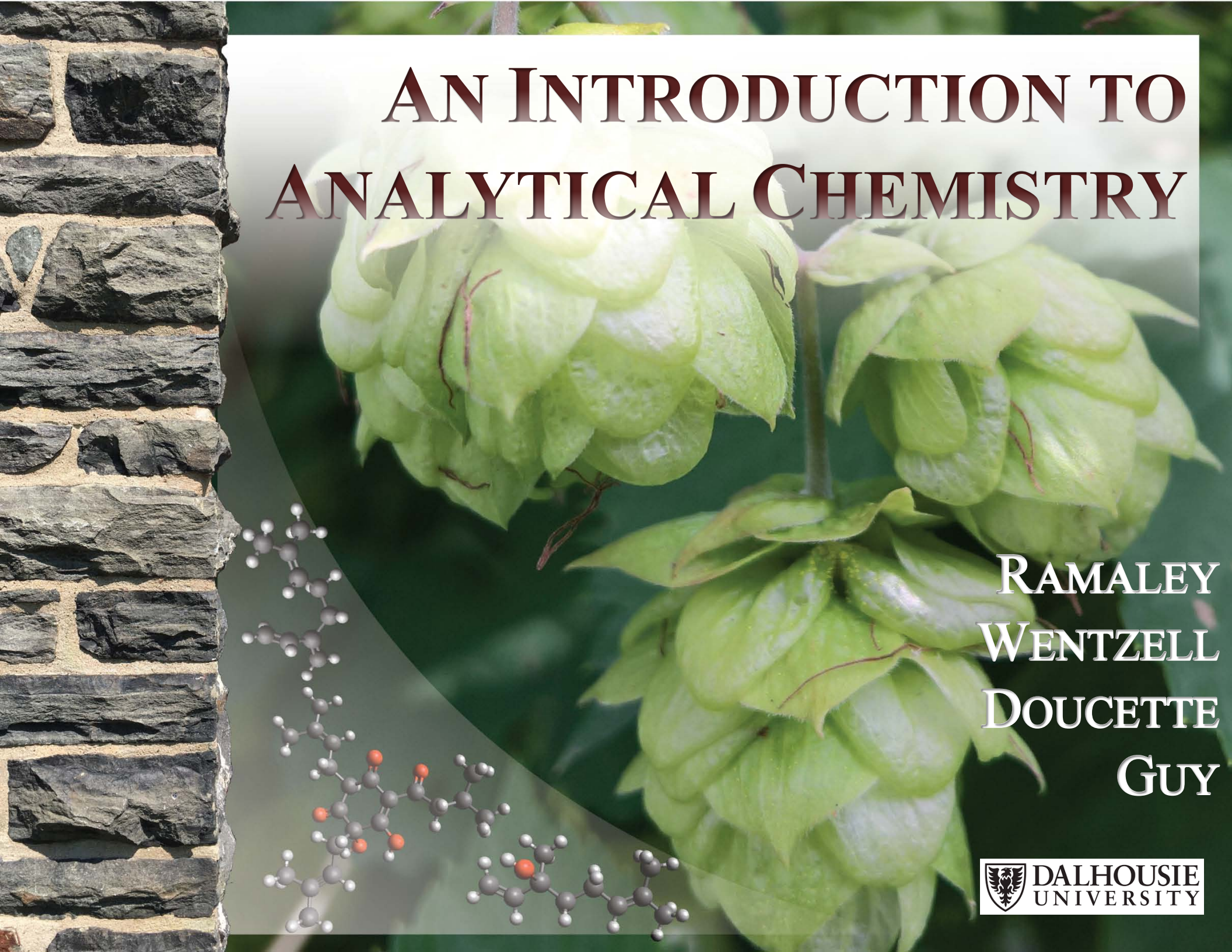
An Introduction to Analytical Chemistry



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Periodic Table of the Elements

1 **H** Hydrogen 1.00794±7																	2 **He** Helium 4.002602±2
3 **Li** Lithium 6.941±2	4 **Be** Beryllium 9.012182±3											5 **B** Boron 10.811±7	6 **C** Carbon 12.0107±8	7 **N** Nitrogen 14.00674±7	8 **O** Oxygen 15.9994±3	9 **F** Fluorine 18.9984032±5	10 **Ne** Neon 20.1797±6
11 **Na** Sodium 22.989770±2	12 **Mg** Magnesium 24.3050±6											13 **Al** Aluminum 26.981538±2	14 **Si** Silicon 28.0855±3	15 **P** Phosphorus 30.973762±4	16 **S** Sulfur 32.066±6	17 **Cl** Chlorine 35.4527±9	18 **Ar** Argon 39.948±1
19 **K** Potassium 39.0983±1	20 **Ca** Calcium 40.078±4	21 **Sc** Scandium 44.955910±8	22 **Ti** Titanium 47.867±1	23 **V** Vanadium 50.9415±1	24 **Cr** Chromium 51.9961±6	25 **Mn** Manganese 54.938049±9	26 **Fe** Iron 55.845±2	27 **Co** Cobalt 58.933200±9	28 **Ni** Nickel 58.6934±2	29 **Cu** Copper 63.546±3	30 **Zn** Zinc 65.39±2	31 **Ga** Gallium 69.723±1	32 **Ge** Germanium 72.61±2	33 **As** Arsenic 74.92160±2	34 **Se** Selenium 78.96±3	35 **Br** Bromine 79.904±1	36 **Kr** Krypton 83.80±1
37 **Rb** Rubidium 85.4678±3	38 **Sr** Strontium 87.62±1	39 **Y** Yttrium 88.90585±2	40 **Zr** Zirconium 91.224±2	41 **Nb** Niobium 92.90638±2	42 **Mo** Molybdenum 95.94±1	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07±2	45 **Rh** Rhodium 102.90550±2	46 **Pd** Palladium 106.42±1	47 **Ag** Silver 107.8682±2	48 **Cd** Cadmium 112.411±8	49 **In** Indium 114.818±3	50 **Sn** Tin 118.710±7	51 **Sb** Antimony 121.760±1	52 **Te** Tellurium 127.60±3	53 **I** Iodine 126.90447±3	54 **Xe** Xenon 131.29±2
55 **Cs** Cesium 132.90545±2	56 **Ba** Barium 137.327±7	57 **La** Lanthanum 138.9055±2	72 **Hf** Hafnium 178.49±2	73 **Ta** Tantalum 180.9479±1	74 **W** Tungsten 183.84±1	75 **Re** Rhenium 186.207±1	76 **Os** Osmium 190.23±3	77 **Ir** Iridium 192.217±3	78 **Pt** Platinum 195.078±2	79 **Au** Gold 196.96655±2	80 **Hg** Mercury 200.59±2	81 **Tl** Thallium 204.3833±2	82 **Pb** Lead 207.2±1	83 **Bi** Bismuth 208.98038±2	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (277)	109 **Mt** Meitnerium (268)	110 **Ds** Darmstadtium (271)	111 **Rg** Roentgenium (272)	112 **Cn** Copernicium (277)	113 **Uut** Ununtrium (?)	114 **Uuq** Ununquadium (285)	115 **Uup** Ununpentium (?)	116 **Uuh** Ununhexium (289)	117 **Uus** Ununheptium (?)	118 **Uuo** Ununoctium (?)

58 **Ce** Cerium 140.116±1	59 **Pr** Praseodymium 140.90765±2	60 **Nd** Neodymium 144.24±3	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36±3	63 **Eu** Europium 151.964±1	64 **Gd** Gadolinium 157.25±3	65 **Tb** Terbium 158.92534±2	66 **Dy** Dysprosium 162.50±3	67 **Ho** Holmium 164.93032±2	68 **Er** Erbium 167.26±3	69 **Tm** Thulium 168.93421±2	70 **Yb** Ytterbium 173.04±3	71 **Lu** Lutetium 174.967±1
90 **Th** Thorium 232.0381±1	91 **Pa** Protactinium 231.03588±2	92 **U** Uranium 238.0289±1	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Standard atomic weights from:
Pure and Applied Chemistry **68**, 2339-2359

Atomic weight uncertainty is in last digit listed
e.g. 65.39 ± 2 (Zinc) means 65.39 ± 0.02

Elements with no stable nuclides list mass number of longest lived isotope of the element

Th, Pa & U are also unstable; a known terrestrial isotopic composition permits listing of atomic mass

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(7th Edition)

A Textbook for Chemistry 2201

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Contents

Topic 1

An Overview of Analytical Chemistry

1.1 Contents in Brief

- Nature and history of analytical chemistry
- Classification of analytical methods by result, technique and concentration
- Applications and scope of analytical chemistry
- Common terms in analytical chemistry

1.2 Introduction

Analytical chemistry can be defined as the science of making and interpreting chemical measurements. Chemistry is a quantitative science, and the ability to make measurements by various means is critical to obtaining a better understanding of nature. Chemical measurements permeate all aspects of our society, from blood tests to food analysis, environmental monitoring, and forensic analysis. It is important to understand the principles and practices underlying these measurements, their capabilities and limitations.

1.3 Historical Perspective

Antoine Lavoisier (1743-1794) was a French nobleman who is most widely regarded as the "father of modern chemistry". He achieved this distinction in large part because of the careful and systematic measurements he made in chemical experiments that allowed him to characterize the stoichiometry of reactions and predict the formulas of compounds. He was the first to recognize the importance of analytical measurements in advancing chemical theory and as a consequence was able to write the first modern chemical textbook.

Early analytical measurements were quite limited by today's standards. Many qualitative tests for various chemical species based on chemical reactions were developed. These included tests for inorganic ions (*e.g.* Pb^{2+}, Ni^{2+}, Cu^{2+}) through the formation of precipitates or coloured solutions, and organic functionalities such as double bonds and aldehydes. Quantitative measurements were limited to mass and other physical properties such as pressure, as well as volumetric techniques such as titrations. Some of these measurements are still used today, and while restricted in their capabilities, were quite sophisticated.

The era of modern analytical chemistry is most often considered to have begun with the introduction of the first electronic pH meter, designed by Arnold Beckman in 1934 to measure the acidity of lemon juice. Although this device, based on vacuum tubes, was cumbersome in comparison with modern pH meters that can be contained in a device the size of a ballpoint pen, it heralded the dawn of modern analytical instrumentation. The pH meter was followed shortly thereafter by infrared and ultraviolet/visible spectrometers, as well as other instruments that made laboratory measurements simpler and more reliable. This was followed by an era of computerization and automation that has led to the very powerful instrumentation we see in laboratories today, instruments such as optical spectrometers, chromatographs, and mass spectrometers.

1.4 Classification of Analytical Methods

The variety of analytical methods available to solve chemical problems today is quite extensive and there are often many techniques that can be used to determine the identity or concentration of a particular analyte. The selection of the most appropriate method to solve

a specific problem is governed by a number of parameters associated with the analyte and the environment in which it exists. To aid in this selection, analytical methods can be classified in a variety of ways, some of which are described below.

Classification by Type of Result

One way to classify analytical problems is in terms the question that is to be answered. In *qualitative analysis*, the fundamental question relates to what is present rather than how much. This question can be formulated in a number of ways. One may simply be looking to determine the presence or absence of a specific analyte (*e.g.* Are there pesticides present in my drinking water?), or may be looking to identify a component of a mixture (*.e.g.* What is the contaminant in the milk?). Alternatively, one may seek the composition of an unknown mixture (*e.g.* What was the white powder found at the crime scene?) on a molecular or elemental level.

Quantitative analysis refers to those cases where the amount or concentration of a particular analyte is to be determined (*e.g.* What is the concentration of lead in my drinking water?, What is my blood sugar level?). In most introductory classes on analytical chemistry, including this one, the emphasis is placed on quantitative analysis. This is not only because of the importance of developing quantitative skills that are useful in all areas of chemistry, but also because many techniques for qualitative analysis (*e.g.* IR and NMR spectroscopy) are closely connected to particular areas of application and are better taught in the context of those subjects.

The distinction between qualitative and quantitative analysis is often blurred. It is necessary, for example, to know the identity of an analyte before it can be measured. Some would argue that the qualitative detection of the presence of an analyte in a sample is simply an indication that its concentration is above some minimum detectable level, and is therefore quantitative. Finally, even quantitative measurements are often ultimately used to make some qualitative decision (*e.g.* Is the water safe to drink? What is the patient's illness? Does the hair at the crime scene match that of the suspect.) Nevertheless, these classifications are often useful in practice.

Classification by Technique

In a broad classification by technique, analytical methods are sometimes distinguished as "wet" chemical methods or instrumental methods. The former classification typically refers to methods where the analytical determination is based on traditional measurements of volume (*i.e.* titrations) or mass (gravimetric methods). These techniques are generally based on chemical reactions. For example, if one wanted to determine the concentration of a hydrochloric acid solution, a titration where it is neutralized with a strong base such as sodium hydroxide could be used. If one wanted to determine the amount of sulfate ion (SO_4^{2-}) present in a solution, it could be reacted with excess barium ions (Ba^{2+}) in another solution to form a solid barium sulfate precipitate ($BaSO_4$) that could be dried and weighed.

In contrast, instrumental methods are those in which the final measurement to be related to analyte concentration is made on an electronic instrument, such as a spectrometer or pH meter. (Students often refer to these as "machines", but "instrument" is more accurate since the primary purpose of the devices is not mechanical work). Again, the distinction between wet chemical and instrumental methods is blurred because modern balances are all electronic and most instrumental methods involve gravimetric and volumetric procedures to prepare samples for analysis.

While both of these strategies are treated in this class, the emphasis is on instrumental methods since these are more widely used for most analytical procedures today. There is often a perception that, because instrumental methods are a more recent development that they give better results than wet chemical methods. In fact, the opposite is generally true and methods such as titrations generally give superior accuracy when they can be employed.

Classification by Analyte Concentration

Often an important parameter to be considered in a chemical analysis is the anticipated concentration of the analyte. This can be broadly classified in the following ways:

Major component:	1% to 100%
Minor component:	0.01% to 1%
Trace component:	1×10^{-5} % to 0.01% (100 ppb to 100 ppm)
Ultratrace component:	<100 ppb

The concentrations given above are in terms of mass fractions of the analyte, and "ppm" and "ppb" refer to "parts per million" and "parts per billion", respectively. (Concentration units are discussed in more detail later.) These categories are only approximate guidelines. In general, the lower the concentration of the analyte, the more difficult it is to determine in a sample, so much effort in analytical research is directed at lowering the level at which a particular analyte can be detected. Most of the emphasis in this class is directed at minor or trace components of a mixture.

Other Classifications

Analytical methods can also be classified in many other ways as well. For example, instrumental techniques can be further divided by the physical means that are used to determine the analyte. Thus, spectroscopic methods exploit the interaction of light and matter, while electrochemical methods utilize various electrical measurements (voltage, current, etc.) to determine concentration. Classification according to sample type is also common. For example, if the analysis relates to biological samples, it is referred to as a bioanalytical method.

1.5 Scope of Analytical Chemistry

Analytical measurements permeate virtually all aspects of our society because the need for chemical information is critical to our general well-being and understanding of nature. If you have ever had a blood test or had your well water tested, then analytical chemistry has been involved. Below are some application areas and samples of questions that may be asked.

Environment:	Are pesticides present in a soil sample?
	What is the concentration of Pb in drinking water?
	What is the acidity of lake?
	Who is responsible for an oil spill?

Health/Medicine:	What is a patient's cholesterol level?
	Is an athelete on steroids?
	Is a woman pregnant?
Law/Forensics:	What was a suspect's blood alcohol level?
	Was a victim drugged or poisoned?
	What type of accelerant was used for arson?

There are many other examples as well. For example, in industry, analytical measurements are widely used to monitor production processes to end product quality to ensure optimum performance. In food science, analytical techniques are used confirm product quality (*e.g.* in breweries) and the absence of harmful contaminants. In geology, the analysis of ore samples is critical to assess the quality of minerals that can be obtained from a site. Even in areas such as art and archeology, analytical chemistry plays a major role in determining the authenticity of paintings or artifacts.

The answers provided by analytical chemistry can often have profound implications to individuals and society. Athletes have been stripped of their medals based on blood tests, artworks have been rendered worthless through an analysis of paint samples, and major projects have been initiated on the basis of geological or environmental analysis. It is therefore important to understand the nature of analytical measurements, their capabilities, and their limitations.

1.6 Terminology in Analytical Chemistry

As with any field, it is important to become familiar with terms used in analytical chemistry as they will come up frequently in discussing the subject matter. While many new terms will be introduced throughout this text, some of the most basic and general definitions are listed below.

Accuracy:	the closeness of a measured value to the true value
Precision:	the reproducibility of a measured value
Analyte:	the chemical constituent for which the analysis is being performed

Matrix: the chemical environment in which an analyte is found (*e.g.* rainwater, seawater, soil, blood)

Interference: a component of the matrix that affects the accuracy with which the concentration of an analyte can be determined

Limit of detection (LOD): smallest concentration of a particular analyte that can be detected by a given method. If one method has a smaller LOD than another, it is often said to be more *sensitive*.

Selectivity: is an indication of how susceptible a method is to interferences in the determination of analyte concentration. A method that is more selective is less affected by interferences.

In addition to the terms above, it is important to recognize that the sample is *analyzed*, but the analyte is *determined*. For example, we would say that "the ore sample was analyzed for iron" or "a titration was used for the determination of iron in the sample", but not "the iron in the sample was analyzed".

1.7 Summary

Analytical chemistry broadly defines the field of chemical measurements for both qualitative and quantitative purposes. It encompasses both wet chemical and instrumental techniques and applications in wide ranging fields. Chemical measurements play an important role in science and society and an understanding of their capabilities and limitations is important.

Topic 2

Statistical Treatment of Data

2.1 Contents in Brief

- Measurement errors: precision and accuracy
- Statistical parameters for central tendency and dispersion
- The normal distribution and confidence intervals
- Outliers: Dixon's Q-test and Grubbs' test
- Comparison of means: the t-test

2.2 Introduction

Quantitative chemical analysis involves making experimental measurements that inherently contain errors. These errors lead to uncertainty in the results and it is necessary to quantify this uncertainty if a result is to be useful. Statistical methods allow us to accomplish this in a meaningful way. This topic introduces basic descriptive parameters used in statistics and the concept of probability distributions. This leads to the treatment of confidence intervals and statistical tests.

2.3 Measurement Errors

The final result of a quantitative analysis is typically one or more numbers that indicate the concentrations of analytes in the sample. There is always some uncertainty associated with each operation or measurement in an analysis, and so there is always some uncertainty in the final result. Knowing the uncertainty is as important as knowing the final result. Having data that are so uncertain as to be useless is no better than having no data at all. Thus there is a need to describe and reduce, if necessary and possible, this uncertainty.

Two terms that are very important in describing measurement errors are *accuracy* and *precision*, as defined in Topic 1. Accuracy relates to the closeness of an experimental result to the actual (correct) value, while precision describes the ability to reproduce the same result (not necessarily the correct one) when the experiment is repeated. Generally, unless we know the true answer, it is not possible to determine the accuracy. Precision can be determined, but a precise result does not necessarily mean an accurate one. However, it is normal to place more "faith" in the results of an analyst who has good precision, since good precision usually means greater attention to detail.

Types of Errors

Good accuracy should be the object of all chemical measurements. The question thus arises, how is accuracy measured? This topic is best introduced by discussing errors, since a measurement will be accurate if there are no errors. There are three general types of errors: blunders, determinate errors, and indeterminate errors.

Gross errors, sometimes called "blunders" are mistakes that are obvious to the analyst and that are unlikely to be repeated when another analysis is performed. An example of a gross error is forgetting to add a reagent that is required for analysis.

Determinate errors, often referred to as "bias", are also mistakes, but are less obvious to the analyst and are likely to be repeated when other analyses are performed. In theory many determinate errors, if recognized, could be eliminated by improving technique. An example of a determinate error would be the use of an analytical balance that has gone out of calibration to weigh a sample, producing results that are always low or high. Determinate errors are unidirectional in that they always produce an error in the same direction.

Indeterminate errors, often referred to as "random errors", are caused by the need to make estimates in the last figure of a measurement, by noise present in instruments, or other unbiased factors that lead to uncertainty in the estimated value. Such errors can be reduced, but never entirely eliminated. An example of indeterminate error is the variation in the values taken from a buret due to the need to estimate the last significant figure. The observer would certainly say, referring to Figure 2.1, that the volume delivered is between 40.2 and 40.3 mL. However, one can and should do better than this. Some observers might say that the volume was 40.24, some 40.25, and others 40.26 mL. This uncertainty in the last place is an example of indeterminate error. It is better to report the volume as 40.26 mL rather than to report its being between 40.2 and 40.3 mL, even though it is realized that the 0.06 is an intelligent estimate. Indeterminate errors are bidirectional; being random in nature they are as likely to produce a high result as a low result.

Note that determinate error may also be involved in estimating the last figure of a measurement. In the case being discussed, parallax error (looking at the meniscus at an angle) and number bias (selecting some numerals, e.g. 0 or 5, more often than others in the estimate) are two examples of determinate error. Since determinate errors are usually unidirectional, they will always cause an error in the final result, even if many measurements are averaged. Indeterminate errors, being bidirectional, will tend to cancel if enough measurements are averaged. These ideas are perhaps best illustrated by Figure 2.2. In Case 1 shown in the figure, the precision is poor, but the accuracy will be good if enough data are taken and averaged, since the errors are approximately equally distributed about the correct answer. In Case 2, the precision is good and the accuracy is also good. In Case 3, the precision is good, but the accuracy is poor due to a determinate error. If determinate error is present, averaging will not help to reduce its contribution.

The precision of the final result can always be improved by making replicate measurements and the extent of improvement is described in the discussion on confidence intervals. Even if many replicates are not required, it is standard practice in most analytical procedures to make two or three separate measurements so that precision can be assessed and gross errors identified.

To evaluate accuracy and assess indeterminate errors, the usual procedure is to analyze a standard (a sample of accurately known composition) and compare the analytical results with

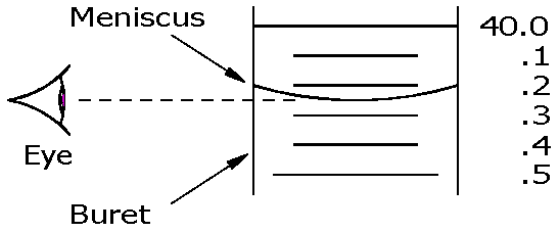


Figure 2.1: Determination of the volume reading in a buret. The final digit is estimated from the position of the meniscus and gives rise to indeterminate errors.

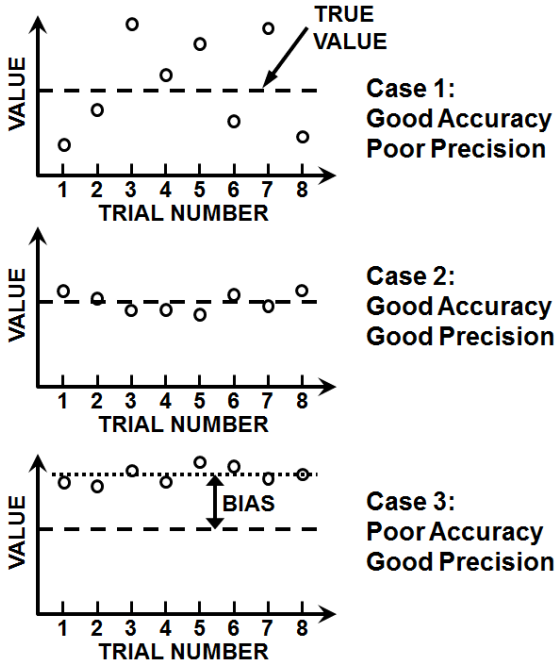


Figure 2.2: Comparison of different situations of accuracy and precision.

the known sample composition. If the values are the same, bias is assumed to be absent. Many organizations, *e.g.* the National Research Council of Canada and the National Institute of Standards and Technology in the U.S.A., provide such standards. A statistical test, described later, can be used to compare the results.

2.4 Statistical Parameters

In statistics we usually distinguish between parameters that pertain to a population and parameters that are estimated from a finite data set. A population would result if a very large number of measurements (strictly an infinite number) were made. A finite data set, or "sample", results when just a few measurements are made, as in the case of experimental measurements. The parameters calculated from a finite data set, usually represented by "English" characters, are only estimates of the population parameters, usually represented by Greek characters. It is the population parameters that one would like to obtain, if possible. Much of statistics is involved with trying to make inferences about the population parameters from the sample parameters.

Since there is always uncertainty involved in measurements, a data population or a data set will consist of a distribution of values rather than a single value. Such distributions have characteristics that are described by statistical parameters. The first such characteristic to be investigated is the "central tendency" of a distribution. Many distributions have some values that are more often observed than other values and these are usually toward the centre of the distribution. Three methods of defining the "central tendency" are listed below.

The mean

The mean, or average, is calculated by summing all the values, x_i, in the set and dividing by the number of trials, N.

$$mean = \bar{x} = \frac{x_1 + x_2 + x_3 + \ldots + x_N}{N} = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad (2.1)$$

As $N \to \infty$, $\bar{x} \to \mu$, where μ is the population mean. In the absence of determinate error, μ is the correct answer, and as N becomes larger the estimate, $\bar{x}$, of the correct answer gets better.

The median

The median is the "central point" in a data set. Half of all the values in a set will lie above the median, half will lie below the median. If the set contains an odd number of data points, the median will be the central point of that set. If the set contains an even number of points, the median will be the average of the two central points.

The mode

The mode is the value that occurs most often (the value with the highest probability). The mode is quite often not obvious in a finite data set where no two values are the same.

In populations where errors are evenly distributed about the mean (the distribution is symmetric), the mean, the median, and the mode will all have the same value. In this text, the mean will be the most useful parameter for indicating the "central tendency" of a data set or population.

Accuracy and how one attempts to achieve and measure it have been discussed. The topic of precision comes next. How does one measure precision? Obviously one must have made more than one measurement to get an estimate of precision. The characteristic of a distribution that relates to precision is its "dispersion". The parameters used to describe the dispersion are listed below.

The standard deviation

The standard deviation (and those parameters related to it) is the only statistically acceptable measure of precision and is the only measure to be discussed in detail here. It is calculated from the mean and the values of the trials in the data set according to:

$$s = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \ldots + (x_N - \bar{x})^2}{N-1}} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}} \qquad (2.2)$$

The values of $(x_i - \bar{x})$ are the deviations from the mean and the quantity in the denominator is called "the degrees of freedom". When the standard deviation is estimated from the sample mean as opposed to the population mean, the degrees of freedom are one less than the number of measurements used in the set, or (N-1). The reason for this is that one degree of freedom is lost when calculating the mean of the data set. As with the mean, as $N \to \infty$, $s \to \sigma$, where

σ is the population standard deviation. The sample standard deviation, s, is only an estimate of σ, but as N gets larger, that estimate gets better.

The relative standard deviation

Often the relative standard deviation (RSD) is often more useful than the absolute standard deviation (given above), since it immediately provides an idea of the precision of the data set relative to its individual values. There are several ways of expressing the RSD.

$$\text{Relative standard deviation} = RSD = s_r = \frac{s}{\bar{x}} \tag{2.3}$$

$$\text{Percent RSD} = \%RSD = s_r \times 100\% = \frac{s}{\bar{x}} \times 100\% \tag{2.4}$$

$$\text{RSD in parts per thousand} = RSD(ppt) = s_r \times 1000 = \frac{s}{\bar{x}} \times 1000 \tag{2.5}$$

The relative standard deviation in percent is often referred to as the "coefficient of variation". Note that the absolute standard deviation has the same units as the mean, whereas the relative standard deviation has no units. In some analytical determinations the relative standard deviation is reported in parts per thousand (ppt).

The variance

The variance is another method of describing dispersion and is often preferred by statisticians because variances are directly additive (as will be seen later). The variance is simply the square of the standard deviation and is normally indicated by the symbol s^2, or σ^2 in the case of population variance.

The range

The range or spread is simply the difference between the largest and smallest values in a data set.

2.5 The Normal Distribution

Many different data distributions are found in nature. Many types of data, including most chemical measurements subject to random errors, follow a Gaussian distribution. This is a symmetrical, bell-shaped distribution. Since so many data types follow this distribution it is usually referred to as the normal distribution and the mathematical equation that describes this distribution is called the normal error curve.

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{(x-\mu)^2}{2\sigma^2}\right\} \tag{2.6}$$

In this equation $f(x)$ is called the probability density function (PDF), x represents the trial values, μ is the population mean, and σ is the population standard deviation. The PDF gives the relative frequency that any value of x will be observed and is a function of the standard deviation and the position of x with respect to the mean. A graph of the normal distribution is shown in Figure 2.3. In this figure the mean is taken as zero and the standard deviation as unity. This is the standard representation of the normal error curve.

The ability to describe the normal distribution mathematically using Eqn. 2.6 is very useful. From Figure 2.3 it is obvious that the mean of a normally distributed data population is the value that occurs most often (has the highest frequency). Since the distribution is symmetrical, the mean, the median, and the mode are all the same. It is less obvious that inflection points occur at $\mu \pm \sigma$. The area under the curve between x_1 and x_2, as determined by integration, gives the probability that any trial value, x, will be found between x_1 and x_2. The area between $+\infty$ and $-\infty$ is exactly 1, as it should be, since the probability of finding any value of x in this range must be unity. The area between μ and $\mu+\sigma$ is 0.3413, which means that 34.13% of all x values in a normally distributed population fall between the mean and the mean plus one standard deviation. Since the distribution is symmetrical, 34.13% of all values will fall between the mean and the mean minus one standard deviation. Thus 68.26% of all values of x will fall within $\pm 1\sigma$ of μ. Likewise it can be shown that 95.44% of all values of x will fall within $\pm 2\sigma$ of μ and 99.74% will fall within $\pm 3\sigma$ of μ. Thus, in a normally distributed population it will be very unlikely (the chances are less than 3 in 1000) that any value of x will be outside the $\pm 3\sigma$ limits.

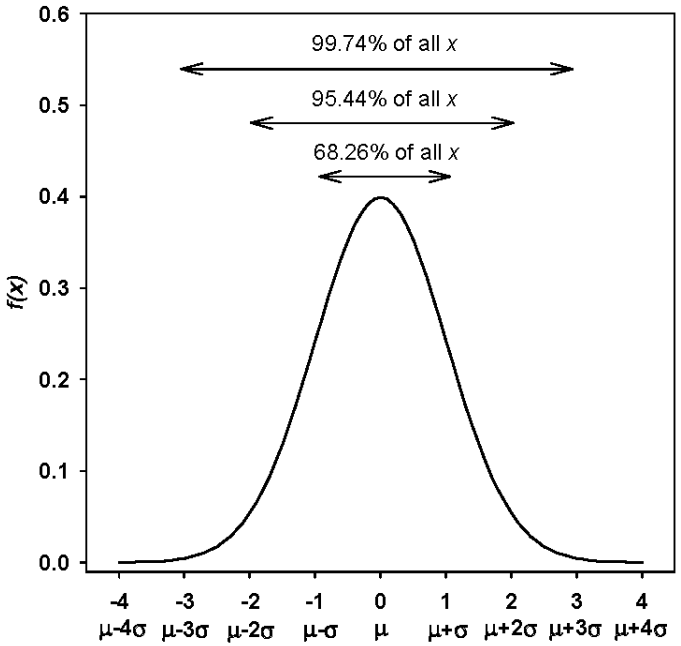


Figure 2.3: Graph of the normal probability density function, which applies to many distributions in nature, including experimental measurement errors.

2.6 The Confidence Interval

One would often like to know how close the mean of a data set is likely to be to the true answer (the population mean), assuming that there is no determinate error. Although we can never know this exactly, we can use the normal distribution to establish a *confidence interval* (CI). This is a region in which we can assume that the true value exists with a certain probability. The bigger this region, the greater the probability that it contains the true value, but because of the nature of the normal distribution, we can never be 100% certain. The confidence interval is given by:

$$\text{Confidence interval, C.I.} = \bar{x} \pm \frac{ts}{\sqrt{N}} \quad \text{with } P\% \text{ confidence} \tag{2.7}$$

As expected, the width of the confidence interval is dependent on the standard deviation (precision) of the measurements, since this defines the spread of the normal distribution. It also depends inversely on the square root of the number of measurements, *N*. This is because we are really interested in the standard deviation of the *mean* and not the individual measurements. The standard deviation of the mean of *N* values is given by:

$$s_{\bar{x}} = s/\sqrt{N} \tag{2.8}$$

The inclusion of this term makes intuitive sense, since we expect the confidence interval to become narrower as we obtain more measurements. Finally, the quantity *t* is a constant that is related to the confidence interval we want to report (*e.g.* 95%). In an ideal situation, where we know the population standard deviation, σ, this would be the only factor defining *t*. However, since we use the sample standard deviation, *s*, the uncertainty in estimating σ must be taken into account, so *t* will become larger as *N* becomes smaller. The values of *t* (called the *critical values*) are taken from what is called a Student's t-distribution, and these are shown in Table 2.1 as a function of degrees of freedom ($N-1$) and the confidence interval.

An example will illustrate the calculation of some of the statistical quantities that have been introduced.

Table 2.1. Critical values for the Student's t-distribution at selected confidence levels.

Deg. of Freedom	Confidence Interval				
	80%	90%	95%	98%	99%
1	3.078	6.314	12.706	31.821	63.657
2	1.886	2.920	4.303	6.965	9.925
3	1.638	2.353	3.182	4.541	5.841
4	1.533	2.132	2.776	3.747	4.604
5	1.476	2.015	2.571	3.365	4.032
6	1.440	1.943	2.447	3.143	3.707
7	1.415	1.895	2.365	2.998	3.499
8	1.397	1.860	2.306	2.896	3.355
9	1.383	1.833	2.262	2.821	3.250
10	1.372	1.812	2.228	2.764	3.169
∞	1.282	1.645	1.960	2.326	2.576

Example 2.1: Statistical Parameters

Assume that the following values were obtained in the analysis of the weight of iron in 2.0000 g portions of a sample: 0.3791, 0.3784, 0.3793, 0.3779, and 0.3797 g. Calculate the mean, variance, standard deviation, relative standard deviation (RSD), the %RSD, the RSD in ppt, the range, the median, and the 80% and 95% confidence intervals.

The calculation of the statistical parameters is carried out as shown below, starting with the mean and degrees of freedom, since these are needed to calculate the variance and standard deviation.

The mean = $\bar{x} = \frac{\sum x_i}{N} = \frac{0.3791 + 0.3784 + \ldots + 0.3797}{5} = \frac{1.8944}{5} = 0.37888\,\text{g}$

The degrees of freedom = DF = $(N-1) = 4$

The variance = $s^2 = \frac{\sum (x_i - \bar{x})^2}{N-1} = \frac{(0.3791 - 0.37888)^2 + \ldots + (0.3797 - 0.37888)^2}{4}$

$= \frac{4.88 \times 10^{-8} + \ldots + 6.72 \times 10^{-7}}{4} = \frac{2.09 \times 10^{-6}\ \text{g}^2}{4} = 5.2 \times 10^{-7}\ \text{g}^2$

The standard deviation = $s = \sqrt{5.2 \times 10^{-7}\ \text{g}^2} = 0.00072\,\text{g}$

Relative standard deviation = RSD = $s_r = \frac{s}{\bar{x}} = \frac{0.00072\,\text{g}}{0.37888\,\text{g}} = 0.0019$

%RSD = $s_r \times 100\% = 0.0019 \times 100\% = 0.19\%$

RSD (ppt) = $s_r \times 1000 = 0.0019 \times 1000 = 1.9$ ppt

To easily see the range and median it is convenient to order the data in terms of increasing or decreasing values. This results in: 0.3779, 0.3784, 0.3791, 0.3793, and 0.3797 g. Since this data set has an odd number of trials, the median is simply the middle or 3rd datum, 0.3791 g. Note that for a finite data set the median and mean are not necessarily identical even if the distribution is symmetric. The range is 0.3797–0.3779 g or 0.0018 g.

From the critical *t* values listed in Table 2.1 (and in the Appendix, the value of *t* for 4 degrees of freedom and 80% confidence is 1.533, while that for 95% confidence is 2.776. With these values, we can calculate the corresponding confidence intervals.

$$\text{80\% C.I.} = x \pm \frac{ts}{\sqrt{N}} = 0.37888\,\text{g} \pm \frac{(1.533)(0.00072\,\text{g})}{\sqrt{5}} = 0.3789 \pm 0.0005\,\text{g}$$

$$\text{95\% C.I.} = x \pm \frac{ts}{\sqrt{N}} = 0.37888\,\text{g} \pm \frac{(2.776)(0.00072\,\text{g})}{\sqrt{5}} = 0.3789 \pm 0.0009\,\text{g}$$

Thus the population mean (and hopefully the true result) will lie between 0.3784 g and 0.3794 g 80% of the time and between 0.3780 g and 0.3798 g 95% of the time.

Although this example illustrates the manual calculations necessary to calculate the statistical parameters directly, many calculators have the ability to evaluate these parameters through built-in functions (see Figure 2.4). You are permitted (and advised) to use these to perform statistical calculations to save time and reduce errors, and *it is not necessary to show all of the calculations presented in the example if you use your calculator functions*. However, you are responsible for knowing how to use these functions on your calculator. This involves knowing how to enter the data and extracting the results. Note that many calculators have two calculations for the standard deviation, one that uses (N–1) in the denominator (called the "sample standard deviation") and one that employs N in the denominator (called the "population standard deviation"). It is the former that should be used. In Figure 2.4, this is indicated by σ_{n-1}, but different designations are used on different calculators.

Figure 2.4: Many calculators can compute statistical parameters automatically, as illustrated with the highlighted buttons shown here. You should learn how to use these.

2.7 Reporting Results

An analytical result, or any experimental result, should be reported with an indication of its uncertainty or else it is not meaningful. In many circumstances, the uncertainty is implied by the last significant digit (±1 in the last digit is assumed), but when more reliable information, such as the standard deviation, is available, it should be used. Typically, the mean is reported as the determined value, since it should be the most precise estimate, and

either the absolute or relative standard deviation is reported as well. For instance, the results in Example 2.1 could be reported in the following ways.

0.3789 g ±0.0007 g, using the absolute standard deviation
0.3789 g with a RSD of 0.0019
0.3789 g ±0.19%
0.3789 g ±1.9 ppt

It is normally assumed that the number following a "±" will be the absolute standard deviation. The use of the various forms of the RSD can be confusing, particularly if a %RSD is given for a concentration that is also given as percentage, so if an RSD is given, this should be clearly indicated.

It is tempting to report the answer as 0.37888 g ±0.00072 g, but this should not be done for two reasons: (1) the rules for significant figures do not allow this (it is assumed that you are familiar with these rules) and (2) the answer itself demonstrates how reporting should be done. The standard deviation indicates that there is an uncertainty of ±7 in the fourth place after the decimal point. Thus it makes no sense to list any figures past this point.

A disadvantage of using the standard deviation of the measurements in reporting is that it does not reflect the improvement in the precision of the result that comes from making more measurements. As the number of replicates increases, the estimate of the population standard deviation will improve ($s \rightarrow \sigma$) but it will not get smaller. Since the mean value is being reported, it is better to report the *standard deviation of the mean* ($s_{\bar{x}} = s/\sqrt{N}$) or the confidence interval ($\mathrm{CI} = ts/\sqrt{N}$). Thus the result could also be reported as:

0.3789 g ±0.0003 g (using the standard deviation of the mean)
0.3789 g ±0.0009 g (using the 95% confidence interval)

Note that, although the confidence interval is wider than the standard deviation of the measurements, it is more statistically meaningful and will decrease as the number of measurements (N) increases.

Important points to remember in reporting analytical results are (1) whatever statistical measure is used to report the uncertainty of the result, it should be clearly indicated to avoid misinterpretation, and (2) when reporting absolute uncertainties, only one significant digit in

of uncertainty should be given with the result and the number of decimal places shown in the result should be consistent with this uncertainty.

Exercise 2.1

Compute the mean, median, range, absolute and relative standard deviations, and the 80% confidence interval for the following set of numbers: 73.8, 73.5, 74.2, 74.1, 73.6, and 73.5.

2.8 Statistical Tests for Outliers

Statistical tests are often used to guide conclusions about experimental results in science. Such tests typically assume that some hypothesis, called the "null hypothesis" is true, and then test it against the "alternate hypothesis". While a statistical test cannot guarantee that the correct conclusion has been reached, it provides a certain level of confidence in the answer. Such tests involve the calculation of a *test statistic*, which is then compared to a tabulated *critical value* at a certain *confidence level*. The null hypothesis is rejected if the test statistic is greater than the critical value.

One of the most useful statistical tests involves testing for erroneous data. Sometimes a value in a set of replicate measurements appears so far from the other measurements that one suspects that the value must have been the result of some large unknown error not present in the other measurements. If this is the case, the suspect value is an *outlier* and, because it does not come from the same distribution as the other measurements, it should be excluded. On the other hand, the value may be just somewhat different from the other measurements. No statistical test can say with absolute certainty whether or not a value is an outlier, but they can provide an objective way to make a decision.

There are two widely used tests for outliers. The first is called **Dixon's Q-test** and uses as the test statistic the value calculated below.

$$Q_{exp} = \frac{\left| \text{suspect value} - \text{nearest value} \right|}{\text{range}} \tag{2.9}$$

Here, Q_{exp} represents the experimental test statistic and the range is the maximum value minus the minimum value (including the suspect value). The test statistic is compared to the critical value, listed in Table 2.2, for the desired confidence level and number of measurements.

The second outlier test is the **Grubbs' test**, and the test statistic in this case is given by the following equation.

$$G_{exp} = \frac{|\text{suspect value} - \bar{x}|}{s} \tag{2.10}$$

Again, the test statistic is calculated and compared to the appropriate critical value, given in Table 2.3 (and the Appendix).

These two tests are essentially equivalent and will lead to the same conclusions in virtually all cases, so it does not matter which one is used. The Q-test has the feature that it does not require the calculation of a mean and standard deviation, which was a big advantage at a time when such calculations had to be done by hand, but this is not as important now.

Example 2.2: Outliers

The following values were reported for the concentration of lead (in parts per million, ppm) in replicate soil samples: 91.2, 80.3, 94.5, 89.6, 93.7, 90.5. Based on a statistical test, should any of the values be rejected as outliers? Carry out the test at the 95% confidence level.

Only one of the two tests needs to be applied, but for illustration, both will be applied in this example.

For the Q-test, it is useful to sort the values first: 80.3, 89.6, 90.5, 91.2, 93.7, 94.5

Possible outliers could be at the high end or the low end, but we only test one of those. Since the difference between the bottom two values is larger than the top two, the lowest value is tested.

$$Q_{exp} = \frac{|80.3 - 89.6|}{94.5 - 80.3} = \frac{9.3}{14.2} = 0.655$$

Table 2.2. Critical values for Dixon's *Q* parameter at selected confidence levels.

No. of Observations	Confidence Interval				
	90%	95%	96%	98%	99%
3	0.941	0.970	0.976	0.988	0.994
4	0.765	0.829	0.846	0.889	0.926
5	0.642	0.710	0.729	0.780	0.821
6	0.560	0.625	0.644	0.698	0.740
7	0.507	0.568	0.586	0.637	0.680
8	0.468	0.526	0.543	0.590	0.634
9	0.437	0.493	0.510	0.555	0.598
10	0.412	0.466	0.483	0.527	0.568

Table 2.3. Critical values for Grubb's parameter at selected confidence levels.

Number of Observations	Confidence Interval				
	90%	95%	96%	98%	99%
3	1.153	1.154	1.154	1.155	1.155
4	1.463	1.481	1.485	1.493	1.496
5	1.671	1.715	1.725	1.749	1.764
6	1.822	1.887	1.904	1.944	1.973
7	1.938	2.020	2.042	2.097	2.139
8	2.032	2.127	2.152	2.221	2.274
9	2.110	2.215	2.244	2.323	2.387
10	2.176	2.290	2.322	2.410	2.482

The critical value for the *Q* statistic, Q_{crit}, at 95% for 6 observations ($N = 6$) is obtained from Table 2.2 as 0.625. Since $Q_{exp} > Q_{crit}$, the null hypothesis (that the suspect value is not an outlier) is rejected, and we conclude that the value is an outlier.

For the Grubbs' test, we need the mean and the standard deviation.

$$\bar{x} = 89.97 \qquad s = 5.097 \qquad G_{exp} = \frac{|80.3 - 89.97|}{5.097} = \frac{9.67}{5.097} = 1.90$$

The critical value for Grubbs' statistic, G_{crit}, from Table 2.3 is 1.887 ($N = 6$, 95%). Since $G_{exp} > G_{crit}$, we again conclude that the suspect value should be rejected.

Based either of these tests, the measured value of 80.7 should be exclude from calculations of the mean, standard deviation and other parameters. It is important to note that these outlier tests can be applied only once to a group of measurements.

What does it mean when a value is rejected in this manner? Since these tests were conducted at the 95% confidence level, it means that we will be correct in rejecting the value 95% of the time, or wrong in doing so 5% of the time. It is up to the analyst to decide the level of the test. If, for example, a 99% level were chosen, we would correctly reject values 99% of the time, but may mistakenly choose to retain outliers more often. In the above example, Q_{crit} at 99% is 0.740, and we would have retained the value. Statistics can never give absolute answers, only assign probabilities that we are correct. If a question does not specify a confidence level, a value of 95% will be assumed in this class.

It should also be noted that, in any given situation, a suspect measurement can always be rejected on the basis of experimental observation rather than a statistical test. This is why it is important to note unusual circumstances (*e.g.* "added too much indicator") in your lab book.

Exercise 2.2

The following data set is available: 17.93, 17.77, 17.47, 17.82, 17.88. Calculate its mean, absolute standard deviation, and confidence intervals at both the 90% and 95% confidence levels.

2.9 Statistical Test to Compare Means

It is quite common in analytical chemistry to want to compare two sets of measurements. For example, we may wish to determine if the amount of calcium in skim milk is the same as that in whole milk, or we may wish to compare the results of two laboratories on the same sample to determine if they are the same. There are several statistical tests that can be used for this purpose, but only one, called the *t*-test, will be discussed here.

It is impossible to determine if two values are the "same" without taking into account their uncertainty. For this reason, the *t*-test uses both the means and uncertainties in calculating the test statistic. The absolute difference in the means is divided by an "average" or pooled standard deviation that accounts for the number of measurements in each group. The test statistic is then compared to the critical value for the corresponding degrees of freedom, with the null hypothesis that the two means are the same. The important equations are given below.

$$t_{exp} = \frac{\left|\bar{x}_1 - \bar{x}_2\right|}{s_{pooled}\sqrt{1/N_1 + 1/N_2}} \tag{2.11}$$

$$s_{pooled} = \sqrt{\frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 - 2}} \tag{2.12}$$

$$\text{Degrees of freedom} = \nu = N_1 + N_2 - 2 \tag{2.13}$$

Critical values for the *t*-statistic are found in Table 2.1 (given earlier) and the Appendix. An example will illustrate the application of the *t*-test.

Example 2.3: Comparison of Means

Two analytical methods are tested to determine the total cholesterol in the same blood sample. The first method gives replicate values of 218, 226, 231, 231 and 211 mg/dL, while the second gives 229, 241, 235 and 248 mg/dL. Are the two sets of results significantly different at the 95% confidence level?

The statistical parameters for each set are first calculated.

$\bar{x}_1 = 223.40 \qquad s_1 = 8.735 \qquad N_1 = 5$

$\bar{x}_2 = 238.25 \qquad s_2 = 8.139 \qquad N_2 = 4$

These can be used to calculate the pooled standard deviation and the *t*-statistic.

$$s_{pooled} = \sqrt{\frac{(5-1)(8.735)^2 + (4-1)(8.139)^2}{5+4-2}} = 8.485$$

$$t_{exp} = \frac{|223.40 - 238.25|}{8.485\sqrt{1/5 + 1/4}} = 2.61 \qquad \nu = 5+4-2 = 7$$

From Table 2.1, the critical value for the test statistic, t_{crit}, at 95% and 7 degrees of freedom is 2.365. Since $t_{exp} > t_{crit}$, we can conclude that we are 95% certain that the two methods are producing different results.

Note that if we had conducted the test at the 99% level (t_{crit} = 3.499), we would not have been able to conclude that results were different. However, we could not say that we are 99% confident that the results are the same under those circumstances, only that we could not detect a difference at the 99% confidence level. The confidence level applies only to the rejection of the null hypothesis.

Exercise 2.3

Two laboratories are contracted to determine the concentration of arsenic in sea water. The first laboratory reports the following values in parts per billion (ppb): 1.34, 1.47, 1.38, 1.43, 1.01, 1.32. The second laboratory reports only five replicates: 1.36, 1.22, 1.12, 1.34, 1.23. Is there a statistically significant difference in the results at the 95% confidence level?

2.10 Summary

Quantitative chemical analysis involves measurements with uncertainty arising from determinate and indeterminate errors that affect the precision and accuracy of results. Measurements can be described through statistical parameters such as the mean, standard deviation, and confidence intervals. Statistical tests can be applied to determine the presence of outliers and also to test whether two sets of measurements provide the same result.

2.11 Additional Exercises

Exercise 2.4

A group of students is asked to read a buret and produces the following data set: 31.45, 31.48, 31.46, 31.46, 31.44, 31.47, and 31.46 mL. Calculate the mean, percent relative standard deviation, and 95% confidence interval of this data set.

Exercise 2.5

Calculate the mean, relative standard deviation in ppt, and the 90% confidence interval of the following data set: 41.29, 41.31, 41.30, 41.29, 41.35, 41.30, 41.28.

Exercise 2.6

A student uses a flame emission spectrometer to measure sodium ion concentrations from drinking water fountains at two different locations on campus. For the first location, she obtains concentrations of 9.21, 9.95, and 8.65 ppm, while the second location gives 8.88, 8.93, 8.50 and 8.69 ppm. If a statistical test is carried out to compare the results, which of the following statement(s) accurately describes the conclusions.

(a) We are 80% confident that the results are different
(b) We are 80% confident that the results are the same
(c) We cannot detect a difference at the 80% confidence level
(d) We are 95% confident that the results are different
(e) We are 95% confident that the results are the same
(f) We cannot detect a difference at the 95% confidence level

2.12 Answers to Exercises 2

2.1 73.8, 73.7, 0.7, 0.3_1, $4._1 \times 10^{-3}$, and 73.6 to 74.0 (or 73.8 ±0.2)

2.2 17.85, 0.07_0, 17.77 – 17.93 (or 17.85 ±0.08); 17.77, 0.18, 17.55 – 17.99 (or 17.77 ±0.22)

2.3 Yes. (t_{exp} = 2.58)

2.4 31.46 mL, 0.041%, 31.45 - 31.47 mL (or 31.46 ±0.01)

2.5 41.30, 0.25, 41.29 - 41.31 (or 41.30 ±0.01)

2.6 (a), (f)

Topic 3

Propagation of Errors

3.1 Contents in Brief

- Review of significant figures in calculations
- Propagation of measurement errors in calculations

3.2 Introduction

Experimental measurements are not meaningful unless there is some indication of their uncertainty. This uncertainty can be represented explicitly, through the use of standard deviations or confidence intervals, or implicitly through the use of significant figures. Whenever inexact (or measured) quantities are used in a calculation to obtain a derived result (such as mass and volume to obtain a concentration), their uncertainties will carry through, or propagate, to the final result. Propagation of error describes how to use the measurement uncertainties to estimate the uncertainty in the calculated result. The rules for significant figures also allow this to be done, but in a much more approximate way. Because so many quantities in science are the result of calculations with measured variables, propagation of error is an important concept in all areas of experimental work.

3.3 Significant Figures

When information about the standard deviation of a measured quantity is not directly available, it is usually implied by the number of digits represented in the value. These digits are called "significant" because they meaningful. For example, if a buret reading is given as 40.24 mL, this implies that there is some reliability in the last digit, although we don't know if its uncertainty is ±0.01 or ±0.07 mL. There is an important difference between 40.24 and 40.240 (although a calculator treats these the same), since the latter implies that the uncertainty is in the third decimal place, normally not a reasonable assumption.

You should already be familiar with significant figures from previous classes, but because of the importance of this topic, the rules for determining significant figures and propagating them through calculations are covered briefly here.

Determining the Number of Significant Digits

Significant digits in a number include any non-zero digits and zeros between non-zero digits. Leading zeros (those to the left of the first non-zero digit) are not significant as they are simply place holders. Trailing zeros are generally not significant unless there is a decimal point shown. Some examples are given below.

532.6	4 SFs	1.87×10^{-3}	3 SFs	19200	3 SFs
101	3 SFs	0.20	2 SFs	19200.	5 SFs
0.0087	2 SFs	1.65×10^{6}	3 SFs	$192\overline{0}0$	4 SFs

The last column of these examples illustrates the case of trailing zeros before a decimal point. If the decimal point is not shown, the trailing zeros are not usually considered to be significant, although this representation is somewhat ambiguous. If the decimal place is shown, the zeros are considered significant. The case where some of the trailing zeros are significant is more problematic. One solution is to represent the number in scientific notation, *e.g.* 1.920×10^{4} when only the first zero is meaningful. An alternative approach used in this text to track significant digits will be to place a bar over the last significant digit, as shown in the last example. This in convenient in situations where it is cumbersome to represent numbers in scientific notation and to avoid rounding in intermediate calculations.

It is important to note that exact constants, such as those resulting from unit conversions (*e.g.* 1 g = 1000 g) or stoichiometric factors (*e.g.* 2 A → B) have no uncertainty and are therefore considered to have an infinite number of significant digits.

Significant Figures in Calculations

To properly represent the results of a calculation involving uncertain measurements, various rules have been developed to determine the number of significant figures that should be retained. These rules are approximations to the more precise methods of error propagation described in the next section, and contradictions sometimes exist. Nevertheless, they are useful when no other information about uncertainty of measurements is available other than that implied by the number of significant digits present. These rules are given below.

Multiplication and Division

When multiplying or dividing two or more numbers, the number of significant digits retained in the result should be the same as that for the quantity with the smallest number of significant digits. For example:

$$4.3 \times 9.71 = 42 \qquad \frac{(6.626\times10^{-34}\ \text{J}\cdot\text{s})(3.00\times10^{8}\ \text{m s}^{-1})}{200.0\times10^{-9}\ \text{m}} = 9.94\times10^{-19}\text{J}$$

This rule is also used when the calculation involves raising a number to a power (including fractional powers such as a square root); *i.e.* the result has the same number of significant digits as the quantity used.

Addition and Subtraction

When adding or subtracting, it is not the number of significant digits that is important, but rather their position. The last significant digit retained in the result is the digit with the greatest uncertainty of any of the quantities involved. If there are digits after the decimal point, this means that the number of decimal places retained is the same as the quantity with the fewest decimal places. Some examples are shown in Figure 3.1. In these examples, the overbar indicates the position of the last significant digit in the calculations. It is important to note

$$\begin{array}{rr} 5.2+3.22 & 6200+173 \\ \downarrow & \downarrow \\ 5.2 & 6200 \\ +\,3.22 & +\ \ 173 \\ \hline 8.\overline{4}2 = 8.4 & 6\overline{3}73 = 6400 \end{array}$$

$$(3.889\times10^{5}) - (1.6\times10^{4})$$

$$\downarrow$$

$$\begin{array}{r} 3.889\times10^{5} \\ -\,0.16\ \times10^{5} \\ \hline 3.7\overline{2}9\times10^{5} = 3.73\times10^{5} \end{array}$$

Figure 3.1: Examples of significant figure rules applied to addition and subtraction.

that, when adding numbers expressed in scientific notation, the numbers need to be raised to the same exponent before the number of decimal places can be compared.

Logarithms and Antilogarithms

Logarithms and antilogarithms are involved in a variety of calculations such as pH. In general, when taking a logarithm the number of decimal places retained in the result is equal to the number of significant digits in the quantity. For antilogarithms, the opposite is true; the number of significant digits retained is equal to the number of decimal places in the quantity. The examples below show this.

$$10^{-10.34} = 4.6\times10^{-11} \qquad \log_{10}(0.00634) = -2.198 \qquad \ln(168.6) = 5.1275$$

Rounding and Rounding Errors

In carrying out calculations involving several steps, a sufficient number of digits should be retained in the intermediate calculations to avoid rounding errors in the final result. In other words, do not truncate the intermediate results to the proper number of significant digits, but only do this when the final result is obtained. The overbar is a useful way to keep track of the last significant digit in the intermediate steps as shown in the example below.

$$\frac{0.680\times(10.23-9.744)}{5.852} = \frac{0.680\times0.4\overline{8}6}{5.852} = \frac{0.3\overline{3}048}{5.852} = 0.05\overline{6}473 = 0.056$$

$$2.985\times3.9\times4.67 = 1\overline{1}.6415\times4.67 = 5\overline{4}.366 = 54$$

Note that, in the second example, rounding of the intermediate result to 12 (the correct number of significant digits) would change the final answer to 56. Only when the final result is obtained do we round for the correct number of digits. If the digit to be dropped is exactly 5, the convention will be to round up in this class.

Exercise 3.1

Report the answers of the following calculations with the correct number of significant digits.

(a) $56.85 - 9.9$

(b) $160.86 \div 3.25$

(c) $(273.15 + 25) \times 0.082058$

(d) $1.18 \times 10^{-6} - 2.06 \times 10^{-5}$

(e) $56.3 + 56.3$

(f) 56.3×2 ("2" is an exact value)

(g) $0.05916 \times \log(7.1 \times 10^{-4})$

(h) $e^{-22.59}$

(i) $$\frac{(3.1 \times 10^{-6})(0.00413 + 1.87 \times 10^{-3})}{12.00}$$

(j) A patient is administered 4 tablets of medication, each of which contains 25 mg of active ingredient. What is the total amount of drug that the patient receives?

3.4 Propagation of Errors in Calculations

In many situations in science, the final quantity of interest is not measured directly, but rather is the result of a calculation involving several other measured values. In these cases, it is critical to know how the errors in individual measured values affect the uncertainty in the final result. This is referred to as *propagation of error*. Propagation of error describes how to calculate the uncertainty in the result of a calculation or procedure if you know the uncertainties of all the numbers entering the calculation. In this text, only indeterminate (random) errors will be considered, since determinate errors propagate somewhat differently and affect the accuracy rather than the precision.

To illustrate, suppose you determined the volume of a rectangular box by measuring its length, width and height with a ruler and taking their product. These measurements could be repeated many times (ideally by multiple individuals to avoid bias) and combined each time to calculate a new volume. The standard deviation of these individual determinations could then be used to express the uncertainty in the volume. However, since the uncertainty of each measurement (*i.e.* the ruler) should be known or easily determined, it should be possible to determine the uncertainty in the volume without actually repeating all of the measurements. This is the idea behind propagation of error.

Significant figures represent a fast and simple way to propagate errors when specific information about measurement uncertainty (*i.e.* standard deviations) are unknown, but this approach is crude and, as shown in the preceding examples, sometimes subject to contradictory results. When more precise information about the uncertainty of a result is desired, error propagation is required. Propagation of error calculations can also provide information on which step in a procedure has the most error associated with it. Improving the precision in this limiting step will have the greatest impact in the overall precision. It can also allow you to select a step which can be done more quickly (and thus less precisely) if the error in the procedure is satisfactory and is not significantly affected by the step to be changed. Finally, such calculations can indicate how low each individual step's standard deviation must be to achieve a result for the overall procedure with a desired standard deviation.

Rules for Propagation of Error

Performing a propagation of error calculation for indeterminate error basically involves applying a set of "rules" to the standard deviations of the numbers entering the calculation. These rules are summarized in Table 3.1 and described in more detail below. In the following discussion "*s*" will represent the estimate of the absolute standard deviation and "*RSD*" that of the relative standard deviation. As indicated above, the rules given below apply only to random errors.

(1) Addition or Subtraction, $y = a \pm b \pm c$

The absolute variance of the result, y, equals the sum of the variances of *a*, *b*, and *c*.

$$s_y^2 = s_a^2 + s_b^2 + s_c^2 + \ldots \qquad (3.1a)$$

or $$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2 + \ldots} \qquad (3.1b)$$

Table 3.1. Summary of equations for propagation of error.

Function	Error propagation formula
$y = a+b$, $y = a-b$	$s_y = \sqrt{s_a^2 + s_b^2}$
$y = a \times b$, $y = a/b$	$RSD_y = \sqrt{(RSD_a)^2 + (RSD_b)^2}$
$y = a+k$, $y = a-k$	$s_y = s_a$
$y = a \times k$, $y = a \div k$	$RSD_y = RSD_a$
$y = a^p$	$RSD_y = p \cdot RSD_a$
$y = \log_b(a)$	$s_y = RSD_a / \ln(b)$
$y = b^a$	$RSD_y = \ln(b) \cdot s_a$

(2) Multiplication and Division, $y = ab/c$

The relative variance of y equals the sum of the relative variances of a, b, and c.

$$(RSD_y)^2 = \left(\frac{s_y}{y}\right)^2 = (RSD_a)^2 + (RSD_b)^2 + (RSD_c)^2 \qquad (3.2a)$$

or $$RSD_y = \sqrt{(RSD_a)^2 + (RSD_b)^2 + (RSD_c)^2} \qquad (3.2b)$$

or $$s_y = y \cdot \sqrt{(s_a/a)^2 + (s_b/b)^2 + (s_c/c)^2} \qquad (3.3)$$

(3) Constants in Arithmetic Calculations, $y = a \pm k$, $y = ka$, $y = a/k$

The case of addition of or multiplication by a constant that is very accurately known (*e.g.* a molar mass or a conversion factor) makes use of the same rules but is often somewhat simpler. In this instance it is assumed that s_k, the standard deviation of the constant, k, is essentially zero. Thus:

For $y = a \pm k$ $\qquad s_y = \sqrt{s_a^2 + s_k^2} = s_a$

For $y = ak$ $\qquad RSD_y = \sqrt{(RSD_a)^2 + (RSD_k)^2} = RSD_a$ or $s_y = k \cdot s_a$

For $y = a/k$ $\qquad RSD_y = \sqrt{(RSD_a)^2 + (RSD_k)^2} = RSD_a$ or $s_y = s_a/k$

In other words, adding or subtracting a constant does not affect the absolute uncertainty, and multiplying or dividing by a constant does not affect the relative uncertainty. In the latter case, the absolute uncertainty is scaled in the same manner as the number.

(4) Raising to a Power, $y = a^p$

In this case p is assumed to be exact, *e.g.* 2 or ½. Here the relative uncertainty in the result is proportional to the relative uncertainty in the measurement, with a proportionality constant equal to the power.

$$RSD_y = p \cdot RSD_a \quad \text{or} \quad s_y = y \cdot p \cdot RSD_a \qquad (3.4)$$

Note that, for a quantity such as a^2, we must apply this rule and not the rule for products as given in rule 2 (*e.g.* for $a \times a$).

(5) Logarithms and Antilogarithms, $y = log_{10}(a)$, $y = ln(a)$, $y = 10^a$, $y = e^a$

When the result is the logarithm of a measured quantity, the absolute uncertainty in the result is proportional to the relative uncertainty in the measurement. For $y = \log_b(a)$:

$$s_y = \frac{RSD_a}{\ln(b)} \tag{3.5a}$$

where "ln" is the natural (base e) logarithm and b is the base used in the calculation. For base 10 logarithms, which are commonly used, this simplifies to:

$$s_y = \frac{RSD_a}{\ln(10)} = \frac{RSD_a}{2.303} = 0.4343 \cdot RSD_a \tag{3.5b}$$

For natural logarithms ($y = \ln(a)$) this becomes $s_y = RSD_a$.

For antilogarithms, the reverse is true and the relative uncertainty in the result is related to the absolute uncertainty in the measurement. For $y = b^a$:

$$RSD_y = \ln(b) \cdot s_a \tag{3.6a}$$

For base 10 antilogarithms, where $y = 10^a$, this becomes:

$$RSD_y = \ln(10) \cdot s_a = 2.303 \cdot s_a \tag{3.6b}$$

For base e antilogarithms ($y = e^a$), the uncertainty is $RSD_y = s_a$.

Example 3.1: Propagation of Error in Addition and Subtraction

Calculate the difference between the values (4.715 ±0.002) and (4.693 ±0.003) and the absolute and relative standard deviations of the result.

It is normal procedure to calculate the result first. Thus,

$$y = 4.715 - 4.693 = 0.022$$

Since the only mathematical operation involved in this calculation is subtraction, the applicable equation for the absolute standard deviation is Eqn. (3.1b).

$$s_y = \sqrt{(0.002)^2 + (0.003)^2} = \sqrt{1.3 \times 10^{-5}} = 0.0036 \approx 0.004$$

The relative standard deviation is calculated directly from the standard deviation calculated above and the mean result.

$$RSD_y = \frac{s_y}{\bar{y}} = \frac{0.0036}{0.022} = 0.16 \quad \text{(or 16\% relative standard deviation)}$$

Notice that the "mean" used in the equation above was simply the result of the original calculation. This is often confusing to students, who are used to calculating a mean from a set of values. However, it is implied that the two quantities used in the original calculation are already mean values, so that the result calculated is also a mean.

In the preceding example, note that both numbers entering the calculation are known with good precision. The number 4.715 has a relative standard deviation of 0.04% and 4.693 has an RSD of 0.06%, yet the result of the calculation has an RSD of 16%. This illustrates that differences between two similar numbers are usually not very precise (on a relative basis), even when the numbers entering the calculation are precisely known.

A comment should also be made about the number of significant digits reported in propagation of error calculations. Generally, standard deviations are not reported with an accuracy of more than one significant digit, so uncertainties reported as the result of propagation of error should also have no more than one or two significant figures. Thus the relative standard deviation could have been reported as 0.2 rather than 0.16. Intermediate calculations, however, should retain additional digits to avoid rounding errors. In this text, answers will sometimes be reported with non-significant digits as subscripts, *e.g.* 0.1_6. This is done so that you may more accurately compare your answer to ensure that you used the correct method.

Example 3.2: Propagation of Errors with Logarithms

A pH meter can normally measure with an accuracy of ±0.01 pH unit. Assuming that pH = −log[H^+], what is the concentration of hydrogen ion and its standard deviation in a solution whose pH is measured as 4.39?

The hydrogen ion concentration is calculated as the antilogarithm of the pH:

$$y = [H^+] = 10^{-4.39} = 4.074 \times 10^{-5} \text{ mol/L}$$

Since the mathematical operation involves t the base 10 antilog, Eqn. (3.6b) applies.

$$RSD_y = 2.303 \cdot s_a = 2.303 \times 0.01 = 0.02303$$

However, the absolute standard deviation is required, so this must be obtained from the mean value.

$$s_y = \bar{y} \cdot RSD_y = (4.074 \times 10^{-5} \text{ mol/L}) \times (0.02303) = 9.4 \times 10^{-7} \text{ mol/L}$$

The final result would be $[H^+] = (4.07 \pm 0.09) \times 10^{-5}$ mol/L.

A point of confusion that sometimes arises among students comes from the fact that the quantity calculated, whether it is an absolute or relative standard deviation, depends on the rule applied, which in turn depends on the calculation. Even though you may want an absolute standard deviation, you may need to calculate a relative RSD first. Remember that one can always be calculated from the other.

Example 3.3: Propagation of Error in Compound Calculations

What is the standard deviation of y in the calculation shown below?

$$y = (1.375 \pm 0.003)(5.893 \pm 0.009) + (8.32 \pm 0.03)$$

This example is a bit more complex since both multiplication and addition are involved. Equations with multiple types of calculations, requiring the application of several rules are referred to as compound calculations. In this case, multiplication will involve relative standard deviations and addition will involve absolute standard

deviations. Thus, this type of problem must be done in steps, involving only one type of standard deviation per step. The order in which this is done should follow the order of calculation for the quantity itself. In this example, the multiplication should be done first, followed by the addition. Care must be exercised not to intermix or confuse the different standard deviations in the various steps.

It is useful in this type of problem to break the calculation into steps until you are left with only one type of calculation. The errors in the individual steps can then be calculated and combined in the final step. This is the approach that will be used here. To start, we will use symbols to represent the calculation.

$$y = 1.375 \times 5.893 + 8.32 = AB + C = D + C = 16.423$$

In this equation, $D = AB$= 1.375 x 5.893 = 8.103, and C = 8.32. From this, it is easy to see that,

$$s_y = \sqrt{s_D^2 + s_C^2}$$

We know that s_C = 0.03, so all that remains is to determine s_D, which can be done by applying the rules for multiplication.

$$D = AB = 1.375 \times 5.893 = 8.10\overline{2}875$$

$$RSD_D = \sqrt{RSD_A^2 + RSD_B^2} = \sqrt{\left(\frac{0.003}{1.375}\right)^2 + \left(\frac{0.009}{5.893}\right)^2} = 0.00\overline{2}663$$

$$s_D = D \times RSD_D = 8.10\overline{2}875 \times 0.00\overline{2}663 = 0.0\overline{2}158$$

Although we have shown too many significant digits here, the error propagation will ultimately tell us how many digits we should retain. Now the final result can be obtained by combining s_C and s_D.

$$s_y = \sqrt{s_D^2 + s_C^2} = \sqrt{(0.0\overline{2}158)^2 + (0.03)^2} = 0.0\overline{3}7 = 0.04$$

Thus the final result would be reported as 16.42 ±0.04.

In the preceding example, the use of Eqn. (3.3) might have saved a step in the calculation. However, when learning how to do these types of problems, the use of "shortcuts" may be counterproductive. Many "real world" problems involve compound calculations and thus involve both absolute and relative standard deviations. Successful application of the rules for propagation of errors requires attention to interconversions between the two types of standard deviations. The final example again illustrates this.

Example 3.4: Propagation of Error in a "Real World" Problem

Assume that you are preparing a solution of NaCl by placing 0.2434 g of the salt (assumed to be 100.00% pure) into a 100 mL volumetric flask, and diluting to the mark with distilled water. The molar mass (MM) of NaCl is 58.443±0.001 g/mol, the uncertainty of the volumetric flask is ±0.02 mL, and the uncertainty of a *single* weighing is ±0.0002 g. What is the molarity of the solution and its standard deviation?

This problem is different from the others presented so far because no equation has been given. Since you need an equation in order to apply the rules for propagation of error, the first step is to derive an equation that presents the result as a function of all of the variables. In this case, we need an equation for the calculation of molarity, which we then apply to calculate the first part of the answer.

$$\text{Molarity} = M = \frac{\text{moles}}{\text{volume}} = \frac{\text{mass}/(\text{molar mass})}{\text{volume}} = \frac{m/MM}{V}$$

$$= \frac{(0.2434\,\text{g})/(58.443\,\text{g/mol})}{0.1000\,\text{L}} = 0.04165\,\text{mol/L}$$

The calculation above involves only multiplications and divisions, so it appears we can propagate the uncertainties using Rule 2 and the relative standard deviations in all of the measurements. While this is true, there is a slight complication involving the measurement of mass because it actually involves the *difference* of two measurements, as shown in Figure 3.2. Although modern balances can be zeroed, or "tared" to automatically remove the mass of the weighing container, this process

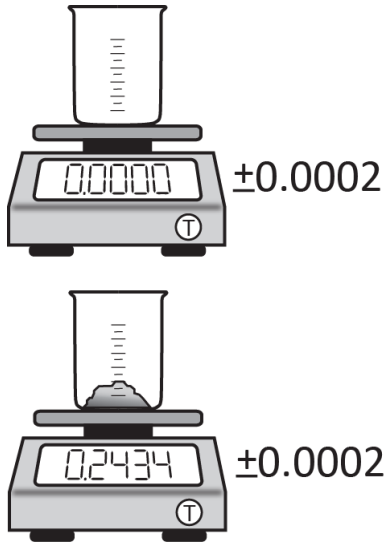


Figure 3.2: Mass measurements on a balance always involve calculating the difference between two independent measurements, even if the balance is zeroed ("tared"). Both measurements have uncertainties that must be taken into account.

introduces uncertainty which must be taken into account. In other words, the calculation of mass involves the difference (0.2434 g – 0.0000 g), and so the uncertainties in *single* weighings (±0.0002 g) must be incorporated using Rule 1 for addition and subtraction. Therefore,

$$s_m = \sqrt{(0.0002\text{ g})^2 + (0.0002\text{ g})^2} = \sqrt{2(0.0002\text{ g})^2} = \sqrt{2} \times (0.0002\text{ g}) = 0.000\overline{2}8\text{ g}$$

In general, **all mass measurements should be considered to result from a subtraction and incorporate uncertainties in a single measurement accordingly.**

Now that we have the uncertainty in mass, Eqn. (3.2b) is used to calculate the relative uncertainty in the overall result of multiplication and division

$$RSD_M = \sqrt{RSD_m^2 + RSD_{MM}^2 + RSD_V^2} = \sqrt{\left(\frac{s_m}{m}\right)^2 + \left(\frac{s_{MM}}{MM}\right)^2 + \left(\frac{s_V}{V}\right)^2}$$

$$= \sqrt{\left(\frac{0.000\overline{2}8\text{ g}}{0.2434\text{ g}}\right)^2 + \left(\frac{0.001\text{ g/mol}}{58.443\text{ g/mol}}\right)^2 + \left(\frac{0.02\text{ mL}}{100\text{ mL}}\right)^2}$$

$$= \sqrt{(\overline{1}.2\times10^{-3})^2 + (\overline{1}.7\times10^{-5})^2 + (\overline{2}.0\times10^{-4})^2}$$

$$= \sqrt{\overline{1}.4\times10^{-6} + \overline{2}.9\times10^{-10} + \overline{4}.0\times10^{-9}} = \overline{1}.2\times10^{-3}$$

Since the result of the above calculation is a relative standard deviation and the absolute deviation is usually desired, the final calculation must convert the RSD to an absolute value.

$$s_M = M \times RSD_M = (0.04165\text{ mol/L})(\overline{1}.2\times10^{-3}) = \overline{5}.0\times10^{-5}\text{ mol/L}$$

The final result would thus be reported as (0.04165 ± 0.00005) M.

Note that in the above example that the uncertainty in the molar mass had no effect on the final result and it could have been ignored in the calculation. This is usually the case and *normally the uncertainty in molar masses is ignored unless it is specifically given*. The step

involving dilution in the volumetric flask also had such a small standard deviation that it did not affect the final result either, but this is not always the case. The only step that contributed significantly to the uncertainty in the answer was the weighing. If a more precise result were desired, the weighing step would be the first to be examined for improvement.

It was noted in this example that *all masses should be considered the result of a subtraction and treated accordingly*. Likewise, any situations involving *volumes delivered from a buret should be treated in the same way* (see Figure 3.3).

Finally, the above example, does not take into account determinate errors that affect the accuracy of the result. For example, if the salt were only 99.8% pure, or the volumetric flask or balance were not properly calibrated, this would introduce an error in the final result (the molarity of the solution) that is not accounted in the uncertainty estimate. These are constant errors (bias) and do not affect the precision of the steps in the procedure in which they are involved. In the absence of determinate error, the standard deviation gives an estimate of the uncertainty in the result (or the accuracy of the result). If determinate error is present, the standard deviation indicates the precision of a measurement, but no longer provides an estimate of the accuracy.

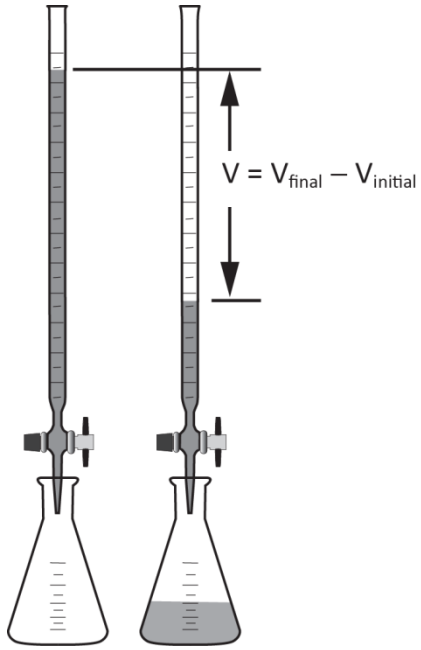


Figure 3.3: Volume measured from a buret, like measurements of mass, always involves two readings even if only one quantity (V) is reported. Propagation of error requires the uncertainties in both readings to be taken into account.

Exercise 3.2

Consider the calculation of a result *X* according to the equation below.

$$X = \frac{(13.50 \pm 0.08) - (14.50 \pm 0.06)}{(2.342 \pm 0.009) - (1.786 \pm 0.003)} \times (6.08 \pm 0.02)$$

(a) Calculate *X* to the correct number of significant figures, ignoring the uncertainties given with each value.

(b) Report the value of *X* with its absolute uncertainty by using propagation of error. The uncertainties shown are all absolute standard deviations. Is this result consistent with part (a)?

3.5 Summary

When a value to be reported is the result of a calculation with uncertain values, there are two common methods that scientists use to indicate the uncertainty in that result. When there is no direct measure of the uncertainty of the input values to the calculation, the uncertainty is assumed to be implied by the number of significant digits shown, and the number of significant figures in the result is determined by applying appropriate rules. This method is simple and widely used, but is not very accurate in estimating uncertainty. When the uncertainties (standard deviations) of the input values are known, the preferred method to determine the uncertainty in the result is through rules for propagation of errors. This approach can also indicate which step limits the precision in a procedure.

3.6 Additional Exercises

Exercise 3.3

What are the values of *Z* and its absolute and relative standard deviations? All standard deviations shown are absolute.

$$Z = \frac{808 \pm 7}{378 \pm 5} - \frac{6.59 \pm 0.09}{4.48 \pm 0.05}$$

Exercise 3.4

What are the values of *X* and its absolute standard deviation? All standard deviations shown are absolute.

$$X = (31.6 \pm 0.9) \times (1.324 \pm 0.018)^3$$

Exercise 3.5

Calculate the values of *Y* and its relative standard deviation. All standard deviations shown are absolute.

$$Y = \log\left(\frac{100.0 \pm 0.5}{38.6 \pm 0.5}\right)$$

Exercise 3.6

An ion selective electrode (ISE) can be use to determine the concentration of an ion based on electrochemical potential, E, that responds logarithmically to concentration. For a chloride ISE, it is found that the concentration of chloride ion (in M) is given by:

$$C = 10^{-\left(\frac{E-K_1}{K_2}\right)}$$

where E = 289.8 ±0.6 mV, K_1 = 101.3 ±0.4 mV, and K_2 = 58.9 ±0.2 mV. Report the concentration with its absolute standard deviation.

3.7 Answers to Exercises 3

3.1 (a) 47.0 (b) 49.5 (c) 24.5 (d) -1.94×10^{-5} (e) 112.6 (f) 113
(Note apparent contradictions in (e) and (f))
(g) −0.186 (h) 1.5×10^{-10} (i) 1.6×10^{-9}
(j) 1.0×10^{2} mg ($1\bar{0}0$ mg) or 1.00×10^{2} mg (100. mg), depending on rule.

3.2 (a) −10.9 (b) −11 ±1, No

3.3 0.67, ±0.04, ±0.06

3.4 73 ±4 (73.3 ±3.6)

3.5 0.413, 0.015

3.6 $(6.3_0 \pm 0.2_4) \times 10^{-4}$ M

Topic 4

Linear Regression

4.1 Contents in Brief

- Linear models in chemistry
- Least squares methods for linear modeling
- Uncertainty in least squares parameter estimates

4.2 Introduction

The ultimate objective of many scientific studies is to create a model to explain some phenomenon under investigation. Often this model takes the form of a mathematical equation that explains the behaviour of a dependent variable as a function of independent variables and model parameters. For example, the Arrhenius Equation in chemical kinetics is a model that describes how the rate constant depends on temperature, with the activation energy and pre-exponential factor as the model parameters. Often, the form of the model and its parameters are determined by regression, or curve fitting, using experimental measurements. There are many types of regression, including straight-line regression, curvilinear regression, and nonlinear regression. In analytical chemistry, straight-line regression is particularly important, and will be described in this topic.

4.3 Straight Line Regression

Straight line regression, often referred to as linear regression (although somewhat incorrectly), is an important modeling technique in science. It is used whenever one variable can be described as a linear function of another variable, where the parameters include the slope and intercept, as given in Eqn. (4.1).

$$y = a + bx \tag{4.1}$$

In this equation, a is the intercept, b is the slope, and x and y are the independent and dependent variables, respectively. The straight line model is widely used because of its simplicity (only two parameters), its wide applicability to many situations, and its ease of physical interpretation.

While Eqn. (4.1) describes the underlying model, it does not adequately describe individual measurements because of the presence of experimental errors. The presence of random errors means that pairs of measurements (x_i, y_i) are likely to deviate from the underlying linear model, as shown in Figure 4.1. If we assume that there are no errors in x (it is known with good accuracy and precision), then the equation for the observed y-value (y_i) can be written as

$$y_i = a + bx_i + e_i = Y_i + e_i \tag{4.2}$$

Here, x_i is the value of the independent variable for measurement I, e_i is the error in the measurement, and Y_i is the true value of the dependent variable in the absence of measurement error. In other words,

$$e_i = y_i - Y_i \tag{4.3}$$

Note that e_i can be positive or negative, as shown in Fig. 4.1. Generally speaking, Y_i and e_i are unknown, as are the parameters a and b (the intercept and slope). It is the goal of linear regression to obtain the best estimates of the true values of a and b based on the available data.

In a typical experiment, a series of N measurement pairs, (x_i, y_i) are obtained and the parameters a and b are estimated by fitting the "best" straight line through the points. This raises the question of what is the "best" straight line. There are a number of criteria that can

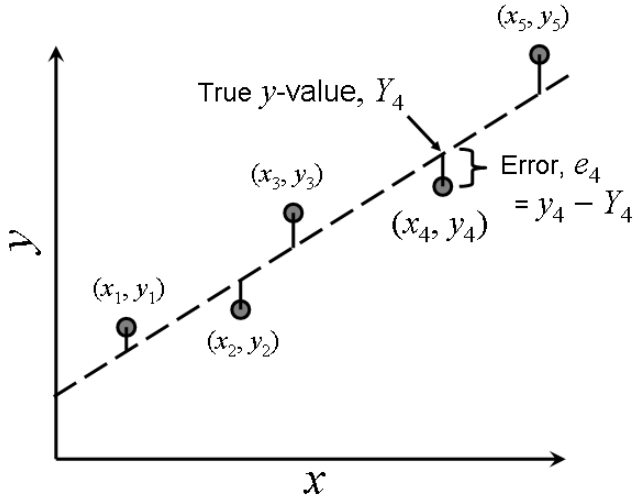


Figure 4.1: Illustration of a linear relationship between x and y. The dashed line shows the true underlying relationship and the points indicate the measured values with errors.

be used to determine this, but one of the most widely used methods (for statistical reasons that won't be detaileded here) is the method of least squares, or least squares regression. This method minimizes the sum of squared residuals (SSR), given by Eqn. (4.4).

$$SSR = \sum_{i=1}^{N} r_i^2 = \sum (y_i - \hat{y}_i)^2 = \sum (y_i - a - bx_i)^2 \tag{4.4}$$

Here, r_i is the *residual*, which is the difference between the measured value for y_i and the fitted value, $\hat{y}_i$, as shown in Figure 4.2 and defined below.

$$r_i = y_i - \hat{y}_i \tag{4.5}$$

$$\hat{y}_i = a + bx_i \tag{4.6}$$

In other words, the "best" (or "most likely") values of *a* and *b* are the ones that minimize the *SSR*. Note that $\hat{y}_i$ and r_i are analogous to Y_i and e_i, but we canot say that they are the same, since we do not know the true model.

The least squares solution is said to be the most likely (or most probable) estimate for model given that the following assumptions are valid: (1) the underlying model is a straight line, (2) the relative uncertainties in the measured *x* values are much smaller than those for the *y* values, and (3) the measured *y* values contain only random errors with the same uncertainty (standard deviation). Violations in each of these assumptions can occur, but for the situations encountered in this class, they will generally be considered to be valid.

Although this section has discussed the principle of least squares regression, it has not described its implementation. Several approaches can be used to obtain the least squares solution and these are described in the following sections.

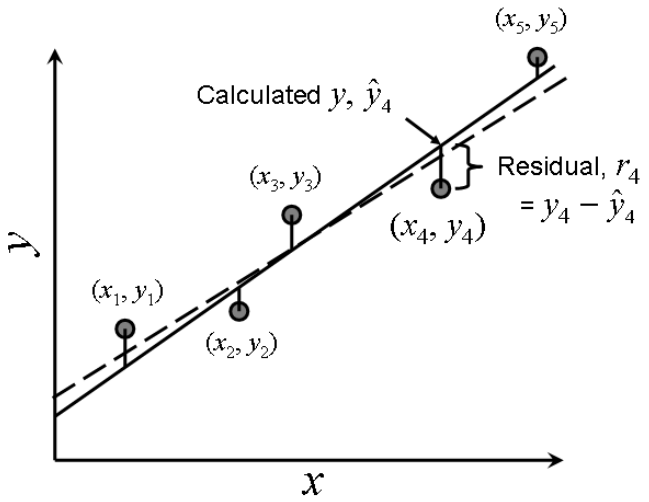


Figure 4.2: Illustration of the relationships in linear regression. The dashed line indicates the true (unknown) linear relationship and the solid line indicates the best a linear fit obtained by least squares. The residuals (*r*) indicate the deviations of the measured points from the fitted line.

4.4 Least Squares Regression: Manual Calculation

The least squares solution in straight line regression corresponds to the values of the slope and intercept that minimize the SSR. Through the application of calculus to minimize this function, analytical solutions for these parameters can be obtained as given in the following equations.

$$b = \frac{\sum (x_i - \bar{x}) y_i}{\sum (x_i - \bar{x})^2} \tag{4.7}$$

$$a = \bar{y} - b\bar{x} \tag{4.8}$$

In these equations, *b* represents the slope and *a* is the intercept and the summation is over the *N* pairs of *x* and *y* values, with $\bar{x}$ and $\bar{y}$ as the corresponding mean values. By applying these equations to a data set, the "best" estimates of the slope and the intercept are obtained. This is illustrated with the following example.

Example 4.1: Manual Calculation of the Least Squares Solution

A student wishes to construct a linear model to describe the relationship between the concentration (*x*) and absorbance (*y*) from the data given below. Use the method of least squares to determine the slope and intercept.

Concentration (μM)	0.0	20.0	40.0	60.0	80.0	100.0
Absorbance	0.017	0.193	0.408	0.561	0.769	0.957

Before carrying out linear regression on any set of data, an important first step is to plot the data whenever possible to confirm the linear relationship and to visually ensure that there are no outliers. If any pair of measurements is an obvious outlier, it should be discarded prior to calculating the fit parameters. The current data set is plotted in Figure 4.3 and all of the points appear to conform to the linear relationship.

The first step in the calculation is to compute the mean values.

$$\bar{x} = (0.0 + 20.0 + 40.0 + 60.0 + 80.0 + 100.0)/6 = 300.0/6 = 50.00$$

$$\bar{y} = (0.017 + 0.193 + 0.408 + 0.561 + 0.769 + 0.957)/6 = 2.905/6 = 0.484\overline{1}667$$

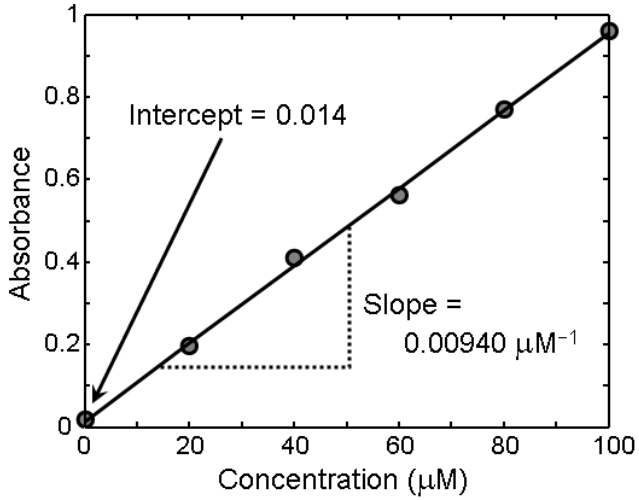


Figure 4.3: A plot of the data in Example 4.1 showing the line fitted by linear least squares.

To simplify the summations, a table can be set up.

x	y	$(x-\bar{x})$	$(x-\bar{x})^2$	$(x-\bar{x})y$
0.0	0.017	-50.0	$25\bar{0}0$	-0.85
20.0	0.193	-30.0	900.	-5.79
40.0	0.408	-10.0	100.	-4.08
60.0	0.561	10.0	100.	5.61
80.0	0.769	30.0	900.	$23.\bar{0}7$
100.0	0.957	50.0	$25\bar{0}0$	$47.\bar{8}5$
Sums			$70\bar{0}0$	$65.\bar{8}1$

The slope (b) and intercept (a) can now be calculated from Eqns. (4.7) and (4.8).

$$b = \frac{\sum (x_i - \bar{x}) y_i}{\sum (x_i - \bar{x})^2} = \frac{65.\bar{8}1}{70\bar{0}0} = 0.0094\bar{0}14 = 0.00940$$

$$a = \bar{y} - b\bar{x} = 0.484\bar{1}667 - (0.0094\bar{0}14)(50.00)$$
$$= 0.484\bar{1}667 - 0.47\bar{0}07 = 0.01\bar{4}0967 = 0.014$$

The best straight line through the points is therefore given by:

$$y = (0.00940)x + 0.014$$

The calculated regression line is shown in Figure 4.3

A question that often arises in calculating regression parameters concerns how many significant figures to retain. In the above example, the number of significant figures was determined in the usual way, but error propagation is a more accurate method. In general, a good rule of thumb is that the number of significant figures reported for the slope should equal the number in the y values, and the number of decimal places retained in the intercept should be the same as the number of decimal places in the y values. When using these parameters in calculations, however, additional digits should be retained.

4.5 Least Squares Regression by Calculator

The manual calculations described above are straightforward, but rather tedious to perform and often prone to errors. As an alternative, many calculators, especially graphing calculators, have built-in functions to carry out the calculations. It is useful to know how to use these functions for regression calculations. Generally, the calculator will have a procedure for entering pairs of x and y values and then retrieving the slope and intercept parameters. Since these procedures are specific for different types of calculators, they will not be covered here. As with the manual calculation, however, it is always advisable to plot the data as well to ensure linearity and the absence of outliers.

4.6 Least Squares Regression by Spreadsheet

The most useful way to carry out linear regression, especially in the laboratory, is through the use of computer software, especially spreadsheets such as Microsoft Excel®. Such software allows both plotting of data with the regression line (sometimes called a trend line) along with the calculation of regression coefficients. You are expected to be familiar with the use of such software for the laboratory. Since particular versions of such software differ in the procedures for this calculation, detailed instructions will not be covered here.

Exercise 4.1

It is found that the amount of protein present in a fixed amount of solution is linearly related to the absorbance of a colored product formed by reaction of the protein. The following data are obtained.

Total protein (μg)	0.00	5.00	10.0	15.0	20.0
Absorbance	0.017	0.193	0.408	0.561	0.769

Using manual and spreadsheet calculation, determine the slope and intercept of a plot of absorbance (y) vs. the amount of protein (x).

4.7 Other Least Squares Parameters

Although the slope and the intercept are the primary parameters of interest in least squares regression, there are several other parameters that relate to the quality of the fitted line that are useful to extract. The first is the *standard error of the regression* or *standard error of the estimate*, which we will designate as s_e.

$$s_e = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{N-2}} = \sqrt{\frac{SSR}{N-2}} \tag{4.9}$$

The standard error can be regarded as the standard deviation of the points around the fitted line. Unlike the standard deviation (which can be regarded as the standard error for a linear model in which the slope is zero), the degrees of freedom is (N–2) because two parameters are estimated for the fitted line. Importantly, the standard error can be regarded as an estimate of the standard deviation (uncertainty) in the y values, *i.e.* $s_y \approx s_e$.

Once the value of s_e is obtained, it can be used to estimate the uncertainty in the intercept and slope through the equations given below.

$$s_a = s_e \sqrt{\frac{1}{N} + \frac{\bar{x}^2}{\sum (x_i - \bar{x})^2}} \tag{4.10}$$

$$s_b = \frac{s_e}{\sqrt{\sum (x_i - \bar{x})^2}} \tag{4.11}$$

These equations are useful when one wishes to provide an uncertainty with the regression parameters. An example will illustrate the use of these equations.

Example 4.2: Uncertainty in Regression Parameters

For Example 4.1, estimate the uncertainty (standard deviation) in the absorbance values and the regression parameters.

First, we need to calculate the standard error, which means we need compute the sum of squared residuals, SSR. This is done by first calculating the estimated *y* values from the regression equation.

$$\hat{y} = 0.01\overline{4}10 + (0.0094\overline{0}14)x$$

Note that we have retained some extra digits in the intercept and slope from Example 4.1 to avoid roundoff errors. This gives the following table.

x	0.0	20.0	40.0	60.0	80.0	100.0
y	0.017	0.193	0.408	0.561	0.769	0.957
$\hat{y}$	$0.01\overline{4}10$	$0.20\overline{2}13$	$0.39\overline{0}16$	$0.57\overline{8}18$	$0.76\overline{6}21$	$0.95\overline{4}24$
$y - \hat{y}$	$0.00\overline{2}90$	$-0.00\overline{9}13$	$0.01\overline{7}84$	$-0.01\overline{7}18$	$0.00\overline{2}79$	$0.00\overline{2}76$

From this, the SSR and s_e can be calculated.

$$SSR = \sum (y_i - \hat{y})^2 = (0.00\overline{2}90)^2 + (-0.00\overline{9}13)^2 + \ldots = 7.\overline{2}06 \times 10^{-4}$$

$$s_e = \sqrt{\frac{SSR}{N-2}} = \sqrt{\frac{7.\overline{2}06 \times 10^{-4}}{6-2}} = 0.01\overline{3}42 = 0.013$$

Therefore, the estimated uncertainty in the absorbance values is s_y = 0.013. To calculate the uncertainty in the slope and the intercept, we can use the value for $\overline{x}$ and $\sum (x_i - \overline{x})^2$ from Example 4.1.

$$s_a = s_e \sqrt{\frac{1}{N} + \frac{\overline{x}^2}{\sum (x_i - \overline{x})^2}} = (0.01\overline{3}42)\sqrt{\frac{1}{6} + \frac{(50.00)^2}{70\overline{0}0}} = 0.0097$$

$$s_b = \frac{s_e}{\sqrt{\sum (x_i - \overline{x})^2}} = \frac{0.01\overline{3}42}{\sqrt{70\overline{0}0}} = 0.00016$$

We can report the intercept as 0.01 ±0.01 and the slope as 0.0094 ±0.0002.

Exercise 4.2

For the regression line determined in Exercise 4.1, determine the standard deviations in the slope and the intercept using a spreadsheet or manual calculations.

4.8 Summary

Linear models are widely used in chemistry and least squares regression is commonly used to estimate the parameters of these models. This is especially true in analytical chemistry, where linear models are important in instrumental calibration, to be discussed later. The least squares method can be implemented through manual calculation, calculator functions, or spreadsheets. In this topic, equations have been provided to estimate the parameters, as well as the uncertainty in those values.

4.9 Additional Exercises

Exercise 4.3

In a technique called chromatography, it is found that the area under a peak is linearly related to the amount of a certain drug. The following data were obtained.

Amount of drug (μg)	3.00	6.00	9.00	12.0	15.0	18.0
Peak Area	239	376	461	593	843	830

Determine the intercept and slope of a plot of peak area (*y*) vs. the amount (*x*) using least squares by any method. (Remember to plot the data.)

Exercise 4.4

In a technique called potentiometry using ion selective electrodes, the following equation holds:

$$E = K_1 + K_2 \cdot \log C$$

where E is the potential (voltage), C is the concentration, and K_1 and K_2 are constants. In one experiment, the following data are obtained.

Concentration (M)	1.0×10^{-1}	1.0×10^{-2}	1.0×10^{-3}	1.0×10^{-4}	1.0×10^{-5}
Potential (mV)	184	244	286	345	401

Report the slope and intercept, with their uncertainties, for a plot of E vs. log$C$.

4.10 Answers to Exercises 4

4.1 intercept = 0.015_2 , slope = 0.0374_4 μg^{-1}

4.2 s_a = 0.012, s_b = 0.00097 μg^{-1}

4.3 intercept = 126, slope = 38.9

4.4 intercept = $131._5 \pm 5._1$ mV, slope = $-53._5 \pm 1._5$ mV

Topic 5

Volumetric Calculations

5.1 Contents in Brief

- Concentration units in analytical measurements
- Calculations involving dilutions
- Calculations involving titrations

5.2 Introduction

The goal of quantitative analytical measurements is to determine the amount of a chemical substance (the analyte) in a sample. Most often this is expressed as a concentration rather than as a mass or number of moles. This is because most analytical methods are performed on solutions, which are homogeneous and easier to manipulate, and because most analytical methods respond directly to concentration. For this reason it is necessary to become familiar with the various concentration units used. It is also important to understand how these concentrations are affected by dilution in the process of preparing standards or carrying out an analysis. Such calculations are also important for one of the most fundamental types of chemical analysis, the titration.

5.3 Mass Based Concentration Units

Three of several methods are presented here. All weight by weight methods are very similar.

(1) **Percent by weight or parts per hundred.** This method is usually used for concentrated reagents such as sulfuric acid or ammonia. Percent by weight is defined simply as the grams of solute in 100 grams of solution (not solvent). More specifically:

$$\%\ \text{by weight} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% = \frac{m_{solute}}{m_{solution}} \times 100\% \tag{5.1}$$

(2) **Parts per million or ppm.** This method is used for dilute solutions. It is defined simply as the grams of solute in 10^6 g of solution.

$$\text{ppm} = \frac{m_{solute}}{m_{solution}} \times 10^6 \tag{5.2}$$

If the solution is very dilute (often true for such solutions), the density can be taken as 1.00 g/mL or 1000 g/L and 1 L will weigh 1000 g. The definition of ppm then becomes:

$$\text{ppm} \approx \frac{\text{mg of solute}}{\text{L of solution}} = \frac{\mu\text{g of solute}}{\text{mL of solution}} \tag{5.3}$$

NOTE: This definition cannot be used for non-aqueous solutions since such solutions rarely have a density of 1.00 g/mL.

(3) **Parts per billion or ppb.** This method is used for extremely dilute solutions. It is defined according to:

$$\text{ppb} = \frac{m_{solute}}{m_{solution}} \times 10^9 \tag{5.4}$$

For solutions that have a density of approximately 1.000 g/mL:

$$\text{ppb} \approx \frac{\mu\text{g of solute}}{\text{L of solution}} \tag{5.5}$$

Some examples are presented to illustrate these methods of specifying concentration.

Example 5.1: Percent by Weight

If 1.00 g of NaCl is dissolved in 10.0 g of water, what is the % by weight of NaCl in the solution?

$$\%\text{NaCl} = \frac{m_{solute}}{m_{solution}} \times 100\% = \frac{1.00\,\text{g}}{(10.0\,\text{g} + 1.00\,\text{g})} \times 100\% = 9.09\%$$

Example 5.2: Percent by Weight

Reagent sulfuric acid is 96% by weight (96 g H_2SO_4 and 4 g of water per 100 g of solution). Compute the volume of 96.0% H_2SO_4 needed to prepare 1 L of a solution containing 0.250 mol of H_2SO_4 if the density of the reagent is 1.81 g/mL.

Note that many acids, like sulfuric acid, are not available in pure form. The first step, however, is to calculate the mass of pure H_2SO_4 needed.

$$\text{mass of pure } H_2SO_4 = m_{H_2SO_4} = (0.250\,\text{mol}) \times (98.08\,\text{g/mol}) = 24.\overline{5}2\,\text{g}$$

To determine the mass of the concentrated acid solution that we need, we use the wt% of the solution as a conversion factor, since 100 g of solution is equivalent 96 g of H_2SO_4.

$$\text{mass of acid} = m_{acid} = 24.\overline{5}2\,\text{g } H_2SO_4 \times \frac{100.0\,\text{g acid}}{96.0\,\text{g } H_2SO_4} = 25.\overline{5}4\,\text{g acid}$$

In the final step of the calculation, the mass of concentrated sulfuric acid is converted to a volume using the density as a conversion factor.

$$\text{volume of acid} = V_{acid} = \frac{m_{acid}}{d_{acid}} = \frac{25.\overline{5}4\,\text{g}}{1.81\,\text{g} \cdot \text{mL}^{-1}} = 14.1\,\text{mL}$$

Therefore, to prepare the desired solution, one would dilute 14.1 mL of the concentrated acid to 1 L. (Note that dilution of concentrated acids is normally done by adding the acid to water rather than the other way around. Why?)

Example 5.3: Calculations with ppm

What is the concentration of sodium ions in ppm if 4.5 mg of NaCl is dissolved in 1000. g of water?

Note that, when working with weight-by-weight methods, the concentration changes with the species considered. In the present example, while the concentrations of NaCl, Na^+, and Cl^- will be the same in mol/L, they will be different in ppm. First, we need to determine the mass of sodium dissolved using the molar masses as conversion factors

$$\text{mass of sodium dissolved} = 0.0045\,\text{g NaCl} \times \frac{22.990\,\text{g/mol Na}}{58.443\,\text{g/mol NaCl}}$$
$$= 0.001\overline{7}70\,\text{g Na}$$

Now the concentration of sodium in ppm can be calculated.

$$\text{ppm Na} = \frac{m_{solute}}{m_{solution}} \times 10^6 = \frac{0.001\overline{7}70\,\text{g}}{(1000.\,\text{g} + 0.0045\,\text{g})} \times 10^6 = 1.8\,\text{ppm}$$

Note that the mass of the solution is taken as the sum of the mass of the solvent (water) and mass of the NaCl, although the latter makes very little difference in dilute solutions, which is why the approximate definition of ppm is typically used.

Example 5.4: Preparation of a Standard Solution in ppm

How much $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (ferrous ammonium sulfate, MM = 392.16 g/mol) must be weighed out to prepare 250 mL of a 10.0 ppm solution of Fe(II) (MM of Fe = 55.847 g/mol)?

Using the approximation, which should be quite valid in this case, it can be stated that a 10.0 ppm solution contains 10.0 mg/L of Fe(II) (NOT 10.0 mg/L of ferrous ammonium sulfate). Therefore, we can calculate the mass present in 250 mL of solution.

$$\text{mass of Fe in 250 mL} = (10.0\,\text{mg Fe/L}) \times (0.250\,\text{L}) = 2.50\,\text{mg Fe}$$

Based on this, the mass of ferrous ammonium sulfate can be calculated, again using the molar masses to relate to the proportion of Fe(II) in the compound.

$$\text{mass of } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O = 2.50 \text{ mg Fe} \times \frac{392.16 \text{ g } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O}{55.847 \text{ g Fe}}$$
$$= 17.6 \text{ mg } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$$

Therefore, the solution could be prepared by dissolving 17.6 mg of ferrous ammonium sulfate in 250. mL of water.

Example 5.5: Calculations with ppb

A 500. mL aqueous solution contains 5.0 µg of NaCl. What is the concentration of chloride ions in the solution in ppb?

As before, we need to calculate the mass of the species of interest in the solution, which is chloride in this case. We use the molar masses to determine the relative proportions.

$$\text{mass of Cl} = 5.0 \text{ µg NaCl} \times \frac{35.453 \text{ g Cl}}{58.443 \text{ g NaCl}} = 3.033 \text{ µg Cl}$$

The concentration in ppb can now be determined using the approximate definition.

$$\text{ppb Cl} = \frac{3.\overline{0}33 \text{ µg Cl}}{0.500 \text{ L}} = 6.1 \text{ µg/L} = 6.1 \text{ ppb Cl}$$

Note that it is acceptable to refer to this either as “6.1 ppb chlorine” or “6.1 ppb chloride”, although the latter is the form present in solution.

In this class, the “approximate” definitions of ppm (mg/L) and ppb (mg/L) will generally be used unless the density of the solution is significantly different from unity.

5.4 Mole Based Concentration Units

There are several concentration units based on moles of dissolved solute, including molarity, formality, and molality. You are probably already familiar with molarity, but less familiar with formality, although it is often (incorrectly) replaced with molarity. Molality (moles per kg of solvent) is rarely used in analytical chemistry and will not be discussed here.

Formality

Formality is used to differentiate that which is dissolved in solution from that which actually exists in solution at equilibrium. The formality of a solution is the number of moles of a substance added to a liter of solution. This does not consider what happens to that substance after it is in the solution (*i.e.* any reactions that occur). Specifically

$$\text{Formality} = F = \frac{\text{moles of solute } \textit{dissolved}}{\text{liters of solution}} = \frac{\text{mol}}{V} \tag{5.6}$$

The units or dimensions are mol/L, sometimes replaced by "F" or "M" (although "M" is technically not as correct, it is often used since both represent mol/L). Some analytical texts do not use formality (most mention it), but it will be used in this text, especially when discussing acid-base equilibria.

Molarity

Molarity is the number of moles of a substance *actually present* per liter of solution, or

$$\text{Molarity} = M = \frac{\text{moles of solute } \textit{present}}{\text{liters of solution}} = \frac{\text{mol}}{V} \tag{5.7}$$

The units of molarity are mol/L or "M". Unfortunately, these are the same units as formality and often molarity and formality are confused. Remember that formality represents what is placed in solution, molarity represents what actually exists in solution at a given time. The molarity of a material is often represented by its chemical symbol or formula written within square brackets, *e.g.* $[Na^+]$ (this indicates the actual material present in solution). Formalities are *never* written this way.

Example 5.6: Molarity and Formality

If one dissolves 15.0 g of copper(II) nitrate, $Cu(NO_3)_2$ (MM= 187.56 g mol^{-1}), in enough water to form 500. mL of solution, determine the molarities and formalities appropriate for the solution.

First, we determine the number of moles of copper nitrate dissolved.

$$\text{mol } Cu(NO_3)_2 = \frac{15.0\,\text{g } Cu(NO_3)_2}{187.56\ \text{g/mol } Cu(NO_3)_2} = 0.079\overline{9}74\ \text{mol}$$

Knowing the total number of moles and the volume allows us to calculate the concentration of the copper nitrate as a formality.

$$F_{Cu(NO_3)_2} = \frac{0.079\overline{9}74\ \text{mol}}{0.500\ \text{L}} = 0.160\ \text{mol/L} = 0.160\ \text{F} = 0.160\ \text{M}$$

Note that "mol/L", "F", and "M" are all equivalent and can be used as units for formality. Because this is an ionic compound, we expect that it dissociates completely in solution according to:

$$Cu(NO_3)_2 \rightarrow Cu^{2+}(aq) + 2NO_3^-(aq)$$

For this reason, it would be inappropriate to talk about the "molarity" of copper nitrate, since it does not exist in solution. Instead, we refer to the molarity of the individual ions.

$$[Cu^{2+}] = 0.160\ \text{mol/L} = 0.160\ \text{M}$$
$$[NO_3^-] = 0.320\ \text{mol/L} = 0.320\ \text{M}$$

Technically, we could also refer to the formality of these ions, since formality makes reference only to the total concentration, but this would not generally be done unless, for example, the copper ions were present in different forms (*e.g.* complexed and free).

Example 5.7: Molarity and Formality

A 6.005 g sample of pure acetic acid (MM = 60.05 g/mol) is dissolved in water to form 1.000 L of solution. What are the formalities and molarities of all the solution components? Assume that acetic acid ionizes 3.0 % in this solution.

Again, we begin by calculating the moles of solute dissolved and divide this by the volume of solution to get the formality.

$$\text{mol of acetic acid } \textit{dissolved} = \frac{6.005 \text{ g}}{60.05 \text{ g/mol}} = 0.1000 \text{ mol}$$

$$F_{CH_3COOH} = \frac{0.1000 \text{ mol}}{1.000 \text{ L}} = 0.1000 \text{ mol/L} = 0.1000 \text{ F}$$

Because acetic acid is a weak acid, it will react as follows when dissolved in water:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

If 3.0% of the acid ionizes, it can be stated that

$$\text{mol } CH_3COO^- = \text{mol } H_3O^+ = (0.030)(0.1000 \text{ mol}) = 0.0030 \text{ mol}$$

$$\text{mol unionized } CH_3COOH = (0.1000 \text{ mol}) - (0.0030 \text{ mol}) = 0.0970 \text{ mol}$$

Therefore, we have

$$[CH_3COO^-] = [H_3O^+] = \frac{0.0030 \text{ mol}}{1.000 \text{ L}} = 0.0030 \text{ M}$$

$$[CH_3COOH] = \frac{0.0970 \text{ mol}}{1.000 \text{ L}} = 0.0970 \text{ M}$$

Note that none of these concentrations is equal to the formality.

Example 5.8: Molarity and ppm

What is the molarity of a dilute solution (d = 1.00 g/mL) of 0.10 ppm Cu^{2+} (MM = 63.546 g/mol)?

If the solution is dilute, the definition of ppm can be taken as ppm = mg/L. Therefore,

$$0.10 \text{ ppm} = 0.10 \text{ mg/L} = 1.0\times10^{-4} \text{ g/L}$$

To go from g/L to mol/L one needs to calculate the number of moles in $1.0\text{x}10^{-4}$ g.

$$\text{mol } Cu^{2+} = \frac{1.0\times10^{-4} \text{ g}}{63.546 \text{ g mol}^{-1}} = 1.\bar{5}7\times10^{-6} \text{ mol}$$

Thus 0.10 ppm Cu^{2+} = $1.6\text{x}10^{-6}$ M Cu^{2+}.

It should be noted that the conventions regarding molarity and formality are not always correctly followed, just as people do not use correct grammar. For example, it would not be unusual to see a bottle in a laboratory incorrectly labeled as "1 M NaCl" instead of "1 F NaCl". Even in many textbooks, especially general chemistry texts, molarity is often used in place of formality. In many cases, the distinction can be made from the context of the situation, but in studying equilibria the difference is important.

5.5 Calculations Involving Dilution

Often samples subjected to analytical procedures are diluted before analysis, yet the results are needed for the original samples, not the diluted solutions. Also many very dilute solutions are prepared by a technique called serial dilution, since the amounts of solute required are too small to weigh directly. In both cases, calculations involving dilution are required.

The process of dilution involves taking a certain amount of a given solution and adding additional solvent so that the concentration is lowered, as shown in Fig. 5.1. The important thing to remember when performing calculations involving dilutions is that the number of moles of material is the same in the solution both before and after dilution.

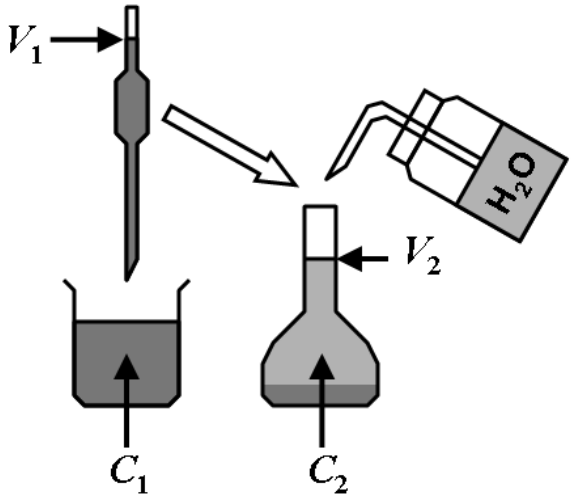


Figure 5.1: A typical dilution procedure. A certain volume, V_1, of the original solution of concentration C_1 is transferred to a second vessel and diluted to a total volume of V_2 with water or other diluent, resulting in a solution with lower concentration, C_2.

Example 5.9: Dilution

A 5.00 mL aliquot of a 0.0400 F solution of HCl is diluted to 100. mL. What is the final concentration of HCl?

Since F = mol/V (by definition), then mol = FV. Also, we know that the number of moles transferred from the first solution is the same as the number of moles in both solutions.

$$\text{mol HCl (in both solutions)} = (0.0400\ \text{mol/L})(0.00500\ \text{L}) = 2.00\times10^{-4}\ \text{mol}$$

$$F_{\text{HCl}}\ \text{(in second solution)} = \frac{\text{mol}}{V} = \frac{2.00\times10^{-4}\ \text{mol}}{0.100\ \text{L}} = 0.00200\ \text{F}$$

Exercise 5.1

What volume of a 1.00 F solution of ammonia (NH_3) is needed to prepare 500. mL of a 0.0250 F solution?

Example 5.10: Dilution

A 10.0 mL sample containing Ca^{2+} is diluted to 50.0 mL before analysis in order to add reagents for the analysis. The concentration of Ca^{2+} in the diluted solution is found to be 0.00354 M. What is the concentration of calcium in the original sample?

The difference in this example is that we are looking for the concentration of the original sample instead of the diluted sample. The principles are the same, however, in that the same number of moles must be present in both solutions.

$$\text{mol } Ca^{2+}\ (\text{in both solutions}) = M_{\text{dil}}V_{\text{dil}} = (0.00354\ \text{mol/L})(0.0500\ \text{L})$$
$$= 1.77\times10^{-4}\ \text{mol}$$

$$[Ca^{2+}]_{\text{orig}} = \frac{1.77\times10^{-4}\ \text{mol}}{0.0100\ \text{L}} = 0.0177\ \text{M}$$

An important principle in these calculations is the fact that the number of moles of the solute remains constant between the original and diluted equation. Since the number of moles is equal to the concentration multiplied by the volume, this leads to the familiar dilution equation.

$$C_1V_1 = C_2V_2 \tag{5.8}$$

In this equation, C_1 and V_1 refer to the concentration and volume of the original solution taken, and C_2 and V_2 refer to the final concentration of the diluted solution, although the symmetry of the equation means that the definitions can be interchanged. The equation is derived with concentrations in mol/L and volumes in L, any unit of volume can be used, as long as it is the same for both sides of the equation. Strictly speaking, the *concentration units must be based on the volume of solution* (*e.g.* molarity or formality), and is not valid with units based on the weight of solution (*e.g.* percent by weight) since the solution density changes. However, *for dilute solutions based on mass* (*e.g.* ppm, ppb), the density changes are so small that the use of Eqn. (5.8) is valid. Finally, it should be noted that, for calculations where molarity is used, the application of the equation will generally not be valid if there is an equilibrium involved, since the dilution also shifts the position of the equilibrium.

Often Eqn. (5.8) is rearranged to express the concentrations in terms of *dilution factors*. These factors are the ratios of the initial volume to the final volume or *vice versa*, depending on whether the final or initial concentration is to be calculated. Thus

$$C_f = C_i \cdot \frac{V_i}{V_f} \tag{5.9}$$

and

$$C_i = C_f \cdot \frac{V_f}{V_i} \tag{5.10}$$

where the subscipt *i* refers to the initial concentration and volume, and *f* refers to the final values. To remember which volume goes in the numerator, recall that the final concentration will always be less than the initial concentration. Thus, when calculating final concentration, the smaller volume generally goes in the numerator of the dilution factor and *vice versa*. In the cases of Examples 5.9 and 5.10 above, application of these equations is as follows.

$$F_{\text{HCl}} = C_i \cdot \frac{V_i}{V_f} = 0.0400\ \text{F} \cdot \frac{5.00\ \text{mL}}{100.\ \text{ML}} = 0.00200\ \text{F}$$

$$[\text{Ca}^{2+}]_i = [\text{Ca}^{2+}]_f \cdot \frac{V_f}{V_i} = 0.00354\ \text{M} \cdot \frac{50.0\ \text{mL}}{10.0\ \text{mL}} = 0.0177\ \text{M}$$

If you are unsure about the use of dilution factors, use the first method involving moles. Although it is longer, it will produce correct results without guessing about which way to set up the ratio of the dilution factor.

5.6 Preparation of Standards by Dilution

A second area in which dilution is often involved is in the preparation of solutions for calibration curves (to be discussed later). An example will best illustrate this type of calculation.

Example 5.11: Preparation of Standards by Dilution

Describe how you would prepare (at least) 50 mL each of solutions containing 0.50, 1.00, 2.00, and 4.00 ppm Pb^{2+} for the calibration curve in a lead analysis, using lead(II) nitrate as your standard.

This is a very common and practical problem in the analytical laboratory, and there is more than one correct approach, as well as others that are not practical. One direct approach is to simply weigh out the correct amount of $Pb(NO_3)_2$ (MM = 331.2 g/mol) for each solution. The most concentrated solution will contain 4.00 mg/L of Pb^{2+} (MM = 207.2 g/mol). If we wanted to make up 50.0 mL of a solution at this concentration of lead, the amount of lead nitrate that we would require would be

$$\text{mass of } Pb(NO_3)_2 \text{ required} = \frac{4.00\ \text{mg } Pb^{2+}}{1\ \text{L}} \times 0.0500\ \text{L} \times \frac{331.2\ \text{g/mol } Pb(NO_3)_2}{207.2\ \text{g/mol } Pb^{2+}}$$

$$= 0.320\ \text{mg } Pb(NO_3)_2$$

Keeping in mind that an ordinary analytical balance has a precision of only about ±0.2 mg, it is clear that such a mass could not be measured with sufficient precision, and this is not a viable approach.

A more accurate and easy approach is to begin with a stock solution with a higher concentration and then perform a series of dilutions. The lowest concentration of stock we could have is 4.00 ppm (the highest concentration we need). However, even if we prepared 1 L of this solution, we would still only need 6.39 mg of lead nitrate, too low to be precisely measured (3% RSD).

The concentration of the stock solution needs to be high enough so that the mass can be measured accurately, but there are also upper limits based on convenience and solubility. If we assume a lower limit of about 100 mg (0.100 g) on the measured mass (*i.e.* 0.2% RSD), a 1 L stock solution of 80.0 ppm Pb^{2+} might be convenient, since it is easily divisible by 4 and gives us the required minimum mass.

$$\text{mass of } Pb(NO_3)_2 \text{ required} = \frac{80.0 \text{ mg } Pb^{2+}}{1 \text{ L}} \times 1.00 \text{ L} \times \frac{331.2 \text{ g/mol } Pb(NO_3)_2}{207.2 \text{ g/mol } Pb^{2+}}$$
$$= 12\overline{7}.9 \text{ mg } Pb(NO_3)_2$$

If this amount of material is dissolved in 1.00 L of water, then the concentration of Pb^{2+} will be 80.0 ppm (80.0 mg/L). This must be diluted by a factor of 20 to make the 4.00 ppm solution desired (80.0 ppm/20 = 4.00 ppm). One way in which this can be accomplished is by diluting 5.00 mL of the 80.0 ppm solution to 100. mL. It could also be done by diluting 25.0 mL to 500. mL - the dilution factor in both cases is 20 (100 mL/5 mL = 500 mL/25 mL = 20).

$$(C_{Pb^{2+}})_f = (C_{Pb^{2+}})_i \cdot \frac{V_i}{V_f} = 80.0 \text{ ppm} \cdot \frac{5.00 \text{ mL}}{100. \text{ mL}} = 4.00 \text{ ppm}$$

Once the stock solution is prepared, the standard solutions can be prepared in a variety of ways. One way is to prepare the 2.00 ppm solution by diluting the 4.00 ppm solution by a factor of two (4.00 ppm/2.00 ppm = 2). This could be

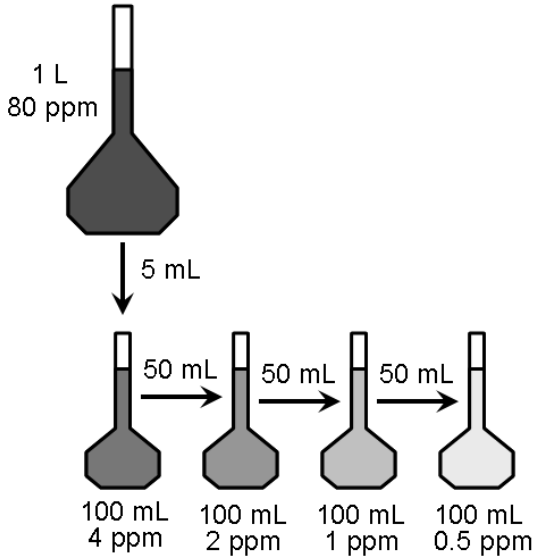


Figure 5.2: One possible scheme for preparing the required set of standard solutions.

achieved by diluting 50.0 mL of the 4.00 ppm solution to 100.0 mL, leaving 50 mL of the 4.00 ppm solution for the calibration curve (assuming it is not needed for any other purpose). Likewise the 1.00 ppm solution can be prepared from the 2.00 ppm solution by a factor of two dilution, and the 0.50 ppm solution can be prepared from the 1.00 ppm solution in a similar fashion. The final result would be 50.0 mL each of 4.00, 2.00, and 1.00 ppm and 100.0 mL of 0.50 ppm for the calibration curve. This dilution sequence is illustrated in Figure 5.2.

Another method could be used if 500.0 mL of the 4.00 ppm solution is prepared (by diluting 25 mL of the stock solution to 500 mL) instead of 100.0 mL. The 2.00 ppm could be prepared in the same fashion (by diluting 50.0 mL of the 4.00 ppm solution to 100.0 mL). However, the 1.00 ppm solution could be prepared from the 4.00 ppm solution using a dilution factor of 4 (dilute 25.0 mL of the 4.00 ppm solution to 100.0 mL). The 0.50 ppm solution could be prepared from the 2.00 ppm solution, also using a dilution factor of 4 (by diluting 25.0 mL of 2.00 ppm to 100.0 mL). The final result would be 425 mL of 4.00 ppm, 75 mL of 2.00 ppm, and 100 mL each of the 1.00 and 0.50 ppm solutions. This sequence is illustrated in Figure 5.3.

This illustrates that there are usually several ways to prepare the same series of serially diluted solutions. The method chosen will depend on several factors including the concentrations desired, the volumes of solutions needed, and the volumetric glassware available. The first scheme explained above would require a 5 mL pipette, a 25 mL (or 50 mL) pipette, and 100 mL volumetric flasks and would provide exactly the amounts of solutions needed. The second scheme would require a 25 mL pipette, one 500 mL and several 100 mL volumetric flasks. It would provide extra solution volumes in case of additional requirements.

There is no general formula that can be applied to such calculations, and each case is unique.

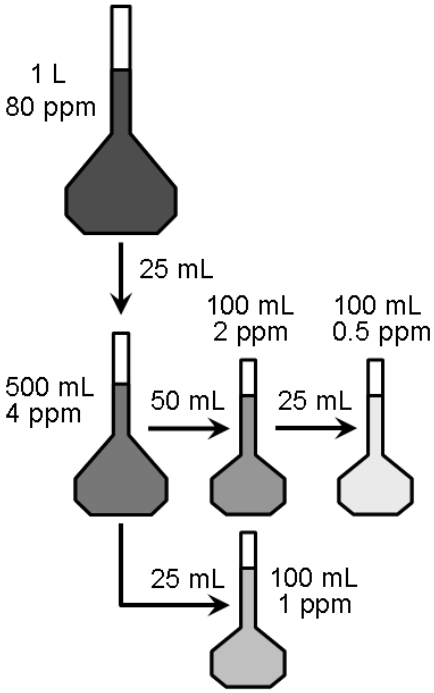


Figure 5.3: An alternative scheme for preparing the required set of standard solutions.

5.7 Quantitative Calculations Involving Titrations

The titration is one of the oldest methods of performing quantitative analyses, yet it is still extremely useful. Titrations have two very important features: they employ very simple and inexpensive "instrumentation", the buret, and they are generally one of the most accurate methods of analysis available. The accuracy often achievable is 0.1% and it can sometimes be extended to 0.01%. However, titrations are usually not capable of trace analysis; that is analysis of components which make up less than 1% of a sample, or components that are less than about 10^{-3} M in solution concentration. Thus, titrations are used for analysis of major sample components or fairly concentrated solutions when high accuracy is required. They are also used when only a few samples need analysis since it is usually easier to set up a titration than a complicated instrumental procedure.

Titrations are nothing more than chemical reactions that are carried out under strictly controlled conditions, with care taken to determine exactly when the reaction is finished. This concept leads to two definitions that should be stressed at this time.

(1) The *equivalence point* is that point in the titration at which exactly enough titrant (the reagent in the buret) has been added to completely consume all the titrand (the reagent in the reaction flask or beaker), "in theory".

(2) The *end point* is that point at which the indicating device or substance signals the equivalence point. It is the point the analyst takes as the equivalence point.

One wants the end point to equal the equivalence point (or else there is an error) and for the present this will be considered to be the case. Titrations will be discussed in general because different types of titrations are very similar.

It is customary to place the reactant whose concentration is known (the standard solution) in the buret, thus making it the *titrant*. The sample which contains the *analyte*, the substance whose concentration is to be determined, is placed in the reaction vessel, making it the *titrand*. This is often (though not always the most convenient way to carry out a titration. In the following discussions T will represent the titrant, U will represent the unknown (the analyte) or titrand, and P_1, P_2, *etc*. will represent the products of the titration reaction.

Direct Titrations

In a direct titration, as shown in Figure 5.4, a known volume or mass of unknown is reacted directly with the titrant. In all titrations the calculations depend on the stoichiometry of the titration reaction; to be specific, the relationship between the moles of T and U in the reaction. The moles of P_1 and P_2 do not enter into the calculation. The following general reaction will be assumed.

$$a\mathrm{T} + b\mathrm{U} \rightarrow c\mathrm{P}_1 + d\mathrm{P}_2 + \ldots$$

At the equivalence point exactly enough T has been added to just react with all the U and there is "no" T or U in the titration flask (assuming that the titration reaction goes completely to the right). Thus, it can be stated that

$$\frac{\text{original mol U}}{\text{mol T added}} = \frac{b}{a} \tag{5.11}$$

Since the moles of U are usually the quantity of interest, this is the quantity to be determined.

$$\text{original mol U} = \frac{b}{a} \cdot (\text{mol T added}) \tag{5.12}$$

Note that the products do not enter the calculation, but that the reaction stoichiometry does through the ratio (*b/a*). Thus one ***must*** have a balanced equation to do such calculations. The moles of titrant are calculated from the formality of the titrant, F_T. This is done using the basic relation between moles, formality, and volume.

$$\text{mol of T added} = (\text{formality}) \times (\text{volume}) = F \cdot V \tag{5.13}$$

Once the moles of the unknown have been determined through Eqn. (5.12) (or a similar calculation), a variety of quantities can be calculated. Because the details of the calculations will vary with the nature of the problem, specific equations will not be given, as they should be derived in each situation rather than memorized. However, some of the quantities that may be calculated are given below.

(1) When the unknown is a solution, the **concentration** of the unknown (M_u or F_u) of the unknown can be determined if the volume of the unknown (V_u) is measured. If the

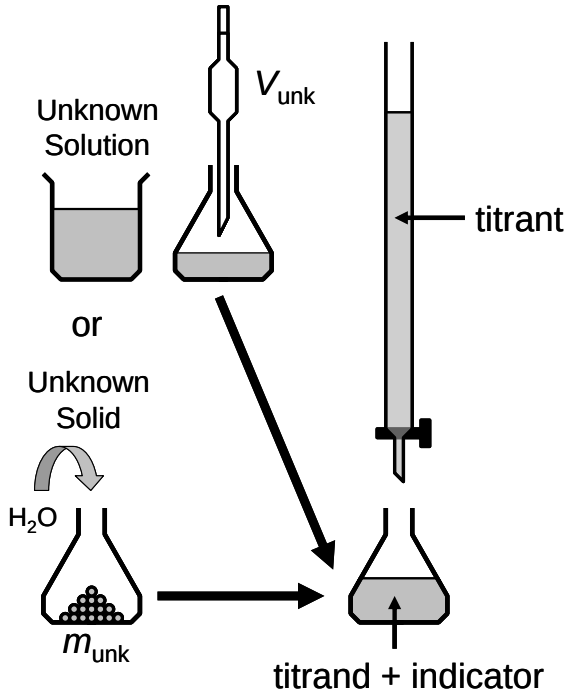


Figure 5.4: Principle of a direct titration. A known volume or mass of the unknown is reacted with a mea-sured volume of a standard solution (titrant) until the endpoint is reached.

chemical formula of the unknown and the density of the solution are available, weight-based concentrations can also be determined.

(2) If the unknown is an *impure* solid which is subsequently dissolved in solution, the **mass** of the analyte can be determined from the number of moles and its chemical formula. For example, an ore sample containing iron is not pure Fe, but the amount of iron present can be determined through titration. If the mass of the unknown sample is also known, the **percent by mass** of the analyte in the sample can also be determined. Note that in this case, the volume of the unknown solution is unimportant.

(3) If the unknown is a *pure* substance dissolved in solution, then its **molar mass** can be determined from the mass and number of moles of the unknown, provided the stoichiometry is available.

Practical Aspects

The calculations outlined above all require the concentration (formality) of the titrant (F_T). to be accurately known. The question arises, how does one know F_T accurately? F_T is usually determined in one of two ways:

(1) Make up the titrant carefully from a primary standard, *e.g.* $K_2Cr_2O_7$.

(2) Make up the titrant from a material the purity of which is less than that of a primary standard, *e.g.* NaOH, and titrate against a primary standard, *e.g.* potassium biphthalate or potassium hydrogen phthalate (KHP – see Figure 5.5). This procedure is called standardization.

This of course raises another question - what is a primary standard? A primary standard is a compound that has the following characteristics:

(1) has an exactly known composition (*e.g.* known waters of hydration),
(2) contains "no" impurities - at least 99.9% pure,
(3) does not react with or take up the components of the atmosphere, *e.g.* CO_2, O_2, or H_2O,
(4) has a form that is easily weighed and transferred (*i.e.* crystalline; not a fine powder).

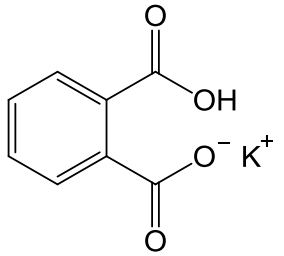


Figure 5.5: Structure of potassium hydrogen phthalate, KHP, a weak acid and primary standard used to standardize solutions of strong bases.

The quantity of primary standard involved in the analysis is determined by a weighing. Thus, the final accuracy in almost all analytical procedures is a function of a weighing. The balance is the most basic analytical tool.

The same equations are used in a standardization titration as in the titration of an unknown. An example will demonstrate this.

Example 5.11: Standardization and Direct Titration

A dilute sulfuric acid solution is standardized by titration with primary standard sodium carbonate, Na_2CO_3. A 0.5032 g sample of dried sodium carbonate requires 44.39 mL of H_2SO_4 solution in the standardization titration. The sulfuric acid is then used to determine the concentration of ammonia, NH_3 in a sample solution. A 50.00 mL aliquot of the sample solution requires 33.68 mL of the sulfuric acid in the titration of the sample. What is the formality of ammonia in the sample?

Since there are no strong acids or strong bases that are primary standards, this is a fairly standard procedure in acid-base titrations and consists of two separate titration steps: (a) standardization of the strong acid or base to determine its concentration, and (b) titration of the unknown with the standardized solution to determine the number of moles of the unknown.

(a) Standardization:

1) Write the balanced chemical equation (always do this).

$$H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$$

2) Substitute the other relations for moles of titrant and titrand.

$$\text{mol } Na_2CO_3 = \frac{m_{Na_2CO_3}}{MM_{Na_2CO_3}} = \frac{0.5032 \text{ g}}{105.99 \text{ g mol}^{-1}} = 0.0047\overline{4}76 \text{ mol}$$

$$\text{mol } H_2SO_4 = \frac{1 \text{ mol } H_2SO_4}{1 \text{ mol } Na_2CO_3} \times (0.0047\overline{4}76 \text{ mol } Na_2CO_3) = 0.0047\overline{4}76 \text{ mol}$$

3) Solve for F_T.

$$F_{H_2SO_4} = \frac{\text{mol } H_2SO_4}{V_{H_2SO_4}} = \frac{0.0047\overline{4}76 \text{ mol}}{0.04439 \text{ L}} = 0.106\overline{9}5 \text{ F}$$

(b) Titration of the sample:

1) Write the balanced chemical equation.

$$H_2SO_4(aq) + 2NH_3(aq) \rightarrow (NH_4)_2SO_4(aq)$$

2) Substitute the other relations for moles.

$$\text{mol } H_2SO_4 = F_{H_2SO_4} V_{H_2SO_4} = (0.106\overline{9}5 \text{ mol L}^{-1})(0.03368 \text{ L}) = 0.0036\overline{2}1 \text{ mol}$$

$$\text{mol } NH_3 = \frac{2 \text{ mol } NH_3}{1 \text{ mol } H_2SO_4} \times (0.0036\overline{2}1 \text{ mol } H_2SO_4) = 0.0072\overline{4}2 \text{ mol}$$

3) Solve for F_U.

$$F_{NH_3} = \frac{\text{mol } NH_3}{V_{NH_3}} = \frac{0.0072\overline{4}2 \text{ mol}}{0.05000 \text{ L}} = 0.1441 \text{ F}$$

It is recommended that the reader not try to memorize all the equations derived earlier, but rather try to solve the problem in a way similar to that presented in the example above.

Exercise 5.2

Titrations can involve reactions other than acid-base reactions. Redox titrations involve oxidation-reduction reactions. Strong oxidizing agents, such as potassium permanganate, $KMnO_4$, are commonly used as titrants in analytical methods. One such method is the determination of hydrogen peroxide, H_2O_2, which is commonly used as a bleaching agent and antiseptic. The reaction with permanganate in acid solution is

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

In the determination of the concentration of hydrogen peroxide in a household antiseptic, a solution of potassium permanganate is first standardized by titration with sodium oxalate, $Na_2C_2O_4$, a primary standard. A 0.2555 g sample of sodium oxalate is dissolved in 100 mL of water and 60 mL of concentrated sulfuric acid and this solution is titrated against a potassium permanganate solution, where the reaction is

$$5\,C_2O_4^{2-} + 2\,MnO_4^- + 16\,H^+ \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

The titration requires 37.31 mL of potassium permanganate solution to reach the end point. To determine the hydrogen peroxide, a 1.1734 g sample of the antiseptic solution is quantitatively transferred to an Erlenmeyer flask where it is diluted with distilled water and sulfuric acid. Titration of this with the standardized permanganate solution requires 17.26 mL to reach the end point. Determine the formality of the potassium permanganate solution and the percent by weight of hydrogen peroxide in the antiseptic.

Back Titrations

Although titrations are a very useful analytical technique, there are some situations where direct titration is not feasible. These include situations where the analyte may not be very soluble, such as calcium hydroxide, $Ca(OH)_2$, or where the titration reaction proceeds slowly. In such situations a *back titration* may be possible. As shown in Figure 5.6, these are titrations in which a *known excess* of a standard material or solution is added to a sample. All of the analyte reacts and some standard remains. The remaining standard is then titrated with a second standard, the titrant. From the known amount of the first standard and the volume and concentration of titrant, the amount or concentration of analyte is calculated. Back titrations are more complicated than simple titrations, involving more manipulations and more standard solutions. Thus, they are used only when a simple titration will not work.

In the following "S" will represent the first standard solution, the one added in excess. All other symbols will retain the same meaning as above.

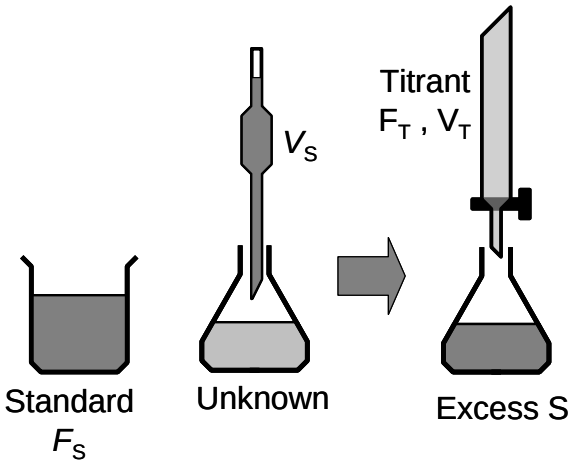


Figure 5.6: Principle of a back-titration. A known number of moles of a standard is first reacted with a known volume or mass of unknown, which is the limiting reagent. Titration of the mixture then allows the determineation of the moles of standard remaining.

(1) Excess standard solution is added to the sample, consuming all U.

$$a\mathrm{S} + b\mathrm{U} \rightarrow \mathrm{P}_1 + \mathrm{P}_2$$

$$\text{mol U} = \frac{b}{a} \cdot (\text{mol of S consumed}) = \frac{b}{a} \cdot (\text{mol of } \mathrm{S}_{\text{Used}}) \tag{5.14}$$

(2) Some S, S_{XS}, remains unused. The S_{XS} is then titrated with T.

$$c\mathrm{T} + d\mathrm{S} \rightarrow \mathrm{P}_3 + \mathrm{P}_4$$

$$\text{mol } \mathrm{S}_{\text{XS}} = \frac{d}{c} \cdot (\text{mol of T at eq. pt.}) \tag{5.15}$$

$$\begin{aligned} \text{Total mol S} = \text{mol } \mathrm{S}_{\text{Tot}} &= \text{mol } \mathrm{S}_{\text{XS}} + \text{mol } \mathrm{S}_{\text{Used}} \\ &= \frac{d}{c} \cdot (\text{mol T}) + \frac{a}{b} \cdot (\text{mol U}) \end{aligned} \tag{5.16}$$

(3) Solve equation (5.16) for the moles of U.

$$\text{mol U} = \left[\text{mol } \mathrm{S}_{\text{Tot}} - \frac{d}{c} \cdot (\text{mol T}) \right] \cdot \frac{b}{a} \tag{5.17}$$

In the final equation, the total moles of S can be determined from its mass or concentration (= $F_S V_S$). One can proceed as was done before to obtain expressions for the mass of U, F_U or %U. An example is presented to illustrate the concept of a back titration.

Example 5.12: Back Titration

A 0.9824 g sample containing $CaCO_3$, a material insoluble in pure water, is dissolved in 100.0 mL of 0.1106 F HCl (an excess) and boiled to expel the CO_2 formed. The remaining HCl is titrated with 0.1058 F NaOH, requiring 21.23 mL to reach the end point. Calculate the percent $CaCO_3$ in the sample.

In this example T is NaOH, S is HCl, and U is $CaCO_3$.

1) Write a balanced equation for the reaction of S with U and establish the stoichiometric ratio.

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O$

2) Write a balanced equation for the reaction of T with the excess S and establish the stoichiometric ratio.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

3) Use the expression for the total moles of HCl added to solve for the moles of U, and finally the %U.

$$(\text{mol HCl})_{\text{Tot}} = F_{\text{HCl}}V_{\text{HCl}} = (0.1106\ \text{mol/L})(0.1000\ \text{L}) = 0.01106\ \text{mol}$$

$$(\text{mol HCl})_{\text{XS}} = \frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}} \times (\text{mol NaOH}) = \frac{1}{1} \times F_{\text{NaOH}}V_{\text{NaOH}}$$
$$= (0.1058\ \text{mol/L})(0.02123\ \text{L}) = 0.002246\ \text{mol}$$

$$(\text{mol HCl})_{\text{Used}} = (\text{mol HCl})_{\text{Tot}} - (\text{mol HCl})_{\text{XS}}$$
$$= (0.01106\ \text{mol}) - (0.002246\ \text{mol})$$
$$= 0.008814\ \text{mol}$$

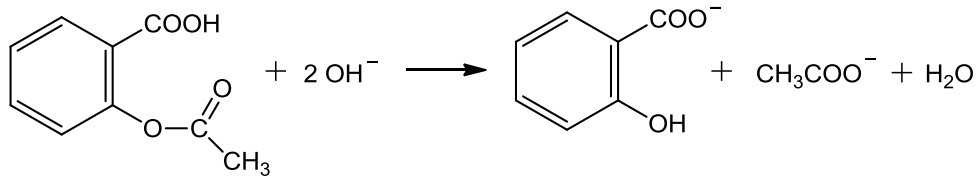
$$\text{mol } CaCO_3 = \frac{1\ \text{mol } CaCO_3}{2\ \text{mol HCl}} \times (\text{mol HCl})_{\text{Used}} = \frac{1}{2} \times (0.008814\ \text{mol})$$
$$= 0.004407\ \text{mol}$$

$$\text{mass of } CaCO_3 = (\text{mol } CaCO_3) \times MM_{CaCO_3}$$
$$= (0.004407\ \text{mol})(100.09\ \text{g/mol}) = 0.4411\ \text{g}$$

$$\%CaCO_3 = \frac{\text{mass of } CaCO_3}{\text{mass of sample}} \times 100\% = \frac{0.4411\ \text{g}}{0.9824\ \text{g}} \times 100\% = 44.9\%$$

Exercise 5.3

Aspirin, or acetylsalicylic acid (ASA), will react with strong base in two steps, the first neutralizing the carboxylic acid group and the second resulting in hydrolysis of the ester. The net reaction is as given below.



ASA

Unfortunately, the rate of the second step is too slow to allow the direct titration of ASA with a strong base. Instead, a back titration of the excess base must be used. In the determination of the amount of ASA in an over-the-counter analgesic tablet, the tablet is first crushed and then dissolved in and reacted with 50.0 mL of 0.09854 F NaOH at an elevated temperature to speed up the reaction. The excess hydroxide is then titrated with 0.1011 F HCl, requiring 13.82 mL to reach the endpoint. How many milligrams of ASA are in the tablet?

5.8 Summary

Concentrations in chemistry can be expressed in a variety of units, such as molarity, formality, percent by weight and parts per million. It is important to know how to use these concentration units and perform the calculations necessary to convert between them. Dilution of solutions is a common operation in chemistry, and familiarity with these calculations is essential. Calculations involving stoichiometry, especially related to titrations, are also important.

5.9 Additional Exercises

Exercise 5.4

You are preparing dilutions of a stock Zn(II) solution using a buret and volumetric flasks. If the concentration of the stock Zn(II) solution is (0.01271±0.00003) M and if you deliver 15.38 mL of stock solution from the buret into a 100 mL volumetric flask, what will be the concentration of Zn(II) in the flask and its absolute standard deviation? Assume that the standard deviation of reading a buret is ±0.02 mL and of filling a 100 mL volumetric flask is ±0.03 mL, and remember that the volume delivered from the buret is the result of two readings, each ±0.02 mL.

Exercise 5.5

Calculate the volume of glacial acetic acid (100%) needed to prepare 500.0 mL of a 0.250 F solution. The density of the reagent is 1.05 g/mL.

Exercise 5.6

Concentrated reagent ammonia is 57.6% by wt. NH_3 and has a density of 0.90 g/mL. What is the formality of ammonia in a solution prepared by addition of 10.0 mL of the concentrated reagent to distilled water followed by dilution to 2.000 L? If only 3.0% of the ammonia reacts to form NH_4^+ and OH^-, what is the molarity of the ammonia in the solution?

Exercise 5.7

Calculate the formality of H_2SO_4 in the concentrated reagent acid if the percent by weight of H_2SO_4 is 96.0% and the density is 1.81 g/mL.

Exercise 5.8

A certain acid (MM = 100. g/mol) is 70.0% by wt. and has a density of 1.69 g/mL. You wish to prepare 2.00 L of a 0.100 F solution of this acid. If you were preparing the solution by weight, how much reagent acid would you need to weigh out? If you were preparing it by volume, what volume of reagent acid would you need?

Exercise 5.9

The upper allowable limit for the concentration of Pb(II) in drinking water is 5.0 ppb. What is this in mol/L?

Exercise 5.10

A 10.0 mL sample of tap water is added to a 25.0 mL volumetric flask, 10 mL of a special buffer is added, and distilled water is used to dilute to the mark. This solution is analyzed and found to contain 2.36×10^{-6} M fluoride. What is the concentration of fluoride in tap water in both mol/L and ppm?

Exercise 5.11

What mass of KI must be weighed out to prepare 500. mL of 10.0 ppm I^- solution (you may use the simple definition of ppm)?

Exercise 5.12

What will be the expected precision of the concentration calculated in the previous problem above if the standard deviation of weighing is ±0.1 mg (remember that a single mass is the result of two weighings), and of using a 500 mL volumetric flask is ±0.05 mL? Assume that the molar masses are accurate.

Exercise 5.13

What mass of KI would have to be weighed out to prepare the same solution as above (500 mL of 10.0 ppm I^-), if the original salt were dissolved in 100. mL of water and 10.0 mL of that solution were diluted to 500. mL?

Exercise 5.14

What would be the expected precision (abs. std. dev.) in the concentration of the solution prepared in the previous problem? In addition to the data given earlier above, assume that the precision of using a 10 mL pipet is ±0.01 mL and that of filling a 100 mL volumetric flask is ±0.02 mL.

Exercise 5.15

Dilute solutions (in the low ppm and the ppb range) cannot be stored for any period of time because adsorption on the walls of the storage container changes the component concentrations. Thus many stock solutions are made up at the 1000 ppm concentration level. What mass of lithium bromide would have to be weighed out to prepare 1.00 L of a 1000 ppm stock solution of Li (use the simple definition of ppm)? If one were to prepare 1.00 L of a 1.00 ppb solution of Li directly by weighing lithium bromide, what mass of the salt would have to be weighed out? If 1.00 L of a 1.00 ppb Li solution were to be prepared by diluting 1.00 mL of the 1000 ppm stock solution to 1.00 L followed by diluting 1.00 mL of this solution to 1.00 L, what would be the expected absolute precision of the final concentration? Assume one can weight to ±0.2 mg, can fill a 1 L volumetric flask to ±0.1 mL, and can use a 1 mL pipet with ±0.02 mL precision. What procedure establishes the overall precision of the final concentration?

Exercise 5.16

A solution of NaOH is standardized by titrating 0.786 g of KHP. The titration requires 37.8 mL. A 0.429 g sample of a pure monoprotic acid is titrated with the same base, requiring 31.7 mL. What is the molecular mass of the monoprotic acid?

Exercise 5.17

Concentrated reagent grade ammonia is reported to be 14.8 F. However, it can lose strength rapidly if not tightly stoppered and should always be checked if needed for exact work. To check a bottle of ammonia, HCl is first standardized against primary standard Na_2CO_3. A 0.2500 g sample of the standard requires 40.00 mL of HCl. A 10.00 mL aliquot of the conc. NH_3 is diluted to 1.000 L. 25.00 mL of the diluted ammonia require 26.39 mL of the HCl for titration. What is the formality of the conc. reagent NH_3?

Exercise 5.18

The acetic acid in a vinegar sample is determined as follows. A solution of NaOH is first standardized by titrating a 0.8323 g sample of KHP. The standardization requires 43.34 mL.

A 2.272 g sample of vinegar is diluted to 50.00 mL and titrated with the NaOH solution, requiring 39.87 mL. Calculate the percentage by weight of acetic acid in the vinegar sample.

Exercise 5.19

A solution of HCl is standardized by titration against 0.277 g of primary standard Na_2CO_3. The titration requires 43.4 mL of HCl. A solid sample weighing 0.183 g and containing sodium oxide is dissolved in water ($Na_2O + H_2O \rightarrow 2\ NaOH$) and titrated with HCl, requiring 47.3 mL. What is the percentage of Na_2O in the sample?

Exercise 5.20

The percentage of $CaCO_3$ in a 1.000 g sample was determined by adding 100.0 mL of 0.1000 F HCl (an excess) to dissolve the sample.

$$CaCO_3(s) + 2\ H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

The solution was boiled to drive off all the CO_2 and the remaining HCl was titrated with 0.1000 F NaOH, requiring 25.00 mL. Calculate the percentage of $CaCO_3$ in the sample.

Exercise 5.21

The hydrochloric acid concentration in a solution is determined by titration with NaOH. A 50.00 mL aliquot of the sample requires 27.31 mL of NaOH solution. The NaOH is standardized against oxalic acid ($H_2C_2O_4$). A 0.4000 g sample of the acid requires 38.77 mL of NaOH (the acid is diprotic). What is the formality of the HCl in the sample? If a 50 mL pipet can be used with a precision of ±0.03 mL, a balance with ±0.2 mg, and a buret with ±0.02 mL, what is the expected absolute precision of the formality? Remember that each mass is the result of two weighings and each volume from a buret is the result of two readings.

5.10 Answers to Exercises 5

5.1 12.5 mL

5.2 0.02044 F, 2.557%

5.3 318.0 mg

5.4 $(1.955 \pm 0.006) \times 10^{-3}$ M

5.5 7.15 mL

5.6 0.15_2 F, 0.14_8 M

5.7 17.7 mol/L

5.8 28.6 g, 16.9 mL

5.9 2.4×10^{-8} M

5.10 5.90×10^{-6} M, 0.112 ppm

5.11 6.5 mg

5.12 $\pm 0.2_2$ ppm

5.13 65.4 mg

5.14 0.02_4 ppm

5.15 12.51 g, 12.51 μg, ±0.03 ppb, the use of the 1.00 mL pipet

5.16 133 g/mol

5.17 12.45 F

5.18 9.910%

5.19 96.5%

5.20 37.5%

5.21 0.1252 F, ±0.0002 F ($\pm 0.0001_{95}$ F)

Topic 6

Introduction to Instrumental Methods

6.1 Contents in Brief

- Linear and nonlinear instrumental response
- Instrument calibration curves
- Figures of merit and limits of detection

6.2 Introduction

Modern analytical chemistry is dominated by the use of instruments such as spectrophotometers, chromatographs, and mass spectrometers. This was not always the case, and the early days of chemical analysis relied on so-called "wet" chemical methods (titration, precipitation, spot tests, *etc.*) for qualitative and quantitative analysis. Although some of these techniques are still used, the introduction of the pH meter and spectrophotometer around 1940 revolutionized analytical chemistry, and instrumental methods are now used for most analytical measurements.

There are a wide variety of instrumental methods making use of many different chemical and physical phenomena. All of these diverse methods have many features in common when it comes to converting their output to a chemical concentration. Therefore, these will be presented here in a general discussion.

6.3 Instrumental Response

In any instrumental method, the instrument measures some chemical or physical property of a sample, such as the amount of light absorbed by a solution containing the analyte, and converts the measurement to a numerical value that relates to the property measured. Figure 6.1 illustrates this process. For example, if a solution absorbs light, the value reported might be the percentage of light transmitted by the sample. The numerical value might be presented as a meter reading on the instrument or reported on a computer screen, or it might be determined from the characteristics of a signal, such as a peak height or area. Regardless of its origins, this value will be referred to as the *instrument response*. The analyst usually has the task of converting this response to the concentration of the analyte of interest.

To convert an instrument response into concentration, the analyst must know the relationship between that response and concentration. Most instruments provide responses that are linear in concentration, although some notable exceptions exist. This chapter will focus on responses that are linear or can be made linear, but much of what is said here can also be applied to other types of instrumental responses.

Linear Instrumental Response

If it is known that an instrumental method provides a response linear in concentration, the following equation applies,

$$R = B + S \cdot C \tag{6.1}$$

where R is the instrument response (the numerical value presented by the instrument), *e.g.* the absorbance of a coloured solution, B is the background, S is the sensitivity, and C is the concentration of analyte.

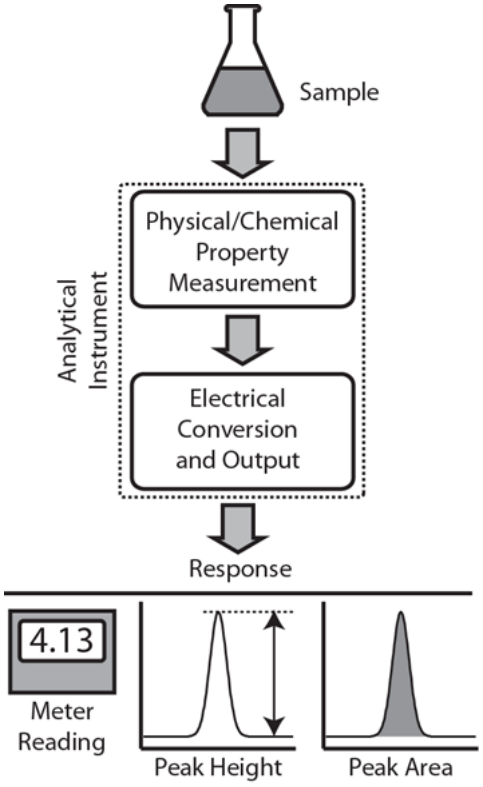


Figure 6.1: Instrumental response for a chemical sample. The analytical instrument converts a property of the sample into an electrical signal (voltage, current) which is then translated into a response such as a meter reading, peak height or peak area.

The background, *B*, is the response of the instrument when the no analyte is present in the sample (*C*=0). One might expect that, if the sample contains no analyte, then the instrument response would be zero. This will be true if there is no background or the background has been removed by instrumental adjustments, but is not always the case. Non-zero background can arise from the instrument itself or from the sample. For example, if light absorption by an analyte is measured, other compounds present may also absorb light at a fixed level, giving rise to a background absorption. Some instruments are provided with controls for "zeroing" the background using a *blank* sample (one with no analyte). In the case where the background is zero or can be properly cancelled, Eqn. (6.1) simplifies to

$$R = S \cdot C \tag{6.2}$$

The sensitivity, *S*, is the slope of the response curve. As sensitivity increases the slope also increases and, often, the ability to measure smaller concentrations of analyte also increases. Much research in modern instrumental analysis is involved with extending limits of analysis to lower and lower concentrations.

A typical linear response curve is shown in Figure 6.2. This plot shows the relationship between the measured response (*y*-axis) and concentration (*x*-axis). This relationship is at the heart of all instrumental analytical measurements, which rely on the indirect measurement of a physical property to estimate chemical concentrations. Much of the emphasis in this class is on understanding the basis of this relationship for various analytical methods, and on the practical application of this model.

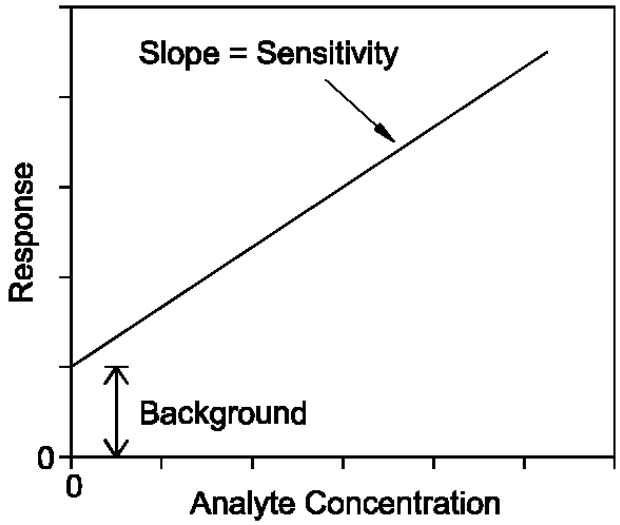


Figure 6.2: Typical linear response curve for an analytical instrument. The linear relationship between the response and the concentration allows the concentration to be indirectly determined.

Linear Transformations

As already noted, some analytical methods do not give a response that is directly linear in concentration; however, it may be possible to apply a mathematical transformation that leads to a linear relationship. In such cases, a function of the measured response can be plotted against a function of the concentration to give the straight line relationship shown in Figure 6.2. An example will illustrate such a case.

Example 6.1: Linear Transformation

In the measurement of light absorption, the following relationship is observed.

$$I = I_o \cdot e^{-kC}$$

Here, I is the intensity of light passing through a sample, I_o is a constant representing the intensity of light passing through a sample with no analyte, k is a constant, and C is the concentration of analyte. Is it possible to transform this into a linear relationship and, if so, what is the transformation?

Since the relationship is contains an exponential term in concentration, an obvious approach is to take the natural logarithm of both sides of the equation.

$$\ln(I) = \ln(I_o) - kC$$

Recall that the equation for a straight line is $y = a + bx$, where a is the intercept and b is the slope. Therefore, a plot of $\ln(I)$ as y versus C as x will give a straight line with an intercept of $\ln(I_o)$ and a slope of $-k$. Alternative forms are also possible. For example, negating both sides gives

$$-\ln(I) = -\ln(I_o) + kC$$

so a plot of $-\ln(I)$ *vs.* C will give a line with a positive slope.

Exercise 6.1

Suppose that each of the following relationships is observed in a particular analytical method. In each case, first determine if a linear transformation is possible that will result in a function that is linear when plotted with C as the x-axis. If so, what quantity would be used for y and what would be the slope and the intercept. In each equation, R, represents a measured response, C is the analyte concentration, and the k's are constants.

(a) $R = k_1 \cdot C^2$ (b) $R = k_1 + k_2 C^2$ (c) $R = k_1 + k_2 C + k_3 C^2$

Exercise 6.2

Suppose that a particular instrument exhibits a response that obeys the following relationship.

$$R = k_1 + k_2 \ln\left(\frac{C^2}{2}\right)$$

Will a plot of *R vs.* $\log_{10}(C)$ be linear? If so, what will be the slope and the intercept?

Deviations from Linearity

Almost all linear instrumental methods of analysis have a specific concentration range over which linearity is observed. This range, which is sometimes referred to as the *linear dynamic range*, may be as small as one order of magnitude in concentration, or it may extend to more than six orders of magnitude. There are many reasons why nonlinearity might occur in techniques that should ideally be linear, but these will be discussed later.

Usually the instrument response is linear at low concentrations and deviates from linearity as concentration increases. If the deviation from linearity appears as a decrease in slope (the curve bends toward the concentration axis), the deviation is said to be negative. If the deviation appears as an increase in slope, it is called positive. These deviations are illustrated in Figure 6.3. Negative deviations are more commonly observed.

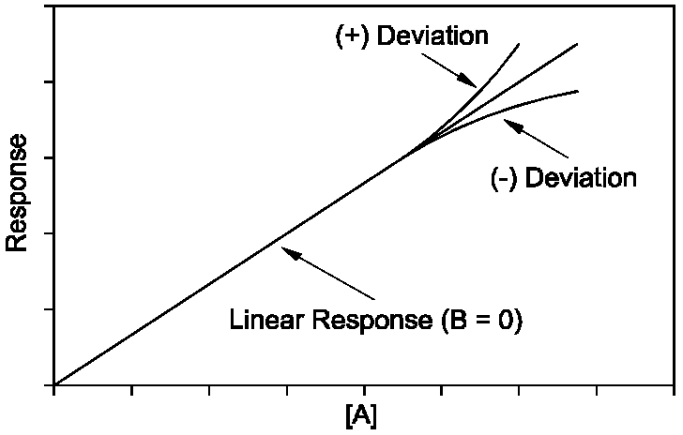


Figure 6.3: Analytical response curve showing deviations from linearity. Such deviations normally occur at high concentrations and may be positive (increased slope) or negative (decreased slope). Negative deviations are more commony observed.

Exercise 6.3

The following data are obtained in the measurement of fluorescence intensity as a function of analyte concentration over a wide range.

Concentration (μM)	1.00	3.00	10.0	50.0	100.	300.
Fluorescence Intensity	20.1	21.0	24.2	41.4	60.8	119.4

Does the relationship between the response and concentration suggest deviations from linearity? If so, are these positive or negative?

A question that is sometimes raised is why analytical chemists, and scientists in general, seem to be preoccupied with establishing linear relationships. There are several reasons for this. The first is quite practical: straight lines are simple and easier to fit than nonlinear relationships. A second reason is that, while there is only one way to fit a straight line, there are many equations that can be applied to a curve and it is more difficult to determine which one is correct unless there is some underlying physical model. Finally, curves are more difficult to use when it comes to the inverse relationship, *i.e.* predicting concentration from the response, which is the ultimate goal of the analyst.

6.4 Relating Response to Concentration

From an analytical perspective, obtaining an instrument response is of no use unless it can be used to accurately predict analyte concentration. This is often more complicated than it might first appear, depending on the nature of the analyte and the sample. Thus, there are several different methods commonly used to relate response to concentration. In most cases, these methods are based on the linear relationship described in Eqn. (6.1).

$$R = B + S \cdot C \tag{6.1}$$

To solve for the concentration of the analyte in some unknown solution, C_{unk}, Eqn. (6.1) is rearranged to

$$C_{\text{unk}} = \frac{R_{\text{unk}} - B}{S} \tag{6.3}$$

where R_{unk} is the measured response for the unknown. Although solution of Eqn. (6.3) is straightforward, it requires that we know the values of the background, B, and sensitivity, S, in other words, the intercept and slope of the linear relationship. The procedure for determining these is known as *calibration*. In general, calibration refers to a process where one quantity, response in this case, is related to another quantity, which is the concentration of the analyte. Most of the time, calibration is performed using one or more samples in which the analyte concentrations are known. These are referred to as *standards*. There are a variety of methods commonly used to perform calibration, and these are described here.

Absolute Calibration

In certain cases, the values of *B* and *S* may be known based on some fundamental principles, in which case they may be substituted directly into Eqn. (6.3) to solve for the concentration of the analyte directly. This will be referred to as *absolute calibration*, although there are actually no calibration standards involved. An example will illustrate this.

Example 6.2: Absolute Calibration

In absorbance spectroscopy, the following relationship is assumed to hold.

$$-\log(I) = -\log(I_o) + \varepsilon bC$$

where I is the intensity of light passing through the sample, I_o is the intensity of light incident on the sample container (cuvette), ε is a constant called the molar absorptivity, b is the width of the cuvette in cm, and C is the concentration of the analyte in mol/L. For a given analyte and experimental set up, it is found that a solution of analyte of unknown concentration gives an intensity reading of 30.2 when the incident intensity is 65.7 in a cuvette with a width (path length) of 0.500 cm. The molar absorptivity of the analyte is known to be 3.64×10^3 M^{-1} cm^{-1}. What is the concentration of analyte in the unknown?

Relating the equation given to Eqn. (6.1), it is clear that

$$R_{unk} = -\log(I) = -\log(30.2) = 1.48\overline{0}0$$
$$B = -\log(I_o) = -\log(65.7) = 1.81\overline{7}6$$
$$S = \varepsilon b = (36\overline{4}0\ M^{-1}\ cm^{-1})(0.500\ cm) = 18\overline{2}0\ M^{-1}$$

Substituting these into Eqn. (6.3) leads to

$$C_{unk} = \frac{R_{unk} - B}{S} = \frac{-1.48\overline{0}0 - (-1.81\overline{7}6)}{18\overline{2}0\ M^{-1}} = \frac{0.33\overline{7}6}{18\overline{2}0\ M^{-1}} = 1.85 \times 10^{-4}\ M$$

Exercise 6.4

In absolute potentiometry, to be discussed later, a fundamental relationship can be established between the measured potential of the electrochemical cell, E, the standard cell potential, E^o, and the analyte concentration. For a copper metal electrode in an electrochemical cell with Cu^{2+} ions in solution, this relationship is

$$E = E^o + \frac{RT}{zF}\ln[Cu^{2+}]$$

where R is the gas constant (8.3145 J $mol^{-1}K^{-1}$), T is the absolute temperature, F is Faraday's constant (96485 C mol^{-1}), z is the charge on the ion, and $[Cu^{2+}]$ is the concentration of Cu^{2+} in M. For this cell, E^o is 0.095 V and an unknown solution containing Cu^{2+} ions gives a reading of 0.032 V at a temperature of 25 °C. What is the concentration of copper in the unknown solution?

Although straightforward in its application and it does not require the use of standard solutions, *absolute calibration is almost never used in practice*. The main reason for this is that, even though the linear relationship may be valid, reliable values for B and S are rarely available from the fundamental principles, either because they involve quantities that are difficult to measure or because deviations from theory make them inaccurate. For this reason, other calibration methods are normally used.

One-Point Calibration

In some instrumental measurements, the background contribution to the signal, B, can either be assumed to be zero or, more commonly, is removed by making adjustments to the instrument while measuring a blank solution (one that contains no analyte). If this is the case, then Eqn. (6.3) reduces to

$$C_{unk} = \frac{R_{unk}}{S} \qquad (6.4)$$

In this case, only one parameter, *S*, needs to be known to solve for the concentration. It is possible to estimate this parameter by measuring the response for one standard solution, providing that the background for that solution is also zero. An example will illustrate this.

Example 6.3: One-Point Calibration

Polarography is an instrumental technique in which the current flowing through an electrochemical cell is measured. This current is linearly related to the concentration of material undergoing reaction in the cell. The cell current measured for a solution containing 1.00 ppm Pb^{2+} is 0.0282 µA. The cell current, measured in the same manner for an unknown, is 0.0426 µA. What is the concentration of Pb^{2+} in the unknown?

Again, since the instrument response (current) is linear in concentration (assuming that the background is zero),

$$R_{std} = S \cdot C_{std}$$

or $$S = \frac{R_{std}}{C_{std}} = \frac{0.0282\ \mu A}{1.00\ ppm} = 0.0282\ \mu A \cdot ppm^{-1}$$

so $$C_{unk} = \frac{R_{unk}}{S} = \frac{0.0426\ \mu A}{0.0282\ \mu A \cdot ppm^{-1}} = 1.51\ ppm$$

An alternative way to do this calculation that avoids the direct calculation of the sensitivity (slope) is as follows.

$$\frac{R_u}{R_s} = \frac{S \cdot C_u}{S \cdot C_s} = \frac{C_u}{C_s} \quad \text{or} \quad C_u = \frac{R_u}{R_s} C_s = \frac{0.0426\ \mu A}{0.0282\ \mu A} \times 1.00\ ppm = 1.51\ ppm$$

Either of these methods may be used in this class.

Exercise 6.5

Because of the expense, pennies are no longer made in Canada, but even when they were, they were only copper-plated. A penny weighing 2.321 g is dissolved in acid, which converts the copper to Cu^{2+}. A 50 mL aliquot of ammonia solution is added, forming an intense blue complex. Distilled water is added to bring the total volume of the solution to 200. mL. The absorbance of this solution, A_{unk} is measured as 0.423 (see figure). A standard solution containing 0.0100 M of the copper-ammonia complex has an absorbance, A_{std}, of 0.523. What is the percentage by mass of copper in the penny. Assume absorbance is linearly related to concentration and the background is zero.

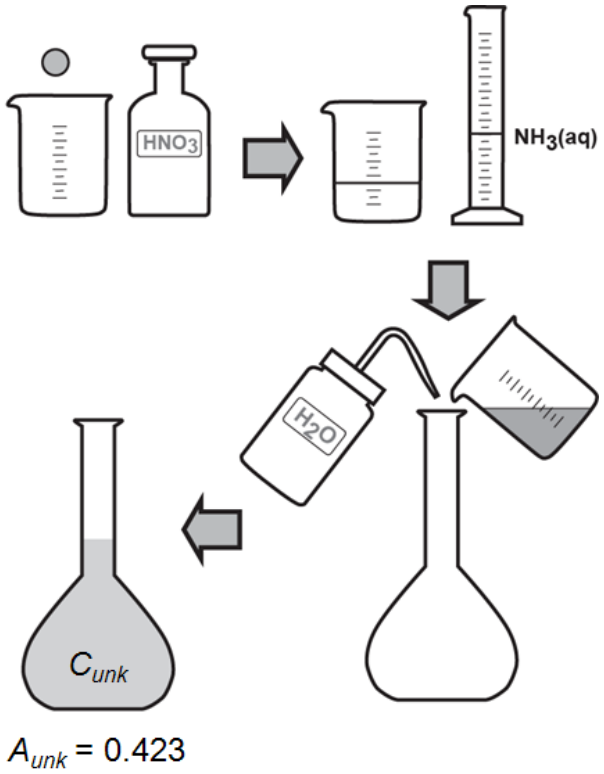


Figure 6.4: Illustration of analytical procedure used in Exercise 6.5.

Note that one does not have to understand either spectrophotometry (the measurement of light intensity) or polarography to solve the above problems. All one needs to know is that instrument response is linear in concentration. However, one should never use an instrumental method without understanding the fundamentals behind it.

The one-point calibration method has the advantages of being simple and requiring only one standard. It is much more reliable than the absolute method in that the sensitivity is determined experimentally and relies only on the assumption of linearity and zero background, so it can account for non-idealities that may cause deviations from theoretical values of the sensitivity. However, because only one standard is used, it is less accurate than other methods and prone to errors if the assumptions of linearity and zero background are violated. Also, in some cases, it may not be possible to set the background to zero using a blank. For these reasons, other calibration methods are usually preferred when more accurate results are required.

Two-Point Calibration

Equation (6.1) has two unknown parameters, the background and the sensitivity. If the background cannot be assumed to be zero, then the determination of these parameters requires a minimum of two standard solutions (two equations for two unknowns). This is the principle behind the two-point calibration method, as shown in Figure 6.5, where two standards are

used to solve for *B* and *S*. The assumption of linearity is still retained. Ideally, the two standards should bracket the concentration of the unknown, and one of the standards may be a blank (zero analyte concentration), but this is not required. An example will illustrate this concept.

Example 6.4: Two-Point Calibration

A detector in chromatography (a technique to be discussed later) gives a signal that is linear with the concentration of toluene ($C_6H_5CH_3$) in water. Standard solutions with concentrations of 10.0 ppm and 50.0 ppm toluene give measurements of 213 and 768, respectively. An unknown gives a reading of 529. What is the concentration of toluene in the unknown in ppm? In moles per liter?

We can write Eqn. (6.1) in terms of the two measurements.

$$R_1 = B + S \cdot C_1 \qquad R_2 = B + S \cdot C_2$$

Here we will use R_1 = 213, C_1 = 10 ppm, R_2 = 768, and C_2 = 50 ppm. To solve for the sensitivity (slope), *S*, we can subtract R_1 from R_2 to eliminate *B*.

$$R_2 - R_1 = (B + S \cdot C_2) - (B + S \cdot C_1) = S(C_2 - C_1)$$

$$S = \frac{R_2 - R_1}{C_2 - C_1} = \frac{768 - 213}{50.0\,\text{ppm} - 10.0\,\text{ppm}} = \frac{555}{40.0\,\text{ppm}} = 13.\overline{8}75\ \text{ppm}^{-1}$$

We can now substitute this quantity back into either equation for the standards and we can get the intercept. The 10 ppm standard will be used here.

$$B = R_1 - SC_1 = 213 - (13.\overline{8}75\ \text{ppm}^{-1})(10.0\ \text{ppm}) = 213 - 13\overline{8}.75 = 7\overline{4}.25$$

These values can now be used to determine the concentration in the unknown.

$$C_u = \frac{R_u - B}{S} = \frac{529 - 7\overline{4}.25}{13.\overline{8}75\ \text{ppm}^{-1}} = \frac{45\overline{4}.75}{13.\overline{8}75\ \text{ppm}^{-1}} = 32.8\ \text{ppm}$$

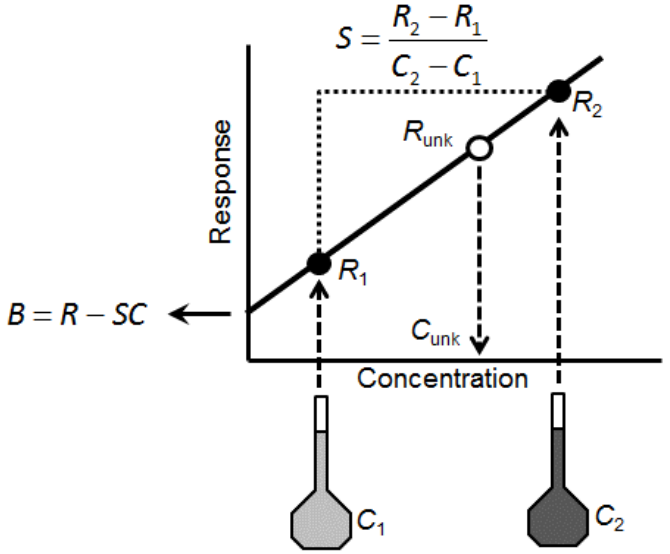


Figure 6.5: Principle of two-point calibration. Note that the two calibration standards define the slope and intercept of the calibration line.

The final step is to calculate the molarity of the toluene solution. Because the solution is quite dilute, we will use the definition that 1 ppm = 1 μg/mL = 1 mg/L. The conversion is then as follows.

$$C_u = \frac{32.8\ \text{mg}}{1\ \text{L}} \times \frac{1\ \text{g}}{1000\ \text{mg}} \times \frac{1\ \text{mol}\ C_7H_8}{92.141\ \text{g}} = 3.56 \times 10^{-4}\ \text{mol/L} = 3.56 \times 10^{-4}\ \text{M}$$

Exercise 6.6

Quinine is a drug used to treat malaria, but it is also used as a flavour ingredient in tonic water. Quinine can be determined by fluorescence spectroscopy in acidic solutions. Fluorescence measurements are linear in concentration at low concentrations. A standard solution of 0.400 μg/mL quinine in 0.1 F H_2SO_4 is found to give a fluorescence reading of 181. A 25.0 mL aliquot of this standard is then diluted to 50.0 mL with 0.1 F H_2SO_4, and this solution gives a fluorescence reading of 95. A 1.00 mL sample of tonic water diluted to 250. mL with 0.1 F H_2SO_4 gives a reading of 153. What is the concentration of quinine in the tonic water? (See Figure 6.6 for a visualization of these operations.)

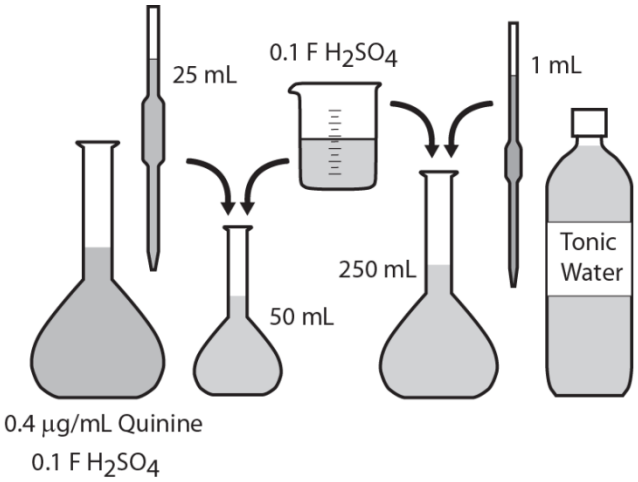


Figure 6.6: Illustration of volumetric operations in Exercise 6.6.

The two-point calibration method is generally superior to the one-point calibration in that an additional standard is used and a zero background is not assumed. However, like the one-point method, it is rarely used in practice. The principle reason for this is that it relies on the assumption of linearity, which cannot be confirmed with only two points, since any two points will define a straight line. In addition, errors in the measurement of either of the two measurements can significantly change the slope of the calibration curve. These principles are illustrated in Figure 6.7.

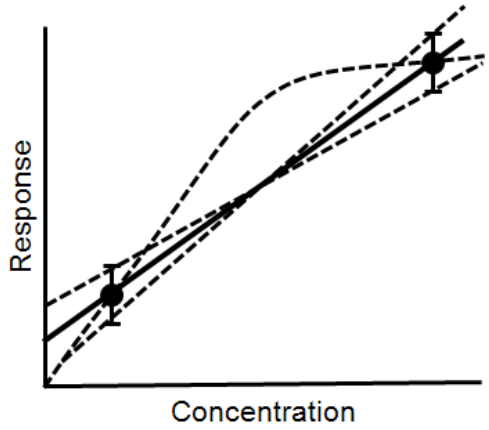


Figure 6.7: Two-point calibration is susceptible to errors in the measurements and nonlinearities.

Multipoint Calibration

Multipoint calibration refers to any calibration method that makes use of more than two standard solutions. These methods are graphical techniques in which the instrument response (or some function of it) is plotted against the concentration (or some transformation of the concentration, such as the logarithm). The resulting graph is referred to as a *calibration curve*. This is somewhat of a misnomer because it is generally assumed that the underlying function is a straight line, although this is not strictly required. When linearity is assumed, the parameters for the slope (S) and intercept (B) are usually obtained by linear least squares (linear regression), but the graph should always be drawn to ensure linearity is obeyed and that there are no outliers that deviate significantly from the line. Multipoint calibration is the most widely used technique in instrumental analytical methods. There are several advantages to this approach, as given below.

(1) The use of multiple standards improves the reliability of the estimates of the slope and intercept. The more solutions that are used, the more accurate these values become.
(2) The plot of the calibration curve allows the linearity of the method to be visually confirmed. Outliers in the data can also be readily identified.
(3) Deviations of the measurements around the fitted line allow the measurement uncertainty to be assessed. This is useful in determining the precision of the method and the limit of detection (to be discussed later).
(4) In cases where linearity is not observed, the calibration curve can still be used to predict unknown concentrations by fitting another equation or visually interpolating a smooth curve through the data.

To prepare a calibration curve, one prepares a series of standard solutions (typically five to ten) and measures their response. These standards are usually evenly spaced along the x-axis, although this is not required, and may include a blank solution. The response of the unknown solution is then measured and the parameters of the calibration curve are used to calculate its concentration. This is illustrated with the example below.

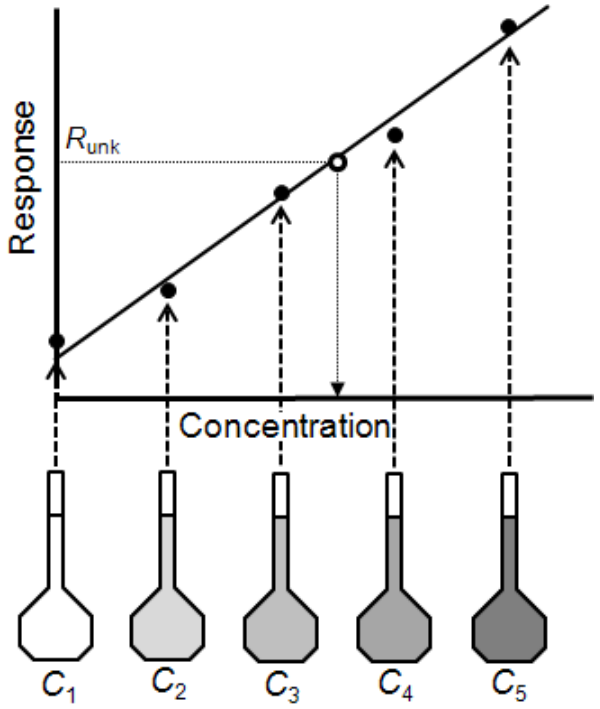


Figure 6.8: Principle of multipoint calibration. Note that the calibration points generally do not fall exactly on the line due to measurement errors.

Example 6.5: Multipoint Calibration

An analyst prepared a set of standards containing a colour-forming reagent and various concentrations of Fe(II). The instrument response (absorbance) for these solutions was measured with a spectrophotometer (an instrument that measures light intensity) and the following results were obtained:

Concentration (μM)	0.00	20.0	40.0	60.0	80.0	100.0
Absorbance	0.017	0.193	0.408	0.561	0.769	0.957

An unknown solution, treated in the same way with the colour-forming reagent, gives a measurement of 0.634. What is the concentration of Fe(II) in the unknown?

The first step is to plot the calibration curve as shown as Figure 6.9. Note that the plot shows the fitted line, as determined below. It is important that when you plot the data that you *do not connect the dots*. Because of measurement errors, the data will not generally fall exactly on a straight line. In this case, we have a calibration curve that is practically ideal. No deviations from linearity are observed, all of the points fall close to the line, and the intercept is close to zero.

The next step is to determine the intercept and slope. Although this can be done by visually drawing the best line through the data, the standard method is to use linear least squares as discussed in the earlier topic on linear regression. If any outliers are observed, they should be removed before this calculation is done. In this case, the numbers are exactly the same as those used in the first example in the regression chapter, so the slope and intercept have already been calculated.

slope = $S = 0.00940\ \mu M^{-1}$

intercept = $B = 0.014$

Based on these values, the unknown concentration can now be determined.

$$[\text{Fe(II)}]_u = \frac{R_u - B}{S} = \frac{0.634 - 0.014}{0.00940\ \mu M^{-1}} = 66.0\ \mu M$$

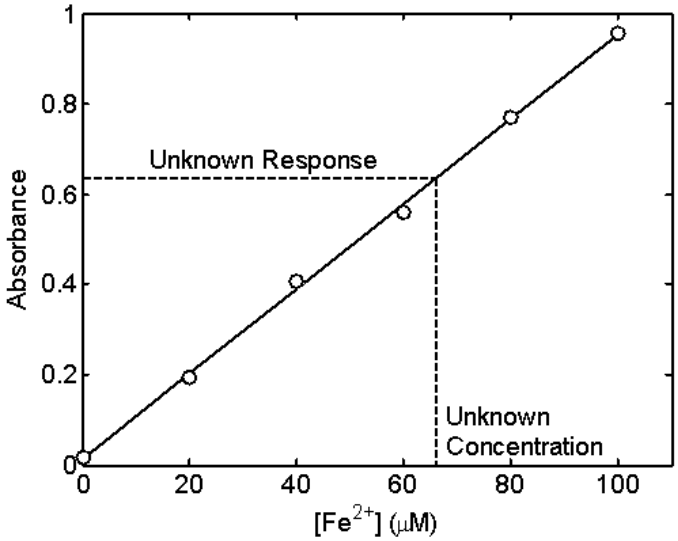


Figure 6.9: Calibration curve for the data in Example 6.5. The line drawn is the best fit line from linear least squares.

Exercise 6.7

In flame atomic emission spectroscopy, the intensity of light at a particular wavelength is linearly related to the concentration of a metal ion in solution. In the determination of lithium by this method the following calibration data were obtained.

[Li^+] (ppm)	1.00	2.00	3.00	5.00	7.00
Intensity	0.161	0.255	0.426	0.708	0.949

An unknown solution containing lithium gives a reading of 0.389. Determine the slope and intercept of the calibration curve and the concentration of lithium ion in the unknown. For convenience the calibration graph has been included as Figure 6.10 to assess linearity and outliers.

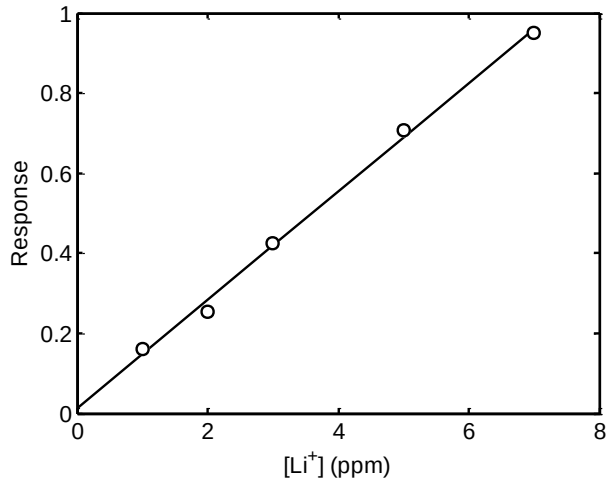


Figure 6.10: Calibration curve for data in Exercise 6.7.

Exercise 6.8

A device called a calcium ion selective electrode can be used to measure calcium in aqueous solution. This device exhibits a linear relationship between the measured potential and the logarithm of the concentration. The following measurements were obtained for six calibration solutions prepared in a special buffer.

[Ca^{2+}] (M)	1.0×10^{-8}	1.0×10^{-7}	1.0×10^{-6}	1.0×10^{-5}	1.0×10^{-4}	1.0×10^{-3}
Potential (mV)	−171	−164	−131	−105	−73	−49

A 2.00 mL sample of blood plasma is diluted to 100. mL with the same buffer solution gives a reading of −84 mV. Determine the slope and intercept of the calibration curve and the concentration of Ca^{2+} in the blood plasma. For convenience the calibration graph has been included as Figure 6.11 to assess linearity and outliers.

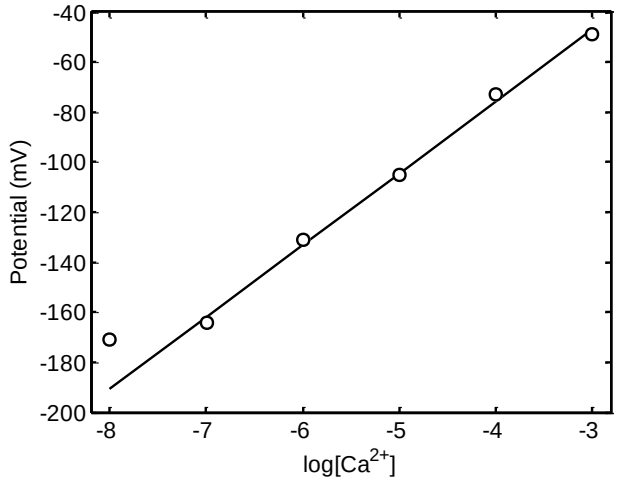


Figure 6.11: Calibration curve for data in Exercise 6.8.

6.5 Sensitivity, Selectivity and Detection Limits

One of the goals of research in analytical chemistry is to develop instruments and sensors that can detect the lowest amount of material possible in increasingly complex samples. This is driven by the need to be able to determine the concentrations of compounds that have an impact even at very low concentrations, such as toxic metals or pesticides in food or soil, or steroids, drugs, or carcinogens in biological fluids. Thus, when choosing an analytical method, it is important to consider the characteristics of the instrument employed and whether or not it is suited to the problem to be solved. It is natural to ask questions such as "what is the lowest concentration that can be detected by this method?" and "are there substances present that are likely to affect my determination of the analyte?". To address these questions, analytical methods are often characterized by *figures of merit* that summarize their capabilities. Some of these figures of merit are discussed in this section.

Analytical chemists often compare methods in terms of their *sensitivity*. In saying that one instrument is more sensitive than another, one normally means that it can detect lower levels of analyte. Although this usage of "sensitivity" is common and will be employed in this class, it is not very precise in describing how much analyte can be detected and there is some ambiguity in its usage. The formal definition of sensitivity is simply the slope of the calibration curve, typically expressed in units of response value per unit concentration, such as μA/ppm. However, such a definition is not very useful when comparing methods which have different units of response. Moreover, the magnitude of the response, and hence the sensitivity, can often be increased by electronic amplification of the signal, but this does not necessarily improve the quality of the measurement. By analogy, if a radio signal has poor reception, tuning up the volume does not normally make it easier to hear the content, since the level of static also increases. Therefore, we need a more precise means of quantifying the amount of analyte that a method can detect.

The amount of information contained in a measurement, or signal, is closely related to the level of measurement error, or *noise*. All measurements contain noise, which is a random variation from the true value. Noise can arise from characteristic variations in the instrument itself, such as fluctuations in the intensity of a light source, and from other aspects of the method, such as the preparation of sample or standards, that lead to errors in the observed

measurement. The noise is characterized by the standard deviation in the response for replicated samples. An important indicator of the information content is the *signal-to-noise ratio* (*S/N*), which is simply the ratio of the instrument response to its standard deviation (*i.e.* the inverse of the relative standard deviation).

$$S/N = \frac{\bar{R} - \bar{B}}{s_R} \tag{6.5}$$

Here, $\bar{R}$ represents the average response for a particular sample, $\bar{B}$ is the average background signal, and s_R is the standard deviation in the response. Often, an average response is not available and a single measurement is used with the assumption that the noise (standard deviation) is the same for all measurements. A higher signal-to-noise ratio means that there is more information in the measurement. Put another way, when the *S/N* becomes too low, the measurement becomes indistinguishable from the noise and contains no information. At that point, we are unable to quantify the analyte. However, we need to be able to express this in a more useful way.

A common way to express the capabilities of an instrument or method is in terms of its *limit of detection* (LOD), or simply *detection limit*. A variety of definitions have been proposed for the detection limit, but in this class the LOD for a method is defined as the level of the analyte (normally expressed as a concentration or amount) at which the measurement (response, signal) has a magnitude three times that of the baseline noise (*i.e.* the standard deviation of the measurement when there is no analyte present). In other words, it is the concentration where the *S/N* equals three. This is illustrated in Figure 6.12, which shows 100 measurements of a response at the detection limit surrounded on each side by 100 measurements at the background (blank) level. The solid lines indicate the true measurements, while the points indicate the measurements contaminated with noise. With this definition of the LOD, there is only a 0.14% probability that a sample with no analyte would give a signal above the detection limit (assuming a normal distribution). This means that the probability of a *false positive*, *i.e.* concluding that the analyte is present when it is not, is very low. On the other hand, if the analyte is present at the detection limit, it will be classified as not detected (*false negative*) 50% of the time. The probability of a false negative decreases rapidly as the concentration of the analyte becomes higher, however.

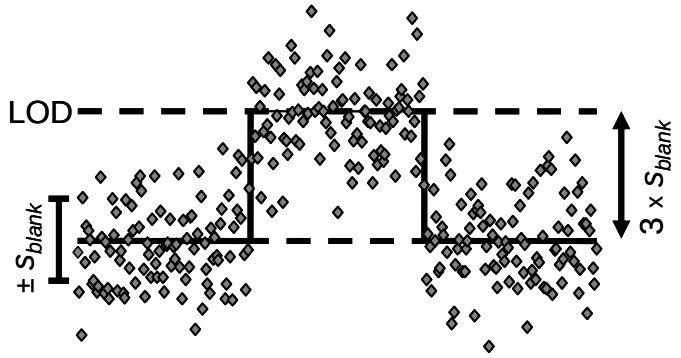


Figure 6.12: Illustration of the concept of the limit of detection (LOD). The measurements in the center result from a concentration at the detection limit, while those at the edges are from the baseline.

To be useful, the LOD needs to be expressed in terms of a concentration and not a response, which means it is related to the slope of the linear relationship, or sensitivity. This is illustrated in Figure 6.13, where the limit of detection is shown to be the concentration corresponding to a response three standard deviations above the blank. Note that the signal background does not affect the LOD. Expressed mathematically, this gives

$$\text{LOD} = \frac{3 \cdot s_{\text{blank}}}{S} \tag{6.6}$$

where S represents the sensitivity (slope of the calibration curve) and s_{blank} is the standard deviation of the blank measurement. Often, as illustrated in Figure 6.13, it is assumed that the standard deviations of the analyte responses are the same as for the blank, especially near the limit of detection, so these values can be used instead. Moreover, if a calibration curve is made using a multipoint approach, the standard deviation does not need to be measured directly, but instead can be estimated directly from the sum-of-squared residuals (SSR) of the linear regression. Thus, the standard deviation in the measurements is given by

$$s_y = \sqrt{\frac{SSR}{N-2}} = \sqrt{\frac{\sum (y - \hat{y})^2}{N-2}} \tag{6.7}$$

In this equation, y is the measured response, $\hat{y}$ is the response calculated from the regression equation, N is the number of calibration points, and the summation is over all of the calibration measurements. The degrees of freedom is (N–2) to account for the estimation of the slope and the intercept. Based on this, the LOD can be estimated as

$$\text{LOD} = \frac{3 \cdot s_y}{S} \tag{6.8}$$

Note that this equation applies to any linear multipoint calibration where concentration appears on the x-axis. It should be noted that the LOD refers to the concentration in the final solution and does not take into account any dilutions of the original sample that are carried out as part of the overall method, so the limit of detection for the method as a whole may be higher. Because standard deviations are usually not estimated to more than one significant digit, limits of detection are also normally given with this precision.

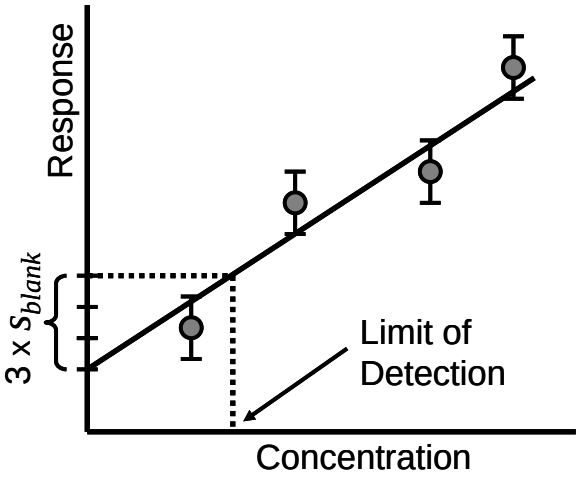


Figure 6.13: Relationship between the standard deviation of the blank signal and the limit of detection from the calibration curve.

A figure of merit related to the LOD is the *limit of quantitation* (LOQ). While the LOD gives a concentration at which the analyte might reasonably be detected, the *S/N* at that level is only 3, corresponding to a relative standard deviation of 33%. Such a high RSD would lead to a poor concentration estimate, so a higher level of signal is generally needed for a reasonably precise estimate of the concentration. This is normally taken as the level at which the *S/N* is ten (10% RSD), leading to a definition similar to the LOD.

$$\mathrm{LOQ} = \frac{10 \cdot s_{\mathrm{blank}}}{S} = \frac{10 \cdot s_y}{S} = \frac{10}{3}\mathrm{LOD} \tag{6.9}$$

The same comments that applied to the LOD also apply to the LOQ.

Another important consideration in an analytical method is the presence of *interferences*. An interference is a substance that produces a measurement above the background under the same conditions under which the analyte is measured. Since real samples are complex mixtures of many substances, it is not uncommon for one or more of these substances to have similar chemical properties to the analyte and respond to the measurement in a similar fashion. The *selectivity* of an analytical method is a measure of the relative magnitudes of the signals from the analyte and interference under the same conditions. The selectivity is defined for each potential interference as the ratio of the analyte response to the interference response at the same concentration, or simply as the ratio of the two sensitivities. If the response of analyte "*a*" is R_a at concentration C_a and the response of interference "*i*" is R_i at concentration C_i, then the selectivity for analyte "*a*" over interference "*i*" is therefore given by

$$\mathrm{SEL}_i = \frac{S_a}{S_i} = \frac{R_a - B_a}{R_i - B_i} \cdot \frac{C_i}{C_a} \tag{6.10}$$

where the *B*'s represent the background measurements, if present. The higher the selectivity, the easier it will be to determine the analyte in the presence of the interferent, although the concentration of the interferent is also a factor. If a potential interferent produces no signal, the selectivity is infinite and the presence of that substance can be ignored. If this is true for all substances that could potentially interfere, then the method is said to be *specific* for the analyte.

Example 6.6: Figures of Merit

A polarographic method is used for the determination of zinc. A solution with a 0.0500 mM concentration of Zn^{2+} gives a reading of 0.295 ±0.002 μA. A solution containing 1.00 mM Cd^{2+}, a potential interferent gives a reading of 0.112 ±0.003 μA under the same conditions. The background measurement is 0.027 μA in both cases. Determine (a) the sensitivity for zinc, (b) the S/N for cadmium, (c) the limits of detection and quantitation for zinc, and (d) the selectivity of the method for zinc over cadmium.

(a) Assuming a linear response, the sensitivity for zinc is given by

$$S_{Zn} = \frac{R_{Zn} - B_{Zn}}{C_{Zn}} = \frac{0.295\,\mu A - 0.027\,\mu A}{0.0500\ mM} = 5.36\ \mu A\,mM^{-1}$$

(b) Assuming that the uncertainty given represents one standard deviation,

$$S/N = \frac{R_{Cd} - B_{Cd}}{s_{Cd}} = \frac{0.112\,\mu A - 0.027\,\mu A}{0.003\,\mu A} = \bar{2}8$$

(c) To determine the LOD and LOQ, we will assume that the blank uncertainty is similar to the measurement uncertainty for zinc. Therefore, we can write

$$LOD_{Zn} = \frac{3 \cdot s_{Zn}}{S_{Zn}} = \frac{3(0.002\,\mu A)}{5.36\,\mu A\,mM^{-1}} = 0.00\bar{1}1\ mM$$

$$LOQ_{Zn} = \frac{10 \cdot s_{Zn}}{S_{Zn}} = \frac{10(0.002\,\mu A)}{5.36\,\mu A\,mM^{-1}} = 0.00\bar{3}7\ mM$$

(d) The selectivity can be determined by using the sensitivities directly or from the measurement information given.

$$SEL_{Cd} = \frac{S_{Zn}}{S_{Cd}} = \frac{R_{Zn} - B_{Zn}}{R_{Cd} - B_{Cd}} \times \frac{C_{Cd}}{C_{Zn}} = \frac{(0.295 - 0.027)\ \mu A}{(0.112 - 0.027)\ \mu A} \times \frac{1.00\,mM}{0.0500\ mM} = 63.1$$

■

Example 6.7: Limit of Detection

From the calibration data given in Exercise 6.7 for the determination of lithium, determine the limit of detection for lithium.

The original data given are:

$[Li^+]$ (ppm)	1.00	2.00	3.00	5.00	7.00
Intensity	0.161	0.255	0.426	0.708	0.949

Based on these data, a linear least squares fit gives the following parameters:

Slope = 0.1352 ppm^{-1} Intercept = 0.0132

Using these values and the concentrations as *x*, the calculated intensities and the residuals can be obtained, as shown in the table below.

x	1.00	2.00	3.00	5.00	7.00
y	0.161	0.255	0.426	0.708	0.949
$\hat{y}$	0.1484	0.2836	0.4188	0.6892	0.9596
$y-\hat{y}$	0.0126	–0.0286	0.0072	0.0188	–0.0106

Now the sum of squared residuals can be calculated and used to estimate the measurement standard deviation.

$$SSR = (0.01\overline{2}6)^2 + (-0.02\overline{8}6)^2 + (0.00\overline{7}2)^2 + (0.01\overline{8}8)^2 + (-0.01\overline{0}6)^2 = 0.001\overline{4}94$$

$$s_y = \sqrt{\frac{SSR}{N-2}} = \sqrt{\frac{0.001\overline{4}94}{3}} = 0.02\overline{2}3$$

From this, the LOD can be calculated using the sensitivity, which is the slope.

$$\text{LOD} = \frac{3 \cdot s_y}{S} = \frac{3(0.02\overline{2}3)}{0.1352\ \text{ppm}^{-1}} = 0.49\ \text{ppm}\ \text{ or }\ 0.5\ \text{ppm}$$

Exercise 6.9

Using the data in Example 6.5, calculate the limit of detection (LOD) and limit of quantitation (LOQ) for Fe(II) using the calibration data provided.

Exercise 6.10

Is it possible to calculate a limit of detection (LOD) for calcium from the data provided in Exercise 6.8? If not, why not? If so, what is it?

6.6 Summary

Many analytical methods are based on the indirect measurement of concentration through an instrumental response that follows a linear behaviour. Usually the linear relationship needs to be determined through calibration, which can be performed using one, two or multiple calibration standards. For one-point calibration, a zero intercept is assumed and the calibration standard is used to determine the slope, or sensitivity. In two-point calibration, both the slope and intercept can be determined. The multipoint calibration curve, in conjunction with linear regression, is the most widely used method in analytical chemistry because it is the most precise and confirms the linearity of the relationship. Analytical methods are normally characterized using standard figures of merit, such as sensitivity, limit of detection and selectivity. Linear regression parameters from multipoint calibration can be used to calculate some of these parameters.

6.7 Additional Exercises

Exercise 6.11

A 25.0 mL aliquot of a colour-forming reagent are added to 25.0 mL of a sample containing iron and the sample is placed in an instrument capable of measuring the amount of light absorbed (a spectrophotometer). The absorbance (the instrument response), which is linearly related to concentration, is given by the instrument as 0.493. The sensitivity (which will be shown later to be a combination of a constant called the molar absorptivity and the distance the light travels through the sample) is found to be 9754 L/mol from a handbook. What is the concentration of iron in the unknown? Assume that the background is zero.

Exercise 6.12

Flame photometry is a technique in which the light given off by metal atoms in a flame is measured. The light intensity is usually linear in the concentration of atoms in the flame and thus also linear in the concentration of the metal ions aspirated into the flame. The flame photometer reading from a sample containing no Li was adjusted to zero. When a 1.00 ppm Li solution was aspirated, the reading was 139.0 and when an unknown was aspirated, the reading was 34.2. What is the concentration of lithium in the unknown?

Exercise 6.13

Irv Gratch, a former student of analytical chemistry, decides to establish a commercial analysis laboratory. He fails to obtain a government grant and has to buy an inexpensive flame photometer without a zero adjustment. When he aspirates a sample containing no Li into his instrument, the reading produced is 13.6. A 2.00 ppm lithium solution and an unknown read 47.6 and 61.9, respectively. What should Irv report (assuming constant background) as the concentration of Li in the unknown?

Exercise 6.14

In fluorescence, the light emitted by a molecule is linear in concentration at low concentrations. The amount of quinine in tonic water is determined by fluorescence as follows. A fluorometer is set to zero with distilled water. A 5.0×10^{-6} M solution of pure quinine sulfate in distilled water reads 78.6 on the instrument. A sample of tonic water reads 69.5 on the instrument. A 20.0 mL sample of the tonic water is then treated with 5.0 mL of a reagent that destroys the quinine but does not change any other physical or chemical property of the solution. This solution reads 11.8 in the fluorometer. Assuming a linear response and constant sensitivity, what is the concentration of quinine in the original sample?

Exercise 6.15

Sodium is often determined by flame photometry. A flame photometer is zeroed with distilled water and the following readings taken with standard solutions.

$[Na^+]$ (ppm)	5.00	10.00	15.00	20.00	25.00
Response	43.4	78.6	104.0	121.0	132.9

What is the concentration of sodium in a river water sample that reads 115.0?

Exercise 6.16

Cu(II) is naturally coloured and the colour intensity is increased in the presence of a large excess of NH_3. The following copper standards were prepared in 1 M NH_3 and their absorbance measured in a spectrophotometer.

[Cu(II)] (M)	1.00×10^{-3}	2.00×10^{-3}	3.00×10^{-3}	4.00×10^{-3}
Absorbance	0.158	0.320	0.475	0.638

1.00 mL of 10 M NH_3 is placed in a 10.0 mL volumetric flask and diluted to the mark with an unknown. This solution (after mixing) produces an absorbance of 0.385. What is the concentration of Cu(II) in the original unknown?

Exercise 6.17
Estimate the limit of detection for copper from the calibration curve in the previous exercise.

Exercise 6.18
Stripping voltammetry is a trace electrochemical technique in which the current is linearly proportional to concentration. A solution of 1.00×10^{-7} M Pb(II) gave a current of 0.139 μA (after baseline subtraction). If the baseline noise is found to be 0.0036 μA, what is the detection limit for the determination of Pb(II) and what is the limit for reasonable quantification?

6.8 Answers to Exercises 6

6.1 (a) yes, $y = \sqrt{R}$, slope $= \sqrt{k_1}$, intercept = 0

(b) yes, if k_1 can be independently measured, $y = \sqrt{R - k_1}$, slope $= \sqrt{k_2}$, int. $= 0$

(c) no

6.2 yes, slope = 2 (2.303) k_2 , intercept = $k_1 - k_2 \ln 2$

6.3 yes, negative

6.4 $\bar{7}.4 \times 10^{-3}$ M

6.5 4.43%

6.6 84 μg/mL

6.7 $S = 0.135_2$ ppm^{-1}, $B = 0.013_2$, $[Li^+]_u = 2.78$ ppm

6.8 slope = 28.8 mV, intercept = 39.6 mV, $[Ca^{2+}]_{blood} = 2.6 \times 10^{-3}$ M

6.9 $\bar{4}.2$ μM, $\bar{1}4$ μM

6.10 No, it is not possible because the of the logarithmic concentration axis.

6.11 1.01×10^{-4} M

6.12 0.246 ppm

6.13 2.84 ppm

6.14 3.5×10^{-6} M

6.15 17.9 ppm

6.16 2.69×10^{-3} M

6.17 $\bar{4}.5 \times 10^{-5}$ M

6.18 7.8×10^{-9} M, 2.6×10^{-8} M

Topic 7

Standard Addition and Internal Standards

7.1 Contents in Brief

- Matrix effects in instrumental analysis
- Two-point standard addition methods
- Multipoint standard addition methods
- Internal standard methods

7.2 Introduction

The instrumental analysis of "real world" samples often involves complex mixtures such as blood, urine, or food that contain many chemical components. While standard calibration methods such as those previously discussed work well for laboratory standards and simple unknowns, the presence other constituents in real samples often leads to inaccuracies. In the discussion that follows, some common methods to correct for these problems in the calibration process are described.

7.3 Matrix Effects

The *matrix* of a sample is simply the background of all the chemical constituents in which the analyte exists. For instance, if we wish to determine the concentration of calcium in blood plasma, the matrix would consist of all of the other components present (proteins, sugars, salts, etc.). A *matrix effect* is a change in the instrumental response for the analyte caused by the presence of other components in the sample. For example, in the determination of magnesium in sea water, it is found that the instrumental response for magnesium ion (as magnesium chloride) in distilled water is not the same as for magnesium ion in sea water. In this case, sea water is the matrix in which the analyte is present and the change in response is mainly due to the presence of high concentrations of sodium, chloride, and sulfate ions. Thus, if the sensitivity (slope of the calibration curve) for magnesium is measured with standards prepared from magnesium chloride in distilled water, accurate results for magnesium might be obtained in measurements on rain water, but inaccurate results will be obtained on sea water samples, where the calibration curve is no longer valid.

As indicated in Figure 7.1, the sample matrix may affect the background (the intercept of the calibration curve), the sensitivity (the slope of the curve), or both. Matrix effects that change the background are often the most difficult to correct. Several measures can often be used to overcome matrix effects that change the sensitivity. Depending on the instrumental method, matrix effects may arise from changes in the chemical environment (*e.g.* the presence of other ions or compounds that change the form of the analyte) or physical properties (*e.g.* viscosity). In many methods of analysis, matrix effects can cause large errors and therefore techniques for dealing with them must be considered. Some of the more useful methods are listed below.

(1) *Matrix matching*. If the matrix is known and reasonably constant, chemical components that simulate the matrix can be added to all of the standards used to prepare the calibration curve. All measurements will then be made under the same conditions (with the same matrix). This method is effective for situations where the components of the matrix are simple and well known (*e.g.* sea water), but not so if the matrix is more complex (*e.g.* blood plasma) or likely to vary from sample to sample.

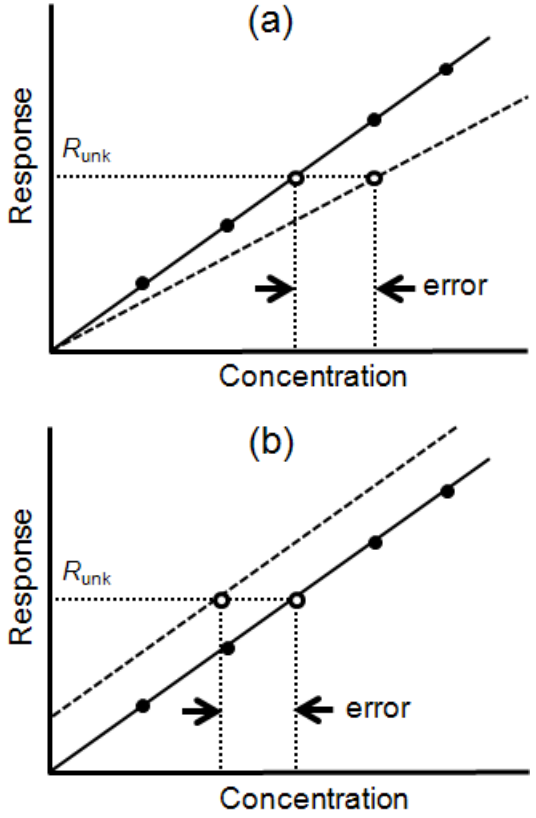


Figure 7.1: Matrix effects on calibration curves: (a) change in sensitivity (slope), and (b) change in background (intercept). The solid line indicates the calibration curve constructed from laboratory samples, the dashed line indicates the (unknown) calibration curve in the presence of the matrix, and the dotted line indicates the error in the unknown concentration.

(2) *Dilution*. This is an alternate form matrix matching in which the sample is sufficiently diluted to remove the effects of the matrix on the sensitivity. Unfortunately, the dilution required is often so large that it may reduce the ability to detect the analyte.

(3) *Matrix buffering*. This is another form of matrix matching in which very high concentrations of a matrix component are added to both the standards and the sample to "mask" the influence of the original sample matrix. For example, enough sodium chloride could be added a seawater sample to mask the effects of the ions already present. Unfortunately, this may also complicate the analysis in other ways.

(4) *Matrix destruction*. In certain cases, it may be possible to destroy the sample matrix (but not the analyte). For example, in the determination of metals in organic substances (*e.g.* hair, food), the organic matrix may be destroyed by dissolving it in acid and heating (called "ashing"). This is not always possible, however, and may result in the loss of analyte.

(5) *Matrix separation*. For many complex samples, it is possible to separate the analyte(s) from the other components of the sample and make the measurements in the absence of a matrix. This may, for example, involve precipitation or extraction of the analyte (or the matrix components). More advanced methods of separation (chromatography) are discussed later. These techniques are widely used, but complicate the analytical procedure.

(6) *Standard addition*. This is a relatively simple procedure in which the sample itself is used to prepare the standards. In this way the sample provides the matrix and ensures that the matrix effects are the same for all measurements.

(7) *Internal standard*. In this method, a substance similar to the analyte, but not present in the sample, is added to each sample and standard and the ratio of the responses of the two substances is used for quantitative purposes.

The method used to reduce or eliminate the matrix effect (when necessary) depends on the nature of the analyte and matrix, as well as the type of analytical technique used. In this chapter, the focus will be on standard addition and internal standards, which are relatively simple techniques that are widely used.

7.4 Calibration with Standard Addition Methods

In the method of standard addition, the sample is made to act as both the standard and the unknown. As the name "standard addition" implies, a standard with a known amount of the analyte is added to a sample with an unknown amount of the same analyte. This is done in such a manner that the matrix is similar for all solutions. Therefore the slope of the calibration curve should not change and the problem of matrix effects should be eliminated. For this method to work, the instrument response must obey a specific relationship to the concentration of analyte, usually the linear relationship that we have already seen. It is also critical with the methods presented here that the *background contribution can be considered to be zero* (*i.e.* the calibration curve has a zero intercept).

Although not a strict requirement, the "standard" and the "unknown" which are mixed together are normally in the form of solutions, and these will be designated to have analyte concentrations of C_s and C_u prior to mixing. Although the analyte comes from different sources, as shown in Figure 7.2, the instrument measuring the response makes no distinction between the two, so the effect of the combined concentrations (in the presence of the matrix) is recorded.

In performing calibration by standard addition, there are two unknown quantities: the sensitivity (S, the slope of the calibration curve) and the concentration of the analyte in the unknown, C_u (recall that the background, B, is assumed to be zero). For this reason, we need response measurements for at least two different solutions to solve for the unknown concentration (two equations, two unknowns). Therefore, there is no one-point calibration method for standard addition, only two-point and multipoint methods. Both of these will be discussed in this topic.

As in traditional calibration, multipoint standard addition methods are preferred in practice since they produce more precise results and are able to detect nonlinearity in the response. However, two-point standard addition methods are faster to carry out and do not require the use of regression. (For the latter reason, they are also more likely to be asked by analytical chemistry professors on tests.) Another disadvantage of multipoint methods is that, if the matrix changes significantly between samples, a new calibration curve may be required each time, which is very time-consuming.

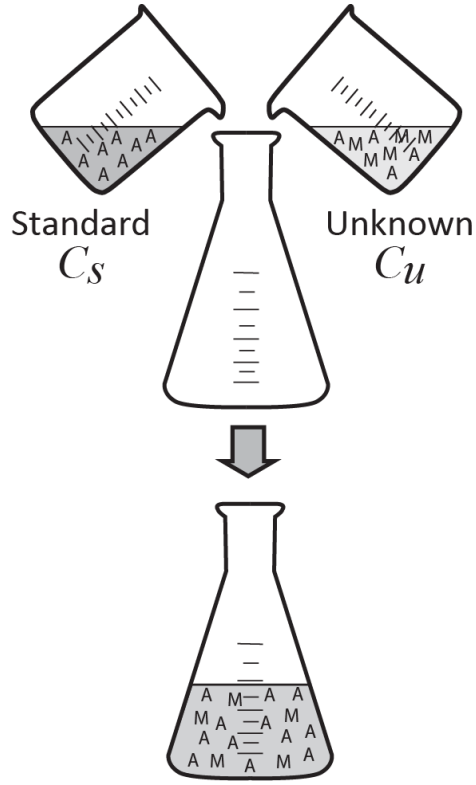


Figure 7.2: In standard addition, a standard solution with a known concentration (C_s) of analyte (A) and no matrix components (M) is combined with the sample solution which contains matrix components and an unknown concentration of analyte.

7.5 Two-Point Standard Addition Method

The approach used in two-point standard addition methods is simply to use a set of two equations to solve for the concentration of the unknown, C_u. However, it is important to recognize that there is *no single equation* that can be used for every situation, since this will depend on the actual procedures employed. Therefore, the equations to be used need to be derived in each situation. Fortunately, there is a standard approach that can be applied and this is described below.

(1) From the procedures described to prepare the two solutions, write expressions for the analyte concentrations in each of the solutions prepared, C_1 and C_2, as functions of C_s and C_u, as well as any volumes specified to account for dilution.

(2) The measured instrument responses for the two solutions, R_1 and R_2, will be given. Write equations for these as functions of C_1 and C_2, expanding these further using the relations in step (1) to give functions of C_s and C_u. Although not strictly required, in virtually all cases, a linear instrument response will be assumed, so the appropriate equations will be

$$\begin{aligned} R_1 &= S \cdot C_1 = \ldots \\ R_2 &= S \cdot C_2 = \ldots \end{aligned} \qquad (7.1)$$

Recall that the background, B, is assumed to be zero. The ellipsis (…) indicates that the full equation in terms of C_s and C_u follows.

(3) Solve the equations given in previous step for C_u, substituting in the numerical values for R_1, R_2, C_s and other necessary quantities. Generally, it is not necessary to directly solve for the sensitivity, S, unless this is needed for other calculations.

It should be noted that, depending on how quantities are defined, there may be more than one set of equations that give rise to valid solutions.

Although it has been stated that each standard addition problem should be treated individually and there is no universal equation, there are two general procedures that apply to most cases encountered. These are referred to as the *variable volume method* and the *fixed volume method*, and are described in the sections that follow.

The Variable Volume Method

In the variable volume standard addition method, a known amount of standard is added to the unknown. For a two-point calibration, two responses are measured. These are typically the responses for the unknown solution and for a solution to which a known volume of standard, V_s, has been added to a known volume of the unknown, V_u. This is illustrated in Figure 7.3. The principle here is that the addition of the standard to the sample makes the matrix similar between the two samples. It is called the variable volume method because the total volume of the solution changes on the addition of the standard (this terminology will become clearer when we discuss the fixed volume method).

Following step (1) in the defined procedure, we can write expressions for the concentration of the analyte in the two solutions.

$$C_1 = C_u \qquad C_2 = \left(\frac{V_u}{V_u + V_s}\right)C_u + \left(\frac{V_s}{V_u + V_s}\right)C_s \tag{7.2}$$

Note that the concentration in the second solution is affected by both the standard and the unknown, as well as the dilution of each of those solutions to the total volume. Assuming a linear response with no background, the measurements for the two solutions, represented as R_1 and R_2, will be given by

$$R_1 = S \cdot C_1 = S \cdot C_u \tag{7.3}$$

$$R_2 = S \cdot C_2 = S \cdot \left(\frac{V_u}{V_u + V_s}\right)C_u + S \cdot \left(\frac{V_s}{V_u + V_s}\right)C_s \tag{7.4}$$

Equations 7.3 and 7.4 represent the two equations needed to solve for the two unknowns, C_u and S (the quantities R_1, R_2, V_u, and V_s are all known from the measurements and procedure). To solve for C_u, some mathematical manipulation will be necessary and you need to be proficient at this. Since there are different (equally valid) approaches to the solution, and because the solutions may vary from one situation to another, no general solution is presented. However, some examples will illustrate how to approach this.

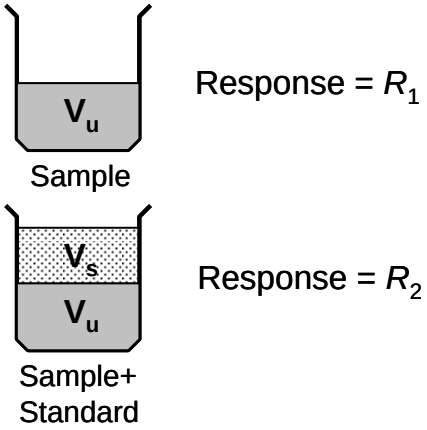


Figure 7.3: Principle of the two-point, variable volume, standard addition method. A known volume of standard, V_s, is added to a known volume of unknown, V_u.

Example 7.1: Two-Point Variable Volume Standard Addition

The absorbance (spectrophotometric response) of a solution containing an unknown amount of iron and a large excess of thiocyanate ion is measured as 0.346. When 1.00 mL of a 100. ppm iron standard is added to 10.00 mL of the unknown, the absorbance of this solution is measured as 0.515. Assuming that absorbance is linear in concentration, what is the iron concentration in the sample?

As with all problems of this type, we begin by writing the equations that define the response as a linear function of the concentrations, taking into account any dilution factors. Here, we will use C_u to represent the original concentration of the unknown and C_s to represent the original concentration of the standard. For the two solutions, we have:

$$C_1 = C_u \qquad C_2 = \frac{V_u}{V_u + V_s} C_u + \frac{V_s}{V_u + V_s} C_s = \frac{10.00\ \text{mL}}{11.00\ \text{mL}} C_u + \frac{10.00\ \text{mL}}{11.00\ \text{mL}} C_s$$

Substituting these into the linear relationship $R = SC$ gives the two equations:

$$R_1 = 0.346 = S \cdot C_1 = S \cdot C_u$$

$$R_2 = 0.515 = S \cdot C_2 = S\left(\frac{10.00}{11.00} C_u + \frac{1.00}{11.00}(100.\ \text{ppm})\right)$$

There are different ways to solve for C_u in these equations. Two solutions are presented below.

Solution 1:

In situations such as this, where one equation only has one term, perhaps the easiest solution is to divide the second equation by the first, thereby eliminating the unknown S, as shown below:

$$\frac{R_2}{R_1} = \frac{0.515}{0.346} = \frac{\cancel{S}\left(\frac{10.00}{11.00} C_u + \frac{(1.00)(100.\ \text{ppm})}{11.00}\right)}{\cancel{S} C_u}$$

$$\frac{0.515}{0.346} = \frac{\frac{10.00}{11.00}\cancel{C_u}}{\cancel{C_u}} + \frac{\frac{(1.00)(100.\text{ ppm})}{11.00}}{C_u} = \frac{10.00}{11.00} + \frac{100.\text{ ppm}}{(11.00)C_u}$$

$$\left(\frac{0.515}{0.346} - \frac{10.00}{11.00}\right) = \frac{100.\text{ ppm}}{(11.00)C_u} \quad \text{or} \quad \left(\frac{0.515}{0.346} - \frac{10.00}{11.00}\right)C_u = \frac{100.\text{ ppm}}{11.00}$$

$$C_u = \left(\frac{100.\text{ ppm}}{11.00}\right) \Big/ \left(\frac{0.515}{0.346} - \frac{10.00}{11.00}\right) = \frac{9.0\overline{9}09\text{ ppm}}{1.4\overline{8}844 - 0.909\overline{0}9}$$

$$= \frac{9.0\overline{9}09\text{ ppm}}{0.5\overline{7}93} = 1\overline{5}.7 \text{ or } 16\text{ ppm}$$

Solution 2:

An alternative solution involves rearranging the equation for R_1 to give $S = R_1/C_u$ and then substituting this into the equation for R_2.

$$R_2 = \frac{R_1}{C_u}\left(\frac{10.00}{11.00}C_u + \frac{1.00}{11.00}\cdot(100.\text{ ppm})\right) = \frac{(10.00)R_1}{11.00} + \frac{(100.\text{ ppm})R_1}{(11.00)C_u}$$

$$\left(R_2 - \frac{(10.00)R_1}{11.00}\right) = \frac{(100.\text{ ppm})R_1}{(11.00)C_u} \quad \text{or} \quad \left(R_2 - \frac{(10.00)R_1}{11.00}\right)C_u = \frac{(100.\text{ ppm})R_1}{(11.00)}$$

$$C_u = \frac{(100.\text{ ppm})R_1}{(11.00)} \Big/ \left(R_2 - \frac{(10.00)R_1}{11.00}\right)$$

$$= \frac{(100.\text{ ppm})(0.346)}{(11.00)} \Big/ \left(0.515 - \frac{(10.00)(0.346)}{11.00}\right)$$

$$= \frac{3.1\overline{4}55}{0.515 - 0.31\overline{4}55} = \frac{3.1\overline{4}55}{0.20\overline{0}45} = 15.7\,\text{ppm}$$

The two different approaches used to solve for C_u in the previous example produced the same answer and both approaches are equally valid. Attentive readers will note, however, that the second calculation results in three significant digits while the first gives only two. This is a consequence of the of the fact that rules for significant figures are only approximate and the application of propagation of error methods would produce more consistent results (uncertainty of ±0.3 ppm assuming ±1 in the last digit of all of the variables). In this class, as long as the answer is consistent with the method employed, that is satisfactory.

It is important in standard addition methods that the matrix remain constant between samples, but a drawback of the variable volume method is that the matrix is diluted by the addition of the standard. For this reason, it is important that the volume of the standard solution, often referred to as a "spike" in quantitative analysis, be small relative to the volume of the sample. If the concentration of the standard spiked into the sample is high enough, the volume of the standard can be quite low and possibly even ignored in the calculations, making the solution easier.

Another consideration is the concentration of the standard used to spike the sample, C_s. In general, the smaller the concentration of the spike in the diluted sample, the larger will be the errors in the estimated concentration because the difference in the measured responses becomes small. This is illustrated in Figure 7.4, which shows the effect of C_s on the errors in the calculated unknown concentration, C_u, under certain conditions (10:1 volume ratio and 1% or 0.1% errors in responses and volumetric quantities). What is important is the ratio of the standard in the *diluted* sample to the concentration of the unknown. Note that there is not much change until this ratio becomes less than unity, but when the concentration of the standard becomes too low, the errors increase rapidly. Choosing a value for C_s is complicated by the fact that we don't know C_u, so normally we would make an estimate of the upper limit of C_u. In general, the concentration of the standard *after dilution* should be around the value of C_u (in the above example, the ratio was about 0.6). It is better to make it too high than too low, but the upper limit of C_s may be limited by solubility or the range of the instrument response.

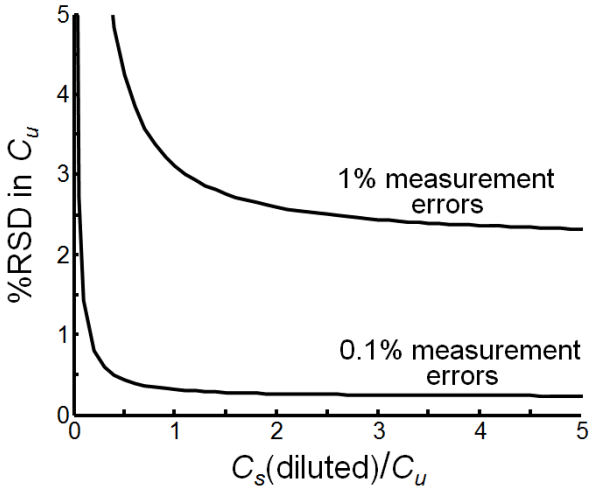


Figure 7.4: Effect of standard concentration, C_s, on the precision of variable volume standard addition under different measurement error conditions. Note that the errors can increase rapidly when the concentration of the diluted standard becomes less than the concentration of the unknown.

Exercise 7.1

Consider the same problem and data as in the previous example, except in this case the second solution consists of 100. μL of 1000. ppm Fe added to 10.00 mL of the unknown sample, giving a reading of 0.561.

(a) Calculate the concentration of Fe in the unknown.

(b) Calculate the concentration of Fe in the unknown assuming no volume change. Is there much difference?

(c) Repeat the calculation in (b) using the original measurements in Example 7.1, again assuming no volume change when the standard is added. What is the calculated concentration? Is the difference bigger or smaller than in part (b)?

Exercise 7.2

The standard addition method is used to determine the concentration of vitamin C in apple juice by polarography, a method that produces a current that is proportional to concentration. A 1.00 mL sample of apple juice is diluted to a total volume of 10.00 mL, which gives a current reading of 0.78 μA. This solution is then spiked with a 2.00 mL aliquot of a 326 mg/L solution of vitamin C, producing a reading of 2.26 μA. What is the concentration of vitamin C in the apple juice?

Exercise 7.3

In the previous exercise, it was assumed that the background was zero. Suppose that the background was actually 0.22 μA. Taking this into consideration, what, would be the calculated concentration of vitamin C in the apple juice?

The Fixed Volume Method

As with the variable volume method, the fixed volume standard addition method involves adding a specified amount of standard to a fixed volume of unknown solution. The difference here is that all of the solutions prepared are diluted to the same total final volume, V_t, in contrast to the variable volume method where the total volume depends on the volumes of the standard and unknown (hence the name). With the two-point fixed volume method, one of the solutions prepared typically contains only the unknown and the other contains the unknown and the standard, but this is not a requirement as long as both solutions contain different amounts of standard. This principle is illustrated in Figure 7.5. A convenient aspect of this approach is that the denominator of the dilution factor does not change, as seen in the derivation below.

Using the same definitions and assumptions (linearity and zero background) as for the variable volume method, equations can be written for the two measured responses.

$$R_1 = S \cdot C_1 = S \cdot C_u^{dil} = S \cdot C_u \cdot \frac{V_u}{V_t} \tag{7.5}$$

$$R_2 = S \cdot C_2 = S \cdot (C_u^{dil} + C_s^{dil}) = S \cdot \left(C_u \cdot \frac{V_u}{V_t} + C_s \cdot \frac{V_s}{V_t} \right) \tag{7.6}$$

Note that the superscript "dil" has been added here to indicate the concentrations of the unknown and standard after dilution. As before, there are two equations and two unknowns (S and C_u) and a variety of methods can be used to solve for the unknown concentration. These equations can change with the problem under consideration, however, so a general equation will not be given and should be derived for each problem.

A major advantage of the fixed volume method compared to the variable volume method is that the concentration of the matrix is the same for both measurements, so the sensitivity should remain constant. However, the fixed volume method requires more solution manipulation (more pipetting and dilution), and the solutions can be more dilute, resulting in lower sensitivity relative to the original concentration of the unknown.

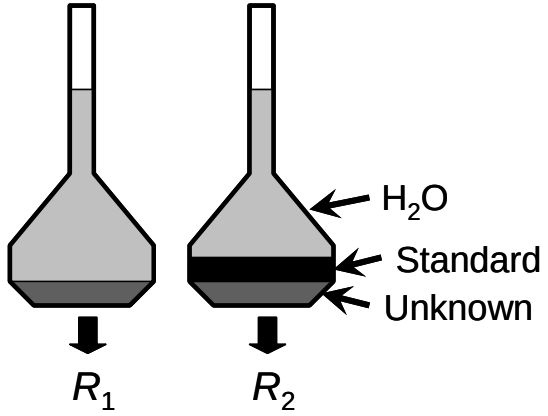


Figure 7.5: Principle of the two-point, fixed volume, standard addition method. One solution contains only unknown, while the other contains the unknown plus standard. Both solutions are diluted to the same final volume.

Example 7.2: Two-Point Fixed Volume Standard Addition

Dextromethorphan, an active ingredient in cough syrups can be determined by fluorescence spectroscopy. A 5.00 mL sample of cough syrup is first diluted to 100.0 mL. A 2.00 mL aliquot of this solution is then diluted to 100.0 mL with distilled water and the fluorescence is recorded as 158. A second 2.00 mL aliquot is combined with 3.00 mL of a standard containing 80.0 ppm of dextromethorpham and the mixture is again diluted to 100.0 mL. This gives a fluorescence reading of 353. Assuming a linear response and zero background, determine the number of milligrams of dextromethorpham in one dose (15 mL) of the cough syrup.

This is a fixed volume standard addition problem since both samples are diluted to 100 mL. To illustrate that there is more than one way to solve these problems, two solutions will be presented.

Solution 1:

In setting up these problems, the definition of the variables is important. In this case, we will define C_u to be the concentration of the analyte in the sample after the first dilution and C_s to be the concentration of the standard. Thus, we can write:

$$R_1 = S \cdot C_u \frac{2.00\ \text{mL}}{100.0\ \text{mL}} \qquad R_2 = S\left(C_u \frac{2.00\ \text{mL}}{100.0\ \text{mL}} + C_s \frac{3.00\ \text{mL}}{100.0\ \text{mL}} \right)$$

In this case, we will take the ratio of the two equations to eliminate S,

$$\frac{R_2}{R_1} = \frac{\cancel{S}\left(C_u \frac{2.00}{100.0} + C_s \frac{3.00}{100.0} \right)}{\cancel{S} \cdot C_u \frac{2.00}{100.0}} = \left(C_u \frac{2.00}{100.0} + C_s \frac{3.00}{100.0} \right) \cdot \frac{100.0}{(2.00)C_u} = 1.00 + \frac{(3.00)C_s}{(2.00)C_u}$$

Rearranging this, we can solve for C_u:

$$C_u = \frac{(3.00)C_s}{(2.00)(R_2/R_1 - 1.00)} = \frac{(3.00)(80.0\ \text{ppm})}{(2.00)(353/158 - 1.00)} = \frac{240.\ \text{ppm}}{(2.00)(2.2\overline{3}42 - 1.00)}$$
$$= \frac{240.\ \text{ppm}}{(2.00)(1.2\overline{3}42)} = 97.\overline{2}3\ \text{ppm}$$

We still need to take into account the initial dilution, so

$$C_u^{\text{original}} = (97.23\ \text{ppm}) \times \frac{100.0\ \text{mL}}{5.00\ \text{mL}} = 19\overline{4}5\ \text{ppm} = 19\overline{4}5\ \text{mg/L} = 1.9\overline{4}5\ \text{mg/mL}$$

Here we have used the equivalence that 1 ppm = 1 mg/L for dilute solutions. Finally, we can calculate the amount in 1 dose.

$$\text{dextromethorphan in one dose} = (1.9\overline{4}5\ \text{mg/mL})(15\ \text{mL/dose}) = 29\ \text{mg}$$

Solution 2:

To illustrate an alternative approach, we will define C_u as the concentration in the cough syrup before the initial dilution and use the first equation to substitute for S (these two changes are not related to one another).

$$R_1 = S \cdot C_u \frac{5.00\,\text{mL}}{100.0\,\text{mL}} \cdot \frac{2.00\ \text{mL}}{100.0\ \text{mL}} = S \cdot C_u \frac{10.0}{10,0\overline{0}0.} = S \cdot C_u(0.00100)$$

$$R_2 = S\left(C_u \frac{5.00\,\text{mL}}{100.0\,\text{mL}} \cdot \frac{2.00\ \text{mL}}{100.0\ \text{mL}} + C_s \frac{3.00\ \text{mL}}{100.0\ \text{mL}} \right) = S[C_u(0.00100) + C_s(0.0300)]$$

$$= \frac{R_1}{C_u(0.00100)} \cdot [C_u(0.00100) + C_s(0.0300)] = R_1 + \frac{(30.0)R_1C_s}{C_u}$$

$$C_u = \frac{(30.0)R_1C_s}{(R_2 - R_1)} = \frac{(30.0)(158)(80.0\,\text{ppm})}{(353 - 158)} = \frac{37\overline{9},200\,\text{ppm}}{195} = 1,9\overline{4}5\,\text{ppm}$$

Note that in this case, we do not need to solve for the initial dilution because this has already been included in the definition of C_u.

■

Exercise 7.4

What is the sensitivity of the fluorescence method in the previous example?

Exercise 7.5

Following the measurements in the previous example, another 5.00 mL is taken from a second bottle of cough syrup and diluted to 100 mL. A 2.00 mL aliquot of this solution is then diluted to 100.0 mL with distilled water and gives a fluorescence reading of 186.

(a) What is the estimated dose of dextromethorpham in 15 mL of this second bottle?
(b) What assumption(s) did you make in calculating the result in part (a)?

Exercise 7.6

In an atomic emission experiment to determine sodium in a sample, 5.00 mL of the unknown solution are mixed with 5.00 mL of a sodium standard containing 104 ppm Na and diluted to 100.0 mL. Another 5.00 mL aliquot of the unknown is mixed with 15.00 mL of the same standard and also diluted to 100.0 mL. These give readings of 149 and 198, respectively. A sample blank containing no sodium gives a reading of 28±3.

(a) What is the concentration of sodium in the unknown solution?
(b) What is the sensitivity of the method?
(c) What is the limit of detection of the method?

7.6 Multipoint Standard Addition Methods

The use of multiple calibration samples can enhance the quality of traditional calibration methods by improving precision and detecting nonlinearities, and the same is true for standard addition methods. Although multipoint methods exist for both the variable volume and fixed volume approaches, the former is almost never used in practice, so this section will focus on fixed volume multipoint methods.

For fixed volume multipoint calibration, a series of solutions is prepared in which the volume of the unknown added, V_u, and the total volume of the solution, V_t, remain constant, but the concentration of the standard solution varies for each of the solutions prepared. For simplicity, the concentration of the standard is usually varied by adding a different volume of a single standard solution to each of the calibration solutions, as indicated in Figure 7.6. Under these conditions, the equation for the instrument response is:

$$R = \frac{SC_u V_u}{V_t} + \frac{SC_s}{V_t} \cdot V_s \tag{7.7}$$

From this, it can be seen that a plot of R *vs.* V_s should be a straight line with a slope of (SC_s/V_t) and a *y*-intercept of (SC_uV_s/V_t). Although this is one way to plot the graph, a more common method is based on the equation

$$R = \frac{SC_u V_u}{V_t} + S \cdot C_s^{dil} \tag{7.8}$$

In this equation, C_s^{dil} represents the concentration of the standard in the *diluted* sample rather than the original. Thus, a plot of R *vs.* C_s^{dil} will also give a straight line with the same *y*-intercept as before, but with a slope equal to S. This is illustrated in Figure 7.6. From this, we can see that the concentration in the original (undiluted) unknown will be

$$C_u = \frac{y\text{-intercept}}{\text{slope}} \cdot \frac{V_t}{V_u} \tag{7.9}$$

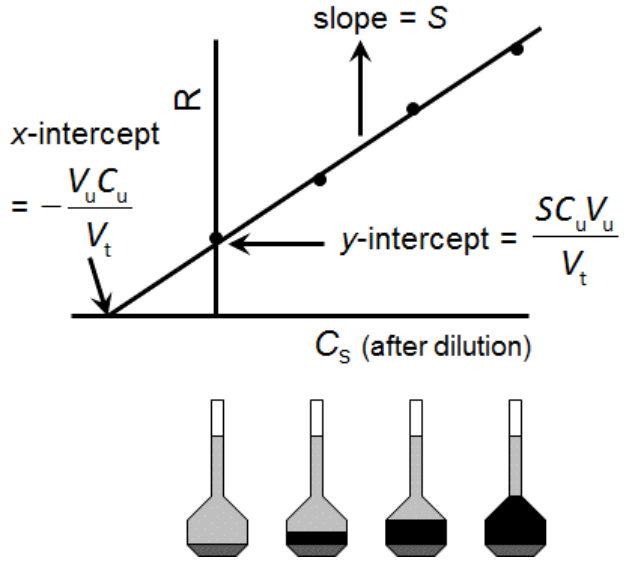


Figure 7.6: Illustration of the graphical approach to the multipoint, fixed volume standard addition method. Variable volumes of standard solution are added to a fixed volume of unknown, then all solutions are diluted to the same total volume.

Another way to determine the unknown concentration is simply to use the *x*-intercept, which will be the negative of the concentration of the unknown in the diluted samples. Therefore, correcting for the dilution, we can write

$$C_u = -(x\text{-intercept}) \cdot \frac{V_t}{V_u} \tag{7.10}$$

This equation can be easier to use, especially if the *x*-intercept is read directly from the graph.

Exercise 7.7

Absorbance spectroscopy is used to determine the amount of phosphate in a urine sample by the standard addition method. Four solutions are prepared, each containing a 1.00 mL of urine, 50.0 mL of colour-forming reagent, varying amounts of a 0.500 mM phosphate standard solution, and enough distilled water to give a total volume of 100.0 mL. The following data were recorded.

Volume of standard (mL)	0	4.00	8.00	12.00
Absorbance	0.205	0.312	0.402	0.534

What is the concentration of phosphate in the urine? (For convenience, the data are plotted in Figure 7.7.)

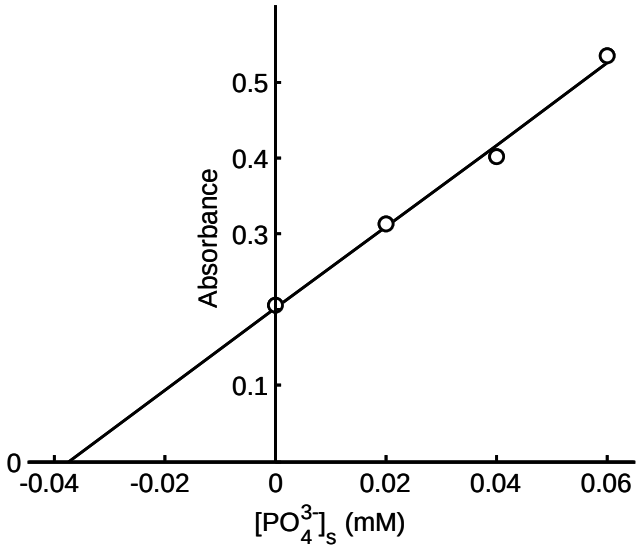


Figure 7.7: Plot of data for multipoint, fixed volume standard addition problem in Exercise 7.7.

Exercise 7.8

Imagine that 1.00 mL of urine from another subject is treated with 50.0 mL of colour-forming reagent and diluted to 100.0 mL. This gives an absorbance reading of 0.242.

(a) Based on the results in the previous exercise estimate the concentration of phosphate in this urine sample.
(b) What important assumption is made in making this estimate?
(c) Is this assumption likely to be valid? Why or why not?

Exercise 7.9

In addition to improved precision, an advantage of multipoint methods is that they allow the determination of the standard error of regression, s_e (see preceding topic), which is an estimate of measurement uncertainty.

(a) Estimate the value of s_e in Exercise 7.7.
(b) Estimate the limit of detection (LOD) for the *measurement* (*i.e.* in the diluted sample).
(c) Estimate the LOD for the *method* (*i.e.* in the original sample).
(d) Based on this, how many significant figures *should* be reported in the answers to the two previous exercises?
(e) Estimate the limit of quantitation (LOQ) for the method.

Summary of Standard Addition Methods

Standard addition is an analytical approach intended to minimize the effect of differences between the matrix of the sample and standards that affect the sensitivity of the measurement. By adding standards to the sample, the matrix is made similar for all measurements. In all of the methods presented, it was assumed that the instrument response is linear and that the background signal is zero or can be subtracted out. If the matrix affects the background, the standard addition method cannot be used.

It is important to recognize that standard addition is a principle rather than a single method or equation, and the necessary relationships should be derived in each case. Nevertheless, the classifications of "variable volume" and "fixed volume" methods can be useful. The variable volume method has the advantage that fewer solution manipulations are required, since there is no final dilution and the dilution of the sample is minimized, resulting in improved sensitivity. However, a drawback of the variable volume method is that the matrix is not identical between measurements. The extent to which this is a problem depends on the magnitude of the matrix effect and the magnitude of the dilution in each solution, but the volume of standard added should be small relative to the volume of the unknown. This is not a factor in the fixed volume method, since the matrix is diluted to the same extent in every

sample, but the sample manipulations are more complicated and the solutions are typically more dilute, resulting in lower method sensitivity.

Multipoint standard addition methods result in greater precision and can establish linearity and limits of detection, but are more time consuming. Traditional multipoint calibration methods assume that matrix effects are negligible and the same calibration curve can be applied to multiple unknowns. For standard addition, this is only possible if the matrix remains essentially constant between samples. If this is not the case, a new calibration curve is necessary for each unknown. This is often impractical, so two-point methods are more commonly used when standard addition is involved. Another approach, referred to as "internal standards" is a way to circumvent this problem.

7.7 Internal Standards

The method of internal standards is another technique to account for changes in the sensitivity of an instrument. It can account not only for matrix effects, but also changes in sensitivity due to drift in instrument components or other factors. To illustrate, imagine that you are going on a long trip and also starting a diet. Weighing yourself along the way is difficult because every scale you use is adjusted slightly differently. Suppose, however, that you had an object, such as a suitcase, that always weighed the same. If you measured the ratio of your weight to that of the object, then you would always be able to tell if you were gaining or losing weight, as long as the scale response was linear. This is the same principle behind the use of internal standards, where the ratio of the measurement for the analyte to the measurement for a fixed amount of a second analyte is used.

An internal standard is a compound which is added to *all samples* and used to correct for changes in sensitivity. The internal standard must not to be present originally in any of the samples, must not interfere in the measurement of the analyte, must give an independent response, and must mirror the behavior of the analyte as closely as possible. It is usually added in the same amount to all samples and standards. The response of the instrument to both the analyte and the internal standard is recorded. The ratio of these responses is then used in any of the calibration strategies already discussed to calculate the concentration of analyte. This principle is illustrated in Figure 7.8.

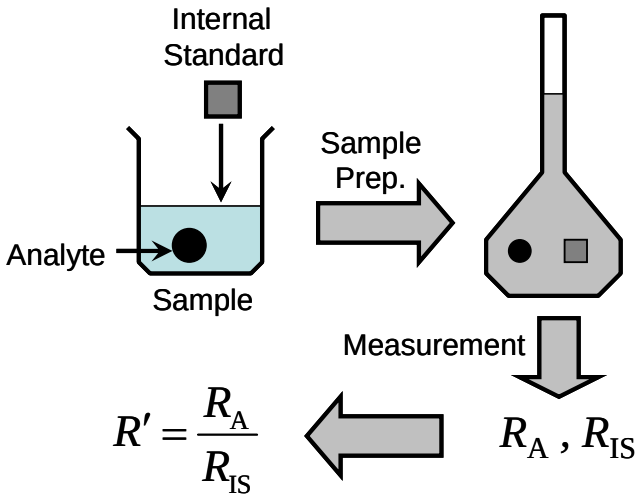


Figure 7.8: Principle of the method of internal standards. The internal standard, which is a secondary analyte not present in the sample, is added to all samples, typically in the same amount. Factors affecting the sensitivity for both analytes are removed by using the ratio of responses.

Assume that instrument response is linear for both the internal standard and analyte and that the background is zero. Then, using the basic linear response equation, we can write

$R_A = S_A C_A$ for the analyte, and

$R_{IS} = S_{IS} C_{IS}$ for the internal standard

where C_{IS} is the concentration of internal standard in the sample. Note that the sensitivity of the instrument for the analyte and the internal standard is generally different. When the ratio of the responses is calculated

$$\frac{R_A}{R_{IS}} = \frac{S_A C_A}{S_{IS} C_{IS}} = k \frac{C_A}{C_{IS}} \qquad (7.11)$$

where k is a constant (the ratio of two sensitivities). If the concentration of internal standard is always maintained constant, then the above expression becomes even simpler.

$$\frac{R_A}{R_{IS}} = R' = k' C_A \qquad (7.12)$$

Note that, when the ratio of the responses is used in place of the analyte response and the concentration of the internal standard is constant, this becomes an alternative form of the basic response equation, so any of the basic calibration methods can be used (including standard addition).

The use of an internal standard corrects for matrix effects in a more subtle manner than the method of standard addition. A matrix effect that acts upon sensitivity causes S_A to change from unknown to standard. If the internal standard is chosen to behave like the analyte, then the matrix effect will change S_{IS} to approximately the same extent as S_A. In this case k, the ratio of the two sensitivities, will change very little or not at all. Thus, the equations above involving k or k' will be almost independent of matrix effects. The same can be said for changes in instrument characteristics that affect the sensitivities. This is illustrated in Figure 7.9. If the sensitivity of the instrument changes between calibration standards, this will cause the analyte response, R_A, to be erratic and deviate from linearity, as shown in the figure. Since the response of the internal standard, R_{IS}, changes proportionately in the same way, taking the ratio of the two responses reduces these deviations.

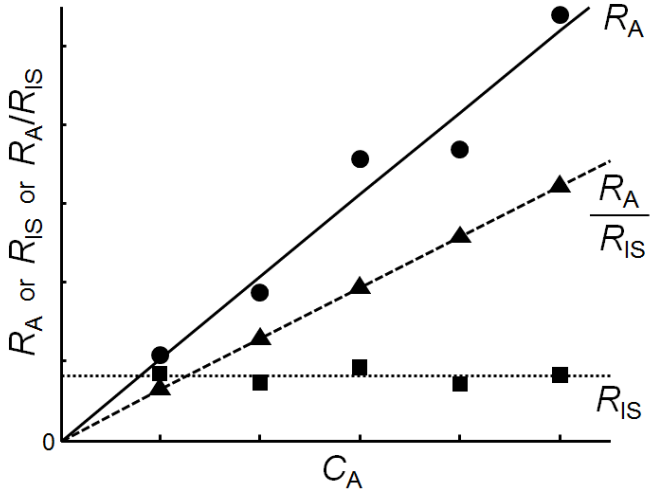


Figure 7.9: Effect of changes in instrument sensitivity on calibration. The responses of the analyte (●), the internal standard (■) and their ratio (▲) are shown, where the concentration of the internal standard is constant. Note that the ratio corrects for deviations in linearity caused by changes in sensitivity.

Internal standards exhibit other advantages as well. Many analytical procedures have steps that involve large systematic errors. For example, some procedures require that the analyte be extracted from the original sample prior to instrumental analysis. This extraction is often incomplete and, worse, the percentage recovery varies considerably from sample to sample. If an internal standard is added to the original sample, the proportion of analyte and internal standard that are lost should be the same, so the ratio of responses should not be affected by this change. Thus, an internal standard can cancel the effects of such problems.

When internal standards are used in a one-point calibration method, a standard solution is prepared containing both the analyte and the internal standard in known concentrations and k (or k') is determined from the measured responses of this standard. The internal standard is then added to the unknown, the responses measured, and the analyte concentration calculated using the value of k (or k'). In this case, it is not necessary that the internal standard be added to all samples in the same concentration.

Example 7.3: Internal Standards in a One-Point Calibration

Cu^{2+} is to be used as an internal standard in the polarographic analysis of Pb^{2+}. A standard solution containing 2.00 ppm of both Cu^{2+} and Pb^{2+} gives currents of 0.0505 μA for Cu^{2+} and 0.0584 μA for Pb^{2+}. A 25.0 mL aliquot of a 2.00 ppm solution of Cu^{2+} is added to 25.0 mL of an unknown containing Pb^{2+} but no copper. The currents measured for the unknown are 0.0226 and 0.0393 μA for Cu^{2+} and Pb^{2+}, respectively. Assuming that measured current is linear in concentration, what is the concentration of Pb^{2+} in the original unknown using: (a) a basic one-point calibration for Pb^{2+}, and (b) using a one-point calibration with copper as the internal standard?

(a) Ignoring the internal standard and considering only the response of the lead, we can write

$$R_{Pb} = S_{Pb} C_{Pb}$$

$$S_{Pb} = \frac{R_{Pb}^{std}}{C_{Pb}^{std}} = \frac{0.0584\ \mu A}{2.00\ ppm} = 0.0292\ \mu A \cdot ppm^{-1}$$

$$C_{Pb}^{unk} = \frac{R_{Pb}^{unk}}{S_{Pb}} = \frac{0.0393\ \mu A}{0.0292\ \mu A \cdot ppm^{-1}} = 1.3\overline{4}59\ ppm$$

Since the second solution was diluted by the internal standard, we need to account for this in determining the concentration of lead in the original unknown.

$$C_{Pb}^{orig} = (1.3\overline{4}59\ ppm) \times \frac{50.0\ mL}{25.0\ mL} = 2.69\ ppm$$

(b) Since the concentration of the internal standard changes between the two solutions, we must use Eqn. (7.11) rather than Eqn. (7.12).

$$R' = \frac{R_{Pb}}{R_{Cu}} = k\frac{C_{Pb}}{C_{Cu}}$$

$$k = \frac{R_{Pb}^{std}}{R_{Cu}^{std}} \cdot \frac{C_{Cu}^{std}}{C_{Pb}^{std}} = \frac{0.0584\ \mu A}{0.0505\ \mu A} \cdot \frac{2.00\ ppm}{2.00\ ppm} = 1.1\overline{5}64$$

$$C_{Pb}^{unk} = \frac{R_{Pb}^{unk}}{R_{Cu}^{unk}} \cdot \frac{C_{Cu}^{unk}}{k} = \frac{0.0393\ \mu A}{0.0226\ \mu A} \cdot \frac{1.00\ ppm}{1.1\overline{5}64} = 1.5\overline{0}37\ ppm$$

Note that both C_{Pb}^{unk} and C_{Cu}^{unk} represent concentrations <u>in</u> the unknown solution, but the copper concentration is actually known because it is the internal standard. Its concentration in this solution is 1.00 ppm because of the 2:1 dilution. Again, we need to account for dilution of Pb^{2+} in the original unknown.

$$C_{Pb}^{orig} = (1.5\overline{0}37\ ppm) \times \frac{50.0\ mL}{25.0\ mL} = 3.01\ ppm$$

Obviously, since the two results do not agree, some factor changed between the measurements on the standard and those on the unknown. This change will have affected both the response for Cu(II) and Pb(II). Since the responses and the concentrations of the internal standard are known for both solutions, they can be used to correct those of the unknown and provide a more accurate result.

Exercise 7.10

In the preceding example:

(a) What is the sensitivity for Cu^{2+} in the first solution?
(b) What is the sensitivity for Cu^{2+} in the second solution?
(c) If the assumptions for internal standards hold, what would you expect the sensitivity for Pb^{2+} to be in the second solution? Why might it have changed?

Exercise 7.11

In Example 7.3(b), suppose the same measurements were obtained but, unknown to the analyst, there was some Cu^{2+} present in the unknown sample before the addition of the internal standard. Would the true concentration of the Pb^{2+} be higher, lower, or the same as that calculated? Support your answer.

Multipoint Calibration with Internal Standards

As with standard addition, the use of internal standards assumes that the background signal for both the analyte and internal standard responses is zero or can be removed. Otherwise, the ratio will not be constant. Because of this, a two-point calibration is not really useful, unless it is to check this assumption. However, internal standards can be used in a multipoint calibration to improve reliability and check linearity. A set of standard solutions, each containing the internal standard (at the same concentration) and the analyte (at different known concentrations), are prepared and the responses measured. The ratio of responses, R_A/R_{IS}, for these standards is then plotted *vs.* the concentration of analyte, C_A, to produce a graph such as that shown in Figure 7.10. The internal standard is then added to all unknowns, in the same concentration as in the standards, and the responses measured. The ratio of these responses is then calculated and the concentration of the analyte is determined from this ratio

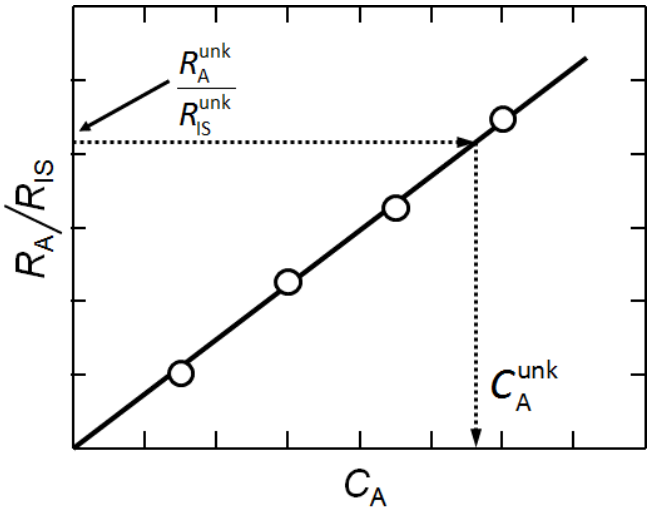


Figure 7.10: A multipoint calibration using internal standards. The ratio of the analyte response to the response for a fixed concentration of internal standard is plotted against the concentration of the analyte. Likewise, the ratio for the unknown is used to determine the concentration of analyte present.

using the calibration graph in the usual manner. The calibration curve method has all the advantages of the use of internal standards plus the usual advantages of multipoint methods.

In terms of ability to reduce matrix effects, the method of standard addition is usually superior to the use of an internal standard, since in the former method the analyte itself is used as the standard. It is almost impossible to select an internal standard that reacts to the matrix in exactly the same fashion as the analyte itself, and in many cases it is impossible to find an internal standard that meets the criteria of being absent in the sample and providing an independent signal. However, as previously noted, the use of internal standards can correct for systematic errors in sample preparation and instrumental drift that cannot be corrected by standard addition. Moreover, standard addition often requires a separate calibration for each sample, whereas the calibration using internal standards can be applied to multiple unknown samples. In certain cases, it is possible to combine the standard addition and internal standard approaches.

Exercise 7.12

The sensitivity of atomic emission spectroscopy (described in a later topic) can be affected by instrumental parameters, such as variations in flame temperature, which can be compensated for by using an internal standard. In the determination of sodium by atomic emission spectroscopy, lithium is used as an internal standard. For each standard solution, a certain volume of a 50.0 ppm Na^+ stock solution is mixed with 5.00 mL of a 20.0 ppm Li^+ stock solution and diluted to 50.0 mL with distilled water. The following data are obtained.

Volume of Na standard (mL)	1.00	2.00	3.00	5.00
Sodium emission intensity	99	242	336	438
Lithium emission intensity	196	213	200	163

A 2.00 mL sample of an unknown (containing no lithium) is added to 5.00 mL of the lithium stock solution and diluted to 50.0 mL. This gives a sodium intensity of 298 and a lithium intensity of 205. Determine the concentration of sodium in the unknown by (a) a standard multipoint calibration, and (b) a multipoint internal standard calibration. Graphs for the two situations are presented in Figure 7.11.

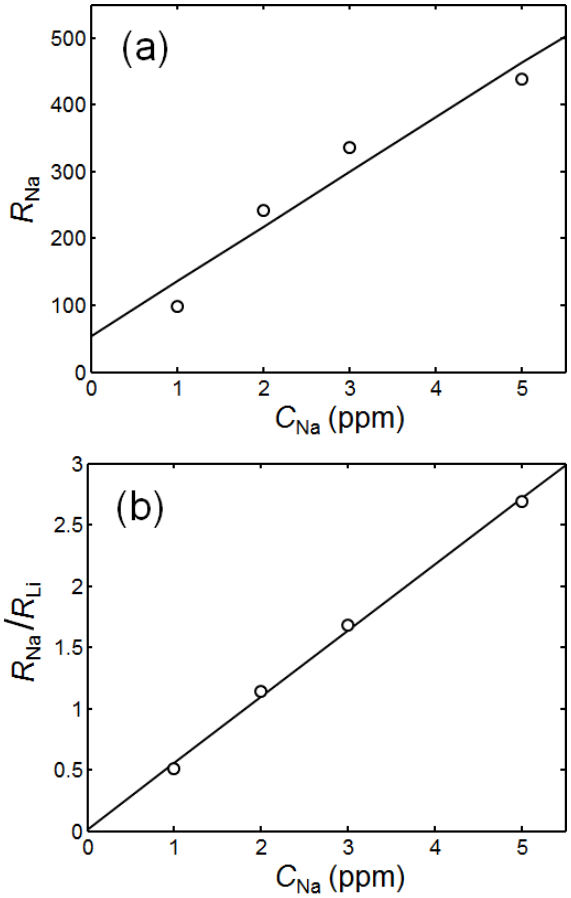


Figure 7.11: Calibration curves used for Exercise 7.12: (a) standard multipoint calibration, and (b) multipoint calibration using an internal standard.

Exercise 7.13

Using the data in preceding exercise, calculate the limit of detection for Na for both the conventional calibration and using internal standards. Is there a difference? Which is better? Why is this the case?

Exercise 7.14

Suggest what might make a good internal standard in the following situations.

(a) the determination of ethanol in beer?
(b) the determination of sodium in lake water?
(c) the determination of glucose in blood?
(d) the determination of a steroid in urine?

7.8 Summary

Matrix effects, which arise from the physical or chemical characteristics of the sample, can be a problem because they cause changes in the sensitivity of the instrument. There are several ways to deal with this problem, two of which were treated in detail here. Standard addition involves adding a known standard to the unknown sample and is commonly applied using fixed or variable volume strategies. The method of internal standards, which employs a secondary analyte, can also reduce matrix effects. It can also correct for certain kinds of systematic errors and instrument drift. For standard addition methods, two-point and multipoint calibration methods are used, while for internal standards, one-point and multipoint calibrations are common. These methods can be used in combination. Both methods assume that the background contribution is zero or can be removed.

7.9 Additional Exercises

Exercise 7.15

Irvina Gratch (Irv's sister) has just purchased a house in a suburb of Halifax and finds that her new white porcelain plumbing is turning brown. She suspects her water has a high iron content and gives a sample of her well water to Irv for analysis. To 10.0 mL of her water sample he adds 10.0 mL of a commercial colour-forming reagent and measures the absorbance in a spectrophotometer as 0.592. To a second 10.0 mL aliquot of her sample he adds 10.0 mL of colour-forming reagent and 5.00 mL of 5.00 ppm Fe(II). This solution reads 0.635 absorbance units. Assuming that absorbance is linear in concentration, what is the concentration of iron in Irvina's well water?

Exercise 7.16

Atomic absorption spectroscopy with graphite furnace atomization is an extremely sensitive technique. The standard addition method is used with this technique to determine the concentration of copper in urine. A 20.00 mL sample of urine is spiked with 1.00 mL of 300. ppb Cu^{2+} and this mixture gives a response of 0.168. Another 1.00 mL aliquot of 300. ppb Cu^{2+} is added to this mixture and gives a reading of 0.235. Determine the concentration of copper in the urine sample.

Exercise 7.17

Suppose you wish to determine calcium in an unknown sample using atomic absorption spectrometry in conjunction with the two-point variable-volume standard addition method. You expect that the maximum concentration of calcium in your sample will be about 1.5 ppm, and you plan to add 1.00 mL of your standard to 100. mL of your sample. For maximum accuracy, the ratio of the diluted standard to the original unknown concentration should not fall below 1 (see Figure 7.4), but you also know that the maximum linear range of the instrument is 4.0 ppm. What is the allowable range of concentration for your calcium standard solution (in ppm)? If the standard is to be prepared by dissolving calcium carbonate (MM = 100.09 g/mol) in 1.00 L of water, what mass range of $CaCO_3$ could be used?

Exercise 7.18

At concentrations below 2 ppm, the light intensity given off by potassium in a flame is linear in concentration provided that matrix effects are taken into account. A 10.0 mL aliquot of an aqueous sample containing potassium is placed in a 25.0 mL volumetric flask and diluted to the mark with distilled water. This solution reads 86.3 when introduced into the flame photometer. Another 10.0 mL aliquot of the sample and 2.00 mL of a 2.00 ppm solution of K^+ are placed in a second 25.0 mL volumetric flask and diluted to the mark with distilled water. This solution reads 98.4. What is the concentration of potassium ion in the sample? Is this concentration in the linear region? Is the answer still valid? Explain.

Exercise 7.19

In a modified two-point standard addition experiment, a student prepares the first solution by adding 10.0 mL of unknown and 10.0 mL of standard and dilutes the mixture to 100.0 mL with distilled water. The second solution is prepared in one of two ways:

(a) 20.0 mL of unknown and 20.0 mL of standard diluted to 100.0 mL, or
(b) 20.0 mL of unknown and 10.0 mL of standard diluted to 100.0 mL

For each of these cases, can you write an equation to solve for the concentration of the original unknown in terms of the volumes, standard concentration, and measured responses? Are there disadvantages to these approaches, or are they just different?

Exercise 7.20

The flame photometric detector for sulfur measures the light given off by sulfur-containing molecules in a cool hydrogen/air flame. The response of this detector follows the law (under certain circumstances)

$$R = S \cdot [\mathrm{RS}]^2$$

where RS represents a molecule containing a sulfur atom. Thiophene is a sulfur-containing impurity often found in benzene. A 2.00 mL benzene sample is diluted to

10.0 mL with hexane, injected into the detector, and reads 42.3. A second 2.00 mL sample of benzene is added to 2.00 mL of a 0.0100 M solution of thiophene in hexane and diluted to 10.0 mL with pure hexane. When injected into the detector, it reads 68.4. What is the concentration of thiophene in the benzene sample, assuming that the response equation above applies?

Exercise 7.21

The response of Ca^{2+} in a flame photometer is known to be linear over a wide concentration range. An aqueous sample with an unknown amount of calcium sample is treated as follows. A 10.0 mL aliquot of the sample and differing amounts of a 20.0 ppm Ca^{2+} standard are mixed and always diluted to 25.0 mL. The flame photometer readings for these solutions are:

Volume of 20 ppm Ca^{2+} (mL)	3.00	6.00	9.00	12.00
Response	53.0	62.2	71.5	80.8

What is the concentration of Ca^{2+} in the sample?

Exercise 7.22

Indium is seldom found in lead-containing samples and thus makes a good internal standard for lead analyses. A 10.0 mL aliquot of a 1.00×10^{-4} M Pb(II) solution is added to 10.0 mL of a 1.00×10^{-4} M solution of In(III). The resulting currents, measured polarographically, are 0.485 and 0.873 μA for Pb(II) and In(III), respectively. Then, 2.00 mL of a 2.00×10^{-4} M In(III) solution are added to 10.0 mL of a sample and the currents for Pb(II) and In(III) are 0.186 and 0.504 μA, respectively. Assuming a linear response between current and concentration, calculate the concentration of Pb(II) in the sample by (a) neglecting the information provided by the internal standard, and (b) taking the internal standard into account.

Exercise 7.23

Manual sampling in the technique of gas chromatography is rather imprecise since a very small sample size is produced with a μL syringe. The use of an internal standard

might be useful to avoid the imprecision of sampling. The following data are available:

Run #	Response for C_6H_{12}	$[C_6H_{12}]$ (M)	Response for C_6H_{14}	$[C_6H_{14}]$ (M)
1	275	0.100	162	0.0500
2	248	0.100	298	0.100
3	213	0.100	506	0.200

Would cyclohexane (C_6H_{12}) make a good internal standard for hexane (C_6H_{14})? Why? When 1.00 mL of a 0.500 M solution of cyclohexane is added to 4.00 mL of a sample (containing no cyclohexane) and the resulting solution was analyzed chromatographically, the responses for cyclohexane and hexane were 261 and 483, respectively. What is the concentration of hexane in the sample?

Exercise 7.24

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, discussed in a later topic) can detect elemental concentrations at very low levels. The following solutions are prepared in a standard addition experiment to determine the concentration of cadmium, a toxic metal, in urine. Solution 1 contains 5.00 mL of urine and 1.00 mL of a 10.0 μg/mL bismuth standard. Solution 2 contains these components, plus 1.00 mL of a 50.0 μg/mL cadmium standard. Both solutions are diluted to a total volume of 10.00 mL. The ICP-AES measurements for Cd are 11.9 and 42.0 in solutions 1 and 2, respectively. The corresponding measurements for Bi, used as an internal standard, are 93.7 and 79.6. Calculate the concentration of Cd in the urine sample by (a) considering only the response of Cd, and (2) using Bi as an internal standard.

7.10 Answers to Exercises 7

7.1 (a) 15.7 ppm (b) 16.1 ppm, no
(c) 20.5 ppm, larger

7.2 $2\bar{6}0$ mg/L

7.3 $1\bar{9}0$ mg/L

7.4 81.3 ppm^{-1}

7.5 (a) $3\bar{4}.3$ mg

7.6 (a) $4\bar{1}0$ ppm, (b) $4.\bar{7}1$ ppm^{-1}
(c) 2 ppm

7.7 3.75 mM

7.8 (a) 4.49 mM, (c) Probably not.

7.9 (a) 0.01_3, (b) 0.007_2 mM,
(c) 0.7_2 mM, (d) two, (e) 2.4 mM

7.10 (a) 0.0252_5 µA ppm^{-1},
(b) 0.0226 µA ppm^{-1},
(c) 0.0261 µA ppm^{-1}

7.11 Higher

7.12 (a) 74.6 ppm, (b) 66.5 ppm

7.13 $1._6$ ppm, 0.3_3 ppm

7.14

7.15 7.3_4 ppm

7.16 $17._2$ ppb

7.17 152 – 254 ppm, 0.380 – 0.634 g

7.18 2.8_5 ppm, no, yes

7.19 (a) No equation,
(b) $C_u = (R_2 - R_1)C_s/(2R_1 - R_2)$

7.20 0.0368 M

7.21 28.3 ppm

7.22 (a) 2.30×10^{-5} M, (b) 2.66×10^{-5} M

7.23 Yes; 0.194 M

7.24 (a) 3.95 µg/mL, (b) 3.17 µg/mL

Topic 8

Introduction to Solution Equilibria

8.1 Contents in Brief

- Definition of the equilibrium constant, *K*
- Applications to acid-base reactions, solubility, and complexation
- Calculations involving equilibria

8.2 Introduction

Chemical equilibrium is an important subject, not only in the study of chemistry, but more generally to any science in which chemistry plays a part, such as biology, geology, and biochemistry, to name a few. Understanding chemical equilibrium is also critical to the study of analytical chemistry, since it relates to the concentrations of species in solution. In this chapter, the basic principles of chemical equilibria are reviewed and applied to several types of solution equilibria important in analytical chemistry.

8.3 Chemical Equilibria

Consider a generic chemical reaction represented by Equation 8.1, where the upper case letters represent chemical species and the lower case letters represent the stoichiometric coefficients.

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \tag{8.1}$$

All chemical reactions are at equilibrium (at least in principle), and this is indicated by the double arrows ($\rightleftharpoons$). The term "equilibrium" implies that we will reach a point at which the concentrations of the chemical species remains fixed (even though the forward and reverse reactions may continue). In writing some reactions, a single arrow ($\rightarrow$) is often used, which may mean that the equilibrium is implied, or that the equilibrium lies well to the right, or that only the forward reaction is being considered.

Figure 8.1 shows a typical reaction profile that should be familiar to you. The rate at which the equilibrium is achieved is determined by the kinetics of the reaction, which depends on such things as the activation energy (E_a) and temperature. For our purposes in discussing chemical equilibria, we will assume that the equilibrium is established quickly (although this is not always true). The position of the equilibrium (*i.e.* the final concentrations of reactants and products) is determined by the initial concentrations and the thermodynamics of the reaction, specifically the Gibbs energy change for the reaction under standard conditions, ΔG°. This is reflected by the equilibrium constant, K, which for the generic case would be:

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \tag{8.2}$$

In this equation, which is valid for solution equilibria, the square brackets represent molar concentrations. The equilibrium constant is related to the standard Gibbs energy of the reaction by:

$$\Delta G^\circ = -RT \ln K \tag{8.3}$$

In general, this means that for reactions where the products are lower in energy than the reactants ($\Delta G^\circ < 0$), the products are favored in the equilibrium ($K > 1$), and vice-versa.

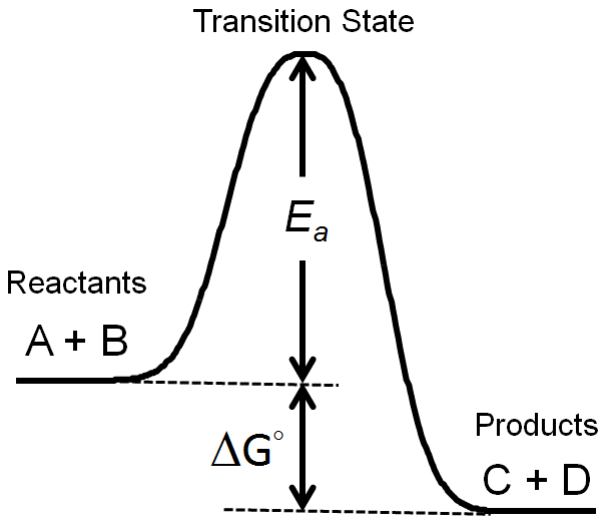


Figure 8.1: A reaction profile for a generic chemical reaction showing the activation energy, E_a, and the standard free energy of the reaction, ΔG°.

You should already be familiar with writing equilibrium constant expressions and manipulating them. For example, you should know that if the reverse chemical reaction is written, the equilibrium constant for the reversed reaction is the inverse of that for the reaction written in the forward direction.

forward: $aA + bB \rightleftharpoons cC$ $\qquad K_{for} = \dfrac{[C]^c}{[A]^a[B]^b}$

reverse: $cC \rightleftharpoons aA + bB$ $\qquad K_{rev} = \dfrac{[A]^a[B]^b}{[C]^c} = \dfrac{1}{K_{for}}$

In addition, when two reactions are added to form a third reaction, the equilibrium constant for the third reaction is the product of the other two equilibrium constants.

$$H_2A \rightleftharpoons HA^- + H^+ \qquad K_1 = [H^+][HA^-]/[H_2A]$$
$$\underline{HA^- \rightleftharpoons A^{2-} + H^+} \qquad K_2 = [H^+][A^{2-}]/[HA^-]$$
$$H_2A \rightleftharpoons A^{2-} + 2H^+ \qquad K_3 = [H^+]^2[A^{2-}]/[H_2A] = K_1 \times K_2$$

8.4 Equilibria in Analytical Chemistry

Chemical equilibria are important, either directly or indirectly, in virtually all aspects of analytical chemistry. In this section, some examples will be present to illustrate this. While the focus here will be on solution equilibria, you should be aware that gas phase equilibria can also be important in areas such as chromatography and atomic spectroscopy (covered later).

Perhaps the most widely studied type of chemical equilibrium is the reactions between acids and bases. You should already be familiar with aspects of acid-base equilibria and the subject will be treated extensively in this class because of the importance of these reactions in analytical chemistry. Aside from the obvious role that these reactions play in acid-base titrations, changes in pH affect many other chemical systems, including those that are used in chemical analysis. The pH of a chemical system is normally controlled through the use of acid-base buffers, so it is important to understand how these work and how to prepare them. Equilibrium constants employed in the study of acid-base equilibria are referred to as *acid*

and base dissociation constants, or K_a and K_b, respectively. Examples of these are given below:

$$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq) \qquad K_a = \frac{[F^-][H_3O^+]}{[HF]} = 6.8\times10^{-4}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.7\times10^{-5}$$

In these equations, hydrofluoric acid is a weak acid and ammonia is a weak base. Note that the equilibrium constants are quite small ($K \ll 1$), meaning that the equilibrium strongly favors the reactants. Note also that water is not included in the equilibrium constant expression, since solvents (as well as pure liquids and solids) are defined to have a concentration of unity.

Another area where equilibrium constants are important is in the formation of complex ions. Such reactions are often used to enhance the detection of analytes. For example, the ferric ion, Fe^{3+}, can be detected in solution from its reaction with the thiocyanate ion, SCN^- to form the complex ion $FeSCN^{2+}$, which has a blood-red color. Likewise, copper ions can be detected by the deep blue color they form with ammonia as the ligand, as indicated below.

$$Cu^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) \qquad K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 1.1\times10^{13}$$

Note that the equilibrium constant in this case is much greater than unity, indicating that the products are highly favored, unlike the previous example. As with acid-base equilibria, the equilibrium constant in this case is given a special name and symbol, referred to as the *formation constant*, K_f (also known as the *stablity constant*).

Equilibria are also relevant to analytical chemistry because they are used for chemical separation during analytical procedures. For example, chloride ions can be removed from solution by reacting them with an excess of silver ions, to form a solid precipitate that settles onto the bottom of the container. The relevant equilibrium is:

$$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-] = 1.8\times10^{-10}$$

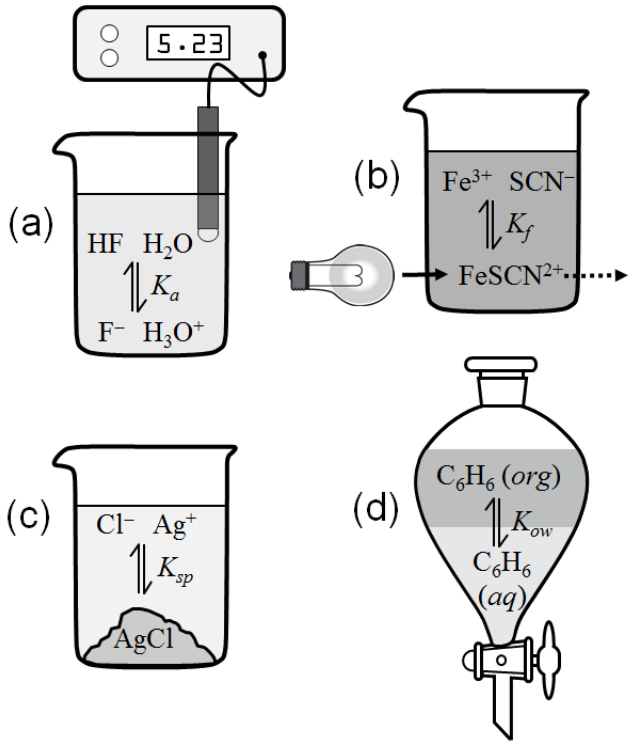


Figure 8.2: Some applications of equilibria in analytical chemistry: (a) acid-base equilibrium, (b) a complex ion formation which is used to form a colored product with the analyte, (c) a precipitation reaction used to remove ions from solution, and (d) an extraction used to separate mixture components.

The equilibrium constant in this case is called the *solubility product constant*, K_{sp}. Note that it does not include AgCl, since this is a pure solid. Also, note that this reaction favors the reactants, which means that most of the chloride ions should precipitate out of solution.

All of these examples have dealt with aqueous equilibria, but the same principle applies to the equilibrium of a chemical species between two phases. Such equilibria are important in separation methods used in analytical chemistry, such as solvent extraction and chromatography (discussed later). For example, a small amount of benzene (C_6H_6) dissolved in water could be extracted in to an immiscible organic solvent like octanol ($C_8H_{17}OH$) using a separatory funnel (see Figure 8.2). In this case, the equilibrium can be written as:

$$C_6H_6\ (aq) \rightleftharpoons C_6H_6\ (org) \qquad K_{ow} = \frac{[C_6H_6\ (org)]}{[C_6H_6\ (aq)]} = 135$$

Here "*org*" is used to indicate the organic phase, and the equilibrium coefficient is given a special designation as the *octanol-water partition coefficient*, K_{ow} (often used to characterize the hydrophobicity/lipophilicity of compounds). The high value in this case indicates that benzene favors the organic phase, as expected.

In a typical chemical system, there may be several reactions in equilibrium at the same time and these may interact with one another. For example, the ligands in a complex ion formation may also have acid-base characteristics. It is therefore important to understand how the concentrations of chemical species are affected, both qualitatively and quantitatively.

Exercise 8.1

For each of the following descriptions of an equilibrium, write a chemical equation for the equilibrium and an expression for the equilibrium constant.

(a) Acetic acid, CH_3COOH is a weak acid in aqueous solution.
(b) Methylamine, CH_3NH_2 is a weak base in aqueous solution.
(c) The ammonium ion, NH_4^+ is a weak acid in aqueous solution.
(d) The fluoride ion, F^-, is a weak base in aqueous solution.
(e) The cadmium ion (Cd^{2+}) reacts with six ammonia ligands to form a complex in water.

(f) Zinc ions react with chloride ions to form the complex $[ZnCl_4]^{2-}$ in water.
(g) Lead chloride ($PbCl_2$) precipitates from aqueous solution.

Exercise 8.2

Given the following equilibrium constants, write the corresponding chemical equilibria.

(a) $K = \dfrac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$

(b) $K = \dfrac{[Fe(CN)_6^{3-}]}{[Fe^{3+}][CN^-]^6}$

(c) $K = [Ca^{2+}]^3[PO_4^{3-}]^2$

(d) $K = \dfrac{[H_3O^+][NO_2^-]}{[HNO_2]}$

Exercise 8.3

Consider the following equilibria that involve the iron (III) ion and thiocyanate ion (SCN^-) in solution.

$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$ $\quad K_f = 8.9 \times 10^2$

$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$ $\quad K_{sp} = 2.5 \times 10^{-39}$

$HSCN(aq) + H_2O(l) \rightleftharpoons SCN^-(aq) + H_3O^+(aq)$ $\quad K_a = 71$

Based on this information, calculate the equilibrium constants for the following reactions.

(a) $Fe(OH)_3(s) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq) + 3\,OH^-(aq)$

(b) $[Fe(SCN)]^{2+}(aq) + H_3O^+(aq) \rightleftharpoons Fe^{3+}(aq) + HSCN(aq) + H_2O(l)$

Exercise 8.4

The iron-thiocyanate complex ion ($[Fe(SCN)]^{2+}$) gives a red color in solution. Based on the equilibria above, predict qualitatively what might happen to the concentration of the complex ion when the pH is increased or decreased. (This is an application of LeChâtelier's Principle.) Why is it important to control the pH of the solution if one wishes to measure the absorbance of the complex ion?

8.5 Equilibrium Calculations: Complex Ions

It is important to evaluate, both qualitatively and quantitatively, the concentrations of the species participating in an equilibrium so that their relative contributions to the overall mixture can be assessed. In the previous exercise, for example, it was important to know whether the absorbing species was present at significant concentrations at a particular set of conditions. These calculations are also important in determining the pH of a solution or the solubility of a substance.

You should already be familiar with equilibrium calculations from introductory chemistry classes, but these methods will be reviewed briefly here. In calculating concentrations, we start with the so called ICE table ("initial-change-equilibrium"). The first entries in the table are the initial conditions (concentrations), while the second row expresses the changes that occur in approaching equilibrium, typically shown in terms of an unknown quantity, *x*. The final row of the table, giving the equilibrium concentrations, is the sum of the first two rows and these values are substituted into the equilibrium constant expression to solve for *x*. An example will illustrate.

Example 8.1: Equilibrium Concentrations using K_f

A solution containing 0.0100 F Fe^{3+} is mixed with an equal volume of a solution containing 0.0100 F SCN^-. Given that the formation constant of $[Fe(SCN)]^{2+}$ is 8.9×10^2, calculate the equilibrium concentrations of Fe^{3+}, SCN^-, and $[Fe(SCN)]^{2+}$.

Note that, because the solutions are mixed together, the initial concentrations of the species will be half of their original values, or 0.00500 F. With these values and the equilibrium, we can set up our table.

	$Fe^{3+}(aq)$	+ $SCN^{-}(aq)$	$\rightleftharpoons$	$[Fe(SCN)]^{2+}(aq)$	
Initial:	0.00500	0.00500		0	mol/L
Change:	$-x$	$-x$		$+x$	mol/L
Equilibrium:	$0.00500-x$	$0.00500-x$		x	mol/L

We can now substitute these into our equilibrium constant expression.

$$K_f = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^{-}]} = \frac{x}{(0.00500-x)(0.00500-x)} = \frac{x}{(2.50\times10^{-5} - 0.0100x + x^2)}$$

Rearranging, this becomes a quadratic equation.

$$(2.50\times10^{-5})K - (0.0100)Kx + Kx^2 = x$$

or $$Kx^2 - (0.0100K + 1)x + (2.50\times10^{-5})K = 0$$

This has the quadratic form of ($ax^2 + bx + c = 0$), where:

$a = K = 8.9 \times 10^2$, $b = -(0.0100K + 1) = -9.9$, $c = (2.50 \times 10^{-5})K = 0.02\overline{2}25$

Substituting these into the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 0.007\overline{9}98 \text{ or } 0.003\overline{1}26$$

Since the first solution would give negative concentrations for $Fe^{3+}$and SCN^{-}, the second solution is the valid one. This gives equilibrium concentrations of:

$$[Fe^{3+}] = [SCN^{-}] = 0.00500\ M - 0.003\overline{1}26\ M = 0.001\overline{8}7\ M$$

$$[FeSCN^{2+}] = 0.003\overline{1}3\ M$$

Exercise 8.5

Using the formation constant from the previous example, calculate the equilibrium concentrations of all species in solution when equal volumes of 0.00600 F Fe^{3+} and 0.00400 F SCN^- are mixed.

Stoichiometric Equivalence

An important principle of chemical equilibria is that the same equilibrium position is always attained regardless of the starting conditions, as long as those conditions are *stoichiometrically equivalent*. This means that all of the conditions represent states that could be achieved simply by reacting stoichiometric amounts of reactants or products. Typically, a problem is solved by considering the reaction driven all of the way to the left (reactants) or to the right (products), but any intermediate state can also be used.

To illustrate this, consider the previous example where the initial conditions were taken to be $[Fe^{3+}] = [SCN^-] = 0.00500$ M and $[FeSCN^{2+}] = 0$. A stoichiometrically equivalent starting point would be one in which all of the reactants were converted to products, or $[Fe^{3+}] = [SCN^-] = 0$ and $[FeSCN^{2+}] = 0.00500$ M. From this starting point, our equilibrium conditions would be:

$$\begin{array}{ccccc} Fe^{3+}(aq) & + & SCN^-(aq) & \rightleftharpoons & [Fe(SCN)]^{2+}(aq) \\ x & & x & & 0.00500-x \quad \text{mol/L} \end{array}$$

Note that here we have left out the first two rows of the ICE table, a practice that will be used throughout the rest of this book. In this case, the equilibrium expression becomes:

$$K_f = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{(0.00500 - x)}{x^2}$$

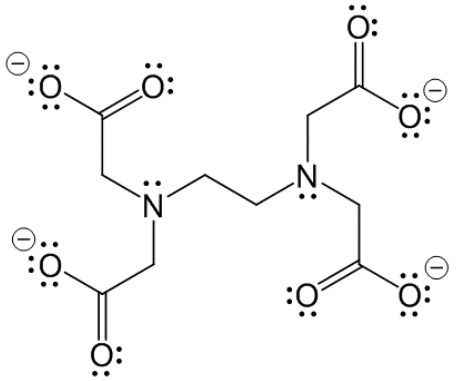
This leads to the quadratic equation ($Kx^2 + x - 0.00500 = 0$) with solutions of $x = 0.00187$ M and -0.00300 M. The first solution is the only valid one and leads to the same equilibrium concentrations as previously obtained by starting with only reactants. Thus, the equilibrium position remains unchanged regardless of where we start.

The concept of stoichiometric equivalence is important because, for certain problems, it may be more difficult to arrive at a solution from a particular starting point. This is especially true when the equilibrium constant is very large or very small (products or reactants are strongly favored). The following example is an illustration of this.

Example 8.2: Equilibrium Concentrations using K_f

EDTA (ethylenediaminetetraacetate, see figure at left) is a complexing agent with multiple uses, such as binding metal ions that can catalyze oxidation in food and chelation therapy in medicine. A solution containing 0.500 F EDTA (represented below as Y^{4-}) is mixed with an equal volume of a solution containing 0.0200 M Fe^{3+} forming the complex ion FeY^- according to the reaction below. What is the concentration of the free ferric ion, Fe^{3+} in the solution at equilibrium?

$$Fe^{3+}(aq) + Y^{4-}(aq) \rightleftharpoons FeY^-(aq) \qquad K_f = 1.7 \times 10^{24}$$



Ethylenediaminetetraacetate (EDTA)

As before, mixing equal volumes of the two solutions will dilute the initial concentrations by a factor of two, so we can set up the equilibrium calculation as given below.

$Fe^{3+}(aq)$	+	$Y^{4-}(aq)$	$\rightleftharpoons$	$FeY^-(aq)$	
$0.0100-x$		$0.250-x$		x	mol/L

This leads to the equation:

$$K_f = \frac{[FeY^-]}{[Fe^{3+}][Y^-]} = \frac{x}{(0.0100-x)(0.250-x)}$$

The resulting quadratic equation is:

$$Kx^2 - (K(0.260)+1)x + K(0.00250) = 0$$

Although this equation is technically correct, solving the quadratic formula leads to the result $x = 0.01$, which leads to a value of $[Fe^{3+}] = 0$. This is clearly wrong, since there must be at least a small amount of Fe^{3+} present to satisfy the equilibrium

expression. Although it is set up correctly, the value of K_f is so large that it causes numerical problems on most calculators, which have limited precision.

The solution to this problem is to first drive all of the reactants to products and start from that point, which is stoichiometrically equivalent. Since Fe^{3+} is the limiting reagent, the maximum concentration of the complex will be 0.0100 M and the remaining concentration of Fe^{3+} will be zero. The concentration of EDTA remaining will be (0.250 – 0.0100) = 0.240 M. We can now write the initial conditions as given below.

$$\begin{array}{ccccc} Fe^{3+}(aq) & + & Y^{4-}(aq) & \rightleftharpoons & FeY^{-}(aq) \\ x & & 0.240+x & & 0.0100-x \quad \text{mol/L} \end{array}$$

This leads to the equation:

$$K_f = \frac{[FeY^-]}{[Fe^{3+}][Y^-]} = \frac{(0.0100-x)}{(x)(0.240+x)} \qquad \text{or} \qquad Kx^2 + (K(0.240)+1)x - 0.0100 = 0$$

This gives results of $x = 0$ and $x = -0.240$. The second solution is clearly invalid, but the first is also not really any more informative than the previous case. The difference here, however, is that x is very small ($x \ll 0.0100$) so we can make the following approximation.

$$K_f \approx \frac{0.0100}{(x)(0.240)}$$

or $$x \approx \frac{0.0100}{K_f(0.240)} = \frac{0.0100}{(1.7 \times 10^{24})(0.240)} = 2.5 \times 10^{-26}\ \text{M} = [Fe^{3+}]$$

Clearly the approximation is valid in this case.

Note that we will typically use stoichiometric equivalence to push the reactants to the product side when the value of K is very large (*e.g.* in the case of formation constants- see Table 8.1), and to push the products to the reactant side when K is very small. For intermediate values of K, either starting point should result in a solution.

Table 8.1. Formation constants of some metal complex ions at 25 °C.

Ion	K_f
$[Ag(NH_3)_2]^+$	1.6×10^7
$[Ag(S_2O_3)_2]^{3-}$	1.7×10^{13}
$[Cu(EDTA)]^{2-}$	5×10^{18}
$[Cu(NH_3)_4]^{2+}$	1.1×10^{13}
$[Fe(CN)_6]^{3-}$	1×10^{42}
$[Fe(EDTA)]^-$	1.7×10^{24}
$[Fe(SCN)]^{2+}$	8.9×10^2
$[Ni(EDTA)]^{2-}$	3.6×10^{18}
$[Ni(NH_3)_6]^{2+}$	5.5×10^8
$[Zn(EDTA)]^{2-}$	3×10^{16}
$[Zn(NH_3)_4]^{2+}$	4.1×10^8

Approximations

The previous example made use of the approximation that x was small enough that it could be ignored in any term in the equilibrium expression in which it was added to or subtracted from a fixed value. This approach can greatly simplify the solution and is widely used in solving equilibrium problems. There are essentially three situations where this strategy is employed:

(i) when the quadratic form can be solved, but the approximation is easier to calculate and does not significantly change the results,
(ii) when the quadratic form results in a solution of $x = 0$ due to calculator rounding errors,
(iii) when the solution involves higher order equations for which there is no analytical solution

A common question that surfaces when using such approximations concerns when the approximation can be considered to be valid. There is no universal answer for this, since it depends on the degree of precision required in the answer and the nature of the problem. For this course, we will consider the approximation to be valid when the determined quantity is less than 5% of the smallest concentration it is added to or subtracted from as indicated below.

$$\left(\frac{x}{C_{\text{min}}}\times 100\%\right) < 5\% \quad \text{or} \quad \left(\frac{C_{\text{min}}}{x}\right) > 20$$

For instance, in the previous example, $C_{\text{min}}/x = 0.01/2.5\text{x}10^{-26} = 4\text{x}10^{23}$, so the approximation is clearly valid. This example is one in which case (ii) applied. A situation where case (iii) applies is given in the following exercise.

Exercise 8.6

A solution containing 0.500 F NH_3 is mixed with an equal volume of a solution containing 0.0200 F $Cu(NO_3)_2$, resulting in an intense blue color from the formation of the complex ion $[Cu(NH_3)_4]^{2+}$. What is the concentration of the free copper ion, Cu^{2+} in the solution at equilibrium? The K_f value for the copper-ammonia complex is $1.1 \text{ x } 10^{13}$ (see Table 8.1).

8.6 Equilibrium Calculations: Solubility

When two or more ions dissolved in solution encounter one another, they may react to form a neutral ionic compound that precipitates from solution as an insoluble solid. For example, if a solution of silver nitrate, $AgNO_3$, is mixed with a solution of sodium chloride, NaCl, the silver ions will react with the chloride ions to form insoluble silver chloride, AgCl, as given by the reaction below and shown in Figure 8.3.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

The reason AgCl precipitates, while $AgNO_3$, NaCl and $NaNO_3$ do not, has to do with the Gibbs energy of the forward reaction, which is a balance between the higher entropy of ions in solution (ΔS contribution) and the negative enthalpy change of crystal formation (ΔH contribution). In this example, the sodium and nitrate ions are "spectator ions" and do not directly participate in the reaction.

Because solubility depends on thermodynamics, it is not immediately apparent which ionic compounds will be insoluble, but observations allow us to formulate some general rules.

- Compounds with Group 1 (Na^+, K^+, etc.), ammonium (NH_4^+), acetate (CH_3COO^-), nitrate (NO_3^-), or perchlorate (ClO_4^-) ions are generally soluble.
- Halides (containing Cl^-, Br^-, I^-) are usually soluble, except with Ag^+, Pb^{2+}, and Hg_2^{2+}.
- Sulfates (SO_4^{2-}) are usually soluble except with Ag^+, Pb^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}.
- Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), hydroxides (OH^-), and sulfides (S^{2-}) are usually insoluble, except when the first rule applies.

The term "insoluble" is not entirely accurate, since equilibrium conditions demand that a small amount of the compound is always dissolved, and so it usually taken to mean "sparingly soluble". The amount dissolved is determined by the conditions and the value of the solubility product constant, K_{sp}, as defined below for AgCl.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

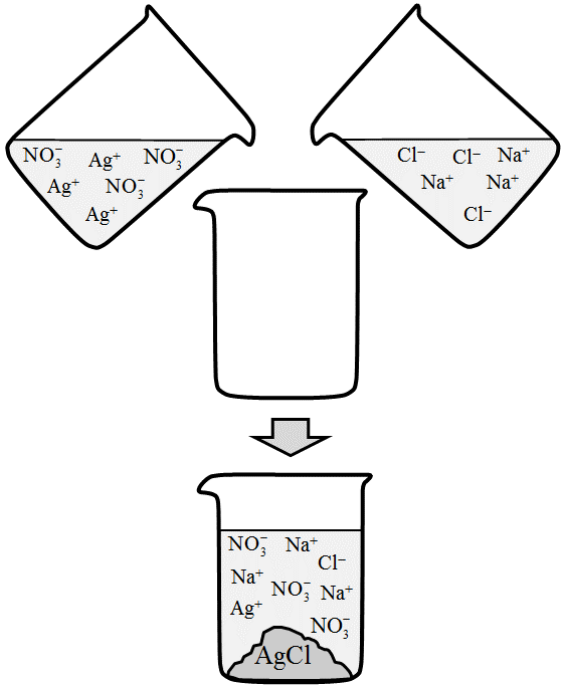


Figure 8.3: Precipitation of silver chloride by mixing solutions of silver nitrate and sodium chloride.

The value of K_{sp} is quite small for compounds that are classified as insoluble (see Table 8.2) and the equilibrium expression differs from other such equations in that there is no contribution from the product, which is a pure solid. This means that calculations involving K_{sp} are a little different from other kinds of equilibria.

The *solubility* of an ionic compound is defined as the concentration of that compound in a *saturated solution*, meaning that no more of the solute will dissolve. Conditions of saturation exist when the dissolved ions are in equilibrium with the solid form. Because of this, the K_{sp} can be used to determine solubility, as illustrated in the following examples.

Example 8.3: Solubility Calculations using K_{sp}

Determine the solubility of (a) AgCl and (b) PbI_2 in water using the K_{sp} values given in Table 8.2.

(a) A solution saturated with silver chloride will follow the equilibrium given below:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

-		x	x	mol/L

Note that the amount of solid AgCl is not important in this equilibrium as long as it is present so that the solution is at equilibrium. The quantities above can be substituted into the equilibrium expression to solve for x.

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.8 \times 10^{-10}$$

$$x = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}\ \text{M}$$

Therefore, the solubility of silver chloride is 1.3×10^{-5} M.

(b) A similar calculation can be performed for lead(II) iodide, but note that there are important differences in the stoichiometry and the expression for K_{sp}.

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

-		x	$2x$	mol/L

$$K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 4x^3 = 9.8 \times 10^{-9}$$

Table 8.2. Solubility product constants of some ionic compounds at 25 °C*.

Formula	Name	K_{sp}
AgBr	Silver bromide	5.4×10^{-13}
AgCl	Silver chloride	1.8×10^{-10}
AgI	Silver iodide	8.5×10^{-17}
$Ba(OH)_2$	Barium hydroxide	2.6×10^{-4}
$BaSO_4$	Barium sulfate	1.1×10^{-10}
CaC_2O_4	Calcium oxalate	2.3×10^{-9}
$CaCO_3$	Calcium carbonate	3.4×10^{-9}
CaF_2	Calcium fluoride	3.4×10^{-11}
$Ca(OH)_2$	Calcium hydroxide	5.0×10^{-6}
$Ca_3(PO_4)_2$	Calcium phosphate	2.1×10^{-33}
$Fe(OH)_2$	Iron(II) hydroxide	4.9×10^{-17}
$Mg(OH)_2$	Magnesium hydroxide	5.6×10^{-12}
$Ni(OH)_2$	Nickel(II) hydroxide	5.5×10^{-16}
$PbCl_2$	Lead(II) chloride	1.7×10^{-5}
PbI_2	Lead(II) iodide	9.8×10^{-9}
$PbSO_4$	Lead(II) sulfate	2.5×10^{-8}

*Values obtained from *CRC Handbook of Chemistry and Physics, 84th edn.*, CRC Press, 2004.

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{9.8\times10^{-9}}{4}} = 1.3\times10^{-3}\ \text{M}$$

As before, *x* corresponds to the formality of lead iodide in solution, so its solubility is 1.3 x 10^{-3} mol/L.

Exercise 8.7

Determine the solubility of AgBr in water in mg/L.

Exercise 8.8

Determine the solubility (in mol/L) of the following compounds in water: (a) calcium carbonate, (b) calcium hydroxide, (c) calcium phosphate. What is the concentration of calcium ions in each solution?

It is important that solubility equilibria, as with all solution equilibria, are often influenced by other chemical equilibria that exist in solution. For example, all of the anions in the previous exercise have acid/base characteristics and their concentrations can be affected by acid-base equilibria. For the purposes of these calculations, however, those complications have been ignored.

Common Ion Effects

It is quite common for ionic equilibria to be affected by ions in solution that appear in the equilibrium expression but arise from an independent source. Because such ions appear from two or more solutes independently, they are referred to as *common ions*. An example of this

is buffer solutions, where the common ion arises from conjugate acid/base pairs. In solubility equilibria, such ions also play an important role, as illustrated in the examples that follow.

Example 8.4: Solubility Calculations with Common Ions

Determine the solubility of $PbCl_2$ in: (a) pure water, and (b) a solution that contains 0.100 F NaCl. Use the K_{sp} values given in Table 8.2

(a) For pure water, we proceed as we did in the earlier examples.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$$

-	x	$2x$	mol/L

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = (x)(2x)^2 = 4x^3 = 1.7\times10^{-5}$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.7\times10^{-5}}{4}} = 0.016\ \text{M}$$

(b) For 0.100 F NaCl, we need to account for chloride ion already present.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$$

-	x	$0.100+2x$	mol/L

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = (x)(0.100+2x)^2 \approx (x)(0.100)^2 = (0.0100)x = 1.7\times10^{-5}$$

$$x = \frac{K_{sp}}{0.0100} = \frac{1.7\times10^{-5}}{0.0100} = 0.0017\ \text{M}$$

In this calculation, we have made the assumption that $2x \ll 0.100$ to avoid solving the cubic equation. This result is valid, since 0.0034 is 3.4% of 0.1.

Note that, in the preceding example, the solubility of the lead chloride decreased in the presence of the common ion, which is the chloride ion in this case. This is a quantitative illustration of LeChâtelier's Principle.

One might wonder in this problem what would have happened if the assumption was not valid. One approach to avoid solving the cubic equation would be to calculate the solution *iteratively*. To do this, the total chloride ion concentration calculated here (0.100+2(0.0017)) would be used in place of the NaCl concentration and the result would be recalculated. Repetition of this process leads to only a slight adjustment of the answer to 0.0016 M.

Example 8.5: Solubility Calculations and pH

Determine the solubility of iron(II) hydroxide (K_{sp} = 4.9 x 10^{-17}) in: (a) pure water, (b) a solution buffered at a pH of 9.00, and (c) a solution buffered at a pH of 6.00.

(a) For pure water, we proceed as before.

$$\mathrm{Fe(OH)_2}(s) \rightleftharpoons \mathrm{Fe^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

-	x	$2x$	mol/L

$$K_{sp} = [\mathrm{Fe^{2+}}][\mathrm{OH^-}]^2 = (x)(2x)^2 = 4x^3 = 4.9\times10^{-17}$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4.9\times10^{-17}}{4}} = 2.3\times10^{-6}\ \mathrm{M}$$

(b) When the solution is pH buffered, the concentration of H_3O^+ is fixed, and therefore so is the concentration of OH^-. This simplifies the calculations.

$$\mathrm{pOH} = 14.00 - \mathrm{pH} = 14.00 - 9.00 = 5.00 \quad \therefore\ [\mathrm{OH^-}] = 10^{-5.00} = 1.00\times10^{-5}\ \mathrm{M}$$

$$\mathrm{Fe(OH)_2}(s) \rightleftharpoons \mathrm{Fe^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

-	x	1.0 x 10^{-5}	mol/L

$$K_{sp} = [\mathrm{Fe^{2+}}][\mathrm{OH^-}]^2 = (x)(1.0\times10^{-5})^2 = (1.0\times10^{-10})x = 4.9\times10^{-17}$$

$$x = \frac{K_{sp}}{1.0\times10^{-10}} = \frac{4.9\times10^{-17}}{1.0\times10^{-10}} = 4.9\times10^{-7}\ \mathrm{M}$$

(c) The same pattern of calculation as in part (b) is followed below.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 6.00 = 8.00 \quad \therefore\ [\text{OH}^-] = 10^{-8.00} = 1.00 \times 10^{-8}\ \text{M}$$

$$K_{sp} = [\text{Fe}^{2+}][\text{OH}^-]^2 = (x)(1.0 \times 10^{-8})^2 = (1.0 \times 10^{-16})x = 4.9 \times 10^{-17}$$

$$x = \frac{4.9 \times 10^{-17}}{1.0 \times 10^{-16}} = 0.49\ \text{M}$$

Note that the concentration is much higher under acidic conditions, indicating how pH plays a role in determining solubility.

Exercise 8.9

The K_{sp} for silver sulfate (MM = 311.80 g/mol) is 1.2 x 10^{-5}. How many grams of silver sulfate can be dissolved in: (a) 100.0 mL of pure water, and (b) 100.0 mL of a 0.200 F sodium sulfate solution?

Exercise 8.10

The term "milk of magnesia" is used to refer to an aqueous suspension of insoluble magnesium hydroxide ($Mg(OH)_2$, MM = 58.32 g/mol) that is sometimes used as an antacid and laxative. For the following questions, assume that the suspension has a total of 8.00 g of $Mg(OH)_2$ in 100.0 mL of water.

(a) What mass of $Mg(OH)_2$ (K_{sp} = 5.6 x 10^{-12}) is *dissolved* in the water?
(b) What is the pH of the suspension?
(c) To what value would the pH need to be lowered to dissolve all of the $Mg(OH)_2$ present (assume no volume change).

Precipitation Reactions

A *precipitation reaction* occurs when two solutions are mixed and ions present in the two solutions react to form an insoluble precipitate. Such reactions are important in chemical analysis because they can be used in *gravimetric analysis*, a technique in which the amount of ion dissolved in solution can be determined from the mass of product formed, assuming that the counter ion is added in excess. Calculations generally assume that all of the analyte ion has been removed from solution. The extent to which this is true can be verified by equilibrium calculations.

Example 8.6: Precipitation Reactions

Determine the mass of any precipitate formed and the concentration of all ions in solution when 25.00 mL of 0.100 F NaCl is added to 100.0 mL of 8.00 x 10^{-3} F $AgNO_3$.

The first step in this problem is to determine what, if any precipitate forms. The ions present are Na^+, Cl^-, Ag^+ and NO_3^-. We know that NaCl and $AgNO_3$ are soluble, since they are already in solution, leaving $NaNO_3$ and AgCl as possible products. $NaNO_3$ should be soluble (see solubility rules), but AgCl is listed with a K_{sp} value in Table 8.2, which means that it has limited solubility. The possible reaction is:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

The second step is to determine if the reaction will occur by calculating the initial concentrations and the reaction quotient, Q_{sp}. The initial concentrations will be different from the original values due to dilution and can be readily calculated.

$$[Na^+]_o = [Cl^-]_o = 0.100\,\text{M} \times \frac{25.00\,\text{mL}}{125.0\,\text{mL}} = 0.0200\,\text{M}$$

$$[Ag^+]_o = [NO_3^-]_o = 8.00 \times 10^{-3}\,\text{M} \times \frac{100.0\,\text{mL}}{125.0\,\text{mL}} = 6.40 \times 10^{-3}\,\text{M}$$

Recall that the reaction quotient, Q, is calculated in the same way as the equilibrium constant, but applies when we are not at equilibrium. The applicable equilibrium is:

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$

$Q_{sp} = [Ag^+]_o[Cl^-]_o = (6.40\times10^{-3})(0.0200) = 1.28\times10^{-4}$

Since $Q_{sp}>K_{sp}$, the reaction will proceed in the reverse direction, so we know that a precipitate will form. We can now set up the equilibrium calculation.

$AgCl(s)$	$\rightleftharpoons$	$Ag^+(aq)$	+	$Cl^-(aq)$
-		$(0.00640-x)$		$(0.0200-x)$

Although this is technically correct, because K is very small it will lead to a quadratic equation with the valid solution $x = 0.0064$, which implies there is no Ag^+ left in solution. In this situation (small K) we need to shift everything to the reactant side. Because Ag^+ is the limiting reagent, the stoichiometrically equivalent set up is:

$AgCl(s)$	$\rightleftharpoons$	$Ag^+(aq)$	+	$Cl^-(aq)$
-		x		$(0.0136+x)$

From this, we obtain a quadratic equation that can be simplified to determine x.

$K_{sp} = [Ag^+][Cl^-] = (x)(0.0136 + x) \approx (0.0136)x \quad \text{if } x \ll 0.0136$

$$x \approx \frac{K_{sp}}{0.0136} = \frac{1.8\times10^{-10}}{0.0136} = 1.3\times10^{-8}\ \text{M} \quad \text{(assumption valid)}$$

Therefore, we have as final concentrations:

$[Ag^+] = x = 1.3 \times 10^{-8}$ M, $[Cl^-] = (0.0136 + x) = 0.0136$ M,

$[Na^+] = [Na^+]_o = 0.0200$ M, $[NO_3^-] = [NO_3^-]_o = 0.00640$ M

To determine the mass of product formed, we use the moles of Ag^+ reacted, since it is the limiting reagent.

$$\text{moles AgCl formed} = \text{moles } Ag^+ \text{ reacted} = (0.00640\,\text{M} - x)\cdot(0.125\,\text{L})$$
$$\approx (0.00640\,\text{mol/L})\cdot(0.125\,\text{L}) = 8.00\times10^{-4}\ \text{mol}$$

$$\text{mass of AgCl} = (8.00\times10^{-4}\ \text{mol})\times(143.32\,\text{g/mol}) = 0.115\,\text{g}$$

Note that essentially all of the Ag^+ is converted to silver chloride.

Example 8.7: Gravimetric Analysis

A 0.1405 g solid sample of an organic compound containing bromine is treated in such a way to release the bromine as bromide ions in 50.0 mL of an aqueous solution. A 10.0 mL aliquot of 0.100 F $AgNO_3$ is added to precipitate the bromide ions as AgBr. The dried precipitate has a mass of 0.1027 g. What is the percentage by mass of bromine in the original sample? What are the concentrations of Ag^+ and Br^- remaining in solution? What percentage of the bromine remains unprecipitated?

Since the K_{sp} for AgBr is quite small (5.4×10^{-13}), we can assume that the precipitation reaction below goes essentially to completion.

$$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$$

$$\text{moles of AgBr} = \frac{0.1027\,\text{g AgBr}}{187.77\,\text{g/mol AgBr}} = 5.469 \times 10^{-4}\,\text{mol}$$

This will also equal the moles of Ag^+ and Br^- reacted, and will be equal to the moles of Br in the original compound if Ag^+ is not the limiting reactant. To check this, we can determine the moles of Ag^+ remaining.

$$\text{initial moles } Ag^+ = (0.100\,\text{mol/L})(0.0100\,\text{L}) = 0.00100\,\text{mol}$$

$$\text{moles } Ag^+ \text{ remaining} = 0.00100\,\text{mol} - 0.0005469\,\text{mol} = 0.00045\,\text{mol}$$

Therefore, Br^- is limiting and we can calculate the %Br in the original sample.

$$\text{mass of Br} = 5.469 \times 10^{-4}\,\text{mol AgBr} \times \frac{1\,\text{mol Br}}{1\,\text{mol AgBr}} \times 79.90\,\text{g/mol Br} = 0.4370\,\text{g}$$

$$\%\text{Br} = \frac{0.04370\,\text{g}}{0.1405\,\text{g}} \times 100\% = 31.10\%$$

The solution concentrations of Ag^+ and Br^- can be determined from the excess and the K_{sp}, since at equilibrium $K_{sp} = [Ag^+][Br^-]$.

$$[Ag^+] = \frac{\text{moles } Ag^+ \text{ remaining}}{\text{total volume}} = \frac{0.00045\,\text{mol}}{0.060\,\text{L}} = 0.0075\,\text{M}$$

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5.4\times10^{-13}}{0.0075\,\text{M}} = 7.2\times10^{-11}\,\text{M}$$

$$\text{mol Br in solution} = (7.2\times10^{-11}\,\text{mol/L})(0.0600\,\text{L}) = 4.3\times10^{-12}\,\text{mol}$$

$$\%\,\text{unprecipitated} = \frac{4.3\times10^{-12}\,\text{mol}}{5.469\times10^{-4}\,\text{mol}}\times100\% = 7.9\times10^{-7}\,\%$$

Since the amount that remains unprecipitated is so small, the original assumption that the reaction is essentially complete was valid.

Exercise 8.11

The K_{sp} for lead(II) iodide (MM = 462.0 g/mol) is 9.8 x 10^{-9}. Consider the addition of 10.0 mL of 0.800 F potassium iodide solution to 90.0 mL of a 5.00 x 10^{-3} F solution of lead(II) nitrate. When equilibrium is achieved, determine the concentration of Pb^{2+} and I^- ions in solution, and the mass of solid PbI_2 formed.

Exercise 8.12

A 0.5715 g sample of limestone is dissolved in hydrochloric acid. The calcium in the sample is precipitated as calcium oxalate by adding an excess amount of $(NH_4)_2C_2O_4$ in solution. The mass of the dried precipitate is 0.6744 g. What is the percentage of calcium in the limestone?

8.7 Summary

Chemical equilibria are important in determining what species are present in solution and what reactions will occur. Here, the focus was on several kinds of equilibria that are important in analytical chemistry, including acid-base equilibria (characterized by acid/base dissociation constants, K_a and K_b), complex ion formation (characterized by the formation constant, K_f) and precipitation reactions (characterized by the solubility product constant, K_{sp}). You should be familiar with equilibrium calculations, including the use of approximations and the application of stoichiometric equivalence to solve problems. You should also be familiar with the use of precipitation reactions for quantitative analysis.

8.8 Additional Exercises

Exercise 8.13

The complexing agent EDTA is sometimes used to treat heavy metal poisoning because it forms strong, soluble complexes that prevent the metal ions from reacting. Given that the formation constant of $[Pb(EDTA)]^{2-}$ is 1.1×10^{18}, calculate the percentage of Pb present as free Pb^{2+} ion when 10.0 mL of a solution containing 0.0500 M EDTA is added to 90.0 mL of 0.00400 F lead(II) nitrate solution.

Exercise 8.14

What is the concentration of free Ag^+ ion in a solution prepared by mixing 50.0 mL of a solution containing 0.00200 M Ag^+ with 50.0 mL of a solution containing 0.0100 M NH_3?

Exercise 8.15
In the "old days", the final step in developing black and white photographic film (known as "fixing") involved dissolving unexposed silver halide in a solution of sodium thiosulfate, $Na_2S_2O_3$. Using the equilibrium constants in Tables 8.1 and 8.2, calculate the equilibrium constant for the following reaction.

$$AgBr(s) + 2\,S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$$

Exercise 8.16
Based on the answer to the previous question, how many grams of silver bromide will dissolve in 100.0 mL of 0.100 F $Na_2S_2O_3$? (Assume no volume change.) What is the concentration of free Ag^+ ions in this solution?

Exercise 8.17
Estimate the solubility of the following compounds in water in mg/L?
(a) $BaSO_4$ (b) $Ni(OH)_2$

Exercise 8.18
What is the solubility of lead(II) chloride in 0.200 F lithium chloride? Would the same calculation be valid for 0.0200 F LiCl? How would you proceed in this case?

Exercise 8.19
Estimate the pH of a solution saturated with barium hydroxide.

Exercise 8.20
A main component of tooth enamel is calcium hydroxyapatite, $Ca_5(PO_4)_3OH$ (MM = 502.31 g/mol). The solubility product constant for this material has been reported as 5.5×10^{-55}. Estimate the solubility of this material (in mg/L) at pH = 7.00 and pH = 2.00. What assumption is made in this calculation?

Exercise 8.21

A solution containing 5.00 x 10^{-6} M Ag^+ is titrated with 50.00 mL of a solution containing chloride ions at an unknown concentration. A precipitate begins to appear after the addition of 7.32 mL of the silver solution. What is the concentration of chloride in the unknown solution?

Exercise 8.22

A 0.2090 g solid sample which is a mixture of NaCl and KCl is dissolved in 100.0 mL of water. A 10.00 mL aliquot of 0.500 F $AgNO_3$ is added to this solution to precipitate the chloride ion as silver chloride. The dried precipitate weighs 0.4973 g. How many moles of chlorine are present in the original solid? What is the mole fraction of KCl in the solid? What is the percentage by mass of KCl in the solid? What is the concentration of chloride ion in the solution after the precipitate has formed?

Exercise 8.23

An unknown solid with the formula $BaCl_2{\cdot}xH_2O$ and a mass of 0.8786 g is dissolved in 50.0 mL of water and 50.0 mL of a 0.100 F sodium sulfate solution is added to precipitate barium sulfate. The dried precipitate weighs 0.8395 g. What is the value of *x* in the unknown formula? What is the concentration of Ba^{2+} remaining in solution?

8.9 Answers to Exercises 8

8.1 (a) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$, $K_a = [CH_3COO^-][H_3O^+]/[CH_3COOH]$

(b) $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$, $K_b = [CH_3NH_3^+][OH^-]/[CH_3NH_2]$

(c) $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$, $K_a = [NH_3][H_3O^+]/[NH_4^+]$

(d) $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$, $K_b = [HF][OH^-]/[F^-]$

(e) $Cd^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons [Cd(NH_3)_6]^{2+}(aq)$, $K_f = [Cd(NH_3)_6^{2+}]/[Cd^{2+}][NH_3]^6$

(f) $Zn^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons [ZnCl_4]^{2-}(aq)$, $K_f = [ZnCl_4^{2-}]/[Zn^{2+}][Cl^-]^4$

(g) $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq)$, $K_{sp} = [Pb^{2+}][Cl^-]^2$

8.2 (a) $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$

(b) $Fe^{3+}(aq) + 6\,CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$

(c) $Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq)$

(d) $HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$

8.3 (a) $K = 2.2 \times 10^{-36}$
(b) $K = 1.6 \times 10^{-5}$

8.4 -

8.5 $[Fe^{3+}] = 0.001\overline{7}8\ M$
$[SCN^-] = 0.000\overline{7}8\ M$
$[FeSCN^{2+}] = 0.001\overline{2}2\ M$

8.6 4.7×10^{-13} M

8.7 0.14 mg/L

8.8 (a) 5.8×10^{-5} mol/L
(b) 0.011 mol/L
(c) 1.1×10^{-7} mol/L
$[Ca^{2+}] = 5.8 \times 10^{-5}$ M, 0.011 M, 3.4×10^{-7} mol/L

8.9 (a) 0.45_0 g, (b) 0.12_1 g

8.10 (a) $6.5_2 \times 10^{-4}$ g, (b) 10.35, (c) 8.31

8.11 $[Pb^{2+}] = 1.9 \times 10^{-6}$ M,
$[I^-] = 0.0710$ M, $m_{PbI2} = 0.208$ g

8.12 36.92%

8.13 6.5×10^{-14} %

8.14 6.9×10^{-6} M

8.15 9.2

8.16 0.80_6 g, $1.2_6 \times 10^{-11}$ M

8.17 (a) 2.4 mg/L, (b) 0.48 mg/L

8.18 4.3×10^{-4} M; No

8.19 12.91

8.20 0.15 mg/L, 0.63 mg/L;
It is assumed that all of the phosphate remains as PO_4^{3-}.

8.21 3.2×10^{-4} M

8.22 3.470×10^{-3}, 0.111_2, 13.8%, 1.3×10^{-8} M

8.23 2, 7.8×10^{-9} M

Topic 9

Non-Ideal Solutions

9.1 Contents in Brief

- Non-ideal behavior, activities and activity coefficients
- Calculation of activities with the Debye-Hückel Equation
- Equilibrium calculations in non-ideal solutions

9.2 Introduction

You should be familiar with the concept of an ideal gas as one that follows the ideal gas law (*PV=nRT*). Under certain conditions, such as high pressures, gases will no longer obey this law and become "non-ideal". In the same way, solutions can become non-ideal as the concentration increases and don't follow the expected behavior as predicted by the equilibrium constant expressions. Chemical equilibria are governed by thermodynamics, and deviations from assumed thermodynamic relationships can occur when there are interactions among species in solution. This can lead to non-ideal behavior, which is examined here.

9.3 Activities and Non-ideal Solutions

The discussion of chemical equilibria that has been presented so far would be entirely correct if the solution were "ideal". In simple terms, an ideal solution is one in which the solute-solute interactions are the same as the solute-solvent interactions. A solution of toluene in benzene (see Figure 9.1) should be close to ideal since the two compounds will interact similarly. However, in an ionic solution, such as NaCl in water, this is no longer true. A solution of NaCl is really composed of Na^+ and Cl^- ions. As shown in Figure 9.2, the charges carried by ions give rise to ion-dipole interactions between the solute ions and the solvent, which are weaker than ion-ion interactions between the solute ions. For this reason, ionic solutions tend to be less ideal than molecular solutions and deserve special attention.

The coulombic forces between ions in solution depend on distance. In a dilute solution the ions are far apart and do not "see" each other, they only "see" water molecules. However, as the ionic concentration increases, the ions come closer to each other and begin to affect each other's behavior. Their environment begins to change from one of just water molecules to one of water molecules and other ions. This change in environment causes a change in the free energy of the species in solution, which in turn shifts the position of the equilibrium from the ideal case. In effect, this means that the equilibrium constant, as expressed with concentrations, is not constant in a non-ideal solution, which makes it less useful.

Another perspective on this behavior is to consider the equilibrium constant as a fixed value and adopt an alternative view of the concentrations. In this approach, each concentration in the equilibrium expression is replaced by an "apparent concentration" or "thermodynamic concentration", which is referred to as the *activity*. While the activity of each species is related to the analytical concentration, it is an adjusted value to account for the non-deal behavior. We will use the symbol "*a*" to represent activity. With this definition, the equilibrium constant for our general reaction now becomes

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D} \qquad K = \frac{(a_\mathrm{C})^c (a_\mathrm{D})^d}{(a_\mathrm{A})^a (a_\mathrm{B})^b} \tag{9.1}$$

where "a_X" indicates the activity of species "X" in solution (not to be confused with the reaction coefficient "*a*" in this particular example). Note that the only change that we have

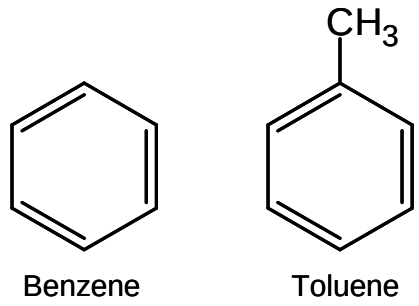


Figure 9.1: A solution of benzene in toluene should be close to ideal since the solute and solvent have similar properties.

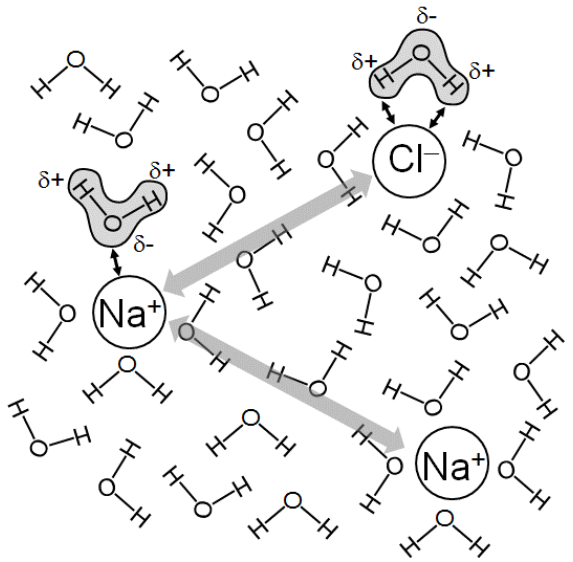


Figure 9.2: Interactions of an ionic solute in aqueous solution. The black arrows show the ion-dipole interactions of the solute with the solvent, while the gray arrows indicate the ion-ion interactions.

made in defining the equilibrium constant is to replace the analytical concentrations with activities (thermodynamic concentrations). In very dilute solutions, the concentrations and activities will be the same, but as the solution becomes more concentrated, the activity of a particular species will deviate from its concentration.

For ionic solutions, the activity of the ions is generally lower than their analytical concentrations, and the relative difference increases with the concentration. It should be noted that, while the analytical concentrations of the ions may be constrained by the stoichiometry, the same is not true for the activities. For example, in a solution of NaCl, it is required that $[Na^+] = [Cl^-]$, but it is not required that $a_{Na} = a_{Cl}$. This is because the free energies of each ion is affected differently by its surrounding environment.

While this approach solves the thermodynamic inconsistency, the problem of knowing or measuring activities now arises. Measuring concentrations is a relatively simple matter, but activities can't be measured directly. The activity of a species in solutions depends not only on its characteristics and concentration, but also on those of other species also present. Sodium ions could be present at a concentration of 0.10 M in two solutions, and have an activity of 0.08 in one and 0.07 in the other. This poses a problem in equilibrium calculations.

Another way of expressing activities is in terms of the *activity coefficient*, γ, which relates the activity to the analytical concentration as given below. This is usually shown as follows:

$$a_X = [X] \cdot \gamma_X \tag{9.2}$$

Here, γ_X is the activity coefficient for species X. It essentially converts concentration into activity and can be regarded as a measure of ideal behavior. In ideal or very dilute solutions, $\gamma_X = 1$ (activities and concentrations are the same), but as ionic concentration increases, γ_X decreases and activity increases less rapidly than concentration. For an ion that has an activity coefficient of 0.80, the apparent or thermodynamic concentration is 80% of its real concentration.

Each species in our generic chemical reaction will have an associated activity coefficient, so we can write:

$$a_A = [A] \cdot \gamma_A \,,\; a_B = [B] \cdot \gamma_B \,,\; a_C = [C] \cdot \gamma_C \,,\; a_D = [D] \cdot \gamma_D$$

The expression for the equilibrium constant now becomes:

$$K = \left\{\frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}\right\}\left\{\frac{\gamma_\mathrm{C}^c\,\gamma_\mathrm{D}^d}{\gamma_\mathrm{A}^a\,\gamma_\mathrm{B}^b}\right\} \tag{9.3}$$

This has not solved the problem, however, since the activity coefficient, like the activity, varies with concentration.

9.4 Debye-Hückel Theory

A solution to the dilemma of how to determine activities of ions in solution was provided by Peter Debye and Erich Hückel, who developed a theory, named in their honor, that can be employed to estimate activity coefficients in ionic solutions. There are several variations of equations derived from this work, but we will focus on one known as the extended Debye-Hückel equation, which is given below:

$$\log(\gamma_\mathrm{X}) = \frac{-0.509\,Z_\mathrm{X}^2\sqrt{\mu}}{1+\dfrac{\alpha_\mathrm{X}\sqrt{\mu}}{305}} \tag{9.4}$$

In this equation, Z_X is the charge on the ion (–2 for the sulfate ion, for example), μ is the ionic strength of the solution (see below), and α_X is the ion size parameter (the effective diameter of the *hydrated* ion) in pm (1 pm = 10^{-12} m = 10^{-9} mm). Values of the ion size parameter for some common ions are listed in Table 9.1. The constants 0.509 and 305 only apply to aqueous solutions at 25°C.

The ionic strength, μ, is a total ionic concentration that takes account of both the molar concentration and the charge of all ions, I, since both the concentrations and charges affect the environment of other ions. The ionic strength is calculated as:

$$\begin{aligned}\mu &= \frac{1}{2}\left([\mathrm{I}_1]\,Z_1^2 + [\mathrm{I}_2]\,Z_2^2 + \ldots + [\mathrm{I}_n]\,Z_n^2\right)\\ &= \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2\end{aligned} \tag{9.5}$$

Table 9.1. Ion size parameters (α) for some common ions.

Ion size (pm)	Ions
1100 pm	Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}
900 pm	H^+, Al^{3+}, Fe^{3+}, Cr^{3+}, In^{3+}
800 pm	Mg^{2+}, Be^{2+}
600 pm	Li^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}
500 pm	Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $Fe(CN)_6^{4-}$
450 pm	Na^+, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, Pb^{2+}, CO_3^{2-}, SO_3^{2-},$C_2O_4^{2-}$, CH_3COO^-
400 pm	Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}, PO_4^{3-}, $Fe(CN)_6^{3-}$
350 pm	OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, $HCOO^-$
300 pm	K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-
250 pm	Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+

where C_i represents the molar concentration of ion i, Z_i represents the charge on ion i, and the summation is over *all* ionic species in solution. It is important to recognize that the ionic strength is a property of the *solution* and not of a particular solute or ion.

Note that Equation 9.5 calculates log(γ) rather than γ. Since the right-hand side of the equation is always negative, γ is always less than 1, but as $\mu \rightarrow 0$, $\gamma \rightarrow 1$, and $a_X \rightarrow [X]$. The equation also indicates that γ is sensitive to the charge of the ion and suggests that a solution with doubly charged ions will be less ideal than one with only singly charged ions at the same concentration. This is because the non-ideality is caused by Coulombic interactions.

Figure 9.3 shows the behavior of the activity coefficient (as calculated with Equation 9.4) as concentration is increased. For simplicity, only the activity coefficient of the positive ion is shown and this is plotted as a function of the ion concentration (as opposed to the salt concentration) so curves for different salts can be compared. Concentrations are plotted on a logarithmic scale over the range of 0.001 M to 0.1 M. For all of the salts, γ_+ decreases as the ion concentration increases, meaning the solution becomes less ideal, as expected. The decrease happens slightly faster for RbCl than LiCl, which reflects the smaller ion size parameter for Rb^+. Likewise, curve for $RbSO_4$ falls off slightly faster than that for RbCl, an effect that is due to the difference in ionic strength arising from the anions involved (Cl^- and SO_4^{2-}). The most dramatic difference is observed for $CaCl_2$ and this is due to two effects, the charge on the ion (+2 *vs* +1) and the difference in ionic strength of such ions at the same concentration. A few examples are presented to illustrate these concepts.

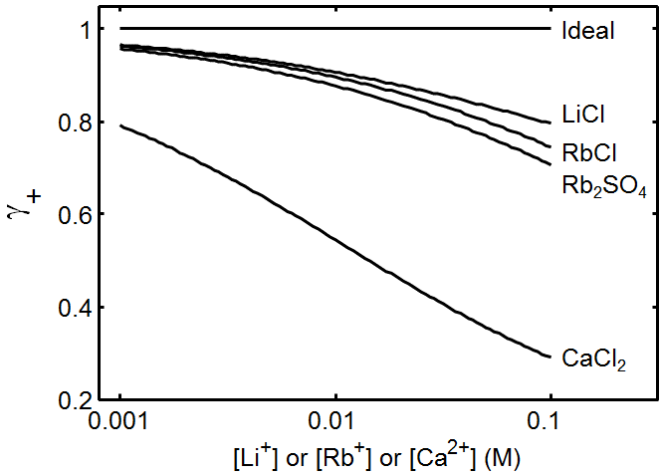


Figure 9.3: Dependence of activity coefficient of various positive ions on concentration and salt composition.

Example 9.1: Ionic Strength

What is the ionic strength of: (a) a 0.10 F solution of NaCl, and (b) a 0.10 F solution of $CaCl_2$?

(a) Since this is an ionic solution, we know that the ionic concentrations are directly related the formality of the salt, so $[Na^+] = [Cl^-] = 0.10$ M. The ionic strength can be calculated from these concentrations.

$$\mu = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 = \frac{1}{2}\left([Na^+](+1)^2 + [Cl^-](-1)^2\right) = \frac{1}{2}\left((0.10\,M)(1) + (0.10\,M)(1)\right) = 0.10\,M$$

(b) In this case we have, $[Ca^{2+}] = 0.10$ M, $[Cl^{-}] = 0.20$ M, which gives,

$$\mu = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 = \frac{1}{2}\left((0.10\,\text{M})(+2)^2 + (0.20\,\text{M})(-1)^2\right) = \frac{1}{2}(0.40\,\text{M} + 0.20\,\text{M}) = 0.30\,\text{M}$$

Note that for a salt consisting of two singly charged ions, the ionic strength of the solution will be the same as its concentration. This is not true for salts containing ions with multiple charges, however, where the ionic strength will be higher than the concentration.

Exercise 9.1

Calculate the ionic strength of the following:

(a) 0.200 F KCl

(b) 0.100 F Na_2SO_4

(c) 0.0500 F $Ca_3(PO_4)_2$

(d) A solution containing 0.20 mol/L $CaSO_4$ and 0.10 mol/L $CaCl_2$

It is important to recognize that the ionic strength is a property of the *solution* and not of the individual salts or species dissolved. Once the ionic strength has been calculated, the activity coefficient, γ, and hence the activity of ions in solution, can be determined. Note that the activity is a property of the individual ion (or other species dissolved) and is not a property of the solution or the original salt dissolved. Two ions can have the same concentration but different activities in the same solution.

Example 9.2: Activity Calculation

Determine the activity of Na^+ in a solution that contains 0.00100 F NaCl.

First, we need to determine the ionic strength of the solution.

$$\mu = \frac{1}{2}\left((0.00100\,\text{M})(+1)^2 + (0.00100\,\text{M})(-1)^2\right) = 0.00100\,\text{M}$$

Now the activity coefficient can be determined using the extended Debye-Hückel equation (Equation 9.4) with the ion size parameter for Na^+ given in Table 9.1 (450 pm).

$$\log(\gamma_{Na^+}) = \frac{-0.509\, Z_{Na^+}^2 \sqrt{\mu}}{1 + \dfrac{\alpha_{Na^+}\sqrt{\mu}}{305}}$$

$$= \frac{-0.509\,(+1)^2 \sqrt{0.00100\,\text{M}}}{1 + \dfrac{(450)\sqrt{0.00100\,\text{M}}}{305}} = \frac{-0.509\sqrt{0.00100\,\text{M}}}{1 + 0.04\overline{66}} = -0.0154$$

$$\gamma_{Na^+} = 10^{-0.0154} = 0.9652$$

In the final step, the activity coefficient and the concentration of the ion are used to determine its activity using Equation 9.2.

$$a_{Na^+} = \gamma_{Na^+}[Na^+] = (0.9652)(0.00100\,\text{M}) = 0.000965\,\text{M}$$

Several points are worth noting about these calculations.

- Activity vs. activity coefficient. Make sure that you understand the distinction between *activity* and *activity coefficient*. Activity, *a*, can be viewed as the "thermodynamic" concentration, whereas the activity coefficient, γ, is used to calculate the activity from the actual concentration. In this case, the activity coefficient indicates that the thermodynamic concentration is 96.5% of the actual concentration.
- Units. Although units have been shown for activity to match the original concentration units, it technically has no units since, from a thermodynamic perspective, it is referenced to a standard state with an activity of 1 M. This is why equilibrium constants have no units.
- Significant figures. The activity and activity coefficient in this example have been expressed to three significant digits. Although the ion size parameter only has two significant digits, the addition results in four significant digits in the denominator of the expression for $\log(\gamma)$. In taking the antilogarithm to calculate γ, recall that the = number of significant figures retained in the antilog should be equal to the number of decimal places in the exponent, or four in this case. In the last calculation, the number of significant digits

is limited by the concentration. In general, for these calculations, the number of significant digits retained in the activity should be the same as for the concentration, but this should not exceed three because of the limitations of the Debye-Hückel equation.

- Range. The extended Debye-Hückel equation is really only valid up to ionic strengths of about 0.1 M, although there are variations that can extend this further. There may be cases in this class where we apply the equation beyond this range, but it becomes less accurate under those conditions.
- Calculation Errors. In doing these kinds of calculations, mistakes are fairly common. Note that the logarithm of the activity coefficient should always be negative number and the activity coefficient should always be between 0 and 1. An activity coefficient less than 0.1 probably means an error has been made.

Example 9.3: Activity Calculation in a Mixed Salt Solution

Find the activity of Na^+ in a solution that contains 0.00100 F NaCl and 0.100 F KCl.

This is essentially the same as the previous calculation, except that the ionic strength will be altered by the presence of potassium chloride in solution.

$$\mu = \frac{1}{2}\left((0.100\,\text{M})\,(+1)^2 + (0.100\,\text{M})\,(-1)^2 + (0.00100\,\text{M})(+1)^2 + (0.00100\,\text{M})(-1)^2\right)$$

$$= \frac{1}{2}(0.100\,\text{M} + 0.100\,\text{M} + 0.00100\,\text{M} + 0.00100\,\text{M}) = 0.101\,\text{M}$$

Now the activity of Na^+ can be determined as before using the new ionic strength.

$$\log(\gamma_{Na^+}) = \frac{-0.509\,Z_{Na^+}^2\sqrt{\mu}}{1 + \frac{\alpha_{Na^+}\sqrt{\mu}}{305}} = \frac{-0.509\,(+1)^2\sqrt{0.101\,\text{M}}}{1 + \frac{(450)\sqrt{0.101\,\text{M}}}{305}} = \frac{-0.509\sqrt{0.101\,\text{M}}}{1 + 0.4\overline{6}89} = -0.110$$

$$\gamma_{Na^+} = 10^{-0.110} = 0.776$$

$$a_{Na^+} = \gamma_{Na^+}[Na^+] = (0.776)(0.00100\,\text{M}) = 0.000776\,\text{M}$$

There are two important points to note in the above calculation.

- Although [Na^+] is the same as in the preceding example (1 mM), the activity is significantly lower in this example (0.776 mM vs. 0.965 mM) to presence of KCl, which increases the ionic strength.
- In this example, notice that the concentration of NaCl has very little effect on the ionic strength of the solution since the concentration of the KCl is much higher. This means that, as long as the concentration of NaCl remains relatively low, its activity coefficient will remain essentially constant (since μ does not change) and the concentration will be proportional to concentration. In this situation, the KCl is called a *total ionic strength buffer* (TISB) since it keeps the ionic strength constant when the concentration of NaCl changes. The use of such buffers is common in certain applications in chemistry.

Exercise 9.2

Determine the activity of the potassium ion in a solution that contains 0.0200 F K_2SO_4.

9.5 Activities and Solubility Equilibria

While the activities calculated in the manner described above can be thought of in the same way as concentrations, they have no bearing on stoichiometric calculations involving moles or mass. A 0.10 F NaCl solution will contain 0.10 moles of Na^+ per liter of solution regardless of the activity of the Na^+ ions. In addition, most analytical methods respond to concentration rather than activity, with some exceptions (*e.g.* potentiometry). However, activities are relevant in any thermodynamic calculations, most notably those involving chemical equilibria. In this section, the influence of activity on equilibrium calculations will be illustrated with solubility equilibria because of their relative simplicity.

Recall that the equilibrium relevant to the solubility of a sparingly soluble salt is defined by the solubility product constant, K_{sp}. As an example, we consider the dissolution of silver chloride:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = a_{Ag^+} \cdot a_{Cl^-} \quad \text{(in general)}$$

$$K_{sp} = [Ag^+][Cl^-] \quad \text{(ideal)}$$

Equilibrium constants should, in principle, always be written in terms of activities, but if an ideal solution can be assumed, the activities can be repalced with concentrations since the activity coefficients will be unity. If this is not the case, the activity coefficients must be included.

$$K_{sp} = a_{Ag^+} a_{Cl^-} = (\gamma_{Ag^+}[Ag^+]) \cdot (\gamma_{Cl^-}[Cl^-]) = \gamma_{Ag^+}\gamma_{Cl^-}[Ag^+][Cl^-]$$

Note that the stoichiometry (sometimes referred to as the mass-balance condition) requires that $[Ag^+] = [Cl^-]$, but there is no requirement that the activities of Ag^+ and Cl^- are equal. Therefore, to determine the equilibrium concentration of the salt, we need to know the activity coefficients of the two ions. An example will illustrate how to carry out this calculation.

Example 9.4: Solubility Calculations in Non-Ideal Solutions

Determine the solubility (in mol/L) of silver bromate, $AgBrO_3$ in pure water assuming (a) ideal behavior and (b) non-deal behavior. The K_{sp} for $AgBrO_3$ is 5.4×10^{-5}.

(a) At equilibrium, we will let the amount of $AgBrO_3$ dissolved in solution to be equal to x mol/L, so we can write the equilibrium as

$$AgBrO_3(s) \rightleftharpoons \underset{x}{Ag^+(aq)} + \underset{x}{BrO_3^-(aq)}$$

Since we are assuming ideal conditions, we can write:

$$K_{sp} = [Ag^+][BrO_3^-] = x^2$$

Rearranging this equation, it is straightforward to solve for x, which will be the solubility of $AgBrO_3$.

$$x = \sqrt{K_{sp}} = \sqrt{5.4 \times 10^{-5}} = 0.0073 \text{ mol/L}$$

(b) The set up in this case is the same as in part (a), except that we need to express the equilibrium constant in terms of activities rather than concentrations.

$$K_{sp} = a_{Ag^+} a_{BrO_3^-} = \gamma_+ \gamma_- [Ag^+][BrO_3^-] = \gamma_+ \gamma_- x^2$$

We could solve this equation easily if we knew the values of the activity coefficients for Ag^+ and BrO_3^-. These could be obtained if we knew the ionic strength, but to get that we need to know the concentrations of ions, which is what we are trying to find. So we are in a dilemma in that we can't solve for *x* without knowing the γ's and we can't get the γ's without knowing *x*.

The solution to this dilemma is to use an *iterative* approach (see Figure). To do this, we first assume a value for one set of unknowns and solve for the other. Then we use this solution to solve for the first set of unknowns. This is repeated until the answers do not change.

In this case, we will first assume that $\gamma_+ = \gamma_- = 1$, which leads to the result in the previous example for an ideal solution. Taking $[Ag^+] = [BrO_3^-] = 0.0073$ M, we can now calculate the ionic strength and the activity coefficients.

$$\mu = \frac{1}{2}\left((0.0073\,\text{M})(+1)^2 + (0.0073\,\text{M})(-1)^2\right) = 0.0073\,\text{M}$$

$$\log(\gamma_+) = \frac{-0.509\, Z_+^2 \sqrt{\mu}}{1 + \left(\alpha_{Ag^+}\sqrt{\mu}/305\right)} = \frac{-0.509\,(+1)^2 \sqrt{0.0073\,\text{M}}}{1 + \left(250\sqrt{0.0073\,\text{M}}/305\right)} = -0.041$$

$$\gamma_+ = 10^{-0.041} = 0.910$$

$$\log(\gamma_-) = \frac{-0.509\, Z_-^2 \sqrt{\mu}}{1 + \left(\alpha_{BrO_3^-}\sqrt{\mu}/305\right)} = \frac{-0.509\,(-1)^2 \sqrt{0.0073\,\text{M}}}{1 + \left(350\sqrt{0.0073\,\text{M}}/305\right)} = -0.040$$

$$\gamma_- = 10^{-0.040} = 0.912$$

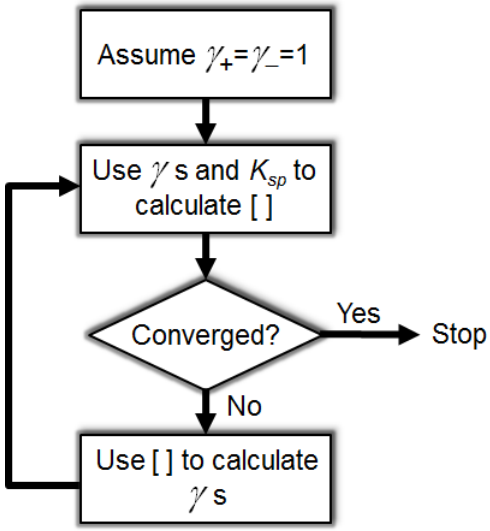


Figure 9.4: Procedure to calculate solubility iteratively in non-ideal solutions.

We see from these calculations that the low concentration of $AgBrO_3$ makes the solution nearly ideal. Substituting these values into the expression for the equilibrium constant, we have,

$$x = \sqrt{\frac{K_{sp}}{\gamma_+ \gamma_-}} = \sqrt{\frac{5.4 \times 10^{-5}}{(0.910)(0.912)}} = 0.0081\,\text{mol/L}$$

We see that the change in the concentration (from 0.0073 M in the ideal case) is small but significant.

Since we have calculated a new value of the concentration, we should do another iteration using this value to calculate the ionic strength and the activity coefficients. Proceeding as before, this gives:

$$\mu = 0.0081\,\text{M}, \quad \gamma_+ = 0.906, \quad \gamma_- = 0.909, \quad x = 0.0081\,\text{mol/L}$$

Although the activity coefficients change slightly on the second iteration, there is no significant change in the concentration of the salt, and we conclude that the iterative calculation has *converged* on a solution. Therefore, the solubility of silver bromate is 0.0081 mol/L.

Notice that the solubility of $AgBrO_3$ is slightly greater when we take non-ideal behavior into account since the activity coefficients must be <1 for any positive concentration. Thus the activity (the "apparent" concentration) will be less than the actual concentration, allowing more of the solute to dissolve. The extent of this effect will depend on the ionic strength, which depends on the K_{sp}. If the K_{sp} is small, the solution will be nearly ideal.

Exercise 9.3

Determine the solubility of the following compounds in pure water assuming ideal and non-ideal behavior.

(a) AgCl (K_{sp} = 1.8 x 10^{-10}) (b) $PbCl_2$ (K_{sp} = 1.7 x 10^{-5})

Solubility in the Presence of Other Salts

The solubility of a compound can be affected by the presence of other dissolved ions. For an ideal solution, this will only happen when there is a *common ion*, which is an ion that is present from two or more compounds in a mixture. For example, if AgCl were placed in a solution of NaCl, its solubility would be affected by the fact that both salts produce the chloride ion.

For non-ideal solutions, solubility can also be affected by other salts even if they don't share a common ion. This is because other salts will increase the ionic strength, which is a property of the solution, and thereby decrease the activity coefficients of the ions present. This decrease in activity coefficient will have the effect of increasing solubility.

Another consequence of secondary salts is that, if they are present in high concentrations, they act as a total ionic strength buffer (TISB) as discussed earlier. This simplifies the calculations since the ionic strength depends only on the TISB and not on the solubility, which is much smaller. An example will illustrate these principles.

Example 9.5: Solubility Calculations with External Salts

Determine the solubility of silver bromide (AgBr, K_{sp} = 5.4 x 10^{-13}) under both ideal and non-ideal conditions in the following solutions.

(a) pure water, (b) 0.0500 F NaBr, (c) 0.0500 F $NaNO_3$

(a) For an ideal solution in pure water, we set up the equilibrium in the usual way.

$$\underset{}{AgBr(s)} \rightleftharpoons \underset{x}{Ag^+(aq)} + \underset{x}{Br^-(aq)}$$

$$K_{sp} = [Ag^+][Br^-] = x^2$$

$$x = \sqrt{K_{sp}} = \sqrt{5.4\times10^{-13}} = 7.3\times10^{-7}\ \text{mol/L}$$

So the solubility in pure water under ideal conditions is 7.3x10^{-7} mol/L. Under non-ideal conditions, we need to use the iterative procedure to estimate the activity coefficients, as was done in the earlier example. Starting with the estimate above, we obtain the following.

$$\mu = 7.3\times10^{-7}\ \text{M},\quad \gamma_+ = 0.999,\quad \gamma_- = 0.999,\quad x = \sqrt{\frac{K_{sp}}{\gamma_+\gamma_-}} = 7.4\times10^{-7}\ \text{mol/L}$$

Because the K_{sp} (and solubility) is so small, the activity coefficients are essentially unity and there is essentially no change in solubility in the non-ideal case. No further iterations are needed.

(b) In the case of 0.0500 F NaBr, the bromide ion is common with AgBr, so we set up the equilibrium taking this into account.

$$\underset{}{\text{AgBr}(s)} \rightleftharpoons \underset{x}{\text{Ag}^+(aq)} + \underset{0.0500+x}{\text{Br}^-(aq)}$$

$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = x(0.0500+x) \approx (0.0500)x$$

$$x \approx \frac{K_{sp}}{0.0500} = \frac{5.4\times10^{-13}}{0.0500} = 1.1\times10^{-11}\ \text{mol/L} \qquad \text{(ideal case)}$$

This calculation makes the assumption that $x \ll 0.0500$, which is clearly valid.

To treat the non-ideal case, we re-formulate the problem in terms of activities.

$$K_{sp} = a_{\text{Ag}^+}a_{\text{Br}^-} = \gamma_+[\text{Ag}^+]\,\gamma_-[\text{Br}^-] = \gamma_+\gamma_-(x)(0.0500+x) \approx \gamma_+\gamma_-(0.0500)x$$

Again, we make the assumption that x is small. Because the concentration of AgBr is likely to be small, the ionic strength is determined by the concentration of NaBr, which is much higher. Therefore, this can be used to calculate the activity coefficients without the need for an iterative solution.

$$\mu \approx 0.0500\ \text{M}$$

$$\log(\gamma_+) = \frac{-0.509\,(+1)^2\sqrt{0.0500\,\text{M}}}{1+\left(250\sqrt{0.0500\,\text{M}}/305\right)} = -0.0962 \qquad \gamma_+ = 10^{-0.0962} = 0.8013$$

$$\log(\gamma_-) = \frac{-0.509\,(-1)^2\sqrt{0.0500\,\text{M}}}{1+\left(300\sqrt{0.0500\,\text{M}}/305\right)} = -0.0933 \qquad \gamma_- = 10^{-0.0933} = 0.8067$$

$$x \approx \frac{K_{sp}}{\gamma_+ \gamma_- (0.0500)} = \frac{5.4\times10^{-13}}{(0.8013)(0.8067)(0.0500)} = 1.7\times10^{-11}\ \text{mol/L} \quad \text{(non-ideal)}$$

Clearly, the concentration of AgBr is low enough that it will not affect the ionic strength. Note that its solubility is about 50% higher than for the ideal case.

(c) In this instance, we have a soluble salt with no ions in common with AgBr. If we assume that the solution is ideal, then the $NaNO_3$ can be considered to be inert and will have no effect on the calculation, which is the same as for pure water.

$$\underset{}{\text{AgBr}(s)} \rightleftharpoons \underset{x}{\text{Ag}^+(aq)} + \underset{x}{\text{Br}^-(aq)}$$

$$x = \sqrt{K_{sp}} = \sqrt{5.4\times10^{-13}} = 7.3\times10^{-7}\ \text{mol/L} \qquad \text{(ideal case)}$$

In the non-deal case, the presence of $NaNO_3$ will affect the ionic strength and therefore the activity. Since the concentration of $NaNO_3$ is much higher than the solubilty, we expect it will define the ionic strength, *i.e.* $\mu = 0.0500$ M). Because this is the same ionic strength as in part (b), the same activity coefficients will result and can be used to determine the solubility.

$$K_{sp} = a_{\text{Ag}^+} a_{\text{Br}^-} = \gamma_+[\text{Ag}^+]\,\gamma_-[\text{Br}^-] = \gamma_+\gamma_- x^2$$

$$\mu = 0.0500\ \text{M}, \quad \gamma_+ = 0.8013, \quad \gamma_- = 0.8067$$

$$x = \sqrt{\frac{K_{sp}}{\gamma_+\gamma_-}} = \sqrt{\frac{5.4\times10^{-13}}{(0.8013)(0.8067)}} = 9.1\times10^{-7}\ \text{mol/L} \qquad \text{(non-deal)}$$

Note that this is higher than the solubility in pure water.

Exercise 9.4

Determine the solubility of lead iodide (PbI_2, K_{sp} = 9.8 x 10^{-9}) under both ideal and non-ideal conditions in the following solutions.

(a) pure water, (b) 0.100 F $LiNO_3$, (c) 0.100 F KI

9.6 Activities and Other Equilibria

The approach to treating other ionic equilibria using activities in place of concentrations is similar to that used for solubility equilibria, but these situations can become even more complicated. For example, if we consider the weak acid HF, we have the equilibrium

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

Under assumptions of non-ideal behaviour, the equilibrium constant becomes

$$K_a = \frac{a_{H^+} a_{F^-}}{a_{HF}} = \frac{(\gamma_{H^+}[H^+])(\gamma_{F^-}[F^-])}{\gamma_{HF}[HF]}$$

To solve this we would need to know all of the activity coefficients. For molecular species such as HF, we can often assume that the activity is equal to the concentration; that is $\gamma_{HF}=1$. However, we would still need to obtain the activity coefficients for the ions. We could use the Debye-Hückel equation for this, but this requires knowing the ionic strength, which requires knowing the concentrations. Thus an iterative solution would likely be required.

When non-ideal behaviour is coupled with the additional complications of solving solution equilibria, especially in cases where there are common ions and multiple equilibria involved, you can imagine that such problems can be quite complex. For this reason, unless otherwise stated, for the remainder of this course, we will make the assumption that

$$a_X \approx [X]$$

That is, we will assume that the activity is the same as concentration. This approximation is generally valid for molecular species or when working with gas phase equilibria. For ionic species, the assumption is less valid, but making it will allow us to explore the general principles of equilibria with greater ease. Nevertheless, you should be aware that to solve an equilibrium problem rigorously, activity corrections should be taken into account.

Exercise 9.5

Based on the definition below, what is the $[H^+]$ in a 0.100 F NaCl solution? What is the activity of H^+? What is the activity of OH^- ? What is the pH based on both the concentration and activity of H^+?

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = a_{H^+} a_{OH^-} = 1.0 \times 10^{-14}$$

9.7 Summary

Non-ideal behavior in ionic solutions results from interactions between charged species. These interactions become more important as solutions become more concentrated. This non-ideal behavior affects thermodynamic properties, including the equilibrium constant, which can be redefined in terms of a thermodynamic concentration, or activity. The activity of an ion in solution can be calculated as the product of its activity coefficient, γ, and its concentration. The activity coefficient can be estimated with the extended Debye-Hückel equation, which depends on the size of the hydrated ion and the ionic strength of the solution. Once calculated, these activities can be applied to equilibrium calculations.

9.8 Additional Exercises

Exercise 9.6

Calculate the ionic strengths of 0.0500 F solutions of the following salts, neglecting any acid-base effects: LiCl, $CaBr_2$, $MgSO_4$, Na_2SO_4, and $La(NO_3)_3$.

Exercise 9.7

Calculate the activity of the cation at 25 °C in the following solutions: 0.100 F LiCl, 0.0500 F Li_2SO_4, 0.100 F $ZnCl_2$, and 0.100 F $ZnSO_4$.

Exercise 9.8

Using the extended Debye-Hückel equation, determine at what salt concentration the activity coefficient of the cation in the following solutions will equal 0.900.
(a) LiCl (b) CsCl (c) Li_2SO_4 (d) $CaCl_2$ (e) $CaSO_4$

Exercise 9.9

Calculate the pH of a 0.100 F solution of HCl, (a) if the definition of pH is $-\log[H_3O^+]$, and (b) if the definition of pH is $-\log(a_{H_3O^+})$.

Exercise 9.10

At the same ionic strength, which ion will be "less ideal" (have a smaller activity coefficient?

(a) An ion with z = +1 or z = +2, assuming the same ion size parameter?

(b) An ion with α = 300 pm or α = 600 pm, assuming the same charge?

Exercise 9.11

What is the solubility of $BaSO_4$ in pure water and in 0.100 F NaCl if the solubility product constant is 1.1×10^{-10}?

Exercise 9.12

The K_{sp} of $Ba(BrO_3)_2$ is 2.4×10^{-4}. Calculate the solubility of this salt in pure water taking activity effects into account.

9.9 Answers to Exercises 9

9.1 (a) 0.200 M, (b) 0.300 M, (c) 0.750 M, (d) 1.10 M

9.2 0.0317 M

9.3 (a) $1.3_4 \times 10^{-5}$ mol/L, $1.3_5 \times 10^{-5}$ mol/L
(b) 0.016_2 mol/L, 0.025_6 mol/L

9.4 (a) 0.0013_5 mol/L, 0.0015_6 mol/L
(b) 0.0013_5 mol/L, 0.0023_1 mol/L
(c) $9.8_0 \times 10^{-7}$ mol/L, $4.7_4 \times 10^{-6}$ mol/L

9.5 $[H^+] = 1.\overline{26} \times 10^{-7}$ M, $a_{H^+} = 1.\overline{04} \times 10^{-7}$ M, $a_{OH^-} = 9.\overline{61} \times 10^{-8}$ M, pH = 6.90, pH = 6.98

9.6 0.0500, 0.150, 0.200, 0.150, 0.300 M

9.7 0.0795, 0.0773, 0.0290, 0.0266

9.8 (a) 1.19×10^{-2} F, (b) 9.42×10^{-3} F, (c) 3.98×10^{-3} F, (d) 1.84×10^{-4} F, (e) 1.38×10^{-4} F

9.9 1.00, 1.08

9.10 (a) z = +2, (b) a = 300 pm

9.11 $1.0_8 \times 10^{-5}$ mol/L, $2.8_9 \times 10^{-5}$ mol/L

9.12 0.075_6 mol/L

Topic 10

Acids and Bases

10.1 Contents in Brief

- Definitions of acids and bases
- Classifications of acids and bases
- Calculations involving strong and weak acids and bases
- Calculations involving buffers

10.2 Introduction

Among the chemical equilibria that are fundamental to an understanding of chemical systems, none are more important than acid-base equilibria. This is because so many chemical species exhibit acid/base properties in solution and interactions or reactions based on those properties. In this section, we are primarily interested in the behavior of acids and bases in aqueous solution. Fundamental to understanding this is the concept that water itself can act as an acid or a base and therefore is a participant in all equilibria.

10.3 Definitions of Acids and Bases

There are several definitions of acids and bases in chemistry, as indicated in Table 10.1. In this class, only Brønsted acid-base reactions will be discussed. In the Brønsted formalism, an acid is a proton donor and a base is a proton acceptor. A general Brønsted acid-base equation can be written as follows:

$$HA + B \rightarrow BH^+ + A^-$$

Here HA is the proton donor and B is the proton acceptor, so HA is the acid and B is the base. Note that BH^+ could be a proton donor and that A^- could be a proton acceptor if the reaction were reversed, so one is really dealing with acid-base pairs; that is, with every acid there is associated a base and *vice versa*. These pairs are called *conjugate acid-base pairs*, as shown in Figure 10.1. HA and A form one conjugate acid-base pair, and HB and B comprise the other.

For the reaction to proceed as written above, HA must be a stronger acid (proton donor) than HB and B must be a stronger base (proton acceptor) than A. In general, the stronger the acid, HA, the weaker its conjugate base, A. A very strong acid has a conjugate base so weak that it may not appear to be a base at all.

Table 10.1. Definitions of acids and bases.

Arrhenius definition	Acid produces H^+ in solution Base produces OH^- in solution
Brønstead definition	Acid donates H^+ Base accepts H^+
Lewis definition	Acid can accept electron pair Base can donate electron pair

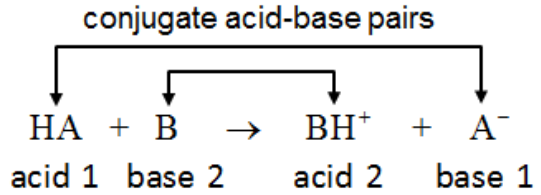


Figure 10.1: Conjugate acid-base pairs for a generic acid-base reaction.

10.4 Acid-Base Properties of Water

Almost all solvents contain protons and many solvents are acids or bases (or both) themselves, with water being the prime example. When acids or bases are dissolved in such solvents, acid-base reactions can occur.

Since water has two unshared electron pairs it can act as a base by accepting a proton, which associates with one of those pairs. The species thus formed, H_3O^+, is called the hydronium ion. The protons on water are not as tightly held as most protons bonded to carbon (for example) and thus water can also act as an acid by donating a proton and forming hydroxide ion (see Figure 10.2).

This behavior leads to the conclusion that the strongest acid that can exist in water is H_3O^+ and the strongest base is OH^-, the hydroxide ion. Why? If a stronger acid than H_3O^+ is placed

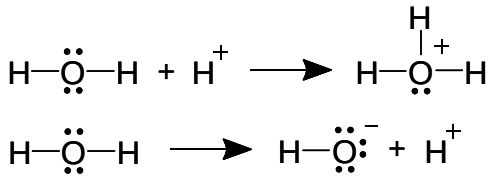


Figure 10.2: Water can act as a base by accepting a proton to form the hydronium ion, H_3O^+, or as an acid by donating a proton to form the hydroxide ion, OH^-.

in solution, it will react with H_2O (acting as a base) to form H_3O^+. For example, HBr is a stronger acid than H_3O^+ and will react with H_2O (acting as a base) to form bromide ion and hydronium ion. Likewise O^{2-} is a stronger base than OH^- and it will react with H_2O (acting as an acid) to form OH^-. This is illustrated in Figure 10.3. This ability to convert all strong acids to H_3O^+ and all strong bases to OH^- is called the *leveling effect*, since all such acids and bases are "leveled" to the strength of H_3O^+ or OH^-.

Solvents that can act as both an acid and a base, like water, are called *amphiprotic* solvents. Examples of such solvents, besides water, are alcohols, carboxylic acids, ammonia and amines. Amphiprotic solvents can undergo *autoionization*, which means that an equilibrium exists between the acid and base forms. For water, this is written as:

$$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-] = 1.007\times10^{-14} \tag{10.1}$$

The equilibrium constant, K_w, is called the autoionization constant or autodissociation constant for water at 25 °C and is sometimes given as the negative logarithm, $pK_w = 13.997$. Generally, we will take this value to be 1.0×10^{-14} ($pK_w = 14.00$) as sufficient for most calculations. In pure water, the concentrations of H_3O^+ and OH^- will be equal, given by:

$$[H_3O^+] = [OH^-] = \sqrt{K_w} = 1.0\times10^{-7}\ \text{M}$$

This will also be true in neutral solutions that contain solutes with no acid-base properties. In other solutions, the concentrations can be several orders of magnitude higher or lower, so the negative logarithm, or "p" scale, is often used, so that in neutral solutions:

$$\text{pH} = -\log[H_3O^+] = 7.00 \qquad \text{pOH} = -\log[OH^-] = 7.00$$

In this calculation, recall that the number of decimal places retained in a logarithm is equal to the number of significant figures in the original value.

Equation 10.1 is valid for any solution, so knowing $[H_3O^+]$ allows $[OH^-]$ to be determined, and vice-versa.

$$[OH^-] = K_w / [H_3O^+] \quad \text{or} \quad \text{pOH} = pK_w - \text{pH} \tag{10.2}$$

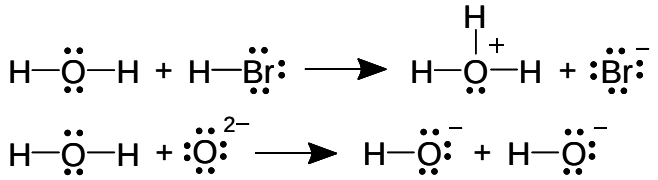


Figure 10.3: Water reacts with stronger acids, such as hydrobromic acid, to form the hydronium ion, and reacts with stronger bases, such as the oxide ion, to form the hydroxide ion.

Note that a higher value for pH means a lower value for $[H_3O^+]$ and higher value for $[OH^-]$.

10.5 Classification of Solutions of Acids and Bases

Quite often in the course of chemical practice it is necessary to understand the acid-base properties of aqueous solutions. This can involve both a qualitative assessment of the solution based on the species present and a subsequent calculation to determine the pH. In general, for aqueous solutions, solutions fall into one of several categories as indicated in Table 10.2. This does not consider all possibilities and is limited to solutions with solutes derived from one or two sources. Except for the buffer solution, which is a mixture of a conjugate acid-base pair, mixtures of weak acids and bases are not considered here. Also not considered are mixtures of strong acids and strong bases, strong acids and weak bases, and strong bases and weak acids, since these all react to form one of the other solutions, as discussed later. The remainder of this chapter is mainly dedicated to the identification of each of these cases and the calculation of solution pH.

Table 10.2. Possible classifications of aqueous solutions in terms of acid-base properties.

Neutral solution	Buffer
Strong acid	Strong acid + weak acid
Strong base	Strong base + weak base
Weak acid	Amphiprotic/polyprotic/ polybasic
Weak base	

10.6 Strong Acids

In an aqueous solution, a strong acid is any acid that is stronger than H_3O^+ so that essentially all of its protons are transferred to water. We say that the acid is completely dissociated and there is effectively no equilibrium. For example, in the case of hydrochloric acid, we write:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad (10.3)$$

Therefore, for a strong acid, the concentration of the hydronium ion is equal to the formality of the acid and the pH can be calculated directly from this value.

$$[H_3O^+] = F_a \qquad pH = -\log[H_3O^+] = -\log(F_a) \qquad (10.4)$$

The identification of strong acids is fairly straightforward, since there are a limited number of them. Some of the most common strong acids, and those that you will be responsible for identifying in this course, are listed in Table 9.3. In the lab, such acids are available in

Table 10.3. Common strong acids along with their formulas and concentrations in concentrated form.

Acid	Formula	Concentration
Hydrochloric acid	HCl	37%, 12 M
Hydrobromic acid	HBr	48%, 9 M
Hydroiodic acid	HI	56%, 8 M
Perchloric acid	$HClO_4$	70%, 12 M
Nitric acid	HNO_3	70%, 16 M
Sulfuric acid (1^{st} H^+)	H_2SO_4	95%, 18 M

concentrated form, and approximate concentrations (weight percent and molarity) are also given in the table.

Since all strong acids are equally strong (*i.e.* they all dissociate completely) the choice of acid might seem arbitrary. However, other factors may be important in their use. All of the hydrogen halides, except for HF, are strong acids, and all are dissolved gases. This can lead to complications, such as irritating fumes when working with the concentrated acid and a gradual reduction of concentration in open containers. Hydroiodic acid is also a useful reducing agent and has been employed in the illicit production of methamphetamine. In contrast, nitric and perchloric acids are oxidizing agents, and the latter usually requires the use of special procedures to avoid the formation of explosive organic perchlorates. Sulfuric acid (Figure 10.4) is unique among the strong acids listed in that it is *diprotic* (two acidic protons), but only the first step in the dissociation goes to completion.

Figure 10.4: A typical container of concentrated acid.

H^+ versus H_3O^+

Reactions such as that presented in Equation 10.3 reflect the Brønsted definition of an acid-base reaction in that the proton is transferred from the acid, HCl in this case, to the base, which is water in this reaction. Although the resulting acid, H_3O^+, is the dominant species produced in this reaction, it should be noted that other transient species exist in water due to complex hydrogen bonding interactions. These include species such as $H_5O_2^+$ and $H_9O_4^+$ as shown in Figure 10.5. However, the presence of these species does not affect the calculations involving acids and bases.

Quite often in textbooks, alternative representations for the dissociation of acids are given which involve direct dissociation of the proton, such as those shown below.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq) \qquad (10.5)$$

$$[H^+] = F_a \qquad pH = -\log[H^+] = -\log(F_a) \qquad (10.6)$$

These equations are not technically correct, since the free proton, H^+, does not actually exist in solution. However, such equations are sometimes simpler to write and are *mathematically equivalent* when used in acid-base calculations. This simplification may be used in this course, but whenever H^+ is written in the context of solution equilibria, H_3O^+ is implied.

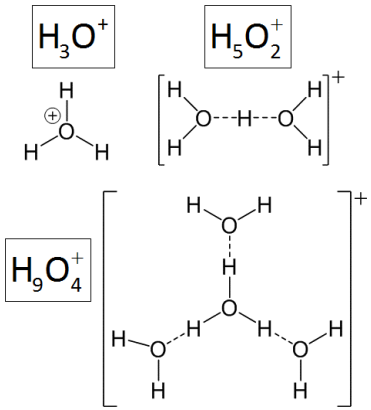


Figure 10.5: Acidic species present in aqueous solution.

10.7 Strong Bases

For the purposes of this course, the strong bases commonly employed are the hydroxides of the Group 1 and 2 elements, as given in Table 10.4. These solids will dissolve in water to produce a stoichiometric amount of hydroxide ion, as shown below.

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$
$$Ba(OH)_2(s) \rightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$$

The Group 2 hydroxides are dibasic, meaning that two moles of base are produced for every mole of the compound. Note, however, that the Group 2 hydroxides are much less soluble than the alkali metal hydroxides and are not routinely used to prepare strong base solutions. The Group 1 hydroxides are deliquescent, which means that they will quickly absorb moisture from the atmosphere. These hydroxides are generally not available in high purity, and normally have to be standardized when exact concentrations are needed.

There are many other strong bases as well, but these are limited in their practicality for preparing analytical solutions, so are not listed. These include other metal hydroxides, such as $Al(OH)_3$ and $Zn(OH)_2$. The use of these is complicated by low solubility and the formation of complex ions (*e.g.* $Zn(OH)_4^{2-}$). Metal oxides (*e.g.* Na_2O, CaO) will also act as strong bases, since the oxide ion will react with water to form two hydroxide ions. Likewise, metal hydrides (*e.g.* CaH_2, $NaBH_4$, $LiAlH_4$) react vigorously with water to form H_2 and OH^-. These substances do not offer an advantage over using the hydroxides directly, however.

For strong bases, the concentration of hydroxide ion is determined directly from the formality of the base solution, F_b, and the $[H_3O^+]$ and pH are calculated through K_w and pK_w. For monobasic strong bases, the relevant equations are given below.

$$[OH^-] = F_b \qquad pOH = -\log[OH^-] \tag{10.7}$$
$$[H_3O^+] = K_w/[OH^-] \qquad pH = pK_w - pOH = -\log[H_3O^+] \tag{10.8}$$

For polybasic strong bases, the equations need to be adjusted according to the number of hydroxide ions. For example, for calcium hydroxide, $[OH^-] = 2F_b$.

Table 10.4. Common strong bases and their approximate solubilities in water.

Compound	Solubility
Lithium hydroxide, LiOH	70 g/L
Sodium hydroxide, NaOH	1300 g/L
Potassium hydroxide, KOH	1100 g/L
Magnesium hydroxide, $Mg(OH)_2$	0.01 g/L
Calcium hydroxide, $Ca(OH)_2$	1 g/L
Strontium hydroxide, $Sr(OH)_2$	9 g/L
Barium hydroxide, $Ba(OH)_2$	40 g/L

Figure 10.6: Sodium hydroxide is generally sold as pellets with about 98% purity. They quickly absorb moisture from the air, eventually forming their own solution.

Exercise 10.1
Calculate the pH for each of the following solutions at 25 °C.

(a) 0.0300 F HNO_3 (b) 5.00 x 10^{-5} F LiOH (c) 0.0020 F $Ca(OH)_2$

Exercise 10.2
The value of pK_w at 10 °C has been reported as 14.535. What are the concentrations of H_3O^+ and OH^- in pure water at that temperature, and what is the pH?

10.8 Weak Acids

Weak acids are those acids which do not dissociate completely in solution, and whose degree of dissociation is defined by the acid dissociation constant, K_a, defined in general terms below.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

or $$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

Some common monoprotic weak acids are listed in Table 10.5 along with their K_a values. While all strong acids are equally strong, weak acids vary in their degree of dissociation. A larger K_a value (or a smaller pK_a) means a larger degree of dissociation, or a "stronger" weak acid. For example, chloroacetic acid (pK_a = 2.87) is stronger than acetic acid (pK_a = 4.76).

Classification of weak acids is more difficult than strong acids since there are many more weak acids and they vary somewhat in structure. Weak acids include:

- carboxylic acids (-COOH)
- compounds/species for which a K_a is given
- acids that are not classified as strong acids
- conjugate acids of weak bases

Table 10.5. Acid dissociation constants (as pK_a values) for some monoprotic weak acids.

Acid	Formula	pK_a
Acetic acid	CH_3COOH	4.76
Arsenious acid	H_3AsO_3	9.29
Benzoic acid	C_6H_5COOH	4.21
Butanoic acid	C_3H_7COOH	4.98
Chloroacetic acid	$ClCH_2COOH$	2.87
Cyanic acid	HOCN	3.66
Dichloroacetic acid	$Cl_2CHCOOH$	1.26
Formic acid	HCOOH	3.75
Hydrazoic acid	HN_3	4.73
Hydrocyanic acid	HCN	9.21
Hydrofluoric acid	HF	3.17
Hydrogen peroxide	HOOH	11.65
Hypobromous acid	HOBr	8.60
Hypochlorous acid	HOCl	7.53
Hypoiodous acid	HOI	10.64
Nitrous acid	HNO_2	3.29
Phenol	C_6H_5OH	9.98
Propanoic acid	CH_3CH_2COOH	4.87
Trichloroacetic acid	Cl_3CCOOH	0.66

Although many compounds contain hydrogens, not all of these will be acidic in aqueous solution. Most acidic protons are bound to electron-withdrawing structures that form stable conjugate bases, and are most often bound to oxygen. Hydrogens bound to carbons are not generally acidic except in special cases (*e.g.* HCN).

To determine the pH of a weak acid solution where the concentration of the weak acid is F_a, we set up the equilibrium in the usual way.

$$\begin{array}{ccccc} \mathrm{HA}(aq) & + & \mathrm{H_2O}(l) & \rightleftharpoons & \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \\ F_a - x & & & & x \qquad\quad x \end{array}$$

Substituting into the equilibrium expression, this gives $K_a = x^2/(F_a - x)$. If we can assume that $x \ll F_a$ (by a factor of 20), we can obtain the approximate solution:

$$x = [\mathrm{H_3O^+}] \approx \sqrt{K_a F_a} \quad \text{if} \quad [\mathrm{H_3O^+}] \ll F_a \tag{10.9}$$

Otherwise, we obtain the quadratic form.

$$x^2 + K_a x - K_a F_a = 0$$

This has the positive solution:

$$x = [\mathrm{H_3O^+}] = \frac{-K_a + \sqrt{K_a^2 + 4K_a F_a}}{2} \tag{10.10}$$

This is the solution that is valid when there is significant dissociation of the acid, which is more likely for stronger weak acids (small pK_a) and low concentrations.

There is sometimes the perception among students that strong acids are somehow more dangerous or corrosive than weak acids, but the terminology refers only to the degree of dissociation. Concentrated weak acids, such as acetic acid, can readily cause acid burns and penetrate latex gloves. Hydrofluoric acid is a weak acid, but it can dissolve glass and requires special handling due to its acute toxicological effects when exposure occurs.

Exercise 10.3

Use both the approximate and exact equations to calculate the pH of solutions with the following concentrations of acetic acid: (a) 0.10 F, (b) 0.010 F, (c) 0.0010 F, (d) 1.0×10^{-4} F. Does the approximation overestimate or underestimate the pH? By how much in each case? For which cases is the approximation taken to be valid?

Exercise 10.4

Compare the pH of a solution containing (a) 0.0100 butanoic acid with solutions containing the same concentration of (b) hypobromous acid, and (c) chloroacetic acid.

Exercise 10.5

The approximation is taken to be valid when $F_a/[H_3O^+] > 20$, where $[H_3O^+]$ is determined by the approximation. Show that this is mathematically equivalent to the condition that $F_a/K_a > 400$. Also show that it is equivalent to the condition that $pK_a - pH > 1.30$.

Weak, Moderate and Strong Weak Acids

As already noted, weak acids differ in their degree of dissociation, or strength. Therefore it is sometimes useful to classify weak acids according to their relative strength as strong, moderate, or weak. The basis of these classifications is given in Table 10.6. The boundaries between each classification are somewhat arbitrary, but being able to make this distinction can help appreciate how a particular weak acid will behave in solution and offer clues as to how proceed with calculations. For example, strong weak acids are more likely to require solution of the quadratic equation especially at low concentration. Weak weak acids can also require special consideration, since the autoionization of water may become a significant factor at low concentrations. This situation will not be considered here, however.

Table 10.6. Classification of weak acids according to their relative strength.

Classification	pK_a range
"Strong" weak acid	$pK_a < 4$
"Moderate" weak acid	$4 < pK_a < 10$
"Weak" weak acid	$pK_a > 10$

10.9 Weak Bases

Unlike strong bases, which produce hydroxide ions by direct dissociation, weak bases generate hydroxide ions by accepting protons from water molecules, as indicated below for a generic base B.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq) \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

For example, in the case of dimethylamine, we have the equilibrium below.

$$(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$$

The base dissociation values, K_b, for some common monobasic weak bases are given in Table 10.7 and Appendix A. As with weak acids, a weak bases with a higher value of K_b, or a lower value of pK_b, are stronger and exhibit a greater degree of dissociation. Weak bases include:

- ammonia, amines (-NR_x), and imines (R_1=N-R_2)
- compounds/species for which a K_b is given
- conjugate bases of weak acids

The most common uncharged organic weak bases are amines, with structures analogous to ammonia and a lone pair of electrons available for binding with the proton (see Figure 10.7).

Equilibrium and pH calculations are exactly analogous to those of weak acids, with the equilibrium conditions set up as shown below for a weak base with formality F_b.

$$\begin{array}{lcccc} BH(aq) & + & H_2O(l) & \rightleftharpoons & BH^+(aq) + OH^-(aq) \\ F_b - x & & & & x \qquad x \end{array}$$

This leads to the same quadratic form and analogous solutions.

$$x = [OH^-] \approx \sqrt{K_b F_b} \qquad \text{if} \quad [OH^-] \ll F_b \tag{10.11}$$

or $$x = [OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_b F_b}}{2} \tag{10.12}$$

Table 10.7. Base dissociation constants (as pK_b values) for some monobasic weak bases.

Base	Formula	pK_b
Ammonia	NH_3	4.76
Aniline	$C_6H_5NH_2$	9.40
Cyclohexylamine	$C_6H_{11}NH_2$	3.36
Dimethylamine	$(CH_3)_2NH$	3.23
Ethylamine	$C_2H_5NH_2$	3.37
Hydrazine	H_2NNH_2	5.77
Hydroxylamine	$HONH_2$	8.04
Methylamine	CH_3NH_2	3.38
Piperidine	$C_5H_{10}NH$	2.88
Propylamine	$C_3H_7NH_2$	3.43
Pyridine	C_5H_5N	8.78
Pyrrolidine	C_4H_8NH	2.69
Triethanolamine	$(HOC_2H_4)_3N$	6.24
Trimethylamine	$(CH_3)_3N$	4.20

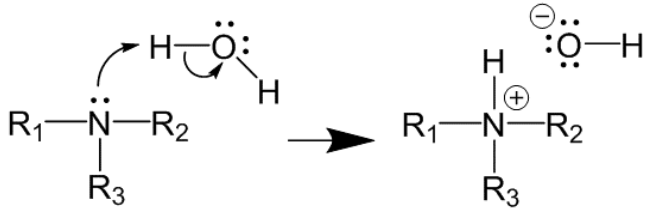


Figure 10.7: An amine acts as a base by accepting a proton from water, resulting in the production of the alkyl-ammonium ion, the conjugate acid.

The same classifications that applied to weak acids also apply to weak bases such that there are strong weak bases (pK_b < 4), moderate weak bases (pK_b = 4-10), and weak weak bases (pK_b > 10). The approximation (Equation 10.11) is likely to be valid for weak and moderate weak acids under most conditions, but the quadratic form (Equation 10.12) is more likely to be required for strong weak bases. The assumptions should always be checked, however.

Conjugate Acid-Base Pairs

It is important to realize that for every weak acid, there is a corresponding conjugate weak base, and likewise, for every weak base there is a conjugate weak acid. By necessity, if the acid or base is one of the uncharged species listed in Tables 10.5 or 10.7, then the conjugate species will be charged and can only be introduced into solution as a salt. For example, hydrofluoric acid, HF, the conjugate base is obtained by removing H^+, leaving the fluoride ion, F^-. This is introduced into solution as an appropriate ionic compound, such as sodium fluoride, NaF, with the reactions as given below.

$$NaF(s) \rightarrow Na^+(aq) + F^-(aq)$$

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq) \qquad K_b = \frac{[HF][OH^-]}{[F^-]}$$

In the first reaction, Na^+ is a neutral cation (which is true for any Group 1 or 2 cations) and so will have no influence on the acid base properties, which are determined by the basic fluoride ion. In the same way, the potassium acetate will generate the acetate ion, which is the conjugate base of acetic acid.

$$CH_3COOK(s) \rightarrow K^+(aq) + CH_3COO^-(aq)$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

For uncharged bases, the conjugate acid will be a cation formed by the addition of H^+. For example, ammonia will form the ammonium cation, which can be placed into a solution as salt such as ammonium chloride as indicated below.

$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

The chloride ion is neutral, so this solution will be acidic due to the presence of the ammonium ion. Other neutral anions include Br^-, I^-, NO_3^-, and ClO_4^-. When the acidic cation derives from an amine, it is an alkylammonium ion. For example, the trimethylammonium ion is derived from trimethylamine in the form of a salt, such as trimethylammonium bromide.

$$(CH_3)_3NHBr(s) \rightarrow (CH_3)_3NH^+(aq) + Br^-(aq)$$

$$(CH_3)_3NH^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + (CH_3)_3N(aq) \qquad K_a = \frac{[H_3O^+][(CH_3)_3N]}{[(CH_3)_3NH^+]}$$

To determine the pH of a solution of the conjugate base or acid, one proceeds as with any weak base or acid. However, to do this, we need to have the corresponding value of K_b or K_a. To obtain these values, we use a straightforward relationship between K_a and K_b for a conjugate acid-base pair, as given in Equation 10.13.

$$K_a \cdot K_b = K_w \quad \text{or} \quad pK_a + pK_b = pK_w = 14.00 \quad @\ 25\ ^oC \qquad (10.13)$$

Based on this, we can calculate $pK_b(F^-) = 14.00 - pK_a(HF) = 14.00 - 3.17 = 10.83$. Likewise, $pK_a(NH_4^+) = 14.00 - 4.76 = 9.24$. The implication of this relationship is that the stronger a weak acid, the weaker its conjugate base, and vice-versa. Therefore, a "weak" weak acid, will give rise to a conjugate base which is a "strong" weak base.

In certain cases, we may have to deal with a mixed salt that contains both an acid and a base, as in the case of ammonium fluoride, NH_4F. The acid-base properties of such a combination can be qualitatively determined by comparison of the relative strengths of the acid and base components. If $pK_a < pK_b$, the solution will be acidic; otherwise it will be basic. Thus, NH_4F will give rise to an acidic solution. Although we can't make a quantitative determination based on the methods we have developed, it can be shown that a good approximation is that the pH will be the average of the pK_a's of BH^+ and HA.

Example 10.1: pH of Weak Acid and Base Solutions

Determine the pH of the following solutions: (a) 0.100 F NH_3, (b) 0.0500 F NH_4NO_3, and (c) 0.0020 F KCN.

(a) An ammonia solution is a weak base, so the first step is to apply the approximation given in Equation 10.11.

$$[OH^-] \approx \sqrt{K_b F_b} = \sqrt{(10^{-4.76})(0.100)} = \sqrt{(1.\overline{7}4 \times 10^{-5})(0.100)} = 0.001\overline{3}2 \text{ M}$$

Since $F_b/[OH^-] < 20$, the approximation is valid and we can determine the pH.

$$\text{pOH} = -\log(0.001\overline{3}2) = 2.88, \quad \text{pH} = 14.00 - \text{pOH} = 11.12$$

(b) Ammonium nitrate is a salt, so we need to determine the acid base properties of both ions, NH_4^+ and NO_3^-. The ammonium ion is the conjugate acid of NH_3, so it will have acidic character. The nitrate ion is the conjugate base, of HNO_3, but since HNO_3 is a strong acid, NO_3^- will be neutral. Therefore, the problem becomes one of finding the pH of 0.0500 F, NH_4^+, a weak acid.

$$\text{p}K_a(NH_4^+) = 14.00 - \text{p}K_b(NH_3) = 14.00 - 4.76 = 9.24$$

$$[H_3O^+] \approx \sqrt{K_a F_a} = \sqrt{(10^{-9.24})(0.0500)} = \sqrt{(5.\overline{7}5 \times 10^{-10})(0.0500)} = 5.\overline{3}6 \times 10^{-6} \text{ M}$$

Once again the assumption is valid (as might be expected with $\text{p}K_a = 9.24$), so,

$$\text{pH} = -\log(5.\overline{3}6 \times 10^{-10}) = 5.27$$

(c) Potassium cyanide dissolves to form K^+ ions, which are neutral, and CN^-, which is the conjugate base of hydrocyanic acid, HCN, so the solution will be basic.

$$\text{p}K_b(CN^-) = 14.00 - \text{p}K_a(HCN) = 14.00 - 9.21 = 4.79$$

$$[OH^-] \approx \sqrt{K_b F_b} = \sqrt{(10^{-4.79})(0.0020)} = \sqrt{(1.\overline{6}2 \times 10^{-5})(0.0020)} = 1.8 \times 10^{-4} \text{ M}$$

In this case, $F_b/[OH^-] = 11$, so the quadratic form (Equation 9.12) must be used. (Although the cyanide ion is a moderate weak base, its concentration is quite low, so this is not unexpected.)

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bF_b}}{2} = \frac{-(1.\overline{6}2\times10^{-5}) + \sqrt{(1.\overline{6}2\times10^{-5})^2 + 4(1.\overline{6}2\times10^{-5})(0.0020)}}{2}$$

$$= \frac{-(1.\overline{6}2\times10^{-5}) + 3.\overline{6}0\times10^{-4}}{2} = \frac{3.\overline{4}4\times10^{-4}}{2} = 1.\overline{7}2\times10^{-4}\ \text{M}$$

$$\text{pOH} = -\log(1.72\times10^{-4}) = 3.76, \quad \text{pH} = 14.00 - 3.76 = 10.24$$

Exercise 10.6

Write equations for the acid-base equilibria that are relevant for solutions of the following: (a) benzoic acid, (b) cyanic acid, (c) dimethylamine, (d) hydroxylamine, (e) sodium nitrite, (f) methylammonium chloride. Also indicate whether the active species is a strong weak acid (SWA), a moderate weak acid (MWA), a weak weak acid (WWA), a strong weak base (SWB), a moderate weak base (MWB), or a weak weak base (WWB).

Exercise 10.7

Determine the pH of the following solutions: (a) 0.050 F chloroacetic acid, $ClCH_2COOH$, (b) 0.050 F trimethylamine, $(CH_3)_3N$, (c) 0.050 F pyridinum chloride (or pyridine hydrochloride), C_5H_5NHCl, (d) 0.050 F sodium hypoiodite, NaOI.

Exercise 10.8

Would you expect a solution of ammonium cyanide to be acidic or basic? Explain.

10.10 Buffers

Buffers represent a very important application of acid-base equilibria. They exist everywhere in nature for pH regulation in biological and ecological systems, and are widely used in laboratories for pH control in experimental systems. From a functional standpoint, the purpose of a buffer is to resist changes in pH when an acid or base is added to a system, either as the result of the flow of material into the system or from chemical reactions occurring within the system. From a compositional standpoint, a simple buffer consists of a conjugate acid-base pair that derive from *independent* sources. The latter condition is necessary to distinguish the buffer from simple weak acids or bases, which will always contain a small amount of the conjugate species. Because of this, a simple buffer can be viewed as being composed of one of three mixtures:

- A weak acid and its salt (*e.g.* acetic acid/ sodium acetate, CH_3COOH/CH_3COONa)
- A weak base and its salt (*e.g.* ammonia/ammonium chloride, NH_3/NH_4Cl)
- A mix of amphiprotic salts (*e.g.* mono- and disodium phosphate, NaH_2PO_4/Na_2HPO_4)

The last possibility is based on polyfunctional acids and bases, to be discussed later.

Because the buffer contains both acid and base components from independent sources, we can consider either the acid equilibrium, based on HA, or the base equilibrium, based on B. Either approach leads to the same result, but it is conventional to work from the acid component. The equilibrium conditions are as shown below.

$$\underset{F_a - x}{HA(aq)} + H_2O(l) \rightleftharpoons \underset{x}{H_3O^+(aq)} + \underset{F_b + x}{A^-(aq)}$$

so $$K_a = \frac{[H_3O^+](F_b + x)}{F_a - x} \qquad (10.14)$$

In this equation, F_a and F_b represent the formalities of the weak acid and its conjugate base, respectively. If we assume the extent of dissociation of these two components to be small, this leads to the approximate form known as the Henderson-Hasselbalch Equation.

$$[H_3O^+] \approx \frac{K_a F_a}{F_b} \quad \text{if} \quad F_a, F_b \gg \left| [H_3O^+] - [OH^-] \right| \tag{10.15}$$

Note that the conditions for the approximation to be valid involve both $[H_3O^+]$ and $[OH^-]$ since the buffer could be acting in either in acidic or basic solution. Generally, this assumption will be valid except at very low or high pH, since buffers are usually prepared at relatively high concentrations. Nevertheless, *the assumption should always be checked*, and we will use the usual rule that both F_a and F_b should be greater than the absolute value of ($[H_3O^+]$-$[OH^-]$) by at least a factor of 20. The case where this is not true needs to be treated with a more complex quadratic form that will not be discussed here.

Equation 10.15 reveals that the pH of the buffer depends only on the *ratio* of F_a to F_b and not on the actual values. When $F_a = F_b$, the pH of the buffer is equal to the pK_a. If the acid component is higher than the base, the pH will be lower than the pK_a, and the pH will be higher than the pK_a if there is more of the base. Although it is the ratio F_a/F_b that is important in determining the pH of the buffer, the concentrations are important in determining *buffer capacity*, which is the extent to which a buffer will change pH on the addition of strong acid or base. Larger values of F_a and F_b will lead to a buffer which has a greater resistance to pH change, or in other words, a higher buffer capacity. Buffer capacity also depends on the pH of the buffer solution and is optimal when pH = pK_a. For that reason, as a rule of thumb, you should try to choose a buffer with a pK_a that is within ±1 pH unit of the desired pH. Other factors also influence the choice of buffer components. For example, hydrocyanic acid would not be a good choice for a buffer because of the toxicity of HCN.

Example 10.2: Preparing a Buffer Solution

Describe how you would prepare 500. mL of a buffer at pH = 10.00 from a stock solution of 2.00 F ammonia and solid ammonium chloride, NH_4Cl (MM= 53.49 g/mol). The formality of the weak base in the buffer should be 0.500 M.

The buffer components in this case are NH_3 and its conjugate acid, NH_4^+, which is formed when ammonium chloride dissolves in solution. Since pK_b(NH_3) = 4.76, the

pK_a of NH_4^+ is 14.00 – 4.76 = 9.24, which is within one pH unit of the desired pH of 10.00. We are also told that F_b = 0.500 in the buffer. Equation 10.15 gives

$$[H_3O^+] \approx \frac{K_a F_a}{F_b}$$

Since we know $[H_3O^+]$, K_a, and F_b, we can solve for F_a.

$$F_a = \frac{[H_3O^+]F_b}{K_a} = \frac{(10^{-10.00})(0.500)}{10^{-9.24}} = \frac{(1.0\times10^{-10})(0.500)}{5.\overline{75}\times10^{-10}} = 0.08\overline{69}\ \text{F}$$

This makes sense, since the pH of the solution is more basic than the pK_a and therefore the formality of the base should be greater than the acid. However, we still need to check the assumptions.

$$\left|\,[H_3O^+] - [OH^-]\,\right| = \left|(10^{-10}\ \text{M}) - (10^{-4}\ \text{M})\right| \approx 10^{-4}\ \text{M}$$

This gives $F_a \Big/ \left|[H_3O^+] - [OH^-]\right| = 868$, so the approximation is valid. (Note that we only need to check the smaller of F_a and F_b.) We can now calculate the moles of NH_4^+ required.

$$\text{moles of } NH_4^+ = 0.08\overline{69}\ \text{mol/L} \times 0.500\ \text{L} = 0.04\overline{34}\ \text{mol} = \text{moles } NH_4Cl$$

The mass of ammonium chloride can be determined from the molar mass.

$$\text{mass of } NH_4Cl = 0.04\overline{34}\ \text{mol} \times 53.49\ \text{g/mol} = 2.\overline{32}\ \text{g}$$

The required moles of NH_3 can be obtained by taking an appropriate amount of the stock solution, calculated using $C_1V_1 = C_2V_2$.

$$V_1 = \frac{C_2}{C_1}V_2 = \frac{0.500\ \text{F}}{2.00\ \text{F}} \cdot 500.\ \text{mL} = 125.\ \text{mL}$$

Therefore, the buffer can be prepared by combining 125.0 mL of 2.00 F NH_3 and 2.3 g of ammonium chloride and diluting the solution to 500. mL.

Exercise 10.9

How many mL of pure acetic acid (called glacial acetic acid, MM = 60.05 g/mol, density = 1.049 g/mL) and what mass of potassium acetate (MM = 98.14 g/mol) would have to be combined and diluted to 400. mL to make a buffer of pH 5.00. The formality of the acid component should be 0.20 F.

Reactions of Buffers

When excess H_3O^+ is generated in a buffer, either through the addition of a strong acid externally or through reactions of other components of the solution, it will react with the weak base component of the buffer to change the formalities of the acid and base components. A generic form of this reaction is as shown below.

$$H_3O^+(aq) + A^-(aq) \rightarrow HA(aq) + H_2O(l)$$

Note that this is shown as a reaction in one direction and not an equilibrium. The actual form of the reaction will depend on the type of buffer. For example, the reactions will differ for an acetate buffer and an ammonia buffer, as shown below.

$$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$
$$H_3O^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + H_2O(l)$$

Regardless of the buffer, the formality of the acid component is increased and the formality of the base component is decreased. Likewise, if hydroxide ion is added, it will react with the acid component, decreasing its concentration and increasing the concentration of the base, as shown below.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$
$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$

The changes in the formality of the acid and base will alter the pH of the solution, decreasing it on the addition of acid and increasing it on the addition of base. However, the pH change

will be much smaller than it would have been if the buffer were not present. This is illustrated in the following example.

Example 10.3: pH Changes in a Buffer Solution

Suppose you prepare 200.0 mL of an acetate buffer in which the formality of the acetic acid, CH_3COOH, is 0.150 F and the formality of the acetate ion, CH_3COO^-, is 0.250 F. Answer the following questions.

(a) What is the initial buffer pH?
(b) What would be the pH after the addition of 10.0 mL of 0.100 F HNO_3?
(c) What would be the pH after the addition of 10.0 mL of 0.100 F NaOH?
(d) Compare these to the pH change if the same additions were made to 200.0 mL of water.

(a) The initial pH is calculated in the usual way using Equation 10.15.

$$[H_3O^+] \approx \frac{K_a F_a}{F_b} = \frac{(10^{-4.76})(0.150)}{0.250} = \frac{(1.\overline{7}4 \times 10^{-5})(0.150)}{0.250} = 1.\overline{0}4 \times 10^{-5}\ \text{M}$$

Since [$F_a/[H_3O^+]>20$, the assumption is valid. Therefore,

$$\text{pH} = -\log(1.\overline{0}4 \times 10^{-5}) = 4.98$$

(b) There are two effects from the addition of the strong acid. The first is a dilution of both buffer components as well as the strong acid. The second is the reaction of the strong acid with the base component to change F_a and F_b.

There are two approaches that can be used here. One is to determine the number of moles of each species at the beginning and end of the reaction, and then convert these to concentrations. The other is to calculate the initial concentrations and work in those units. Both approaches are valid, but we will use the first approach. The initial number of moles can be determined by multiplying the concentrations by the volumes involved.

$$\text{initial moles } CH_3COOH = (0.150\,\text{mol/L}) \times (0.200\,\text{L}) = 0.0300\,\text{mol}$$

$$\text{initial moles } CH_3COO^- = (0.250\,\text{mol/L}) \times (0.200\,\text{L}) = 0.0500\,\text{mol}$$

$$\text{moles of } H_3O^+ \text{ added} = (0.100\,\text{mol/L}) \times (0.0100\,\text{L}) = 0.00100\,\text{mol}$$

We can now write the reaction and determine the number of moles remaining.

	$H_3O^+(aq)$	+ $CH_3COO^-(aq)$	→ $CH_3COOH(aq)$	+ $H_2O(l)$
Initial	0.00100	0.0500	0.0300	mol
Change	–0.00100	–0.00100	+0.00100	mol
Final	≈ 0	0.0490	0.0310	mol

The reaction between the strong acid and weak base is assumed to be complete, but of course the concentration of H_3O^+ is not really zero. The new formalities of the acid and base (in the new volume) can now be determined.

$$F_a = \frac{0.0310\,\text{mol}}{0.210\,\text{L}} = 0.14\overline{7}6\ \text{F} \qquad F_b = \frac{0.0490\,\text{mol}}{0.210\,\text{L}} = 0.23\overline{3}3\ \text{F}$$

$$[H_3O^+] \approx \frac{K_a F_a}{F_b} = \frac{(10^{-4.76})(0.14\overline{7}6)}{0.23\overline{3}3} = 1.\overline{1}0 \times 10^{-5}\ \text{M} \quad \text{(assumption still valid)}$$

$$\text{pH} = -\log(1.\overline{1}0 \times 10^{-5}) = 4.96$$

Note that the pH has only decreased by 0.02 units after adding the strong acid.

One additional thing to note is that, since the total volume is fixed, the H_3O^+ concentration could have been calculated directly from the moles.

$$[H_3O^+] \approx \frac{K_a(\text{moles } CH_3COOH)}{\text{moles } CH_3COO^-} = \frac{(10^{-4.76})(0.0310)}{0.0490} = 1.\overline{1}0 \times 10^{-5}\ \text{M}$$

However, without the calculation of F_a and F_b, the assumptions cannot be checked.

(c) The calculations in this case are nearly identical, except that we are adding an equivalent number of moles of strong base.

$$\text{initial moles } CH_3COOH = 0.0300\,\text{mol} \qquad \text{initial moles } CH_3COO^- = 0.0500\,\text{mol}$$

$$\text{moles of } OH^- \text{ added} = (0.100\,\text{mol/L}) \times (0.0100\,\text{L}) = 0.00100\,\text{mol}$$

The strong base will react with the acid component of the buffer, as shown below.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

Initial	0.0300	0.00100	0.0500	mol
Change	–0.00100	–0.00100	+0.00100	mol
Final	0.0290	≈ 0	0.0510	mol

$$F_a = \frac{0.0290\,\text{mol}}{0.210\,\text{L}} = 0.13\overline{81}\ \text{F} \qquad F_b = \frac{0.0510\,\text{mol}}{0.210\,\text{L}} = 0.24\overline{29}\ \text{F}$$

$$[H_3O^+] \approx \frac{K_a F_a}{F_b} = \frac{(10^{-4.76})(0.13\overline{81})}{0.24\overline{29}} = 9.\overline{88} \times 10^{-6}\ \text{M} \quad \text{(assumption still valid)}$$

$$\text{pH} = -\log(9.\overline{88} \times 10^{-6}) = 5.01$$

In this case, the change is only +0.03 units.

(d) These changes may not seem very impressive until we compare them to what would happen in pure water, which has an initial pH of 7.00. In this case, we are simply diluting the strong acid and strong base. In each case, the concentration of the strong acid or base is (0.100 M)x(10.0 mL)/(210.0 mL) = 4.76×10^{-3} M.

Acid: $[H_3O^+] = 4.76 \times 10^{-3}\ \text{M}$ $\qquad \text{pH} = -\log(4.76 \times 10^{-3}) = 2.322$

Base: $[OH^-] = 4.76 \times 10^{-3}\ \text{M}$ $\qquad \text{pH} = 14.00 - \log(4.76 \times 10^{-3}) = 11.68$

In contrast to the buffer, which has a total change 0.05 units, the unbuffered solution changes by 9.36 units.

Exercise 10.10

Repeat the calculations above for 200.0 mL of an ammonia buffer with an NH_3 concentration of 0.200 F and an NH_4^+ concentration of 0.300 F. Calculate (a) the initial pH, (b) the pH after the addition of 20.0 mL of 0.100 F HCl, (c) the pH after the addition of 20.0 mL of 0.100 F KOH, (d) pH after the addition of the same amounts of strong acid and base to 200.0 mL of water.

10.11 Mixtures of Strong and Weak Acids and Bases

In certain cases, there may be a need to consider the pH of a solution that contains a mixture of a strong acid and a weak acid, or a mixture of a strong base and a weak base. This would be the situation, for example, if enough strong acid was added to a buffer to exceed its capacity, converting essentially all of the base component present to a weak acid. Under these conditions, when both a strong acid and a weak acid are present, the are two sources of H_3O^+. For example, if the mixture contains both hydrochloric and acetic acid, we have:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Because the strong acid dissociates completely, it will generally dominate the contribution of H_3O^+ ions in solution, whereas the weak acid will typically make a smaller contribution. The contribution of the weak acid is further diminished because the H_3O^+ from the strong acid will push the equilibrium to the left (Le Châtelier's Principle). Therefore, we would expect the weak acid to make only a small contribution to lowering the pH. An exception would be if the concentration of the weak acid were high relative to the strong acid and/or we were dealing with a strong weak acid (low pK_a) that dissociates extensively. Otherwise, we can estimate the pH from the formality of the strong acid.

$$[H_3O^+] \approx F_{SA} \quad \text{if } F_{SA} \gg K_a \text{ for weak acid} \tag{10.16}$$

When this condition is not met, a different calculation is needed, but that is not treated here.

For mixtures of strong bases and weak bases (*e.g.* NaOH and NH_3), similar arguments apply and the pH will be largely determined by the concentration of the strong base.

$$[OH^-] \approx F_{SB} \quad \text{if } F_{SB} \gg K_b \text{ for weak base} \tag{10.17}$$

Exercise 10.11

For the acetate buffer employed in the previous example (200.0 mL, F_a = 0.150 F, F_b = 0.250 F), calculate the pH after the addition of the following amounts of 1.00 F HNO_3: (a) 20.0 mL, (b) 40.0 mL, and (c) 60.0 mL.

10.12 Polyfunctional Acids and Bases

Polyfunctional acids and bases refer to those species that are capable of donating or accepting more than one proton. If the uncharged form of such a species can only donate protons, it is termed *polyprotic*. For example, phosphoric acid, H_3PO_4, is a polyprotic acid, or more specifically, a triprotic acid, since it can donate three protons. Some examples of polyprotic acids are given in Table 10.8. Such acids can donate protons in a stepwise fashion, and each successive step has a defined K_a value, as shown below for phosphoric acid.

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \qquad K_{a1} = 7.1\times10^{-3}$$
$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \qquad K_{a2} = 6.3\times10^{-8}$$
$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \qquad K_{a3} = 7.1\times10^{-13}$$

Note that each successive step in this process has a lower K_a (or a larger pK_a), reflecting the fact that it becomes more difficult to remove additional protons. Diprotic acids are also very common, and sulfuric acid, H_2SO_4, is an example of this, although it is unique in that the first proton is a strong acid ($K_{a1} = \infty$).

If a compound can only accept protons in its neutral form, it is said to be *polybasic*. An example of a dibasic compound is ethylenediamine ($NH_2CH_2CH_2NH_2$; abbreviated "en"), which is also a complexing agent. Each of the terminal amines in this compound is capable

Table 10.8. Acid dissociation constants (as pK_a values) for some polyfunctional acids.

Acid	Formula	pK_a
Alanine	$HOOCCH(CH_3)NH_3^+$	2.34 9.69
Arsenic acid	H_3AsO_4	2.22 6.98 11.50
Carbonic acid	H_2CO_3	6.35 10.33
Citric acid	$C_3H_5O(COOH)_3$	3.12 4.76 6.40
Glycine	$HOOCCH_2NH_3^+$	2.34 9.60
Hydrogen sulfide	H_2S	7.02 13.9
Maleic acid	HOOCCH=CHCOOH	1.92 6.22
Malonic acid	$HOOCCH_2COOH$	2.85 5.70
Oxalic acid	HOOCCOOH	1.27 4.27
Phosphoric acid	H_3PO_4	2.15 7.20 12.15
Succinic acid	$HOOCCH_2CH_2COOH$	4.21 5.64
Sulfuric acid	H_2SO_4	$-\infty$ 1.99

of accepting a proton to form the corresponding ammonium species. The equilibria are as shown below.

$$H_2N\text{-}CH_2CH_2\text{-}NH_2 + H_2O \rightleftharpoons H_2N\text{-}CH_2CH_2\text{-}NH_3^+ + OH^- \qquad K_{b1} = 8.5\times10^{-5}$$

$$H_2N\text{-}CH_2CH_2\text{-}NH_3^+ + H_2O \rightleftharpoons {}^+H_3N\text{-}CH_2CH_2\text{-}NH_3^+ + OH^- \qquad K_{b1} = 7.1\times10^{-8}$$

As with acids, the K_b values decrease with each successive proton accepted. A list of some polybasic bases and their pK_b values is given in Table 10.9.

If an uncharged compound is capable of accepting and donating protons, it is said to be *amphiprotic*. Other than water, common examples of amphiprotic compounds are amino acids, such as alanine and glycine, which are also listed in Table 10.8. To avoid listing both K_a and K_b values for amphiprotic substances, it is common to list only K_a values for the fully protonated (charged) species, and this is why the amino acids are the only charged species in the table.

As the pH increases in solution, all polyfunctional acids and bases transition from the acid form, to amphiprotic species and then to the basic form. This is illustrated below for three cases.

	Acid Form		*Amphiprotic Species*		*Base Form*
Phosphoric acid	$\mathbf{H_3PO_4}$	$\rightleftharpoons$	$H_2PO_4^- \rightleftharpoons HPO_4^{2-}$	$\rightleftharpoons$	PO_4^{3-}
Ethylenediamine	${}^+H_2NCH_2CH_2NH_3^+$	$\rightleftharpoons$	$H_2NCH_2CH_2NH_3^+$	$\rightleftharpoons$	$\mathbf{H_2NCH_2CH_2NH_2}$
Glycine	$HOOCCH_2NH_3^+$	$\rightleftharpoons$	$\mathbf{{}^-OOCCH_2NH_3^+}$	$\rightleftharpoons$	${}^-OOCCH_2NH_2$

Phosphoric acid has two intermediate species that are amphiprotic, whereas the other two substances have only one. The uncharged forms are shown in bold. Note that the glycine is a *zwtterion* in this form, which means it has charged groups but a net charge of zero. This is in contrast to the uncharged structure that is normally shown for amino acids (Figure 10.8).

Exercise 10.12

Write the formulas for the acid, amphoteric, and base forms of the following compounds: (a) citric acid, (b) piperazine, and (c) alanine.

Table 10.9. Base dissociation constants (as pK_b values) for some polyfunctional bases.

Base	Formula	pK_b
Butane-1,4-diamine (putrescene)	$NH_2(CH_2)_4NH_2$	3.20 4.37
1,4-Diaminobenzene	$C_6H_4(NH_2)_2$	7.69 11.03
Ethylenediamine	$NH_2(CH_2)_2NH_2$	4.07 7.15
Piperazine	$C_4H_{10}N_2$	4.27 8.67
Propane-1,3-diamine	$NH_2(CH_2)_3NH_2$	3.45 5.12

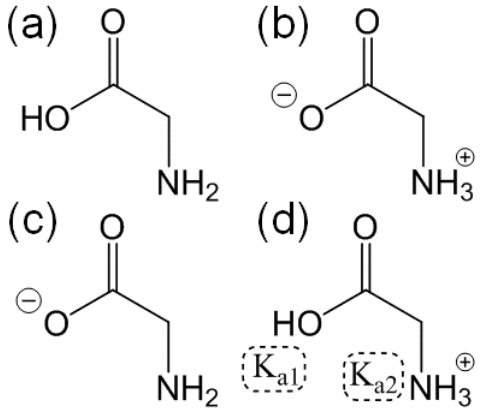


Figure 10.8: Different representations of the amino acid glycine: (a) normal representation, (b) uncharged zwitterionic form, (c) fully deprotonated form, (d) fully protonated form.

Calculations with Polyfunctional Acids and Bases

The presence of multiple acid-base equilibria makes the calculation of pH for polyfunctional species more complex compared to monofunctional acids and bases. However, if the difference between successive K_a or K_b values is sufficiently large, there are certain instances where an approximation to the monofunctional case is possible (*i.e.* other equilibria can be ignored). The accuracy of this approximation depends on a number of factors, but we will employ the rule that the approximations can be used if the difference between successive pK values **greater than or equal to 3** (or K values differ by a factor of at least 10^3).

Even when these conditions are met, there are only some calculations that can be done. These are summarized below, using phosphoric acid as an example, since it meets the requirement of $\Delta pK_a \geq 3$.

(1) *Pure acid or pure base form.* When a species is in a form that is fully protonated (*e.g.* H_3PO_4) or fully deprotonated (*e.g.* PO_4^{3-}) and meets the ΔpK conditions ($pK_2 - pK_1 \geq 3$), then pH can be calculated as if it were a monoprotic weak acid or a monobasic weak base.

(2) *Amphiprotic forms.* A single amphiprotic species in solution (*e.g.* $H_2PO_4^-$ or HPO_4^{2-}) can act simultaneously as an acid or a base and it is <u>*not possible*</u> to accurately calculate the pH of the solution, even if the ΔpK conditions are met. However, it *is possible* to determine if the solution will be acidic or basic. If $pK_a < pK_b$ (or $K_a > K_b$), then the solution will be acidic; otherwise, it will be basic. Note that pK_a and pK_b here refer to the amphiprotic species, and not its conjugate acid or base.

(3) *Buffers.* If a buffer is prepared from a pair of conjugate species (*e.g.* $H_3PO_4/H_2PO_4^-$, $H_2PO_4^-/HPO_4^{2-}$, or HPO_4^{2-}/PO_4^{3-}), then the usual buffer calculations will apply if $\Delta pK \geq 3$. The use of polyfunctional acids and bases (*e.g.* phosphate, carbonate) is useful, since it expands the range of pH available using a single buffer.

Note that if the condition of ΔpK does not hold for cases (1) and (3), calculations can still be done, but they are likely to be less accurate.

Example 10.4: pH Calculations with Polyfunctional Acids and Bases

For each of the following solutions, indicate whether the solution will be acidic or basic and, if possible, determine the pH of the solution.

(a) 0.0500 F H_3PO_4, (b) 0.250 F Na_3PO_4, (c) 0.100 F K_2HPO_4,
(d) a mixture containing 0.150 F LiH_2PO_4 and 0.200 F Li_2HPO_4.

(a) H_3PO_4 represents the fully protonated form of phosphoric acid, which meets the criterion that $\Delta pK_a \geq 3$ (the smallest difference is 4.95). Therefore, we can treat this as a weak acid solution with $pK_a = pK_{a1} = 2.15$.

$$[H_3O^+] \approx \sqrt{K_a F_a} = \sqrt{(10^{-2.15})(0.0500)} = \sqrt{(7.\overline{0}8\times10^{-3})(0.0500)} = 0.01\overline{8}8\,\text{M}$$

This does not satisfy the assumption that $[H_3O^+] \ll F_a$ so the quadratic form is required (expected, since H_3PO_4 is a strong weak acid).

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aF_a}}{2} = \frac{-(7.\overline{0}8\times10^{-3}) + \sqrt{(7.\overline{0}8\times10^{-3})^2 + 4(7.\overline{0}8\times10^{-3})(0.0500)}}{2}$$

$$= \frac{-(7.\overline{0}8\times10^{-3}) + (0.03\overline{8}2)}{2} = 0.01\overline{5}6\,\text{M}$$

$$\text{pH} = -\log(0.01\overline{5}6) = 1.81$$

(b) Trisodium phosphate will dissociate completely into Na^+ ions (neutral) and PO_4^{3-}, which is the fully deprotonated for of phosphoric acid. Therefore, the phosphate ion can be treated as a weak base with $pK_b = 14.00 - pK_{a3} = 1.85$ (since PO_4^{3-} is the conjugate base of HPO_4^{2-}). This is a strong weak base, and since $F_b/K_b < 400$, we will proceed directly to the quadratic form without the approximation.

$$[OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bF_b}}{2} = \frac{-(10^{-1.85}) + \sqrt{(10^{-1.85})^2 + 4(10^{-1.85})(0.250)}}{2}$$

$$= \frac{-(0.01\overline{4}1) + (0.1\overline{2}0)}{2} = 0.05\overline{2}8\,\text{M}$$

$$\text{pH} = 14.00 - \log(0.05\overline{2}8) = 12.72$$

(c) A solution of potassium hydrogen phosphate will produce K^+ ions, which are neutral, and HPO_4^{2-}, which amphiprotic. To determine whether this species will act as an acid or a base, we need to compare its pK_a to its pK_b. The pK_a can be obtained directly from Table 10.8 as pK_a = pK_{a3}(H_3PO_4) = 12.15. To determine the pK_b, we need to use the pK_a of its *conjugate acid*, $H_2PO_4^-$.

$$pK_b(HPO_4^{2-}) = 14.00 - pK_a(H_2PO_4^-) = 14.00 - pK_{a2} = 14.00 - 7.20 = 6.80$$

Since pK_b < pK_a (or $K_b > K_a$), we can conclude that the base is stronger than the acid and the solution will be basic.

Because this is an amphiprotic species, it is not possible to calculate the pH accurately in a simple way. (A calculation assuming F_b = 0.100 and pK_b = 6.80 will give pH = 10.10, but the actual value is 9.65.)

(d) This solution contains $H_2PO_4^-$ and HPO_4^{2-}, a conjugate acid-base pair from independent sources, so it forms a buffer with F_a = 0.150 F, F_b = 0.200 F, and pK_a = pK_{a2} = 7.20. Because the pK_a > 7, we expect the buffer to be basic, but this can be verified by the usual calculation.

$$[H_3O^+] \approx \frac{K_a F_a}{F_b} = \frac{(10^{-7.20})(0.150)}{0.200} = \frac{(6.\overline{3}1\times10^{-8})(0.150)}{0.200} = 4.\overline{7}3\times10^{-8}\ \text{M}$$

The assumption that $F_a, F_b \gg \left| [H_3O^+] - [OH^-] \right|$ is valid, so

$$pH = -\log(4.\overline{7}3\times10^{-8}) = 7.32$$

Exercise 10.13

Of the acids listed in Table 10.8, how many meet the requirement of $\Delta pK_a \geq 3$ for all forms? How many bases meet the requirement in Table 10.9?

Exercise 10.14

For each of the following solutions, indicate whether the solution will be acidic or basic and, if possible, determine the pH of the solution.

(a) 0.200 F oxalic acid (c) 0.100 F K_2SO_4 (e) 0.0100 F trisodium citrate
(b) 0.250 F NaH_2PO_4 (d) 0.500 F Na_2CO_3 (f) 0.300 F $NaHCO_3$

Exercise 10.15

How many grams of sodium hydrogen carbonate and sodium carbonate would be needed to prepare 1.00 L of a buffer at pH = 10.00. The formality of the base component should be 0.100 F.

10.13 Neutral Salts

It may seem from the discussion so far that there are no substances that have no acid-base properties, but there are some ions that can be considered neutral. Among the positive ions, these include the Group 1 and 2 cations, with the exception of Be^{2+}, which is slightly acidic. The neutral anions include the conjugate bases of the strong acids that were listed earlier (chloride, bromide, iodide, nitrate, and perchlorate, but *not* fluoride or sulfate), as well as some others that were not mentioned but are less common (chlorate, bromate, iodate, perbromate, periodate). Some neutral cations and anions are listed in Table 10.10. A solution which contains a salt with a neutral cation and a neutral anion, such as NaCl, will be neutral.

In the same way that neutral anions derive from strong acids, the neutral anions might be viewed as being derived from strong bases such as NaOH or $Ca(OH)_2$. One might wonder if the cations of other metal hydroxides, such as $Fe(OH)_3$, could also be considered as neutral, but transitions metals and such metals form complexes with water in solution. These can hydrolyze as shown below, and therefore will generally be acidic in solution.

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5(OH)_6^{2+}(aq) + H_3O^+(aq)$$

Certain singly charged ions, such as Ag^+, are considered neutral, however.

Table 10.10. Some neutral anions and cations.

Cations:	Li^+, Na^+, K^+, Rb^+, Cs^+
	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}
Anions:	Cl^-, Br^-, I^-, NO_3^-, ClO_4^-
	BrO_4^-, IO_4^-, ClO_3^-, BrO_3^-, IO_3^-

10.14 Summary

Chemical species that act as acids and bases are common in aqueous solution, so it is important to be able to classify such species as strong acids, strong bases, weak acids, weak bases or combinations of these, and to be able to calculate the solution pH using the methods presented here. Buffers are especially important because of their role in regulating pH. Likewise, polyfunctional acids and bases are widely encountered and require special consideration. An understanding of acid-base equilibria is key to many chemical systems in the lab and in nature.

10.15 Additional Exercises

Exercise 10.16
What is the pH of a 0.00734 F solution of tetrafluoroboric acid? HBF_4 is a strong monoprotic acid in water.

Exercise 10.17
Approximately how many mL of concentrated HCl (see Table 10.3) would have to be diluted to 500. mL to give a solution with a pH of 1.50?

Exercise 10.18
Calculate the pH of a solution prepared by mixing 15.0 g of 37.0% by weight concentrated HCl with enough water to make 100.0 mL of solution.

Exercise 10.19
What mass of lithium hydroxide (MM = 23.948 g/mol) must be used to prepare 500. mL of a solution of pH 10.50?

Exercise 10.20
Barium hydroxide is available in several forms, including anhydrous, monohydrate and octahydrate. How many grams of the octahydrate ($Ba(OH)_2 \cdot 8H_2O$) would need to be dissolved to give 100.0 mL of a solution at pH 13.20?

Exercise 10.21
What is the pH of a solution formed by dissolving 4.00×10^{-3} moles of benzoic acid in water to form 100.0 mL of solution?

Exercise 10.22
Calculate the pH of a 0.0100 F solution of dichloroacetic acid.

Exercise 10.23
Calculate the pH of a 0.0125 F solution of trimethylamine.

Exercise 10.24
Calculate the pH of a 0.200 F solution of ethylamine.

Exercise 10.25
What is $[H_3O^+]$ in a solution 0.125 F in sodium formate (HCOONa)?

Exercise 10.26
Assume that you wish to prepare a buffer of pH 4.00 using acetic acid as the acid component and sodium acetate as the base component. What concentration of acetic acid would be required if the concentration of the base component is to be 0.100 F.

Exercise 10.27
Calculate the pH of the buffer in the previous question when 50.0 mL of 1.00 F NaOH is added to 200.0 mL of the buffer. Also, calculate the pH of the buffer after the addition of 50.0 mL of 1.00 F HCl. What is different in the latter case?

Exercise 10.28
What volume of concentrated formic acid (23.6 F) and what mass of sodium formate (MM = 68.01 g/mol) would be needed to make 250.0 mL of a buffer at pH = 4.00 if the formality of the weak acid component is to be 0.500 F?

Exercise 10.29
What is the maximum mass of sodium hydroxide (MM = 40.00 g/mL) that could be dissolved in the buffer prepared in the previous question before the pH exceeds 4.50? Assume there is no change in volume.

Exercise 10.30
What volume of hydroxylamine (MM = 33.03 g/mL, density = 1.21 g/mL) and what mass of hydroxylammonium chloride (hydroxylamine hydrochloride, MM = 69.49 g/mol) would be required to make 500. mL of a buffer with pH = 6.50 if the concentration of the base component is 0.200 F?

Exercise 10.31
What volume of concentrated ammonia (28% by weight, density = 0.88 g/mL) and what mass of ammonium bromide would be required to make 1.00 L of a buffer with pH = 9.00? The *sum* of the acid and base formalities should equal 0.500 F in this buffer.

Exercise 10.32
For each of the following solutions, indicate whether the solution will be acidic, basic, or neutral and, if possible, determine the pH of the solution.

(a) 0.20 F potassium nitrate
(b) 0.20 F potassium nitrite
(c) 0.010 F hydrochloric acid
(d) 0.010 F hydrofluoric acid
(e) 0.050 F calcium hydroxide
(f) 0.050 F calcium bromide
(g) 0.10 F maleic acid
(h) 0.10 F sodium hydrogen maleate
(i) 0.10 F disodium maleate
(j) 0.030 F glycine hydrochloride
(k) 0.020 F sodium hydrogen sulfide
(l) 0.30 F ethylenediamine dihydrochloride

Exercise 10.33
Calculate $[H_3O^+]$ in a solution 0.0100 F in $NaHSO_4$.

Exercise 10.34
Describe how to prepare 500. mL of a buffer at pH = 4.00 in which the concentration of the base component is 0.400 F. You have available solid oxalic acid, sodium hydrogen oxalate and disodium oxalate.

Exercise 10.35
In Section 10.11, it was stated that the pH of a mixture of a strong acid and a weak acid could be determined by assuming $[H_3O^+] \approx F_{SA}$ if $F_{SA} \gg K_a$. Consider the following equations for a generic strong acid (HSt) and weak acid (HA) with concentrations of F_{SA} and F_{WA}.

$$HSt(aq) + H_2O(l) \rightarrow H_3O^+(aq) + St^-(aq)$$

$$\begin{array}{lcll} HA(aq) + H_2O(l) & \rightleftharpoons & H_3O^+(aq) + A^-(aq) \\ F_{WA} - x & & F_{SA} + x \quad x \end{array}$$

Show that the exact solution for $[H_3O^+]$ when the assumption given above does not hold is given by:

$$[H_3O^+] = \frac{F_{SA} - K_a + \sqrt{(F_{SA} + K_a)^2 + 4K_aF_{WA}}}{2}$$

(Hint: note that $[H_3O^+] = F_{SA} + x$.). Using both the approximate and exact formulas, evaluate the pH of the following solutions containing mixtures of strong and weak acids at the given concentrations.

(a) 0.010 F HCl and 0.00010 F dichloroacetic acid
(b) 0.010 F HCl and 0.10 F dichloroacetic acid
(c) 0.010 F HCl and 0.10 F acetic acid

10.16 Answers to Exercises 10

10.1 (a) 1.52, (b) 9.70, (c) 11.60

10.2 $[H_3O^+] = [OH^-] = 5.40 \times 10^{-8}$, pH = 7.268

10.3 (a) 2.88, 2.88, (b) 3.38, 3.39, (c) 3.88, 3.91
Approximation underestimates pH by 0.00, 0.01, 0.03.
Approximation is taken to be valid for cases (a) and (b).

10.4 (a) 3.49, (b) 5.30, (c) 2.51 (pH decreases as pK_a decreases)

10.5 -

10.6 (a) $C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$ MWA
(b) $HOCN(aq) + H_2O(l) \rightleftharpoons OCN^-(aq) + H_3O^+(aq)$ SWA
(c) $(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$, SWB
(d) $HONH_2(aq) + H_2O(l) \rightleftharpoons HONH_3^+(aq) + OH^-(aq)$ MWB
(e) $NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$ WWB
(f) $CH_3NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^+(aq)$ WWA

10.7 (a) 2.12, (b) 11.25, (c) 3.26, (d) 11.65

10.8 Basic.

10.9 4.5_8 mL, $13._6$ g

10.10 (a) 9.06, (b) 9.03, (c) 9.10, (d) 2.04, 11.96

10.11 (a) 4.54, (b) 3.91, (c) 1.41

10.12 (a) Acid: $C_3H_5O(COOH)_3$,
Amphiprotic: $C_3H_5O(COOH)_2(COO)^-$, $C_3H_5O(COOH)(COO)_2^{2-}$,
Base: $C_3H_5O(COO)_3^{3-}$
(b) Acid: $C_4H_{12}N_2^{2+}$, Amphiprotic: $C_4H_{11}N_2^+$, Base: $C_4H_{10}N_2$
(c) Acid: $HOOCCH(CH_3)NH_3^+$, Amphiprotic: $^-OOCCH(CH_3)NH_3^+$,
Base: $^-OOCCH(CH_3)NH_2$

10.13 9/12, 3/5

10.14 (a) acidic, pH = 1.10 (d) basic, pH = 12.01
(b) acidic, pH = ?, (e) basic, pH = ?,
(c) basic, pH = 7.49, (f) basic, pH = ?

10.15 18.0 g, 10.6 g

10.16 2.13

10.17 1.3_2 mL

10.18 −0.182

10.19 3.8 mg

10.20 2.5_0 g

10.21 2.80

10.22 2.06

10.23 10.93

10.24 11.97

10.25 3.8×10^{-9} M

10.26 0.57_5 F

10.27 4.79; 0.92; buffer capacity is exceeded

10.28 5.30 mL, 15.1 g

10.29 2.9 g

10.30 2.73 mL, 2.0_0 g

10.31 12.6 mL, 31.1 g

10.32 (a) N, 7.00, (b) B, 8.30, (c) A, 2.00,
(d) A, 2.64, (e) B, 13.00, (f) N, 7.00,
(g) A, 1.53, (h) A, ???, (i) B, 9.61,
(j) A, 2.02, (k) B. ???, (l) A, 3.69

10.33 0.0062 M

10.34 Dissolve 41.7 g of sodium hydrogen oxalate and 26.8 g of disodium oxalate and dilute to 500. mL.

10.35 Approximate formula gives pH = 2.00 in all cases.
Exact formula gives:
(a) pH = 2.00, (b) pH = 1.23, (c) pH = 1.99

Topic 11

Buffers and Titrations

11.1 Contents in Brief

- Reactions of acids and bases
- Preparation of buffer solutions
- Titration curves

11.2 Introduction

Although the topic of acid-base equilibria has already been introduced, some aspects deserve more detailed attention. One of these is the subject of buffers, which are widely used to regulate pH in chemical systems. Although buffers can be prepared directly from a weak acid and its conjugate base, other methods involve mixing a weak acid and a strong base, or a weak base and a strong acid. In this chapter, these approaches will be discussed. Closely connected to this is the concept of a titration curve, which will also be treated. Both of these require a fundamental understanding of acid-base reactions, which will be the first subject to be addressed.

11.3 Reactions of Strong Acids and Bases

An acid-base reaction involves the transfer of a proton from the acid to the base. When a strong acid or base is involved in the reaction, the reaction can be regarded as complete. In other words, the reaction proceeds from reactants to products until one of the reactants is completely consumed. There are **three** such reactions that you need to know, involving strong acid (SA), strong base (SB), weak acid (WA) and weak base (WB).

SA+SB $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

SA+WB $H_3O^+(aq) + B(aq) \rightarrow BH^+(aq) + H_2O(l)$

SB+WA $OH^-(aq) + HA(aq) \rightarrow A^-(aq) + H_2O(l)$

Alternatively, we could represent these reactions in terms of H^+ rather than H_3O^+.

SA+SB $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

SA+WB $H^+(aq) + B(aq) \rightarrow BH^+(aq)$

SB+WA $OH^-(aq) + HA(aq) \rightarrow A^-(aq) + H_2O(l)$

This representation, while technically not as correct, is simpler to write, and so this form will be used in the remainder of this chapter.

Each of the reactions above has three possible outcomes, depending on the limiting reagent (LR). For SA+SB, the possible outcomes are a strong acid (OH^- is LR), a strong base (H^+ is LR) or a neutral solution (equal moles of reactants). For SA+WB, the possibilities are a strong acid/weak acid mixture (B is LR), a buffer (H^+ is LR), or a weak acid (equal moles). Finally, for SB+WA, we could have a strong base/weak base mixture (HA is LR), a buffer (OH^- is LR), or a weak base (equal moles). For each of these situations, we have equations that can be used to predict the pH of the resulting mixture. Several additional points should be made regarding the reactions given above.

- Although H^+ or OH^- may be the limiting reactant, their concentrations in the resulting mixture is *not* actually zero. This approach simply drives the reaction all the way to the right so that the resulting equilibrium position can be determined.

- The representations of the weak acid (HA) and weak base (B) are generic, but these can be replaced by charged species where appropriate. For example, the ammonium ion, NH_4^+, is a weak acid, so its reaction with a strong base could be represented as

  $$OH^-(aq) + BH^+(aq) \rightarrow B(aq) + H_2O(l)$$

  The products are essentially the same, the conjugate weak base and water. Likewise, the acetate ion (CH_3COO^-) is a weak base (A^-) and will react with a strong acid to form its conjugate acid.

The reactions given above apply to any situations involving monofunctional acids and bases. However, the situation becomes more complicated when a strong acid or base reacts with a polyfunctional species (a polyprotic acid, a polybasic base, or an amphiprotic species). This is because such reactions can generate amphiprotic species that can react further with the strong acid or base. Such reactions will continue until the strong acid or base is completely consumed, or until the polyfunctional species has been completely protonated or deprotonated. As an example, consider the reaction of the diprotic acid, oxalic acid ($H_2C_2O_4$), with strong base. Depending on the molar quantities the reactions are as given below.

$$OH^-(aq) + H_2C_2O_4(aq) \rightarrow HC_2O_4^-(aq) + H_2O(l)$$
$$OH^-(aq) + HC_2O_4^-(aq) \rightarrow C_2O_4^{2-}(aq) + H_2O(l)$$

The hydrogen oxalate ion ($HC_2O_4^-$) produced in the first reaction is amphiprotic (can act as an acid or base), which means that if any OH^- remains after the first reaction is complete, it will continue to be consumed in the second reaction. Depending on the amounts of reactants, the possible resulting mixtures are: $H_2C_2O_4/HC_2O_4^-$ (a buffer), $HC_2O_4^-$ (amphiprotic), $HC_2O_4^-/C_2O_4^{2-}$ (a buffer), $C_2O_4^{2-}$ (weak base), or $C_2O_4^{2-}/OH^-$ (weak base + strong base). Except for the amphiprotic case, methods to calculate the pH in each of these situations has been discussed.

A natural question from this discussion arises from the only case that has been excluded, reactions of weak acids with weak bases (WA+WB). Because the outcome of such reactions depends on relative strength of the acid and the base, these are treated more traditionally as equilibria. For example, a mixture of acetic acid and ammonia will react according to:

$$CH_3COOH(aq) + NH_3(aq) \rightleftharpoons CH_3COO^-(aq) + NH_4^+(aq) \quad K = K_a K_b / K_w$$

Such equilibria can be evaluated by the methods that we have used, but they are not very relevant to the application of buffers and titrations, so they will not be discussed here.

To determine the pH of any mixture that involves a strong acid or base, there are three steps: (1) determine if there are any species that will react with the SA or SB, (2) determine the products of that reaction and classify the resulting mixture (WA, buffer, etc.) and the relevant amounts, and (3) calculate the pH as appropriate for that mixture. Some examples will illustrate these principles.

Example 11.1: Acid-Base Mixtures

For each of the following combinations, classify the solution that results on mixing, and determine, if possible the pH.

(a) 100. mL 0.100 F KOH + 90. mL 0.100 F HNO_3
(b) 100. mL 0.100 F NaOH +100. mL 0.100 F HNO_2
(c) 100. mL 0.100 F LiOH + 100. mL 0.100 F NH_3
(d) 100. mL 0.100 F HCl + 100. mL 0.150 F NH_3
(e) 100. mL 0.100 F $HClO_4$ + 80. mL 0.100 F Na_3PO_4

(a) In this case we have a strong base (potassium hydroxide) and a strong acid (nitric acid), which will obviously react. We first need to know the initial moles of each.

$$\text{moles KOH} = \text{moles } OH^- = 0.100\,\text{mol/L} \times 0.100\,\text{L} = 0.0100\,\text{mol}$$

$$\text{moles } HNO_3 = \text{moles } H^+ = 0.100\,\text{mol/L} \times 0.090\,\text{L} = 0.0090\,\text{mol}$$

Based on these amounts and the reaction below, we see that the SA is the LR, leaving us with a solution of SB when the reaction is complete.

	$H^+(aq)$	+	$OH^-(aq)$	→	$H_2O(l)$	
Initial	0.0090		0.0100			mol
Change	–0.0090		–0.0090			mol
Final	≈ 0		0.0010			mol

To find the pH, the excess moles of hydroxide are converted to a concentration.

$$[OH^-] = 0.0010\,\text{mol}/0.190\,\text{L} = 0.005\overline{2}6\,\text{M},\quad \text{pOH} = 2.28,\ \text{pH} = 11.72$$

(b) A strong base is used here as well, but in this case the acid is nitrous acid, HNO_2, a weak acid with pK_a = 3.29. By a calculation similar to part (a), there are 0.0100 mol of NaOH and 0.0100 mol of HNO_2 initially, resulting in the following reaction.

	$HNO_2(aq)$	+	$OH^-(aq)$	$\rightarrow$	$NO_2^-(aq)$	+	$H_2O(l)$
Initial	0.0100		0.0100		0		mol
Change	–0.0100		–0.0100		+0.0100		mol
Final	≈ 0		≈ 0		0.0100		mol

Here, we are left with a solution of nitrite ion (or sodium nitrite), which is the conjugate base of nitrous acid with pK_b = 14.00 – 3.29 = 10.71 ($K_b = 1.\overline{9}5\times10^{-11}$) and F_b = 0.0100 mol/0.200 L = 0.0500 F. Using the approximate formula:

$$[OH^-] \approx \sqrt{K_b F_b} = \sqrt{(1.\overline{9}5\times10^{-11})(0.0500)} = 9.\overline{8}7\times10^{-7}\,\text{M}$$

Since $F_b/[OH^-] > 20$, the approximation is valid, so,

$$\text{pOH} = -\log(9.\overline{8}7\times10^{-7}) = 6.01,\quad \text{pH} = 7.99$$

(c) Here we have a mixture of a strong base (LiOH) and a weak base (NH_3, pK_b = 4.76), so there is *no reaction*. Recall that for such a mixture (SB+WB) the pH is determined by the strong base as long as $F_{SB} \gg K_b$, so,

$$[OH^-] \approx F_{SB} = 0.0100\,\text{mol} / 0.200\,\text{L} = 0.0500\ \text{M}$$

Since K_b = 1.7x10^{-5}, the condition is met, so the pH can be calculated.

$$\text{pOH} = -\log(0.0500) = 1.30,\quad \text{pH} = 12.70$$

(d) This example involves a mixture of a strong acid (HCl) with an excess amount of weak base (NH_3, pK_b = 4.76) which will produce the conjugate weak acid.

	$H^+(aq)$	+	$NH_3(aq)$	→	$NH_4^+(aq)$	
Initial	0.0100		0.0150		0	mol
Change	−0.0100		−0.0100		+0.0100	mol
Final	≈ 0		0.0050		0.0100	mol

Since both the weak base (NH_3) and its conjugate acid (NH_4^+) remain at the end of the reaction, we have a buffer, where pK_a = 14.00 − 4.76 = 9.24, so the calculations proceed as follows.

$$F_a = 0.0100\,\text{mol}/0.200\,\text{L} = 0.0500\,\text{F}, \quad F_b = 0.0050\,\text{mol}/0.200\,\text{L} = 0.025\,\text{F}$$

$$[H^+] \approx K_a \cdot \frac{F_a}{F_b} = 10^{-9.24} \cdot \frac{0.0500\,\text{F}}{0.025\,\text{F}} = 1.\overline{1}5 \times 10^{-9}\ \text{M} \quad \text{if } F_a, F_b \gg \left|[H^+] - [OH^-]\right|$$

The assumption is valid ([OH^-] = 8.7x10^{-6} M), so the pH can be calculated.

$$\text{pH} = -\log(1.\overline{1}5 \times 10^{-9}) = 8.94$$

(e) The key to this example is to recognize that Na_3PO_4 dissociates to form three Na^+ ions and the phosphate ion, PO_4^{3-}, which is polybasic. This will react with the strong acid as indicated below.

	$H^+(aq)$	+	$PO_4^{3-}(aq)$	→	$HPO_4^{2-}(aq)$	
Initial	0.0100		0.0080		0	mol
Change	−0.0080		−0.0080		+0.0080	mol
Final	0.0020		0		0.0080	mol

The phosphate ion is the LR, so at the end of this reaction, both H^+ and HPO_4^{2-} remain. One might be tempted to think this is a mixture of a strong acid and a weak acid. However, the hydrogen phosphate ion is amphiprotic, which means that it can also act as a base, so it can accept a proton to form the dihydrogen phosphate ion. The starting point for this reaction is the ending point of the first reaction:

	$H^+(aq)$	+	$HPO_4^{2-}(aq)$	→	$H_2PO_4^-(aq)$	
Initial	0.0020		0.0080		0	mol
Change	–0.0020		–0.0020		+0.0020	mol
Final	≈ 0		0.0060		0.0020	mol

Now that all of the strong acid has been consumed, we are left with a buffer consisting of $H_2PO_4^-$ (the weak acid, pK_a = 7.20) and HPO_4^{2-} (its conjugate base). We calculate the $[H^+]$ in the usual way.

$$[H^+] \approx K_a \cdot \frac{\text{moles } H_2PO_4^-}{\text{moles } HPO_4^{2-}} = 10^{-7.20} \cdot \frac{0.0020\,\text{mol}}{0.0060\,\text{mol}} = 2.\overline{1}0 \times 10^{-8}\ \text{M}$$

$$\text{if } F_a, F_b \gg \left|[H^+] - [OH^-]\right|$$

For convenience, we did the calculation with moles rather than concentrations, but we still need to check the assumptions. In this case, the smallest concentration, F_a, is 0.011 F and $[OH^-]$ is 4.8×10^{-7} M, so the assumption is valid.

$$\text{pH} = -\log(2.\overline{1}0 \times 10^{-8}) = 7.68$$

Exercise 11.1

For each of the following combinations, classify the solution that results on mixing, and determine, if possible the pH.

(a) 100. mL 0.100 F LiOH + 50.0 mL 0.200 F $HClO_4$
(b) 50.0 mL 0.200 F KOH +50.0 mL 0.100 F HOCl
(c) 100. mL 0.100 F HCl + 50.0 mL 0.200 F sodium acetate
(d) 100. mL 0.100 F NaOH + 50.0 mL 0.250 F ammonium chloride
(e) 50.0 mL 0.200 F KOH + 50.0 mL 0.150 F $H_2C_2O_4$
(f) 100. mL 0.100 F HCl + 200. mL 0.0750 F NaOH + 200. mL 0.0500 F NaH_2PO_4

11.4 Preparation of Buffer Solutions

The first step in the preparation of a buffer is the selection of a conjugate acid-base pair that has a pK_a near the desired buffer pH and meets other criteria. Once this is done and the amounts required for each component have been specified, the actual preparation of the solution can be performed in several ways.

- By adding the buffer components directly (at least one of these is in the form of a salt).
- By adding a strong base (LR) to the weak acid component to make the weak base.
- By adding a strong acid (LR) to the weak base component to make the weak acid.

It does not matter which of these methods is used to prepare the buffer, since the final composition will be the same.

The pH of the buffer depends only on the *ratio* of the concentrations of acid and base component, which means that some other constraint is necessary to define the actual concentrations or moles used. This can also be done in a number of ways.

- By specifying the concentration of one of the buffer components (F_a or F_b).
- By specifying the total concentration of the buffer components ($F_a + F_b$).
- By specifying the ionic strength of the buffer components.
- By specifying the tolerance of the buffer to the addition of acid or base.

Although the pH is determined by the ratio of buffer components, the amounts present determine the *buffer capacity*, which is the amount that the pH will change on the addition of a specified amount of strong acid or strong base. A higher concentration of buffer components (or a larger buffer volume) means that the buffer capacity is larger and that there is greater resistance to changes in pH.

Regardless of the components used or the constraints imposed, the strategy for the preparation of a buffer follows the same steps, as given below.

(1) Choose the conjugate acid-base pair to be used and the components (WA/WB, SB/WA, or SA/WB) that will be used to prepare the buffer. In problems presented here, these

will usually be specified. The buffer system should have a pK_a close to the desired pH, but other factors affect the choice of components as well.

(2) Determine the ratio of concentrations (F_a/F_b) or moles (mol acid/mol base) that is needed to prepare the buffer at the desired pH.

(3) Apply the constraints to calculate the formalities and moles of acid and base required. In this calculation, you should check to make sure that the assumption $F_a, F_b \gg \left|[H^+] - [OH^-]\right|$ is valid.

(4) Use the components specified to determine the moles required to generate the necessary buffer composition. Convert these to the necessary masses or volumes required.

Several examples will be presented to illustrate these types of calculations.

Example 11.2: Preparation of a Buffer from a Weak Acid and Strong Base

What mass of ammonium chloride (NH_4Cl, MM = 53.49 g/mol) and sodium hydroxide (NaOH, MM = 40.00 g/mol) would be required to make 500. mL of a pH 9.00 buffer in which the concentration of the basic component is 0.0500 F?

The buffer system is specified as NH_4^+/NH_3, and since p$K_b(NH_3)$ = 4.76, the pK_a of the acid component is 9.24. The first step is to determine the ratio of concentrations.

$$[H^+] \approx K_a \cdot \frac{F_a}{F_b}, \quad \text{so} \quad \frac{F_a}{F_b} \approx \frac{[H^+]}{K_a} = \frac{10^{-9.00}}{10^{-9.24}} = 1.\overline{7}38$$

Since we are given the constraint that F_b = 0.0500 F, this means that F_a = $0.08\overline{6}9$ F. The approximation will be valid if $F_a, F_b \gg \left|[H^+] - [OH^-]\right|$, which will be true here, since $[OH^-] = 10^{-5}$ M. The number of moles of each component can now be calculated.

$$\text{moles } NH_3 = (0.0500\,\text{F})(0.500\,\text{L}) = 0.0250\,\text{mol}$$
$$\text{moles } NH_4^+ = (0.08\overline{6}9\,\text{F})(0.500\,\text{L}) = 0.04\overline{3}4\,\text{mol}$$

If the buffer were to be prepared from NH_3 and NH_4Cl, the next step would be straightforward, but in this case, the NH_3 must be prepared by a reaction of NH_4^+ (from ammonium chloride) with a strong base. This is arranged so that the strong base is the limiting reagent and the result is a buffer with the desired quantities

above. This is the reverse of the usual situation in that we know the final concentrations and need to deduce the initial values.

	$NH_4^+(aq)$	+	$OH^-(aq)$	→	$NH_3(aq)$	+	$H_2O(l)$
Final	$0.04\overline{3}4$		≈ 0		0.0250		mol
Change	?		?		?		mol
Initial	?		?		0		mol

We can determine the initial concentrations of reagents by working backwards. Since we know there is initially no NH_3, moles formed must be equal to the moles of the LR, which means that there are initially 0.0250 moles of OH^- present. Likewise, the initial amount of NH_4^+ present must be 0.0250 moles more than its initial amount. The table can now be completed.

	$NH_4^+(aq)$	+	$OH^-(aq)$	→	$NH_3(aq)$	+	$H_2O(l)$
Final	$0.04\overline{3}4$		≈ 0		0.0250		mol
Change	−0.0250		−0.0250		+0.0250		mol
Initial	$0.06\overline{8}4$		0.0250		0		mol

Knowing the initial moles required, the masses of reagents can be calculated.

$$\text{mass of } NH_4Cl = (0.06\overline{8}4 \text{ mol})(53.49 \text{ g/mol}) = 3.\overline{6}6 \text{ g}$$
$$\text{mass of } NaOH = (0.0250 \text{ mol})(40.00 \text{ g/mol}) = 1.00 \text{ g}$$

Therefore, the buffer is prepared by dissolving 3.7 g of ammonium chloride and 1.00 g of sodium hydroxide in a total volume of 500. mL.

Exercise 11.2

Suppose that the buffer prepared in the previous example needs to remain within 0.10 pH unit of 9.00 on the addition of 0.0100 mol of H_3O^+ (assume no change in volume). Would this buffer meet these requirements? What if the concentrations of the buffer components were increased by a factor of ten? What if the volume of the buffer were doubled?

Exercise 11.3

What mass of sodium acetate (MM = 82.03 g/mol) and what volume of 1.00 F HCl would be required to prepare 400. mL of a buffer at pH = 5.00? The formality of the base component should be 0.200 F and the pK_a of acetic acid is 4.76.

Example 11.3: Preparation of a Buffer with a Specified Total Concentration

What mass of sodium carbonate (Na_2CO_3, MM = 105.99 g/mol) and what volume of 0.500 F HCl would be required to prepare 1.00 L of a buffer at pH = 10.00? The total concentration of buffer components should be 0.200 mol/L.

We first need to identify the buffer components. The carbonate ion, CO_3^{2-}, is a dibasic ion derived from carbonic acid (H_2CO_3, pK_{a1} = 6.35, pK_{a2} = 10.33). Since we want to prepare a buffer at pH = 10.00, it is the second pK_a, corresponding to HCO_3^-, that is of importance. (Note that the $\Delta pK_a > 3$, so we can consider the protons independently.) Therefore the buffer components are the hydrogen carbonate ion, HCO_3^- (acid), and the carbonate ion, CO_3^{2-} (base). As before, we first calculate the ratio required.

$$\frac{F_a}{F_b} \approx \frac{[H^+]}{K_a} = \frac{10^{-10.00}}{10^{-10.33}} = 2.\overline{1}38 \quad \text{or} \quad F_a = (2.\overline{1}38)F_b$$

To determine the formality, we must combine this with the constraint that the total concentration is 0.200 F.

$$F_a + F_b = 0.200\ \text{F} = (2.\overline{1}38)F_b + F_b$$
$$= (3.\overline{1}38)F_b \qquad \therefore \quad F_b = \frac{0.200\,\text{F}}{3.\overline{1}38} = 0.06\overline{3}7\ \text{F}$$
$$F_a = 0.200\,\text{F} - 0.06\overline{3}7\,\text{F} = 0.13\overline{6}3\ \text{F}$$

Note that these values satisfy the assumption that $F_a, F_b \gg \left|[H^+] - [OH^-]\right|$. Since 1 L of the buffer is to be prepared, these are also equal to the number of moles needed. In this case, the buffer is to be prepared by reacting the weak base (CO_3^{2-}) with a strong

acid (HCl). This proceeds in a manner similar to the earlier calculation, where we know the final amounts and need to obtain the initial amounts. The results are shown below, where the values shown in bold were the quantities known initially.

	$CO_3^{2-}(aq)$	+ $H^+(aq)$	→ $HCO_3^-(aq)$	
Final	**0.06$\overline{3}$7**	**≈ 0**	**0.13$\overline{6}$3**	mol
Initial	0.200	0.13$\overline{6}$3	**0**	mol

Notice that the number of moles of CO_3^{2-} needed initially is the same as the total moles of acid and base specified in the initial problem. This is not surprising, since both the acid and base components derive from the same source. Now the amounts can be determined.

$$\text{mass of } Na_2CO_3 = (0.200\,\text{mol})(105.99\,\text{g/mol}) = 21.2\ \text{g}$$

$$\text{volume of HCl solution} = \frac{0.13\overline{6}3\,\text{mol}}{0.500\,\text{mol/L}} = 0.273\ \text{L}$$

Therefore, the buffer could be prepared by combining 21.2 g of Na_2CO_3 and 273 mL of 0.500 M HCl and diluting to 1.00 L.

Exercise 11.4

Suppose that you are provide with solutions of 2.00 F NH_3 and 5.00 F HCl. Describe how to prepare 500. mL of a buffer at pH 9.50 in which the total concentration of buffer components is 0.500 M.

Example 11.4: Preparation of a Buffer with a Specified Ionic Strength

What masses of sodium oxalate ($Na_2C_2O_4$, MM = 134.00 g/mol) and sodium hydrogen oxalate monohydrate ($NaHC_2O_4{\cdot}H_2O$, MM = 130.03 g/mol) would be required to make 400.0 mL of a buffer at pH 4.50 in which the ionic strength is 0.400 M? Oxalic acid ($H_2C_2O_4$) is a diprotic acid with pK_{a1} = 1.27 and pK_{a2} = 4.27.

For a pH of 4.50, it is clear that we want to use the second acidic proton (pK_a = 4.27) as the acid component of the buffer. Therefore, the buffer components are $HC_2O_4^-$ (weak acid) and $C_2O_4^{2-}$ (weak base). As before we determine the ratio.

$$\frac{F_a}{F_b} \approx \frac{[H^+]}{K_a} = \frac{10^{-4.50}}{10^{-4.27}} = 0.5\overline{8}88 \quad \text{or} \quad F_a = (0.5\overline{8}88)F_b$$

As before, we need an additional constraint to determine the actual formalities, and in this case the total ionic strength must be 0.400 M. Recall ionic strength, μ, is defined as:

$$\mu = \tfrac{1}{2}\sum c_i z_i^2$$

where c_i is the concentration of ion i and z_i is its charge. In this solution, two salts are being dissolved to generate the buffer components.

$$NaHC_2O_4(s) \rightarrow Na^+(aq) + HC_2O_4^-(aq)$$
$$Na_2C_2O_4(s) \rightarrow 2\,Na^+(aq) + C_2O_4^{2-}(aq)$$

The concentrations of the ions in the first reaction are related to F_a and those in the second reaction are related to F_b, so we can determine the ionic strength.

$$[Na^+] = F_a + 2F_b \qquad [HC_2O_4^-] = F_a \qquad [C_2O_4^{2-}] = F_b$$

$$\mu = \tfrac{1}{2}\left\{[Na^+](+1)^2 + [HC_2O_4^-](-1)^2 + [C_2O_4^{2-}](-2)^2\right\}$$
$$= \tfrac{1}{2}\left\{(F_a + 2F_b)\cdot 1 + F_a \cdot 1 + F_b \cdot 4\right\} = \tfrac{1}{2}\left\{2F_a + 6F_b\right\} = F_a + 3F_b = 0.400\,M$$

(You may wonder why H^+ and OH^- were not included in this calculation, but given the pH, these ions will be too low in concentration to make a difference.) Given this constraint, the formalities can now be calculated.

$$F_a + 3F_b = (0.5\overline{8}88)F_b + 3F_b = 0.400\,mol/L$$

$$F_b = \frac{0.400\,mol/L}{3.5\overline{8}88} = 0.11\overline{1}5\,F, \qquad F_a = 0.400 - 3(0.11\overline{1}5) = 0.06\overline{5}5\,F$$

Note that, as required for the approximation, $F_a, F_b \gg \left|[H^+] - [OH^-]\right|$. In the final step, the masses of the reagents are calculated.

$$\text{mass of } Na_2C_2O_4 = (0.11\overline{1}5\,\text{mol/L})(0.400\,\text{L})(134.00\,\text{g/mol}) = 5.98\,\text{g}$$

$$\text{mass of } NaHC_2O_4 \cdot H_2O = (0.06\overline{5}5\,\text{mol/L})(0.400\,\text{L})(130.03\,\text{g/mol}) = 3.\overline{4}1\,\text{g}$$

The buffer is prepared by dissolving the given masses in 400. mL of solution.

Exercise 11.5

Suppose that you wanted to prepare an acetate buffer with the same properties as the buffer in the previous example (400. mL, pH = 4.50, μ = 0.400 M). What volume of glacial acetic acid (CH_3COOH, MM = 60.05 g/mol, density = 1.049 g/mL) and what mass of potassium hydroxide (MM = 56.11 g/mol) would be needed to prepare the buffer? The pK_a of acetic acid is 4.76.

The use of polyfunctional acids and bases in the preparation of buffers deserves special attention because of the availability of multiple conjugate acid-base pairs to prepare buffers with different optimal pH values. For example, phosphoric acid has three acid forms: H_3PO_4 (pK_{a1} = 2.15), $H_2PO_4^-$ (pK_{a2} = 7.20) and HPO_4^{2-} (pK_{a3} = 12.15). This allows the possibility of preparing buffers in acidic, neutral and basic pH regions. Phosphate buffers are widely used to prepare buffers at physiological pH and phosphate is an important buffer component in living systems.

Another convenient feature of polyfunctional acids and bases is that buffers can be prepared with the appropriate combination of any form of compound (*e.g.* H_3PO_4, NaH_2PO_4, Na_2HPO_4, or Na_3PO_4) and an appropriate amount of strong acid or base. Although the calculations can be somewhat more complicated because multiple steps might be involved, this is a common way to prepare buffers and the general principles are the same. An example will illustrate this approach to buffer preparation.

Example 11.5: Preparation of a Buffer from a Polyprotic Acid

What volume of concentrated phosphoric acid (MM = 98.00 g.mol) and what mass of sodium hydroxide (MM = 40.00 g/mol) are needed to prepare 600.0 mL of a buffer at pH = 7.00 in which the concentration of the weak acid component is 0.400 F. Concentrated phosphoric acid is 85.5% by weight and has a density of 1.685 g/mL.

The first step, as usual, is to select the buffer components. Since we want a pH of 7.00, the acid component should be $H_2PO_4^-$ (pK_a = 7.20), which means the conjugate base will be HPO_4^{2-}. Since we are given the formality of the weak acid, the concentration of the base can be calculated.

$$F_a = 0.400\,\text{F}, \quad F_b = \frac{K_a}{[\text{H}^+]} \cdot F_a = \frac{10^{-7.20}}{10^{-7.00}} \cdot 0.400\,\text{F} = (0.6\overline{3}1)(0.400\,\text{F}) = 0.2\overline{5}2\,\text{F}$$

Note that the assumption $F_a, F_b \gg \left|[\text{H}^+] - [\text{OH}^-]\right|$ is valid here. For calculations, these can be converted to moles.

$$\text{moles } H_2PO_4^- \text{ required} = (0.400\,\text{mol/L})(0.600\,\text{L}) = 0.240 \text{ mol}$$
$$\text{moles } HPO_4^{2-} \text{ required} = (0.2\overline{5}2\,\text{mol/L})(0.600\,\text{L}) = 0.1\overline{5}1 \text{ mol}$$

A complication in preparing the actual buffer is that we are starting with neither of these components, but rather phosphoric acid, H_3PO_4. However, phosphoric acid can be converted to $H_2PO_4^-$ and subsequently to HPO_4^{2-} by reactions with strong base, as shown below.

$$H_3PO_4(aq) + OH^-(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$$
$$H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$$

The first reaction can be carried out to completion, while the second can be used to create the desire amounts of the buffer components. It is important to recognize that, since both buffer components originate from H_3PO_4, the moles of H_3PO_4 required will be the sum of the other two molar quantities.

$$\text{moles } H_3PO_4 \text{ required} = 0.240 \text{ mol} + 0.1\overline{5}1 \text{ mol} = 0.3\overline{9}1 \text{ mol}$$

Although the preparation of the buffer occurs in one step, it is helpful to think of it as two processes. First, the phosphoric acid is converted completely to $H_2PO_4^-$ by adding sufficient strong base, as indicated below.

	$H_3PO_4(aq)$	+ $OH^-(aq)$	→ $H_2PO_4^-(aq)$	+ $H_2O(l)$	
Final	**≈ 0**	**≈ 0**	**0.3$\overline{9}$1**		mol
Initial	0.3$\overline{9}$1	0.3$\overline{9}$1	**0**		mol

As before, the original known quantities are shown as bold. In the second step, the hydroxide ion is the limiting reagent in the conversion of $H_2PO_4^-$ to the required amount of HPO_4^{2-}.

	$H_2PO_4^-(aq)$	+ $OH^-(aq)$	→ $HPO_4^{2-}(aq)$	+ $H_2O(l)$	
Final	**0.2$\overline{4}$0**	**≈ 0**	**0.1$\overline{5}$1**		mol
Initial	**0.3$\overline{9}$1**	0.1$\overline{5}$1	**0**		mol

The total amount of sodium hydroxide required to complete these two steps is the sum of the two processes.

$$\text{moles NaOH required} = 0.3\overline{9}1 \text{ mol} + 0.1\overline{5}1 \text{ mol} = 0.5\overline{4}2 \text{ mol}$$

The amounts of starting reagents can now be calculated.

$$\text{mass of NaOH} = (0.5\overline{4}2 \text{ mol})(40.00 \text{ g/mol}) = 2\overline{1}.7 \text{ g}$$

$$\text{vol. of phosphoric acid} = (0.3\overline{9}1 \text{ mol } H_3PO_4)(98.00 \text{ g/mol}) \cdot \frac{100 \text{ g acid}}{85.5 \text{ g } H_3PO_4} \cdot \frac{1 \text{ mL acid}}{1.685 \text{ g acid}}$$

$$= 2\overline{6}.6 \text{ mL of acid}$$

The buffer can be prepared by combining 22 g of NaOH and 27 mL of concentrated phosphoric acid in 600. mL of solution. (Note that the acid and base should not be combined before dilution, however.)

Exercise 11.6
What mass of trisodium phosphate (Na_3PO_4, MM = 163.94 g/mol) and what volume of concentrated hydrochloric acid (37.2% w/w, 1.18 g/mL, MM(HCl) = 36.46 g/mL) would be required to prepare the same buffer as in the previous example?

11.5 Practical Buffers

In principle, any of the weak acids or bases listed in previous tables can be used as buffer components, but many are not widely used in practice for a variety of reasons. For example, hydrogen cyanide (HCN), the active component of hydrocyanic acid, is a poisonous gas, and hydrofluoric acid (HF) is highly corrosive and dangerous to handle. Nitrous acid (HNO_2) is susceptible to redox reactions. Some acids and bases have an unpleasant odor, such as butanoic acid (rancid butter) or trimethylamine (rotting fish). Other issues with buffers can include low solubility, reactivity, the formation of complex ions with metals in solution, or interference with analytical measurements (*e.g.* absorbance in the UV-visible region).

For these reasons, certain buffers are more widely used in practice than others. These include phosphate, acetate, carbonate and ammonia, as well as many others. Figure 11.1 shows some commonly used buffers with their corresponding pH ranges and pK_a values. Some buffer components in this table (phosphate, citrate, and carbonate) are polyfunctional and therefore can be used over different pH ranges. Both phosphate (pK_{a2} = 7.20) and carbonate (pK_{a1} = 6.35) are important in living systems, but the latter is rarely used in the laboratory under acidic conditions because of the tendency of carbonic acid (H_2CO_3) to decompose to H_2O and CO_2.

Many buffers are employed near physiological conditions (around pH 7.4) for studies of biochemical reactions or biological systems, and a number of weak acids and bases are commonly used for this purpose. These are typically organic compounds with long names, so they are often abbreviated with an acronym. For example, the compound tris(hydroxymethyl)methylamine is simply called "TRIS" (also known as "Tris", "THAM", "Trizma") and the compound 2-(N-morpholino)ethanesulfonic acid is commonly known as MES. The structures of some of these compounds are shown in Figure 11.2. For these compounds, the

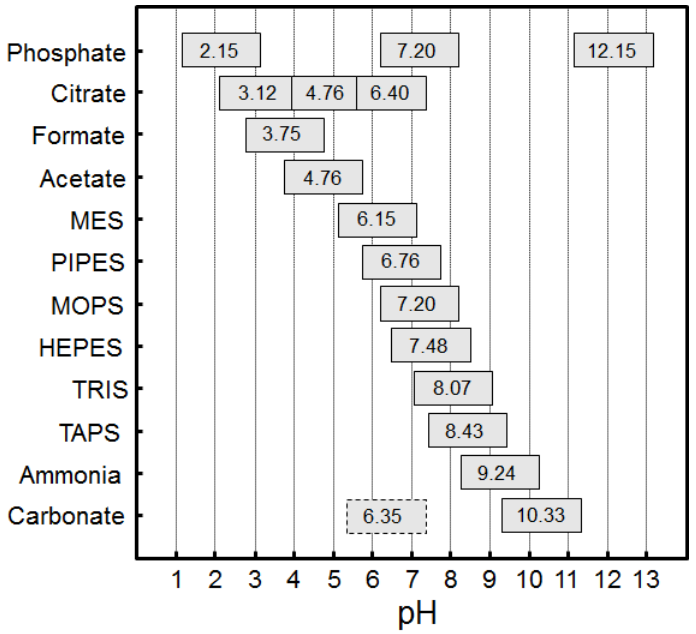
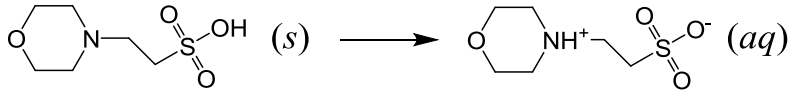
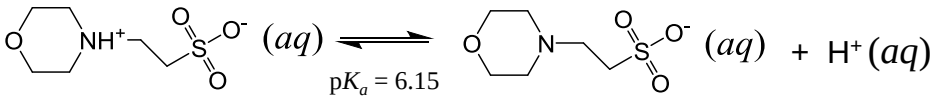


Figure 11.1: Some commonly used buffers and their typical pH ranges. The numbers shown are the pK_a values.

active nitrogen for protonation or deprotonation is shown in bold. Most of the compounds shown have a sulfonic acid group (-SO_3H) as well and as such are polyfunctional. However, the pK_a of the sulfonic acid group is very low (a strong weak acid) and the compounds are not used to buffer in this region, so only the pK_a of the ammonium ion is generally given. In solution, these compounds, like amino acids, are *zwitterions*, which are neutral species with charged sites. This improves their solubility. For example, the sulfonic acid proton in MES is transferred to the amine when the solid is dissolved.



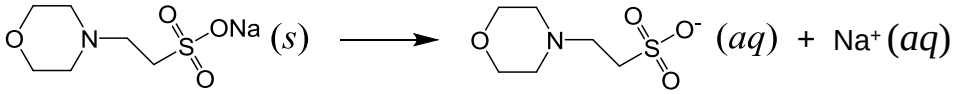
Therefore, to prepare the buffer directly from MES, we would add hydroxide ion to convert some of the ammonium ion to the amine, resulting in the equilibrium below.



This is the equilibrium that is relevant to the behavior of the MES buffer solution. Although it appears more complex than the weak acids we have examined, it still reduces to the usual form:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

On the other hand, if we start with the sodium salt of MES, then the starting point is the basic form, and a strong acid has to be used to make the conjugate acid for the buffer.



Therefore, in preparing buffers from these materials, it is important to know the form of the starting material.

Finally, it should be noted that, when preparing buffers in the laboratory, the final pH may not be exactly as anticipated even if the calculations are correct. This can be due to a variety of factors (non-ideal solutions, temperature differences, reagent impurities, etc.). It is therefore common practice to make up the buffer as calculated and then adjust the final pH (as measured by a pH meter) by adding small drops of acid or based.

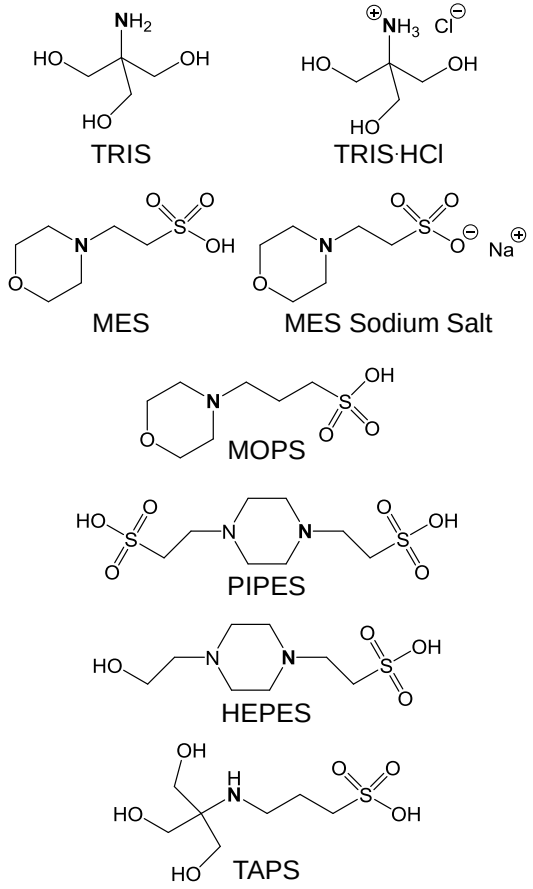


Figure 11.2: Structures of some common biological buffers and some representative salts.

Exercise 11.7
Draw the structures of TAPS and HEPES (see Figure 11.2) when they are dissolved in aqueous solution.

Exercise 11.8
Suppose you are provided with 5.00 F HCl and 5.00 F KOH and you want to make 500. mL of a TRIS buffer at pH = 7.60 for immunohistochemical staining. The sum of the buffer components should be 0.500 F (F_a + F_b = 0.500). (a) Describe how you would prepare the buffer using TRIS (MM = 121.14 g/mol). (b) Describe how you would prepare the buffer using TRIS·HCl (MM = 157.60 g/mol).

Exercise 11.9
Instead of TRIS, describe how you would prepare the buffer in the previous exercise using (a) HEPES (MM = 238.30 g/mol) and (b) the HEPES sodium salt (MM = 260.29 g/mol).

11.6 Titration Curves

In general, a titration is a procedure in which one reactant is added to another in a controlled fashion. Normally, such reactions are carried out in solution (although gas phase titrations are also performed) and the amount of one reactant is known. Titrations can be used to for a variety of different reactions (*e.g.* redox, complexation, precipitation), but in this chapter we will focus on acid-base reactions. Typically the goal of the titration is to determine the point at which there is stoichiometric equivalence of the two reactants (*i.e.* equal moles for a 1:1 reaction). This is called the *equivalence point* and allows the quantitative determination of the concentration of an unknown reactant (the *titrand*) based on the known concentration of the other reactant (the *titrant*).

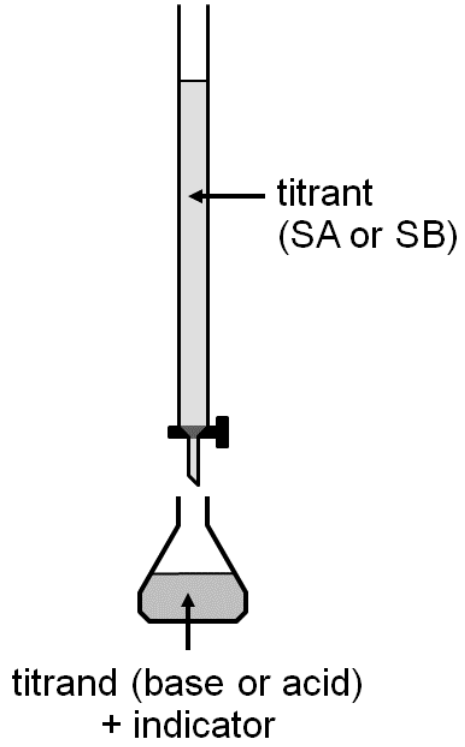


Figure 11.3: Titration of the titrant, from the buret, with the titrand, in the flask.

A typical setup for a titration involving a buret and a titration flask is shown in Figure 11.3. For acid-base titration, an indicator is usually added to the titration flask to indicate the *end point* of the titration by means of a colour change. The end point is the experimentally observed equivalence point (*i.e.* where we *think* we have reached stoichiometric equivalence), which may be slightly different from the actual equivalence point due to a variety of experimental factors. The ability to precisely detect the end point of a titration is critically important in accurate quantitation. In an acid-base titration, the titrant is generally always a strong acid or base, since a weak acid or base would not give us the sharpest equivalence point. The titrand can be a weak or strong acid or base.

A *titration curve* for an acid-base reaction is a plot of the pH *vs.* the volume of titrant added. In this context, the pH may be measured with a pH meter or calculated, as we will do here. A typical titration curve for the titration of a strong base (titrant) with a strong acid (titrand) is shown in Figure 11.4. The purpose of this section is to describe the calculation of such titration curves. Sometimes students wonder why it is necessary to learn to carry out these calculations. For one thing, it would seem that the only important point in the titration curve is the equivalence point, so why bother with other points on the curve? Also, it may be argued that doing the calculations requires a knowledge of the concentrations of both reactants, so why would one perform a titration if there is not an unknown to determine?

There are several reasons why these calculations are important. One is pedagogical: they lead to a better understanding of acid-base reactions. A second reason is more pragmatic in that the calculations form the basis for understanding the shape of the titration curve as a function of variables such as the concentration and strength of the acid or base. In practical applications, this shape is important, since the ability to determine the equivalence point precisely is directly related to the sharpness of the curve. A third reason is that the shape of the titration curve can reveal properties of the titrand, such as its pK_a and the number of acidic protons. Finally, knowing the pH at the equivalence point in a titration allows the selection of an appropriate indicator to detect the end point, which is especially important when the titration curve is not sharp. While it is true that we need to know the concentration of the titrand to calculate the titration curve, usually we only need to have an approximate value to select an indicator, so calculations are applicable even when the exact value is not used.

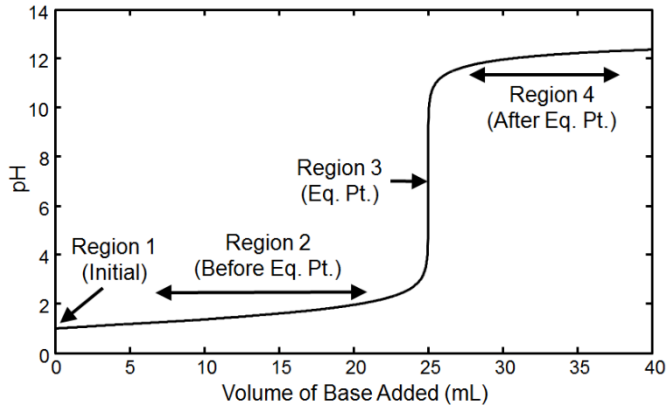


Figure 11.4: Titration curve for the titration of 0.100 F NaOH with 25.00 mL of 0.100 F HCl.

Calculations for titration curves involve the same reactions we have already used, so they will not be repeated in great detail here. In general, there are four steps involved:

(1) Determine the titration reaction (SA+SB, SA+WB, SB+WA).
(2) Determine the initial moles of each reactant present at that point in the titration, the limiting reagent, and the final moles and concentrations.
(3) Classify the resulting solution (SA,SB, Buffer, SA+WA, SB+WB).
(4) Calculate the pH accordingly.

As shown in Figure 11.4, there are four distinct regions in the titration curve for a monoprotic acid or base. Region 1, before any titrant has been added, consists of pure titrand. Region 2, which is sometimes referred to as the "buffer region" since the pH remains relatively constant on the addition of the titrant, is the region before the equivalent point has been reached and where the titrant is the limiting reagent. Region 3 is the equivalence point, where all of the titrant and titrand have reacted, and Region 4, after the equivalence point, is where the titrand is the limiting reagent. Calculations and characteristics of the titration curves for different types of titrations are discussed in the sections that follow.

Strong Acid/Strong Base Titrations

For a strong acid/strong base titration, the titration reaction is the same regardless of the acid or base since these dissociate completely.

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$$

or $$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

For strong acid/strong base titrations, the titrant could be either the strong acid or the strong base. The titration curve for the latter is as shown in Figure 11.4. For Regions 1 and 2, the strong base is the limiting reagent and the solution will be a strong acid. In Region 3, the solution is neutral because the moles of acid and base are the same, and in Region 4, the solution will be a strong base. Note that the shape of the titration curve changes with the formality of the reagents, as shown in Figure 11.5. As the concentration of the acid and base are decreased, the pH before and after the equivalence point come closer together. As a consequence, the end point will be less sharply defined titration curve and it will become more

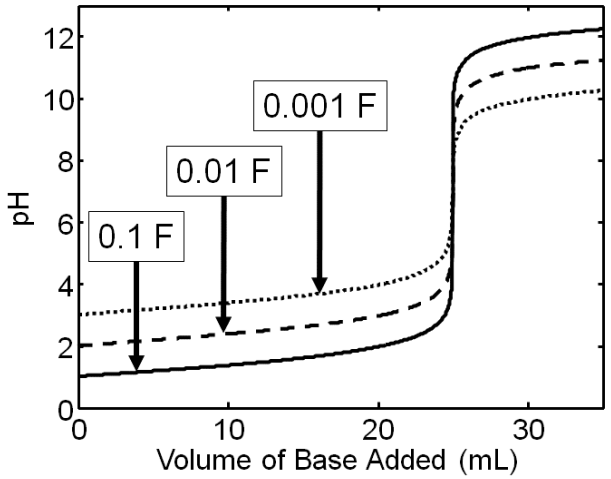


Figure 11.5: Titration curves for the titration of NaOH with 25.00 mL of HCl with various concentrations. In each case, the concentration of the acid and the base are taken to be the same.

difficult to titrate acids and bases at low concentrations. This is a general principle for all acid-base titrations.

In the case where the titrant is a strong acid and the titrand is a strong base, the titration curve is essentially flipped along the y-axis as shown in Figure 11.6. Here the same solutions are used as in Figure 11.4, but in this case the acid is the titrant.

For all titrations of strong acids and bases, the pH at the equivalence point will be neutral (pH = 7), but this is **not true** for titrations with weak acids and bases. It is also important to recognize that the equivalence point occurs when the moles of titrant equals the moles of titrand, and (depending on the concentrations) this is **not** necessarily when the volumes are equal. You should be able to calculate the points on the titration curve of a strong acid with a strong base using the principles of acid-base reactions we have introduced so far.

Exercise 11.10

Consider the titration of 0.1000 F HCl (the titrant) with 25.00 mL of 0.2000 F KOH (the titrand). Calculate the pH in the titration flask after the addition of the following amounts of acid: (a) 0 mL, (b) 25.00 mL, (c) 40.00 mL, (d) 50.00 mL, and (e) 55.00 mL. Also, sketch the general shape of the titration curve.

Weak Acid/Strong Base Titrations

In the titration of a weak acid with a strong base, the relevant titration reaction is:

$$HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(aq)$$

A typical titration curve for a weak acid with a pK_a = 5 is shown in Figure 11.7. The same regions apply as before. At the start of the titration, only the weak acid is present and the pH is equal to 3.00. Note that this starting pH is higher than the pH for a strong acid with the same concentration (pH = 1.00). As base is added, it is the limiting reagent before the equivalence point, so both HA and A^- are present, forming a buffer. This is the reason that Region 2 is sometimes called the "buffer region". Note that the pH does not increase very quickly in this region, but the slope is greater than the corresponding strong acid titration, which will make it harder to detect the end point. At the equivalence point, all of the strong

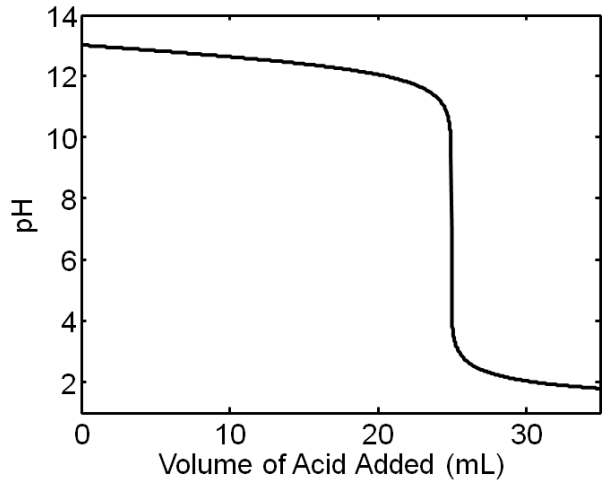


Figure 11.6: Titration curve for the titration of 0.100 F HCl with 25.00 mL of 0.100 F NaOH.

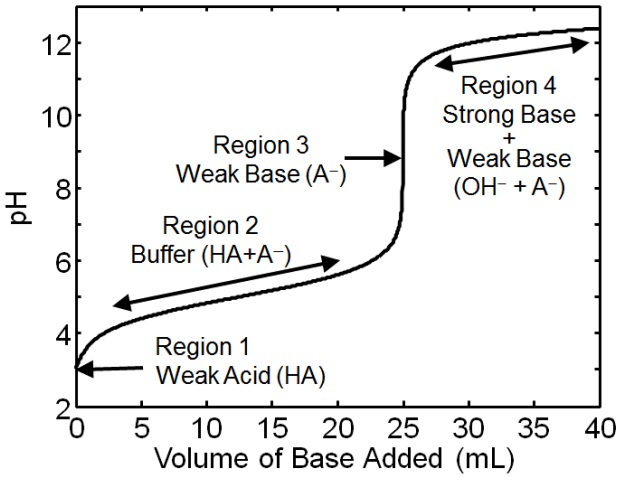


Figure 11.7: Titration curve for the titration of 0.100 F NaOH with 25.00 mL of 0.100 F weak acid (pK_a = 5).

base and weak acid have been consumed, and only the conjugate weak base (A^-) remains. Note that the pH at this point is **greater** than 7 (in this case, it is 8.85), unlike the strong acid titration. After the equivalence point, the strong base is in excess, so the titration flask contains a mixture of strong base and weak base. For calculation purposes, this can be treated as a strong base, except very close to the equivalence point.

You should note the general shape of the WA/SB titration curve (Figure 11.7) compared to the SA/SB titration curve (Figure 11.4). In particular, you should notice that, at the same concentration, the curve for the weak acid is not as sharp and that the pH is above 7, making the end point harder to detect and the selection of an indicator more critical. The shape of the WA/SB titration curve is also dependent on other factors, such as concentration and the pK_a of the acid.

Figure 11.8 shows the effect of changing the weak acid concentration. This has a small effect on the initial pH and virtually no effect in the buffer region, but lower concentrations mean a decrease in the pH at the equivalence point (8.85, 8.35, and 7.85 in the figure) and lower pH values after the equivalence point. The later effect is largely a consequence of the lower concentration of the strong base required. These effects mean the change in the pH at the equivalence point is not as large, so the end point will not be as precise for lower concentrations of the acid.

Figure 11.9 shows the effect of the pK_a of the weak acid on the shape of the titration curves. In contrast to Figure 11.8, the effect here is mainly on the lower part of the titration curve. A lower pK_a (stronger weak acid) means that the initial pH and the buffer region are lower, as one would expect. The pH at the equivalence point also decreases with the pK_a (9.85, 8.85 and 7.85 in the figure), but the pH after the equivalence point is largely unaffected. Because the equivalence point is sharper for acids with a smaller pK_a, these end points can be more reliably determined.

When the titration curve is measured directly with a pH meter during the course of a titration, it can provide useful information. Since the concentration of the weak acid and conjugate base are the same at the point halfway to the equivalence point, the pH will be equal to the pK_a of the weak acid at that point, as indicated in Figure 11.9. This can be a useful way to estimate the pK_a of an unknown weak acid, even if its concentration is unknown.

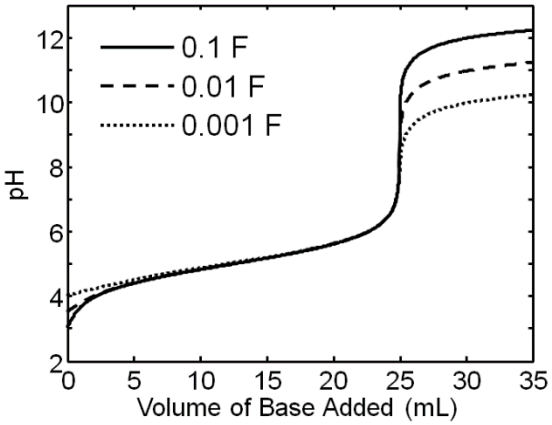


Figure 11.8: Weak acid/strong base titration curves for various concentrations of 25 mL of weak acid (pK_a = 5). The strong base is assumed to have the same concentration as the weak acid.

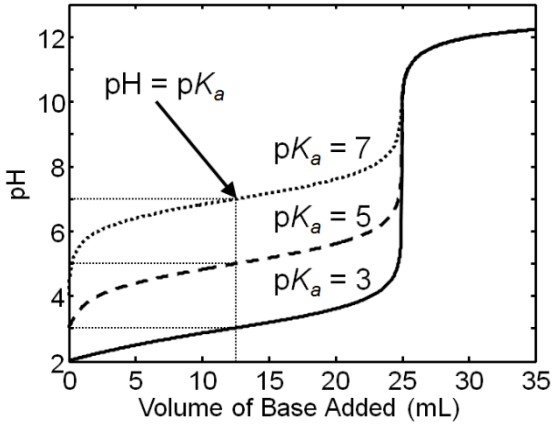
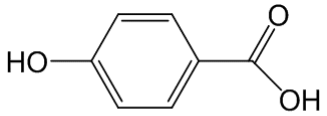


Figure 11.9: Effect of pK_a on weak acid/strong base titration curves for 25 mL of 0.1 F weak acid and 0.1 F strong base.

Example 11.6: Titration curve for weak acid/strong base titration

Consider a titration in which 0.0500 F NaOH is added to 50.00 mL of 0.0300 F 4-hydroxybenzoic acid (pK_a = 4.54). Calculate the pH in the titration flask after the addition of the following volumes of titrant: (a) 0 mL, (b) 15.00 mL, (c) 25.00 mL, (d) 30.00 mL and (e) 35.00 mL.



4-Hydroxybenzoic acid

(a) The structure of 4-hydroxybenzoic acid (HBA, $(C_6H_5O)COOH$) is shown at the right, but we will represent it simply as a generic weak acid, HA, with a pK_a of 4.54. The initial pH will simply be that of the weak acid.

$$[H^+] \approx \sqrt{K_a F_a} = \sqrt{(10^{-4.54})(0.0300)} = \sqrt{(2.\overline{8}8\times10^{-5})(0.0300)} = 9.\overline{3}0\times10^{-4}\ \text{M}$$

$$\text{pH} = -\log(9.\overline{3}0\times10^{-5}) = 3.03$$

Note that the assumption for the approximation is valid here.

(b) The initial quantity of HBA is (0.0300 mol/L)x(0.05000 L) = 0.00150 mol, or 1.50 mmol. Likewise, 15.00 mL of NaOH is (0.0500 mol/L)x(0.01500 L) = 7.50 x 10^{-4} mol, or 0.750 mmol. These amounts can be applied to the titration reaction.

	$HA(aq)$	+ $OH^-(aq)$	$\rightarrow$ $A^-(aq)$	+ $H_2O(l)$	
Initial	1.50	0.750	0		mmol
Change	−0.750	−0.750	+0.750		mmol
Final	0.75	≈ 0	0.750		mmol

Since OH^- is the limiting reagent, we are clearly in the buffer region, and since the moles of the weak acid and its conjugate base are equal, we are halfway to the equivalence point. The concentrations of the weak acid and base can be calculated based on the total volume.

$$F_a = F_b = \frac{0.75\times10^{-3}\ \text{mol}}{(0.05000\text{L} + 0.01500\,\text{L})} = 0.01\overline{1}5\ \text{F} \qquad [H^+] = K_a\frac{F_a}{F_b} = K_a = 2.\overline{8}8\times10^{-5}\ \text{M}$$

$$\text{pH} = \text{p}K_a = 4.54$$

Note that, although this result could have been obtained taking the ratios of moles directly, or by recognizing that we are halfway to the equivalence point, the concentrations are needed to ensure that $F_a, F_b \gg \left|[H^+] - [OH^-]\right|$.

(c) The addition of 25.00 mL of NaOH corresponds to 1.25 mmol of OH^-, with a total volume of 75.00 mL. Proceeding as before, we employ the titration reaction.

	$HA(aq)$	+ $OH^-(aq)$	→ $A^-(aq)$	+ $H_2O(l)$
Initial	1.50	1.25	0	mmol
Final	0.25	≈ 0	1.25	mmol

Here, only the initial and final amounts have been shown. We are still in the buffer region, so the calculations proceed in the same way.

$$F_a = \frac{0.25\ \text{mmol}}{75.00\,\text{mL}} = 0.003\overline{3}\,\text{F} \qquad F_b = \frac{1.25\ \text{mmol}}{75.00\,\text{mL}} = 0.0167\,\text{F}$$

$$[H^+] = K_a \frac{F_a}{F_b} = (2.\overline{8}8 \times 10^{-5}) \frac{0.003\overline{3}\,\text{F}}{0.0167\,\text{F}} = 5.\overline{7}4 \times 10^{-6}\ \text{M}$$

$$\text{pH} = -\log(5.\overline{7}4 \times 10^{-6}\ \text{M}) = 5.24$$

Note that the pH has increased, but not dramatically.

(d) The addition of 30.00 mL of NaOH corresponds to the equivalence point.

	$HA(aq)$	+ $OH^-(aq)$	→ $A^-(aq)$	+ $H_2O(l)$
Initial	1.50	1.50	0	mmol
Final	≈ 0	≈ 0	1.50	mmol

The solution now consists of a weak base with $pK_b = 14.00 - 4.54 = 9.46$.

$$F_b = \frac{1.50\ \text{mmol}}{80.00\ \text{mL}} = 0.018\overline{7}5\ \text{F} \qquad [OH^-] \approx \sqrt{K_b F_b} = 2.\overline{5}5 \times 10^{-6}\ \text{M}$$

$$\text{pOH} = -\log(2.\overline{5}5 \times 10^{-6}) = 5.59 \qquad \text{pH} = 14.00 - 5.59 = 8.41$$

The assumptions are valid here. Note that the pH has increased significantly and is greater than 7 at the equivalence point.

(e) The addition of 35.00 mL of NaOH has passed the equivalence point and the solution is now a mixture of strong base and weak base.

	$HA(aq)$	+ $OH^-(aq)$	→ $A^-(aq)$	+ $H_2O(l)$
Initial	1.50	1.75	0	mmol
Final	≈ 0	0.25	1.50	mmol

In a SB/WB mixture, the pH can normally be determined from the strong base alone if the formality of the strong base is much greater than the K_b of the weak base.

$$[OH^-] \approx F_{SB} = \frac{0.25 \text{ mmol}}{85.00 \text{ mL}} = 0.00294 \text{ M} \quad \text{if } F_{SB} \gg K_b \text{ (OK)}$$

$$\text{pOH} = -\log(0.00294) = 2.53 \qquad \text{pH} = 14.00 - 2.53 = 11.47$$

The complete titration curve, including the calculated points, is shown in Figure 11.10.

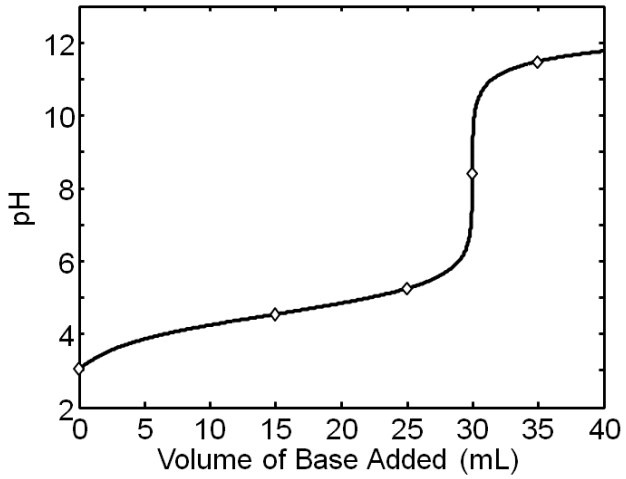


Figure 11.10: Titration curve for Example 11.6 showing the calculated points.

Exercise 11.11

Consider the titration of 50.00 mL 0.0500 F formic acid (HCOOH, pK_a =3.75) with 0.0500 F KOH. Calculate the pH in the titration flask after the addition of the following amounts of base: (a) 0 mL, (b) 45.00 mL, (c) 50.00 mL, and (d) 55.00 mL.

Weak Base/Strong Acid Titrations

The titration of a weak base with a strong acid is analogous to the WA/SB case, with the titration reaction in this case given below.

$$B(aq) + H_3O^+(aq) \rightarrow BH^+(aq) + H_2O(aq)$$

or $$B(aq) + H^+(aq) \rightarrow BH^+(aq)$$

The two reactions above are equivalent and result in the conversion of the generic base, B, to its conjugate acid, BH^+. The titration in this case proceeds from the WB to the buffer, to the

WA, and then finally to a mixture of SA and WA. A typical titration curve for a base with pK_b = 5 is shown in Figure 11.11. Notice that the curve is inverted from the case of the WA/SB, with the pH decreasing as the acid is added. The buffer region is still Region 2, and the pH at the midpoint of this region will correspond to the pK_a of the conjugate weak acid (*i.e.* 14 – pK_b). The equivalence point here corresponds to the weak acid and the pH will be less than 7. Calculations are very similar to the WA/SB case, except that the species involved change. These will not be discussed in detail.

As with the WA/SB titration, the shape of the titration curve here is influenced by the concentration of the weak base and its pK_b value. As before, the equivalence point becomes sharper (and easier to determine) as the concentration increases and the pK_b decreases. The effect of the pK_b on the titration curve is illustrated in Figure 11.12. Notice that the buffer region shifts downward as the pK_b decreases, opposite to the changes observed for the WA/SB titration.

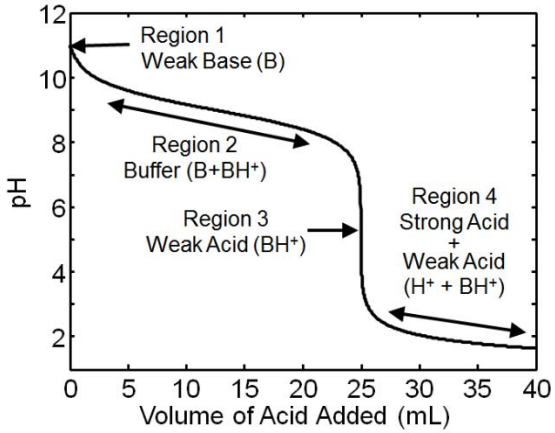


Figure 11.11: Titration curve for the titration of 0.100 F HCl with 25.00 mL of 0.100 F weak base (pK_b = 5).

Exercise 11.12

Trimethylamine, $(CH_3)_3N$, is a weak base with pK_b = 4.20. Calculate the pH in the titration flask after the following volumes of 0.0500 F HCl are added to 40.0 mL of 0.0500 F trimethylamine: (a) 0 mL, (b) 20.0 mL, (c) 40.0 mL, (d) 60.0 mL.

Titration Curves for Polyfunctional Acids and Bases

The general principles developed for the titration of weak acids and bases also apply to polyfunctional weak acids and bases, with the added complication that multiple protons can are added or removed. As an example, we consider the titration of a generic diprotic acid, H_2A, with strong base. The relevant titration reactions occur in succession.

$$H_2A + OH^- \rightarrow HA^- + H_2O$$
$$HA^- + OH^- \rightarrow A^{2-} + H_2O$$

We can view the titration as occurring in two separate steps. On the initial addition of base, the diprotic acid H_2A is converted to the amphiprotic species HA^-, reaching the first

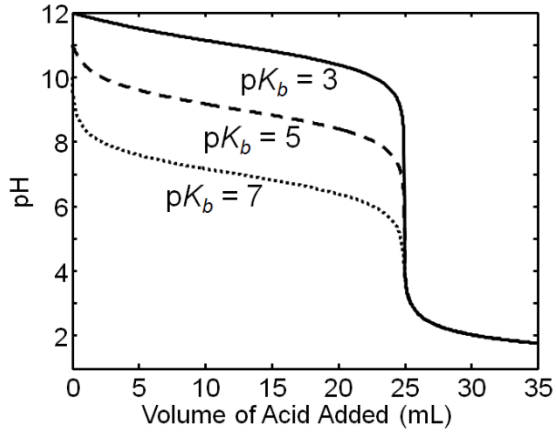


Figure 11.12: Effect of pK_b on weak base/strong acid titration curves for 25 mL of 0.1 F weak base and 0.1 F strong acid.

equivalence point when all of the H_2A has been consumed. Following this, the HA^- is converted to the basic form, A^{2-}, passing through a second buffer region and reaching a second equivalence point after two equivalents of base have been added.

A titration curve for such a process is shown in Figure 11.13. In this case, the buffer regions and equivalence points are clearly evident. However, the titration curves for polyfunctional acids and bases are rarely this straightforward because the shapes are highly dependent on the magnitude of the pK_a values relative to each other, and the assumption of independence in the multiple equilibria is often not valid. As a more practical case, Figure 11.14 shows the titration of 0.1 F oxalic acid, a diprotic acid, with a strong base. Because both pK_a values are quite low, the first equivalence point in this case is virtually indistinguishable, although the second is clearly defined. Likewise, the titration curve for the triprotic phosphoric acid (pK_{a1} = 2.15, pK_{a2} = 7.20, pK_{a3} = 12.15) with a strong base should show three equivalence points. However, this curve, shown in Figure 11.15, only clearly shows the first two equivalence points. The third proton is so weakly acidic that it cannot be easily distinguished in the titration curve.

Based on this discussion, if we wish to titrate a polyfunctional acid or base for quantitative purposes, it is important to know which equivalence point we wish to detect and choose an indicator accordingly. In the case of oxalic acid, for example, it would be much easier to detect the second equivalence point (pH = 8.40), while for phosphoric acid, either of the first two could be used, but very different indicators would be used (pH = 4.70 vs. pH = 9.60). Clearly, then, the choice of indicator is an important consideration.

Exercise 11.13

Sketch the general shape of a titration curve you would expect to see for the titration of 25 mL of a 0.1 F solution of a dibasic weak base (pK_{b1} = 3, pK_{b2} =8) with 0.1 F HCl solution.

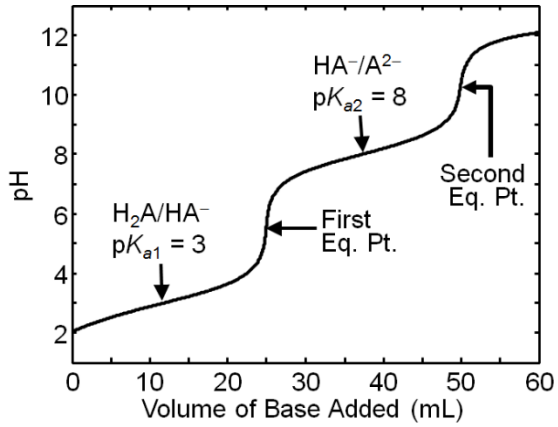


Figure 11.13: Titration curve for titration of 25 mL of a 0.1 F diprotic weak acid (pK_{a1} = 3, pK_{a2} = 8) with 0.1 F strong base.

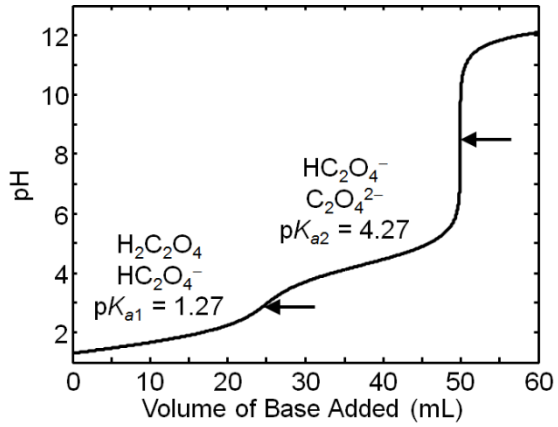


Figure 11.14: Titration curve for titration of 25 mL of 0.1 F oxalic acid ($H_2C_2O_4$) with 0.1 F strong base. Arrows indicate equivalence points.

11.7 Acid-Base Indicators

One way to detect the end point of a titration is the use a chemical indicator, and for acid-base titrations, this is an acid-base indicator. For an indicator to be effective, it must undergo a reaction with the reagents in the titration and undergo a color change. An acid-base indicator is simply a weak acid or base for which the colors of the conjugate acid-base pair are different (one form may be colorless). This is represented below for the acid form of the indicator, but a similar equation could be written starting with the basic form.

$$\underset{\text{Color 1}}{\text{HIn}\,(aq)} \rightleftharpoons \text{H}^+(aq) + \underset{\text{Color 2}}{\text{In}^-(aq)} \qquad K_{In} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

In this reaction, HIn simply indicates the acid form of the indicator and K_{In} is simply the K_a value for this equilibrium (the different notation is used to distinguish it from the K_a of the weak acid being titrated). Indicators tend to be highly conjugated organic structures, which is what leads to their bright colors. The structure of a typical indicator, methyl red, is shown in Figure 11.16, with the acidic proton shown in bold (note that the neutral form is a zwitterion). For our purposes, however, it is the acid base properties that are of interest.

Students sometimes wonder why an indicator, which has acid-base properties, does not affect the acid-base titration. In fact, it does interact with the acid or base we are titrating, but the quantity of indicator added is usually so small that it does not significantly alter the pH. Therefore, we can consider $[\text{H}^+]$ as being independent of the equilibrium above and determined entirely by the titrant and titrand. Because of this, we can write:

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}^+]}{K_{In}}$$

This equation indicates that, when $[\text{H}^+] = K_{In}$ (or when $\text{pH} = \text{p}K_{In}$), there are equal concentrations of the acid and base forms of the indicator. Alternatively, if the pH decreases to one unit below $\text{p}K_{In}$, which is a factor of 10 increase in $[\text{H}^+]$, there will be 10 times as much of the acid form of the indicator, and its color (Color 1) will dominate. If the pH increase, by one unit above $\text{p}K_{In}$, the base form of the indicator (Color 2) will be 10 times more abundant. This relationship is represented in Figure 11.17.

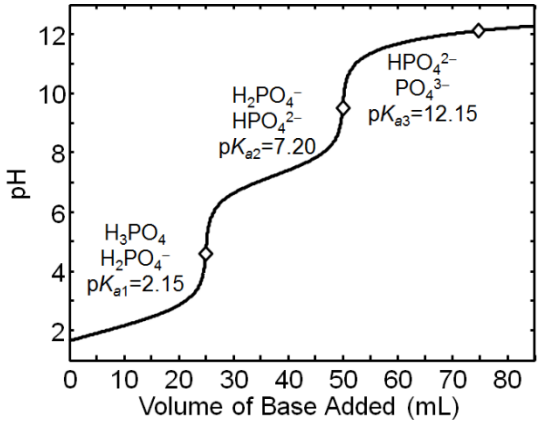


Figure 11.15: Titration curve for titration of 25 mL of 0.1 F phosphoric acid (H_3PO_4) with 0.1 F strong base. The diamonds indicate equivalence points.

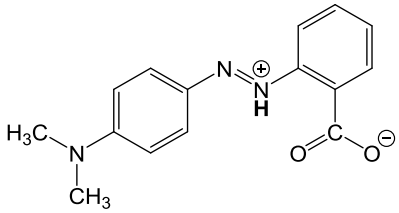


Figure 11.16: Structure of the acid form of the indicator methyl red.

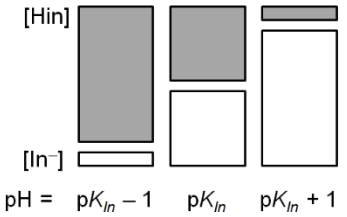


Figure 11.17: Effect of pH on indicator composition.

To illustrate with a more concrete example, methyl red has a pK_a (pK_{In}) of 4.97 and is red in its acid form (Color 1) and yellow in its base form (Color 2). This means that at pH = 3.97, a solution containing methyl red will appear red because 91% of the indicator will be in its acid form. At pH = 4.97, there will be a 1:1 ratio of the two forms and the solution will appear orange. As the pH increases to 5.97, the base form of the indicator will dominate (10:1) and the solution will appear yellow.

The main principle here is that we want the pK_a of the indicator to be as close as possible to the pH at the equivalence point of the titration to ensure that we can accurately determine transition of color at the end point. This is one reason why it is important to be able to estimate the pH at the equivalence point of the titration. Once this is done we can select from a variety of indicators to find the one best suited for the titration. A chart of some indicators and their corresponding pK_a values is given in Figure 11.18 (see also the Appendix).

Matching the pK_a to the equivalence point in the titration still does not guarantee that an accurate result will be obtained. As indicated above, the color transition for an indicator typically takes place over about 2 pH units, so for an accurate determination of the end point, the change in pH at the equivalence point should be as rapid and large as possible. This will depend on the concentration of the solutions and the strength of the acid or base. To illustrate, Table 11.1 indicates the change in pH (ΔpH) around the equivalence point for the titration of 50 mL of acid with equivalent concentrations of strong base under various conditions. The change in pH is taken to be the pH 0.05 mL after the equivalence point minus the pH 0.05 mL before the equivalence point, which corresponds to about three drops from the buret. For the titration of a SA at a relatively high concentration (0.1 F) the change is very sharp and the selection of indicator is not critical. For lower concentrations, the change is less sharp, but still relatively easy to detect. For a moderate WA (pK_a = 5), the end point is relatively sharp for high concentrations, but becomes more difficult to detect as the concentration decreases. For a weak WA (pK_a = 9) the end point is almost impossible to measure accurately at any reasonable concentration.

Based on this discussion, you should be prepared to select the appropriate indicator for a titration and justify your reasoning.

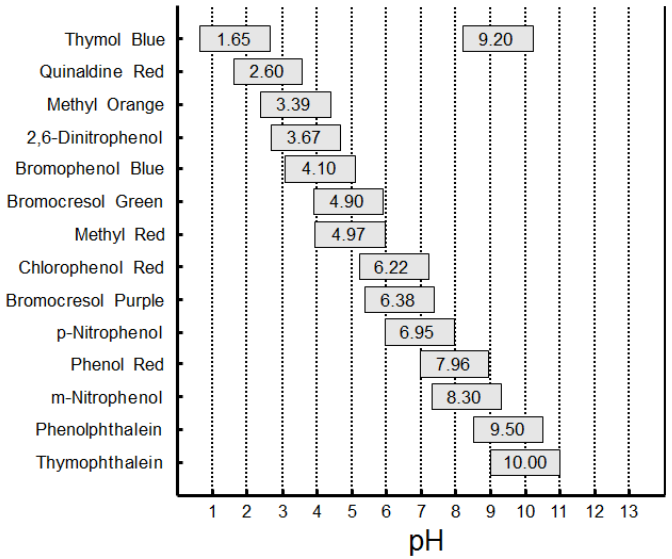


Figure 11.18: Some acid-base indicators and their transition ranges. The pK_a values are given in the boxes.

Table 11.1. Change in pH around the equivalence point for the titration of 50 mL of acid with strong base.

Acid	Formality	ΔpH (49.95 mL - 50.05 mL)
Strong	0.1 F	5.40
Strong	0.001 F	1.40
Weak, pK_a = 5	0.1 F	1.71
Weak, pK_a = 5	0.001 F	0.30
Weak, pK_a = 9	0.1 F	0.03

Exercise 11.14

Based on earlier discussions of titration curves, what would be the best indicator to use for the quantitative determination of oxalic acid, with an approximate concentration of 0.1 F, by titration with 0.1 F NaOH? What about phosphoric acid at this same concentration?

Exercise 11.15

Which of the indicators given are most suitable for titrations involving monoprotic weak acids?

Exercise 11.16

Consider the titration of 0.100 F ammonia (NH_3, the unknown, pK_b = 4.76) with 0.100 F HCl. What would be a suitable indicator to use for this titration?

Exercise 11.17

Would the indicator selected in the previous exercise still be appropriate if the concentration of the ammonia solution were 0.0500 F? (HCl is still 0.100 F.)

11.8 Summary

Acid-base reactions are relevant to many aspects of chemistry, including buffers and titrations. When one of the reactants is a strong acid or base, the final mixture falls into one of several categories: neutral solution, SA, SB, WA, WB, WA+SA, WB+SB, buffer, or an amphiprotic substance. Understanding the acid-base properties of such solutions and being able to predict pH allows the application of different strategies to prepare buffers and the calculation of titration curves, both of which are very useful in the practice of chemistry.

11.9 Additional Exercises

Exercise 11.18
What is the [H_3O^+] in a solution prepared by mixing 50.0 mL of 0.0100 F NH_3 and 50.0 mL of 0.100 F NH_4Cl?.

Exercise 11.19
Calculate the pH of a solution obtained by mixing 10.0 mL of reagent HCl (density = 1.19 g/mL, 37.0% by wt. HCl) and 100.0 mL of 1.00 F NaOH and diluting to 1.00 L.

Exercise 11.20
What is the [H_3O^+] in a solution formed by mixing 40.0 mL of 0.0200 F HCl and 25.00 mL of 0.0320 F ethylamine?

Exercise 11.21
What is the [OH^-] in a solution prepared by adding 50.0 mL of 0.100 F HNO_3 to 75.0 mL of 0.0500 F trimethylamine?

Exercise 11.22
What is the pH of the solution that results from mixing 100.0 mL of 0.0750 F Na_2HPO_4 and 30.0 mL of 0.500 F HCl?

Exercise 11.23
How many moles of acetic acid and sodium acetate would be required to prepare 500. mL of a pH 5.00 buffer with an ionic strength of 0.0100 M?

Exercise 11.24
Describe how you would prepare 1.00 L of a pH 5.00 buffer starting with solid sodium hydroxide (NaOH, MM = 40.00 g/mol) and glacial (pure) acetic acid (CH_3COOH, MM = 60.05 g/mol, density = 1.05 g/mL). The total concentration of the buffer components should be 0.200 mol/L

Exercise 11.25
What masses of sodium bicarbonate (MM=88.01 g/mol) and sodium hydroxide (MM=40.00 g/mol) would be required to make 250. mL of a pH 10.00 buffer in which the concentration of the weak acid component is 0.200 F?

Exercise 11.26
A chemist wishes to prepare a buffer of pH 5.00 using sodium acetate and acetic acid in which the formality of the conjugate base is 0.0100 F. However, no sodium acetate is available. Calculate the weights of sodium hydroxide and acetic acid needed to prepare 1.00 L of the buffer.

Exercise 11.27
Describe how you would prepare 400. mL of a pH = 7.00 MOPS buffer in which you the concentration of the weak acid component is 0.100 F. You have available MOPS (MM = 209.26 g/mol), 2.00 F NaOH and 2.00 F HCl.

Exercise 11.28
Consider a titration in which 0.100 F NaOH is added to 50.0 mL of 0.100 F butanoic acid (*a.k.a.* butyric acid, pK_a = 4.98). Calculate the pH in the titration flask after the addition of the following volumes of titrant: (a) 0 mL, (b) 20.0 mL, (c) 50.0 mL, and (d) 60.00 mL. What would be the best indicator to use for this titration?

Exercise 11.29
Calculate the pH of the solution in the titration flask after 30.0 mL of 0.0500 F NaOH have been added to 50.0 mL of 0.0500 F HCl.

Exercise 11.30
Calculate the change in pH that occurs between the 20% and 80% titrated point in the titration of 50.0 mL of 0.100 F weak acid (pKa = 5.00) with 0.100 F NaOH.

Exercise 11.31
Calculate the pH of the solution in the titration flask after 20.0 mL of 0.0300 F HCl have been added to 50.0 mL of 0.0450 F NaOH.

Exercise 11.32
What is the pH at the equivalence point in the titration of 50.00 mL of 0.100 F NH_3 with 0.200 F HCl?

Exercise 11.33
What volume of 0.100 F LiOH must be added to 50.0 mL of 0.100 F propionic (propanoic) acid to bring the resulting solution to pH 11.00?

Exercise 11.34
It has been suggested that the weakest acid which should be titrated with a strong base has a pK_a of 7.00. Of the indicators given in this chapter, which would be the best one for the titration of such an acid at 0.100 F with 0.100 F NaOH?.

Exercise 11.35
The molecular masses of amines are often determined by titration with a strong acid such as HCl. The pK_b of most aliphatic amines is about 4.0. If the amines and the HCl are both assumed to be about 0.0500 F, select the proper indicator for the titration from those listed in this chapter.

Exercise 11.36
Consider the titration of 50.0 mL of 0.100 F formic acid with 0.100 F NaOH. At what volume of NaOH added will the pH be 7.00?

Exercise 11.37
Predict whether or not reactions will occur between the following species in aqueous solution. If a reaction does occur, write the overall equation.

(a) nitrous acid and ammonia (b) hydrocyanic acid and sodium fluoride

Exercise 11.38
When 100 mL of 0.0500 F KOH are mixed with 50.0 mL of 0.200 F trichloroacetic acid, what is the resulting solution pH?

Exercise 11.39
What kind of solution results from mixing 100.0 mL of 0.0500 F Na_3PO_4 and 100.0 mL of 0.140 F HCl? What is the pH calculated using the approximate equation? Are the assumptions valid? Challenge: Solve for the pH by deriving the exact equation.

Exercise 11.40
What kind of solution results from mixing of 50.0 mL of 0.0200 F Na_3PO_4 and 50.0 mL of 0.0100 F HCl? What is the pH calculated using the approximate equation? Are the assumptions valid? Challenge: Solve for the pH by deriving the exact equation.

Exercise 11.41
Describe how you would prepare 500. mL of a MOPS buffer at pH = 7.00 in which the concentration of the weak base is 0.200 F. You have available MOPS (MM = 209.26 g/mol, pK_a = 7.20) and sodium hydroxide (MM = 40.00 g/mol).

Exercise 11.42
What concentrations of buffer components are required to make an acetate buffer at pH 5.00 such that the pH must not change by more than 0.10 unit when a maximum of 0.005 mol of base (OH^-) is generated in 100 mL of solution.

Exercise 11.43
A buffer of pH 10.00 can be readily prepared from trimethylammonium chloride and trimethylamine. Calculate the initial concentrations of the weak acid and base necessary to prepare a buffer which will not change pH by more than 0.20 units on addition of 0.00100 mol of strong base to 100 mL of the buffer.

Exercise 11.44
You wish to study the saponification of an ester at pH 10.00:

$$RCOOR' + OH^- \rightarrow RCOO^- + HOR'$$

You choose a buffer containing ammonia and ammonium chloride. What must the formalities of these substances be to hold the pH constant to within 0.10 unit if the formality of the ester (RCOOR') at the start of the reaction is 0.0500 F? You may choose a specific volume for the reaction if you wish.

Exercise 11.45
Calculate the masses of trimethylammonium chloride and sodium hydroxide needed to form 1.00 L of a buffer of pH 10.00 such that the addition of 50.00 mL of buffer to 50.00 mL of another solution containing up to 0.0200 F H_3O^+ or OH^- causes the pH to change no more than 0.02 units.

11.10 Answers to Exercises 11

11.1 (a) Neutral, pH=7.00, (b) SB+WB, pH=12.70, (c) WA, pH=2.97,
(d) Buffer, pH=9.84, (e) Buffer, pH=3.97, (f) Buffer, pH=7.20

11.2 No (pH=8.69); Yes (pH=8.97); No (pH=8.86)

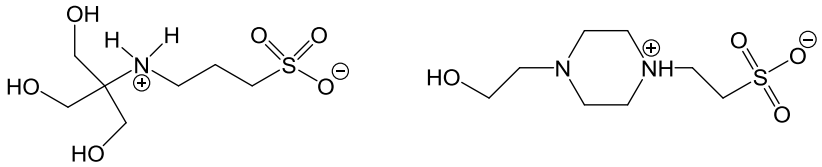
11.3 10.3 g, 46.0 mL

11.4 Mix 17.7 mL of 5.00 F HCl and 125 mL of 2.00 F NH_3 in 500. mL of solution.

11.5 25.8 mL, 8.98 g

11.6 64.2 g, 52.4 mL

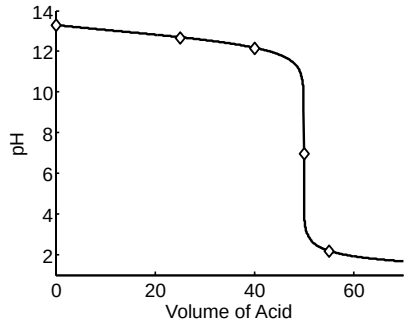
11.7



11.8 (a) Mix 37.3 mL of 5.00 F HCl and 30.3 g TRIS in 500. mL of solution;
(b) Mix 12.7 mL of 5.00 F KOH and 39.4 g TRIS·HCl in 500. mL of solution

11.9 (a) Mix 28.4 mL of 5.00 F NaOH and 59.6 g HEPES in 500. mL of solution;
(b) Mix 21.6 mL of 5.00 F HCl and 65.1 g HEPES salt in 500. mL of solution

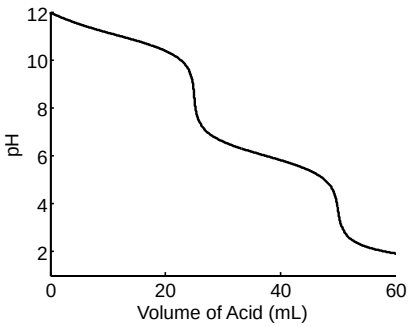
11.10 (a) 13.30, (b) 12.70, (c) 12.19, (d) 7.00, (e) 2.20 (see figure at right)



11.11 (a) 2.53, (b) 4.70, (c) 8.07, (d) 11.38

11.12 (a) 11.25, (b) 9.80, (c) 5.70, (d) 2.00

11.13



11.14 *m*-nitrophenol (pH_{ep} = 8.40); bromocresol green (pH_{ep} = 4.70) or phenolphthalein (pH_{ep} = 9.60)

11.15 Those with pK_a > 7.

11.16 methyl red (pH_{ep} = 5.27)

11.17 yes (pH_{ep} = 5.36)

11.18 5.8×10^{-9} M

11.19 1.68

11.20 5.4×10^{-7} M

11.21 1.0×10^{-12} M

11.22 1.77

11.23 0.00288 mol CH_3COOH, 0.00500 mol CH_3COONa

11.24 Mix 5.08 g of NaOH and 11.4 mL (or 12.0 g) of acetic acid in enough water to make 1.00 L.

11.25 6.46 g $NaHCO_3$, 0.935 g NaOH

11.26 0.400 g NaOH and 0.946 g CH_3COOH

11.27 Mix 13.7 g MOPS and 12.6 mL of 2.00 F NaOH in 400. mL of solution.

11.28 (a) 2.99, (b) 4.80, (c) 8.84, (d) 11.96; *m*-nitrophenol

11.29 1.90

11.30 1.20

11.31 12.37

11.32 5.21

11.33 51.01 mL

11.34 thymolphthalein (pH_{ep} = 9.85)

11.35 chlorophenol red (pH_{ep} = 5.65)

11.36 49.97 mL

11.37 (a) yes,
$HNO_3(aq) + NH_3(aq) \rightarrow NO_2^-(aq) + NH_4^+(aq)$
(b) no

11.38 1.58

11.39 Buffer, 1.55, No, 2.14

11.40 Buffer, 12.15, No, 11.50

11.41 Mix 54.09 g MOPS and 4.00 g NaOH in 500.0 mL of solution.

11.42 F_a = 0.35 F, F_b = 0.62 F

11.43 F_a = 0.038 F, F_b = 0.060 F

11.44 1.35 F and 0.235 F

11.45 45 g NaOH, 176 g of TMAC

Topic 12

Spectroscopy

12.1 Contents in Brief

- Nature of light and its interaction with matter
- Absorption spectroscopy and the Beer-Lambert Law
- Molecular fluorescence spectroscopy
- Atomic absorption and emission spectroscopy
- Spectroscopic instrumentation, applications and measurements

12.2 Introduction

When a chemist uses the term "spectroscopy", it is usually taken to mean the study of the interaction of light and matter. The use of light (strictly speaking electromagnetic radiation) in its many forms to probe matter gives the chemist one of the most powerful techniques available for determining the characteristics of the material under examination. Thus a fairly thorough introduction to some of the spectroscopic techniques most commonly used in analytical chemistry will be presented.

12.3 Wave Description of Light

Light, or more accurately electromagnetic radiation, can be characterized as either a wave or a particle. This dual nature confounded the physicists who pioneered quantum mechanics, but we have since come to recognize that both descriptions are valid and useful, depending on the context. We begin with the classical wave description.

As implied by the term "electromagnetic", light has associated with it both an electric field and a magnetic field. These fields oscillate to give light its periodic, or wave-like, properties. A particle encountering light at a particular point in space would feel an oscillating electric field, analogous to an ocean wave that raises and lowers a boat. At the same time, it would feel a magnetic field which would be perpendicular to the direction of the electric field and to the direction of travel, or propagation. This is illustrated in Figure 12.1, which shows the magnitude of the electric and magnetic fields as a function of distance along the direction of propagation at a particular point in time. Both fields are sinusoidal in shape and the distance required for one full cycle is called the *wavelength*. This is analogous to the distance between the crests of waves on an ocean, and is one of the ways light is characterized. Depending on the nature of the radiation, the wavelength can typically vary between 1 and 10^{-9} m.

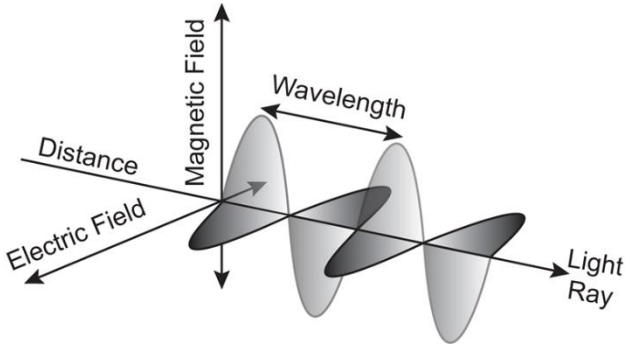


Figure 12.1: Electromagnetic radiation consists of electric and magnetic fields that oscillate perpendicular to each other and the direction of propagation of the light. At a particular point in time, the electric and magnetic fields vary periodically with position (distance). The length of this period is the wavelength.

Alternatively, we could consider the variation in field strength as a function of time at a particular point in space, as shown in Figure 12.2. This would be analogous to the rise and fall of a boat anchored on the ocean. The time required for one full cycle is called the *period* of the wave, T (units of seconds). The number of cycles occurring in one second is called the *frequency* of the wave, ν (Greek letter "nu"), and is the reciprocal of the period ($1/T$). Frequency has units of s^{-1}, or Hertz (Hz) and is another way to characterize light.

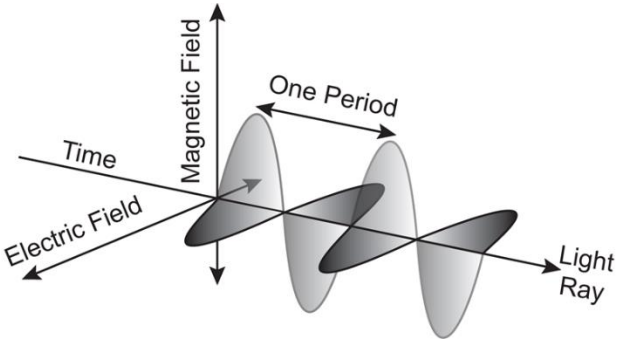


Figure 12.2: At a particular point in space, the electric and magnetic fields vary periodically with time. The time of this period is the reciprocal of the frequency.

For all types of waves (light, sound, etc.), a simple relationship exists between the velocity of the wave, its wavelength and its frequency.

$$\text{velocity} = \nu\lambda \tag{12.1}$$

For a light wave, the symbol for the speed of light is usually taken as "c", so this becomes

$$c = \nu\lambda = 2.998\times10^{8}\ \text{m s}^{-1}\ \text{(in a vacuum)} \tag{12.2}$$

The value of ν remains constant regardless of the medium, but c and λ may change when the light wave passes from one medium to another, *e.g.* from air into water.

12.4 Particle Description of Light

The development of quantum mechanics brought recognition that light could be considered to be a stream of particles consisting of individual packets of energy called *photons*. Photons are different from other particles in that they have no mass (in the traditional sense) and travel at the speed of light. The energy of a photon at a particular wavelength or frequency (*monochromatic* light) is given by the following relationship.

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} \qquad \text{where } h = 6.626 \times 10^{-34}\ \text{J s} \text{ (Planck's constant).} \qquad (12.3)$$

Note that the particle description of light still involves wave properties. As frequency increases (wavelength decreases, since velocity is usually fairly constant), energy increases. Thus one could use the energy, the frequency, or the wavelength to describe different light waves. Since the energy and the frequency are invariant for a given wave, it would be best to use one of these. However, for the "type" of light to be discussed in this text, the wavelength is most commonly used to describe or classify the light being employed in an experiment.

In theory light can have any frequency (or energy) above zero. This gives rise to a wide variety of electromagnetic waves, as shown in Figure 12.3. For example, radio waves (10^8 Hz) and X-rays (10^{18} Hz) are both "light" waves. All the different kinds of light waves are said to make up the electromagnetic spectrum. Photons in different regions of the spectrum interact with matter in different ways, leading to different applications. For example, radio waves are used in nuclear magnetic resonance (NMR) and X-rays are used for crystallographic diffraction measurements.

Virtually all regions of the electromagnetic spectrum have utility in analytical chemistry, but in this chapter, only a very small part of the electromagnetic spectrum, the visible (vis) and ultraviolet (UV) regions, will be discussed. One reason for this restriction is to limit the scope of the material covered, but many of the general principles discussed for visible and ultraviolet spectroscopy will also extend to other regions. The visible and ultraviolet regions, because they are more accessible, were the first regions to be used experimentally and are still very important in chemical analysis. Table 12.1 gives the various characteristics of light in this region of the spectrum, sometimes called the "UV-vis" region.

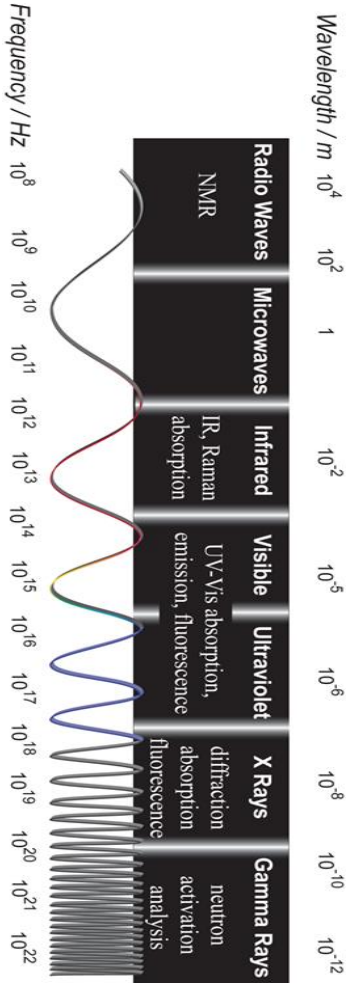


Figure 12.3: The electromagnetic spectrum showing spectral regions and some example applications.

Table 12.1. Characteristics associated with ultraviolet and visible radiation.

Characteristic	Values						
Colour	(UV)	violet	blue	green	yellow	orange	red
λ (nm)	200-380	380-435	435-500	500-565	565-590	590-625	625-740
ν_{avg} (x10^{14} Hz)	10.	7.4	6.4	5.6	5.2	4.9	4.4
E_{avg} (x10^{-19} J)	6.8	4.9	4.2	3.7	3.4	3.3	2.9

Example 12.1: Photon Energies and Wavelength

Calculate the energy per mol of red photons at 700. nm and per mol of ultraviolet photons at 200. nm.

The energy of one red photon is

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ \text{J}\cdot\text{s})(2.998\times10^{8}\ \text{m s}^{-1})}{700.\times10^{-9}\ \text{m}} = 2.84\times10^{-19}\ \text{J}$$

For one mole of photons, we have

$$E_{\text{red}} = (2.84\times10^{-19}\ \text{J/photon})\times(6.022\times10^{23}\ \text{photons/mol})$$
$$= 1.71\times10^{5}\ \text{J/mol} = 171\ \text{kJ/mol}$$

A similar calculation for UV photons at 200 nm gives 598 kJ/mol.

The energies calculated in this example, are to those involved in chemical reactions. This might give a clue as to what happens when light in this region of the spectrum interacts with matter. Chemical reactions involve the rearrangement of valence electrons, and so will the interaction of visible and ultraviolet light with matter.

The colours of the different wavelengths of visible light are given in Table 12.1. It should be noted that white light is a mixture of all the different colours (or wavelengths) of light in the visible region of the spectrum and that the human eye is insensitive to ultraviolet light, which therefore has no colour.

Exercise 12.1

A helium-neon laser can provide mochromatic ("one colour") light at a wavelength 543.5 nm with a power of 1.0 mW (1 Watt = 1 J s^{-1}). What colour is the laser light? How many photons does the laser emit in 1.0 s? Would a laser with the same power at 633 nm emit more or fewer photons?

12.5 Absorption and Emission of Light

The two processes that are most commonly used to monitor the interaction of light with matter are called *absorption* and *emission*. In general, these processes can be described as illustrated in Figure 12.4, although the specific details will vary with the type of spectroscopy, as we will see. In absorption spectroscopy, an atom or molecule typically begins in the *ground state*, which is its lowest energy state. By absorbing a photon, the atom or molecule makes a transition to a higher energy *excited state*, but only if the energy of the photon matches energy difference between the two states. Photons at a wavelength (or frequency) which do not match this energy will not be absorbed, and neither will photons which do not come close enough to the atom or molecule to interact with it. The excited state is usually transitory, and the molecule will typically "relax" back to the ground state by emitting a photon or through other processes that transfer the energy. The photon emitted in this way will also have an energy equal to the difference between the ground and excited state.

A molecule or atom can have many distinct excited states with different energy levels related to combinations of different types of energy it can store. These different types of energy are given below in order of increasing ΔE.

(a) *translational energy* – related to the velocity of an atom or molecule,
(b) *rotational energy* – related to the rotation (tumbling of molecules end-over-end),
(c) *vibrational energy* – related to the vibration of atoms in a molecule about their bonds, and
(d) *electronic energy* – related to the promotion of electrons to higher orbitals.

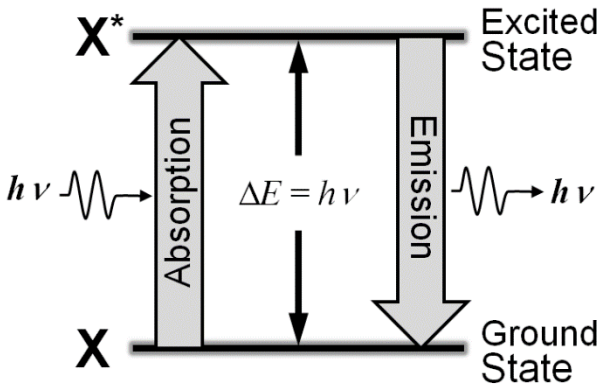


Figure 12.4: Absorption and emission processes in spectroscopy. An atom or molecule in the ground state, X, absorbs a photon with energy corresponding to its transition to an excited state, X^*. The wavelength or frequency of the photon must match the difference in energy between the ground state and the excited state. On returning to the ground state, the atom or molecule will emit a photon with the corresponding energy.

These components of the total energy are illustrated in Figure 12.5 for a formaldehyde molecule. In general, translational energy is involved in spectroscopic transitions, so only the other three will be considered. Transitions between rotational, vibrational or electronic states, or combinations of them, are quantized, meaning that they occur with specific values of ΔE that also depend on the molecule.

A *spectrum* is a plot of the absorption or emission of an atom or molecule as a function of wavelength, frequency or energy. The quantity plotted on the x-axis varies with the type of spectroscopy, but we will always use wavelength in this chapter. The spectrum is a map of the energy levels of the corresponding species, since light is only absorbed or emitted at wavelengths corresponding to the transition energy. In an *absorption spectrum*, the amount of light absorbed or transmitted as it passes through the sample is plotted vs. wavelength. If the light intensity incident on the sample at a particular wavelength is I_o and the intensity passing through is I, three quantities could be measured: percent transmited (%T), percent absorbed (%A), and the absorbance (A). These are related as given below.

$$\%T = \frac{I}{I_o} \times 100\%, \qquad \%A = \frac{I_o - I}{I_o} \times 100\% = 100 - \%T, \qquad A = -\log\left(\frac{\%T}{100}\right) \tag{12.4}$$

A spectrum for gas phase formaldehyde in the infrared region is shown in Figure 12.6 for all three of these representations, and each indicates the presence of six energy transitions. Note that the %A spectrum is just an inversion of the %T spectrum. The absorbance spectrum, A, conveys the same information about energy levels as the other two, but is scaled differently. The reason for the use of this form will become evident when we derive Beer's Law.

An *emission spectrum*, the intensity of light emitted by an atom or molecule as it relaxes from an excited state to a lower energy level is plotted as a function of wavelength. The emission spectrum conveys similar information about the energy levels as the absorption spectrum, although in some cases it may be somewhat different. The collection of an emission spectrum does not require the absorption of a photon since a molecule can be promoted to the excited state by other means (*e.g.* heat, electrical discharge). Unlike absorption measurements, the emission intensity is not normally measured relative to an incident intensity.

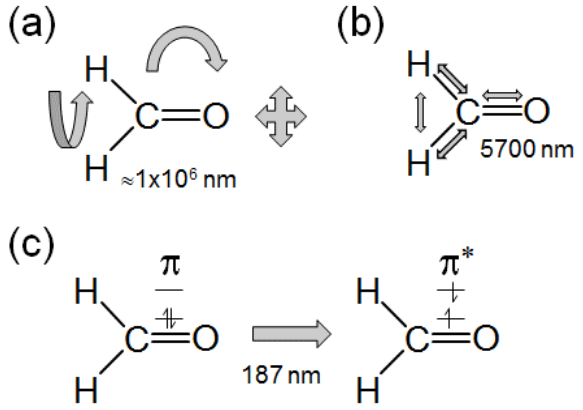


Figure 12.5: Different forms of energy stored in a molecule, along with corresponding transition wavelengths, illustrated with the formaldehyde molecule. (a) rotational and translational energy, (b) vibrational energy, (c) electronic energy ($\pi \rightarrow \pi^*$ transition).

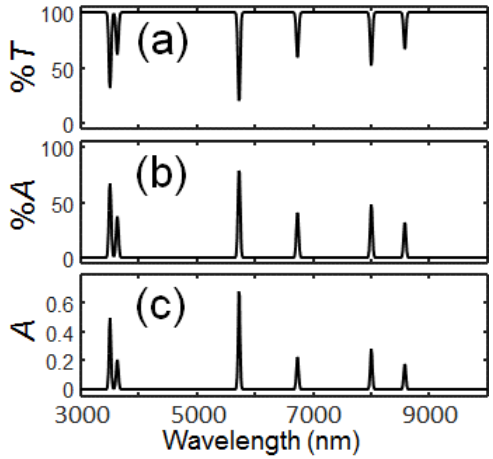


Figure 12.6: Different representations of the infrared spectrum of gas phase formaldehyde (a) % transmitted, (b) % absorbed, (c) absorbance.

In discussing the interaction of light and matter, we have referred to atoms and molecules, but it should be pointed out that such interactions also encompass ionic species. The characteristics of a spectrum will vary with the wavelength region, the nature of the species, and its physical state. In this chapter, we will focus mainly on UV-visible spectra of atomic species in the gas phase and molecular species in solution. We begin with atomic spectra.

Atomic Spectra

The spectrum of an atom or monoatomic ion in the gas phase is much simpler than that for a molecule because an atom has no rotational or vibrational energy states, so all of the energy absorbed or emitted results from transitions between atomic orbitals, usually involving valence electrons. A familiar example is the spectrum of the hydrogen atom, which arises from changes in the principal quantum number, *n*, as shown in Figure 12.7. The emission spectrum of the hydrogen atom in the UV region, shown in the bottom part of the figure, results from transitions between the energy levels shown in the upper part of the figure. The energy levels are calculated using the Rydberg equation, and the photon energies are calculated from the differences in these energy levels, as given below.

$$E_{\text{photon}} = h\nu = \left|\Delta E_{\text{orbitals}}\right| = \left|E_f - E_i\right| \tag{12.5}$$

This can be converted to the corresponding wavelength or frequency, as shown in Table 12.2.

Table 12.2. Characteristics of light absorbed for transitions of the hydrogen atom.

Transition	n=1 ⟶ n=2	n=1 ⟶ n=3	n=1 ⟶ n=4	n=1 ⟶ n=5
Wavelength(nm)	121.6	102.6	97.3	95.0
Frequency (Hz)	$2.47\text{x}10^{15}$	$2.92\text{x}10^{15}$	$3.08\text{x}10^{15}$	$3.16\text{x}10^{15}$
Energy (kJ/mol)	984	1166	1230	1259

Because the energies of electronic transitions in the hydrogen spectrum are well-defined, the resulting spectrum (absorption or emission) is called a *line spectrum*. Unlike the broader bands that are observed in solution spectra (see below), the transition wavelengths are very sharp. The lines shown in Figure 12.7 are called the Lyman series, corresponding to

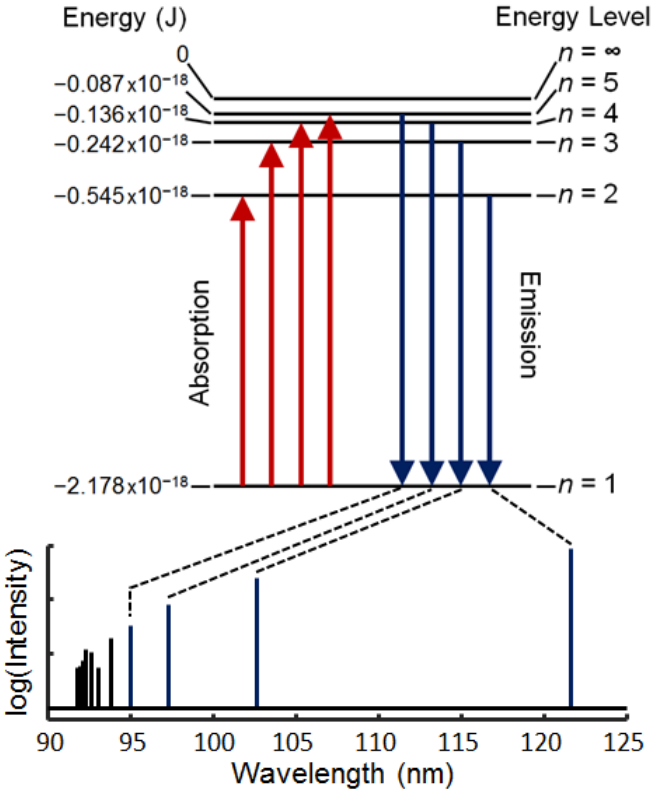


Figure 12.7: Energy levels in the hydrogen atom as a function of the principal quantum number, *n* (top), and the corresponding emission spectrum (bottom). The arrows correspond to absorption (pointing up) and emission (pointing down) of photons. Other transitions are also possible, but are not shown.

transitions to or from the ground state, n=1. However, other transitions are also possible between higher levels. If transitions occur between n=2 and higher levels occur, the lines appear in the visible region and are referred to as the Balmer series.

All atoms and monoatomic ions in the gas phase exhibit line spectra, but unlike hydrogen, the energy levels are not easily calculated. Other atoms will also give more complex spectra because the presence of multiple electrons introduces new energy levels. As an example, Figure 12.8 compares the emission spectra for hydrogen and iron in the visible region. The iron spectrum has many more lines, some of which merge together at the resolution of the image. The iron spectrum is further complicated by lines from iron ions (Fe^{+}, Fe^{2+}, etc.).

Atomic species do not generally form solutions, but ions dissolve readily (*e.g.* Na^{+}). However, the colour of these solutions, such as the blue colour of Cu^{2+} solutions, does not result from transitions within the monoatomic ion, but rather from the molecular ion that forms when water or other species present in solution complex with the metal ion. These spectra have much different characteristics, as described in the next section.

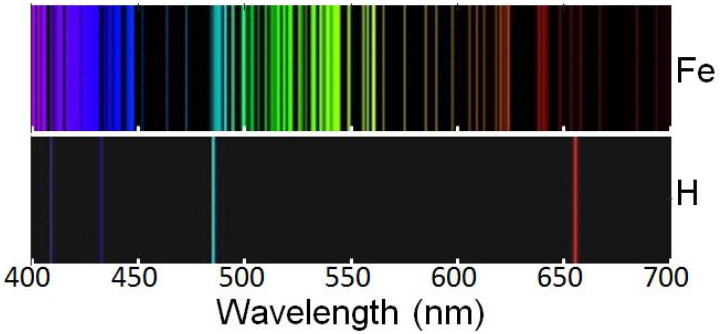


Figure 12.8: Comparison of atomic emission spectra for hydrogen (bottom) and iron (top) in the visible region.

Example 12.2: Energy Levels of the Hydrogen Atom

Using the wavelengths given in Table 12.2, confirm the energy for the transition from n=1 to n=3 in the hydrogen atom.

The wavelength corresponding to the transition is 102.6 nm, and from this we can calculate the energy of the photon.

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\text{J}\cdot\text{s})(2.998\times10^{8}\,\text{m}\,\text{s}^{-1})}{102.6\times10^{-9}\,\text{m}} = 1.936\times10^{-18}\,\text{J}$$

This is the energy of a single photon, but the energy in Table 12.2 is expressed in kJ/mol, so we need to calculate the energy of one mole of photons.

$$E = (1.936\times10^{-18}\,\text{J})\times\frac{6.022\times10^{23}}{\text{mol}}\times\frac{1\,\text{kJ}}{1000\,\text{J}} = 1166\,\text{kJ/mol}$$

This is the value given in Table 12.2.

Exercise 12.2

Using the information in Figure 12.7, calculate the wavelength of light (in nm) that would be absorbed when an electron in a hydrogen atom makes a transition from n=2 to n=4. What would be the colour of the light absorbed?

Exercise 12.3

What is the energy (in kJ/mol) required to ionize a ground state hydrogen atom? (Ionization corresponds to a transition to $n=\infty$.)

Molecular Spectra

The spectra of molecules are both simpler and more complex than those of atoms. On one hand, there are generally fewer electronic transitions in the UV-vis region because of the stability of electrons in a chemical bond. These transitions can include transitions of pi electrons to antibonding orbitals ($\pi \rightarrow \pi^*$), non-bonding (lone pair) electrons ($n \rightarrow \pi^*$), and transitions of d-electrons in complex ions. On the other hand, molecules also have different vibrational and rotational energy states not present in atoms. Each electronic state contains many vibrational states, and each vibrational state has many rotational states, as represented in the energy diagram in Figure 12.9. This is a simplified diagram since it only shows three vibrational states within each electronic state and only five rotational levels with each vibrational state, but there can be many more. In addition, the diagram suggests an equal spacing of the energy levels, but this is not generally true. Because of the large number of energy levels and possible transitions, the spectrum of a molecule in the gas phase contains a large number of closely spaced lines. Often, many of these lines will merge together unless the measurement device has sufficient resolution to distinguish them.

While gas phase molecular spectra are sometimes used in analytical chemistry, such as in atmospheric studies, most measurements are performed on molecules in solution, which causes further changes in the spectra. The presence of interactions with solvent molecules slightly changes the energy levels for individual molecules, causing the transitions shown in the figure to become "smeared", like ink on a page. As a consequence, individual transitions

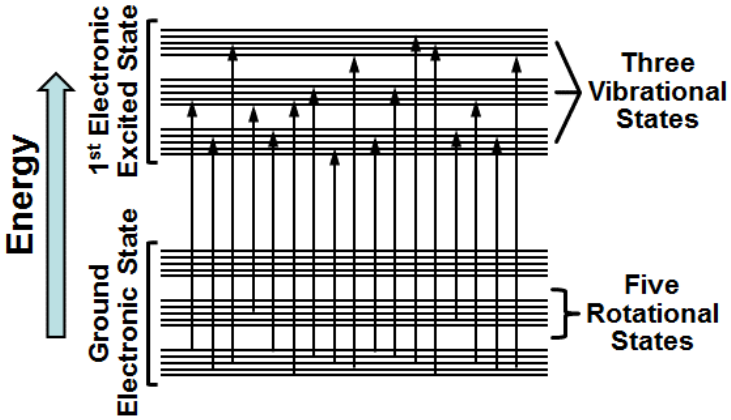


Figure 12.9: Simplified representation of the energy levels in a molecule showing the vibrational and rotational levels of the ground state and first electronic excited state. The arrows indicate transitions corresponding to the absorption of photons.

are not observable in solution and instead they blend together to form broad bands. This is called a *band spectrum* (in contrast to the line spectrum observed for atoms), and typically one to several bands are observed in the UV-visible region for molecules that absorb. Figure 12.10 shows band spectra in the visible region for three molecular ions in solution: iron thiocyanate, a copper-ammonia complex, and the permanganate ion. Also shown are the corresponding solutions in the same order as the spectral peaks. The iron thiocyanate has a band with an absorbance peak at 476 nm (λ_{max} = 476 nm), meaning that it absorbs most strongly in the blue region of the spectrum. The absorbance approaches zero above 600 nm, meaning that light is transmitted in that region and the solution appears orange-red. On the other hand, the copper-ammonia complex has λ_{max} = 605 nm and transmits light most strongly at 420 nm, so it appears blue. Potassium permanganate has a maximum somewhere in the middle of these two at λ_{max} = 526 nm. It transmits most strongly below 500 nm (blue-violet) and above 600 nm (orange-red), giving an overall effect of a pink or purple solution.

All of the absorption bands in Figure12.10 result from the promotion of electrons in the d-orbitals of the transition metals involved. For organic molecules, the electronic transitions usually occur in the UV region unless the molecule is highly conjugated, as is often the case with dyes and indicators. An example is presented in Figure 12.11, which shows two absorption bands in the UV spectrum of acetone. The width of molecular absorption bands (typically 10-100 nm) is much larger than atomic line widths, which are on the order of 0.01 nm. Consequently, we will see that the instrumentation employed for these two cases is quite different.

When a molecule absorbs a photon to enter an excited state, it must subsequently release that energy to return to the ground state. A natural way to do this would be to release another photon by the process we referred to as emission. When this happens in molecules, it is also called *fluorescence*. However, molecular emission in solution is relatively rare, and more often, the energy gained is released by redistributing it to other bonds within the molecule or transferring it to solvent molecules. This non-radiative process is sometimes called *vibrational relaxation* and ultimately transforms the energy into heat. The measurement of molecular emission is examined in a later section.

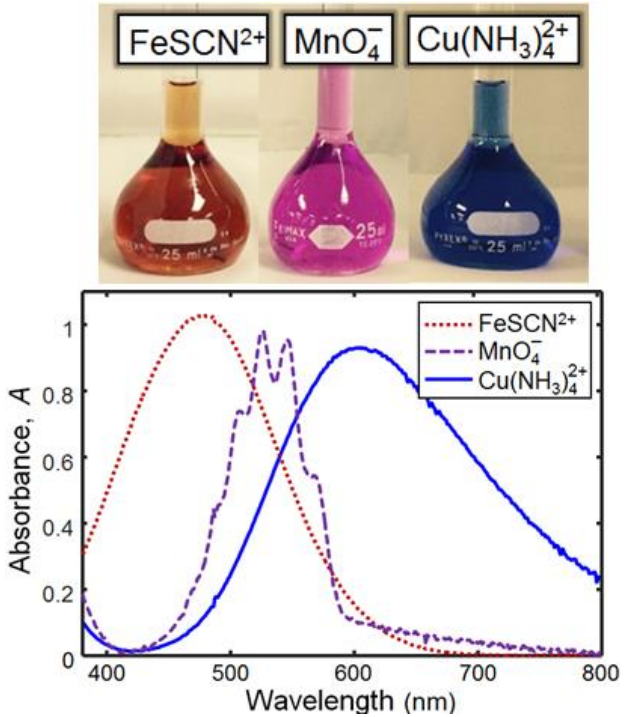


Figure 12.10: Absorption spectra for different species in aqueous solution, along with photographs of the corresponding solutions: iron(III) thiocyanate (red), permanganate ion (purple), and copper(II) in ammonia solution (blue).

12.6 Absorption Spectroscopy in Solution: Beer's Law

One of the goals of analytical spectroscopy is to make quantitative determinations of the amount of analyte in a sample. In this text we will focus on four main ways to do this: (1) molecular absorption, (2) molecular emission, (3) atomic absorption, and (4) atomic emission. Molecular absorption in solution is one of the simplest and oldest methods to measure concentrations, so that will be our starting point.

The measurement of UV-visible absorption in solution typically employs a square or rectangular sample cell which is also called a cuvette. The intensity of light entering the cell will be designated as I_o, and the intensity of light leaving as I, as shown in Figure 12.12. Since the amount of light absorbed depends on the wavelength, we will specify that the light entering is monochromatic (single wavelength). In addition, the amount of light absorbed will depend on the distance it travels through the cell, called the *path length*, b (cm), and the concentration of the absorbing molecule, c (mol/L), with the light absorbed increasing with b and c. The task is to find the relationship between the light absorbed and these variables. This relationship is called the Beer-Lambert Law, or simply Beer's Law, and will be derived here.

To start, we can imagine an infinitely thin slice of solution, 1 cm on each edge, in the path of the light beam as shown in Figure 12.13. Based on this, we can calculate the number of molecules in the slice as follows.

$$\text{Volume of slice (in cm}^3\text{ or mL)} = 1\text{ cm} \times 1\text{ cm} \times dx = dx$$

$$\text{Volume of slice (in L)} = \text{Vol. in mL} \times (0.001\text{ L/mL}) = dx \cdot (0.001\text{ L/mL})$$

$$\text{Moles in slice} = c \cdot V = c \cdot (0.001)dx$$

$$\text{Molecules in slice} = (0.001)c \cdot dx \cdot N \qquad (12.6)$$

In this last equation, N = Avogadro's number = 6.022×10^{-23} mol^{-1}.

The amount of light entering the slice is I and the amount leaving is $(I + dI)$, where dI is negative since light is absorbed. If we imagine that a photon is only absorbed if a molecule is blocking its path, then the fraction of light absorbed will be the ratio the cross-sectional area occupied by molecules to the total area (1 cm^2). In other words, if the molecules occupy 10% of the area of the slice, then 10% of the light would absorbed. To determine the total area

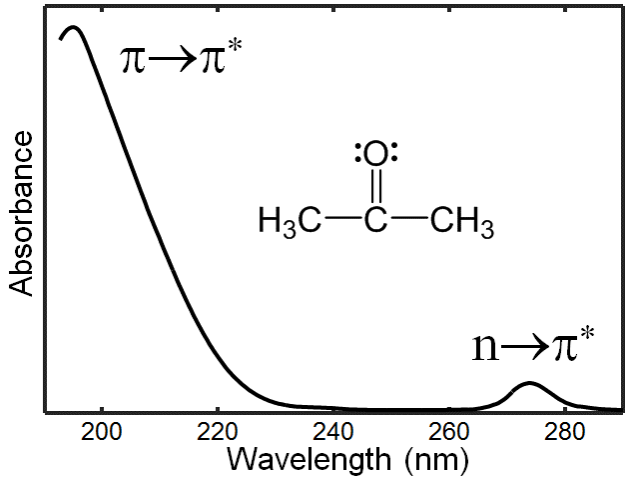


Figure 12.11: Ultraviolet spectrum of acetone in solution.

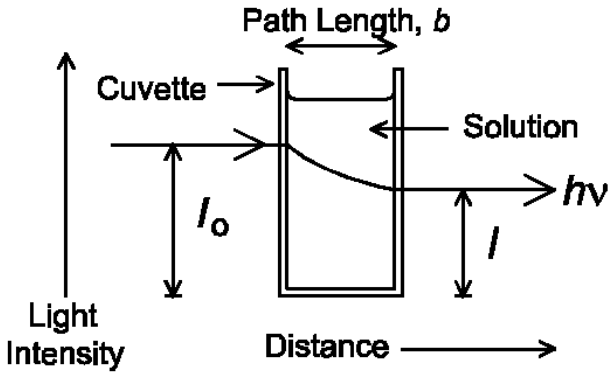


Figure 12.12: Measurement of light absorption in solution. Light entering the cuvette with intensity I_o is absorbed by solute molecules as it passes through the solution over a distance b and exits the solution with a lower intensity, I.

occupied by the molecules, we multiply the number of molecules in each slice by the cross-sectional area of one molecule, which we will designate as σ (in cm^2).

Area occupied by molecules = (No. of molecules) x σ = $(0.001)Nc \cdot dx \cdot \sigma$ (12.7)

Fraction of area occupied $= \dfrac{\text{Area occupied}}{\text{Total area}} = \dfrac{(0.001)Nc\sigma \cdot dx}{1\ \text{cm}^2} = (0.001)Nc\sigma \cdot dx$ (12.8)

This would be equal to the fraction of light absorbed by the slice if every photon encountering a molecule were absorbed. However, the probability of absorption is not likely to be 100%. We will assign this probability the symbol *P*, which can take on a value between 0 and 1. For example, if *P* is 0.5, then 50% of the photons encountering a molecule will be absorbed. The value of *P* will depend on the molecule and the wavelength of light. It will be highest at the absorbance maximum of the absorber, and zero where the absorption spectrum goes to zero. With this defined, we can now determine the proportion of photons absorbed.

$$\text{Fraction of light absorbed} = -\frac{dI}{I} = (0.001)Nc\sigma P \cdot dx \qquad (12.9)$$

Note that the negative sign is present because *dI* will be a negative quantity.

Of course, we are not interested in the light absorbed in this thin slice, but rather that transmitted through the entire cell. To determine this we will have to integrate this equation across the cell. Integration is carried out from $x = 0$, where $I = I_o$, to $x = b$, where $I = I$.

$$-\int_{I_o}^{I} \frac{dI}{I} = (0.001)NP\sigma c\int_0^b dx \qquad (12.10)$$

or $\quad -\left[\ln I\right]_{I_o}^{I} = (0.001)NP\sigma c\left[x\right]_o^b$

or $\quad -\ln I - (-\ln I_o) = (0.001)NP\sigma(b-0)$

or $\quad \ln\left(\dfrac{I_o}{I}\right) = (0.001)NP\sigma cb \qquad (12.11)$

This result is one form of Beer's Law. However, for historical and practical reasons, base 10 logarithms ("log") are typically used in place of natural logarithms ("ln"). Since $\ln x = (2.303)\log x$, Equation (12.11) can be rewritten as

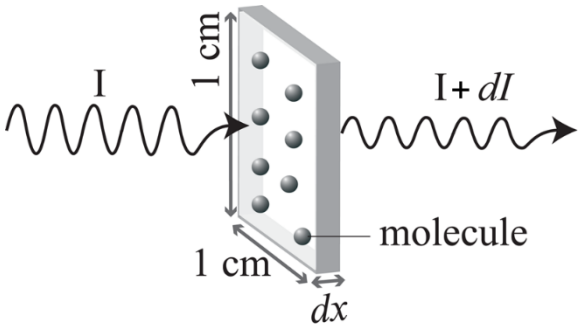


Figure 12.13: Absorption of light in an infinitely thin 1 cm^2 slice of solution. Note that the change in intensity, *dI* is a negative quantity, corresponding to a decrease in intensity.

$$2.303 \log\left(\frac{I_o}{I}\right) = (0.001) NP\sigma bc \qquad (12.12)$$

or $$-\log\left(\frac{I}{I_o}\right) = \frac{0.001}{2.303} NP\sigma bc \qquad (12.13)$$

The quantity on the left hand side is commonly referred to as "absorbance" and given the symbol "*A*". As well, the ratio of the transmitted intensity to the incident intensity, I/I_o, is referred to as the *transmittance* and given the symbol "*T*". For a given molecule at a given wavelength, all of the quantities on the right hand side are constant except for *b* and *c*, and can therefore be collected together. This leads to the usual form of Beer's Law.

$$A = -\log T = \varepsilon bc \qquad (12.14)$$

In this equation, the quantity "ε" is called the *molar absorptivity* and has units of M^{-1} cm^{-1}. It is normally constant for a given molecule in a given solvent at a particular wavelength.

A key aspect of Beer's Law is that it shows that absorbance, rather than intensity, is directly proportional to concentration, suggesting that measurement of absorbance should be an excellent method for performing quantitative analysis. It also indicates that the amount of light transmitted is *not linear* in either concentration or path length, a result that is not necessarily intuitive. The calculation of absorbance can be carried out in a variety of ways depending on the quantities provided (*I*, *T*, %*T*, etc.), and some of these relationships are shown in Table 12.3.

Note that in deriving Beer's law *P*, σ, and *c* have been assumed to be constant. While *c* can be considered constant (*in a given solution*) and probably also σ, the photon absorption probability, *P* will depend strongly on wavelength and, to some extent, on solution refractive index and solution concentration. More will be said about this later.

Table 12.3. Some Beer's Law relationships.

Transmittance	$T = \frac{I}{I_o}$
Percent Transmittance	$\%T = T \times 100\% = \frac{I}{I_o} \times 100\%$
Absorbance	$A = \varepsilon bc$ $A = -\log T = -\log\left(\frac{I}{I_o}\right)$ $= \log(I_o) - \log(I)$ $A = -\log\left(\frac{\%T}{100}\right) = 2 - \log(\%T)$

Example 12.3: Beer's Law

What value of absorbance corresponds to 90.0 % of the light being absorbed by the solution in the cell?

When 90.0% of the light is absorbed, 10% of the light is transmitted through the cell, which means that $T = 0.100$. Substituting this into Equation (12.14) gives

$$A = -\log(T) = -\log(0.100) = 1.000$$

Example 12.4: Molar Absorptivity

Imagine that a molecule has a cross-sectional area equal to 0.53 Å^2 and the probability of absorbing a photon is 0.75 at a particular wavelength. What is the molar absorptivity of the molecule? (Note: 1 Å (angstrom)= 10^{-10} m.)

The molar absorptivity is defined through Equations (12.13) and (12.14) as

$$\varepsilon = \frac{0.001\,\text{L cm}^{-3}}{2.303} NP\sigma$$

Before using this, however, the cross-sectional area needs to be converted to cm^2.

$$\sigma = 0.53\ \text{Å}^2 \times \left(\frac{10^{-10}\,\text{m}}{1\,\text{Å}}\right)^2 \times \left(\frac{100\,\text{cm}}{1\,\text{m}}\right)^2 = 5.3\times10^{-17}\ \text{cm}^2$$

Now the molar absorptivity can be calculated.

$$\varepsilon = \frac{0.001\ \text{L cm}^{-3}}{2.303}(6.022\times10^{23}\ \text{mol}^{-1})(0.75)(5.3\times10^{-17}\text{cm}^2)$$
$$= 3.5\times10^{3}\ \text{L}\cdot\text{cm}^{-3}\cdot\text{mol}^{-1}\cdot\text{cm}^2 = 3.5\times10^{3}\ \text{M}^{-1}\ \text{cm}^{-1}$$

Exercise 12.4

For the molecule given above, what concentration would be necessary to absorb 99% of the light in a cuvette with a path length of 1.00 cm?

12.7 Photometric Instrumentation

The next step in the discussion is to examine how absorbance is measured. This is performed with an instrument called a *spectrophotometer*. A block diagram of this instrument is shown in Figure 12.14. A few words should be said about each component of the spectrophotometer.

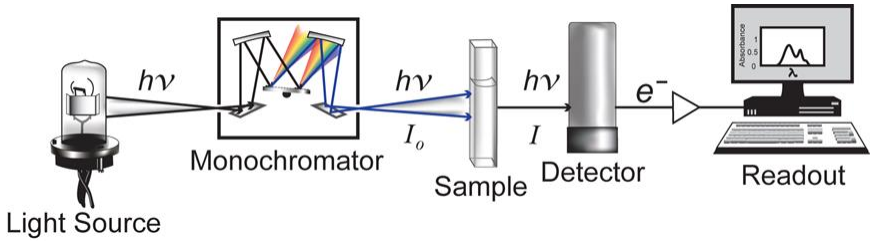


Figure 12.14: Block diagram of a simple absorption spectrometer.

Light Source

If measurements are to be made only in the visible region, then the light source usually used is an ordinary tungsten filament incandescent lamp. These lamps emit wavelengths at useful intensities from the infrared (well above 700 nm) to about 350 nm.

If wavelengths <350 nm are needed, a glowing wire cannot be used because the intensities are too low in this region. An entirely different method of obtaining light must be employed, which usually involves the use of an electric discharge in a tube partially filled with a specific gas. In spectrophotometers this gas is usually hydrogen, H_2, or deuterium, D_2. A diagram of such a gas-discharge tube is shown in Figure 12.15, along with a photograph a deuterium lamp. In this source electrons are "boiled" off the heated cathode and travel across the tube to the anode. Since several hundred volts are usually applied between the cathode and anode, these electrons can acquire a high energy before striking a gas molecule. Such a collision can result in excitation of the gas molecule.

$$e^- \text{ (high energy)} + H_2 \rightarrow H_2^* + e^- \text{ (lower energy)}$$

The excited gas molecule, represented by H_2^*, can then decay to the ground state or a lower excited state by emitting a photon of light, represented by $h\nu$.

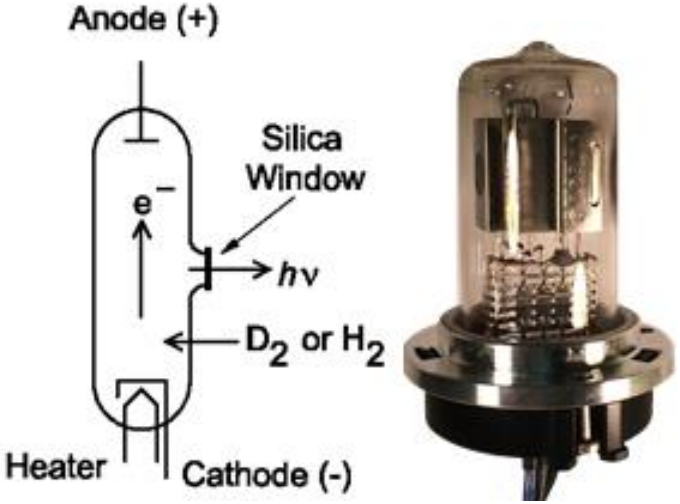


Figure 12.15: Schematic diagram of a hydrogen or deuterium gas discharge tube. Electrons emitted from the negatively charged cathode collide with gas molecules as they travel to the positively charged anode. Light is emitted from the excited state molecules.

$$H_2^* \rightarrow H_2 + h\nu$$

This emitted light can be of very high energy (low wavelength), depending on the gas used in the tube. Fluorescent lights work on the same principle, except that the gas used is mercury, not hydrogen, and the tube is coated with a substance (a phosphor) to convert the short wavelength ultraviolet light given off by the gas discharge to visible light.

Example 12.5: Light Sources

An electron traveling from the cathode to the anode in a hydrogen gas discharge tube has a velocity of 4.19×10^6 m/s when it strikes a hydrogen molecule. After the collision, its velocity is 3.88×10^6 m/s. How much energy was transferred to the hydrogen molecule? What wavelength of light will be emitted when the molecule returns to the ground state?

The electron has kinetic energy (= ½ mv^2) before and after the collision, but because its velocity is less afterwards, some of its energy must have been transferred to the hydrogen molecule. The difference in energy can be calculated using the mass of the electron (= 9.109×10^{-31} kg).

$$\Delta E = E_f - E_i = \tfrac{1}{2} m v_f^2 - \tfrac{1}{2} m v_i^2$$

$$= \frac{(9.109 \times 10^{-31}\ \text{kg})(3.88 \times 10^6\ \text{m/s})^2}{2} - \frac{(9.109 \times 10^{-31}\ \text{kg})(4.19 \times 10^6\ \text{m/s})^2}{2}$$

$$= (6.8\overline{57} \times 10^{-18}\ \text{J}) - (7.9\overline{96} \times 10^{-18}\ \text{J}) = -1.1\overline{39} \times 10^{-18}\ \text{J}$$

Therefore, the H_2 molecule absorbs 1.14×10^{-18} J of energy. When the molecule returns to the ground state, this energy will be released as a photon and the corresponding wavelength can be calculated.

$$E_{photon} = 1.1\bar{3}9 \times 10^{-18}\ \text{J} = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E_{photon}} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{1.1\bar{3}9 \times 10^{-18}\ \text{J}} = 1.74 \times 10^{-7}\ \text{m} = 174\ \text{nm}$$

Monochromator

Almost all light sources used in spectrophotometers emit polychromatic light. This is light that contains a broad range of wavelengths. While this is useful because we often don't know the wavelengths at which a sample absorbs, we usually want to measure the absorbance at a particular wavelength or as a function of wavelength (*i.e.* a spectrum). Moreover, Beer's Law makes the assumption that ε is constant, which is normally only true over a limited wavelength range. Therefore, for best results, the light used should be monochromatic (a single wavelength or a small range of wavelengths). The device that selects a "single" wavelength from polychromatic light is called a monochromator. There are several methods that can be employed to do this. A filter can be used to pass a certain colour (a small band of wavelengths). Filters are inexpensive, but usually pass a wide band of wavelengths and are inflexible since the band of wavelengths cannot be varied (the wavelength cannot be changed) except by changing the filter.

Prisms and diffraction gratings can be used to break white light into its individual wavelengths and then any one of these wavelengths can be selected. Modern instruments almost universally use diffraction gratings. These are mirrors with closely spaced fine lines scribed on them (about 1 μm separation), as shown in 12.16. Compact disks behave in a similar fashion to gratings, and show the effect of breaking white light into its components. A simplified diagram of a grating monochromator is shown in Figure 12.17. The position of the grating is varied to select the wavelength desired for the analysis. Like filters (and all monochromators), grating monochromators pass a band of wavelengths, but the band is much narrower in this case.

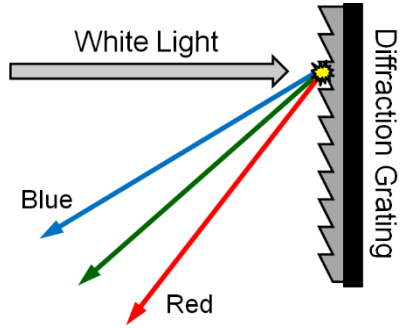


Figure 12.16: Dispersion of white light by a diffraction grating.

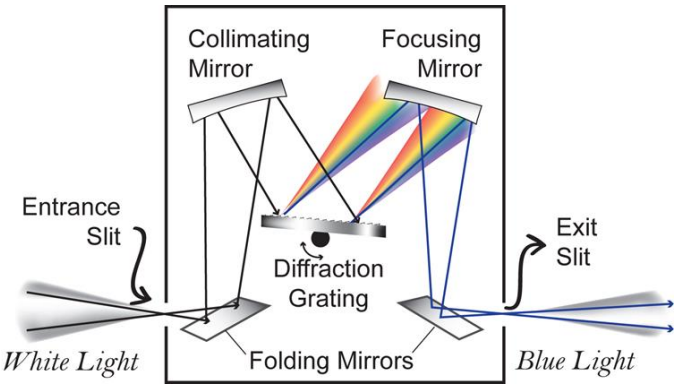


Figure 12.17: Schematic diagram of a grating monochromator. White light entering the device is dispersed by the ruled reflective grating into its individual wavelengths. The angle of the grating controls which wavelengths exit the monochromator.

Sample Cell

The sample cell is usually a square container (see Figure 12.12) made of glass or silica (SiO_2) with a path length of 1.00 cm. Glass, which contains materials that absorb light below 340 nm, is used in the visible and silica (or quartz), which transmits down to 190 nm, is used in the ultraviolet. Silica can also be used in the visible, but is much more expensive and therefore is usually only used when needed.

Some instruments use cylindrical flow cells that are never removed from the instrument. Such cells, shown diagrammatically in Figure 12.18, also normally have path lengths of 1.00 cm, but cells with longer or shorter path lengths are also common. There are certain advantages to the use of flow cells: (a) the cell is never moved and thus is not subject to errors caused by changes in its position, (b) only one cell is ever used, so matched cells are not necessary, (c) the cell is not handled and thus the windows do not get dirty (on the outside), and (d) the measurements can be done very rapidly since cells do not have to be manipulated. However, a pump must be available if a flow cell is used. Such flow cells are useful for monitoring solutions where analyte concentrations change over time and are employed for spectroscopic detectors in chromatography (discussed later).

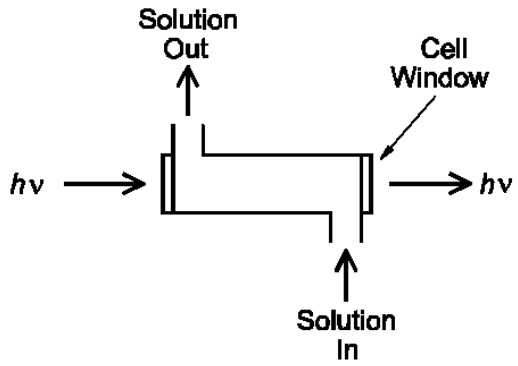


Figure 12.18: Diagram of a simple flow cell used for absorbance measurements.

Example 12.6: Path Length

A solution in a cell with a path length of 1.00 cm allows 34.3% of the light at 592 nm to pass through it. What percentage of the light would pass through the solution if it were placed in a cell with a path length of 10.0 cm?

Recall that Beer's Law tells us that the absorbance of a solution is proportional to the path length. Since 34.3% percent of the light passes through the cell, we know that $I/I_o = 0.343$. Therefore we can calculate the absorbance in the first cell.

$$A_1 = \log\left(\frac{I_o}{I}\right) = -\log\left(\frac{I}{I_o}\right) = -\log(0.343) = 0.465$$

Since absorbance is proportional to path length, we know that the absorbance in the second cell must be ten times greater. In mathematical terms,

$$\frac{A_2}{A_1} = \frac{\varepsilon b_2 c}{\varepsilon b_1 c} = \frac{b_2}{b_1} = \frac{10.0\,\text{cm}}{1.00\,\text{cm}} = 10.0 \quad \text{or} \quad A_2 = 10.0 \times A_1 = 4.65$$

Based on this, we can determine the percentage of light exiting the 10.0 cm cell by rearranging the first equation.

$$\left(\frac{I}{I_o}\right) = 10^{-A_2} = 10^{-4.65} = 2.2 \times 10^{-5}$$

Therefore, the percentage of light exiting the cell will be 0.0022%. (Note that, although there was only a 10-fold increase in the path length, the percentage of light transmitted decreased by more than a factor of 10,000.)

Detector

The light signal from the sample must be converted to an electronic signal (current or voltage) which can be displayed on a meter or recorded by a computer. There are several types of devices that accomplish this. Perhaps the simplest and oldest device, and one often used in simple spectrophotometers, is a vacuum photodiode, or phototube. This is simply an evacuated glass or silica container (depending on whether the light to be detected is visible or UV) which contains two electrodes (thus the name diode), as shown in Figure 12.19. The cathode or negative electrode is a large semicircular metal foil coated with a special material with a low work function, such as cesium metal. This means that electrons can be easily removed from this surface coating. A photon to be detected strikes the cathode and ejects an electron (providing the photon has enough energy to do this). This electron is attracted to the anode, which is usually a thin wire. Thus a current flows through the diode when light strikes the cathode. Since each photon produces an electron, the electric current is directly proportional to the light intensity striking the detector. Actually not every photon produces an electron, but a constant fraction of photons produces electrons, still maintaining the proportionality between intensity and current. This proportionality makes photometric measurements much simpler.

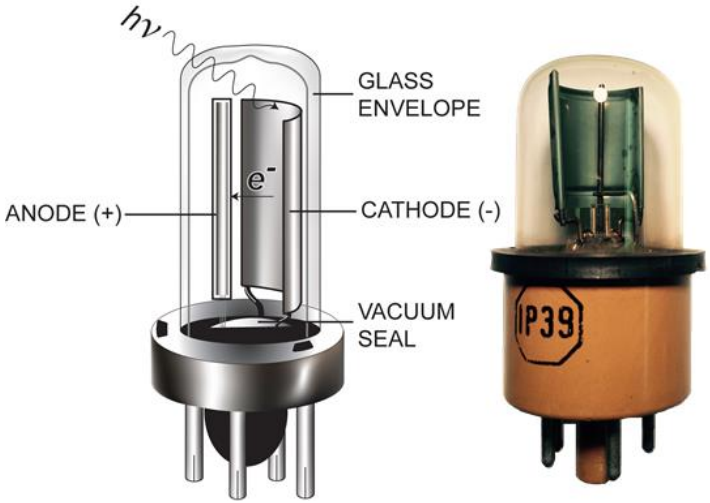


Figure 12.19: Schematic representation of a simple vacuum photodiode, or phototube, with a corresponding photograph Photons of light strike the surface of a metal releasing electrons by the photoelectric effect. The electrons travel to the positive anode, where the electrical current is proportional to the light intensity.

In recent times, many applications of the vacuum photodiode have been replaced by semiconductor photodiodes. A semiconductor diode passes electrical current in only one direction, and in a photodiode this is controlled by the amount of light striking the pn junction of the semiconductor, since photons will promote electrons from the valence band to the conduction band. Figure 12.20 shows the electronic symbol for a photodiode, along with a diagram of the device, which is about 1 cm in diameter. Because light has to enter the device, the top or side is made of a transparent material. Semiconductor photodiodes are smaller and more convenient than phototubes, and have replaced them in many applications, but phototubes have a larger responsive surface and enhanced sensitivity in the UV region. Other semiconductor devices (phototransistors, photoresistors) are also used for detection.

An advantage of the small size possible with a photodiode is that many such devices can be configured side-by-side in an electronic chip called a photodiode array, or PDA. The PDA can have several hundred photodiodes laid out in a package only a couple of centimeters in length. The top of the chip is transparent to allow light to enter, as shown at the right of Figure 12.21. An advantage of the PDA is that light from a diffraction grating can be dispersed directly on to the detector, as shown in Figure 12.21. This removes the need to scan the wavelength by rotating the angle of the diffraction grating and the entire spectrum can be obtained in a single reading, since each photodiode in the PDA will respond to a particular wavelength. The absence of moving parts greatly simplifies the design of the spectrophotometer and most instruments currently used for routine applications are based on this design. However, such instruments are more limited in the quality of measurements that they can make.

For high sensitivity measurements, which are needed when light levels are low, other types of detectors are also available. The most common of these is the photomultiplier tube, or PMT. However, for absorbance measurements, measurements are always made relative to a fairly intense light source (I_o), so high sensitivity is not normally required. Therefore, the discussion of PMTs will be deferred to the topic of molecular emission.

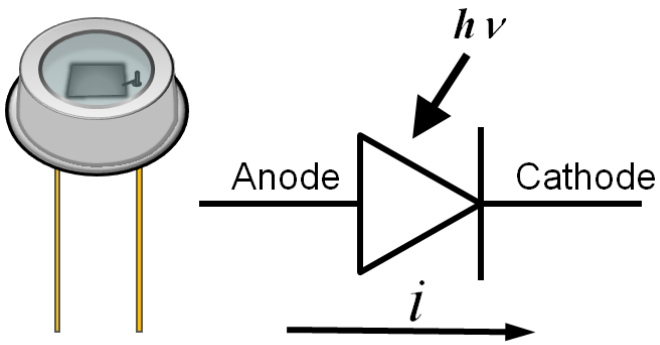


Figure 12.20: Diagram of a photodiode and its electronic symbol.

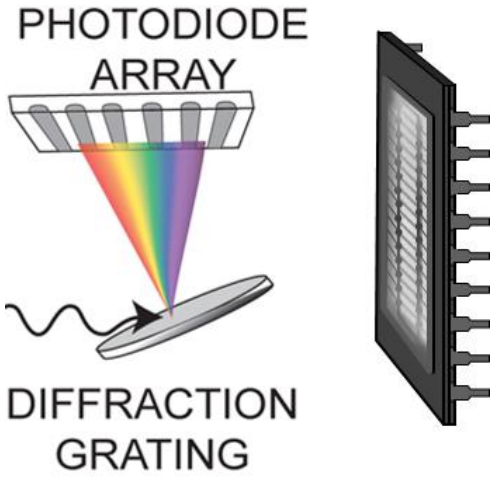


Figure 12.21: Diagram of a photodiode array chip (right) and the dispersion of a spectrum onto its surface by a diffraction grating.

Example 12.7: Detectors

The work function of a metal is the minimum amount of energy required to remove an electron from its surface. Cesium metal has a work function of 3.43×10^{-19} J. If blue light with a wavelength of 453 nm is directed at the surface of cesium metal, what would be the initial velocity of an electron liberated by one of the photons?

The energy of the photons striking the surface is easily calculated from the wavelength.

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{453 \times 10^{-9}\ \text{m}} = 4.39 \times 10^{-19}\ \text{J}$$

Part of this energy will be used to remove the electron from the surface, and the remainder will be transformed into the kinetic energy of that electron.

$$\text{Kinetic energy} = \tfrac{1}{2} mv^2 = \Delta E = (4.39 \times 10^{-19}\ \text{J}) - (3.43 \times 10^{-19}\ \text{J})$$
$$= 0.96 \times 10^{-19}\ \text{J}$$

Knowing the kinetic energy of the electron and its mass (9.109×10^{-31} kg), we can calculate its velocity.

$$v = \sqrt{\frac{2 \cdot \Delta E}{m}} = \sqrt{\frac{2(0.96 \times 10^{-19}\ \text{kg m}^2\text{s}^{-2})}{9.109 \times 10^{-31}\ \text{kg}}} = 4.6 \times 10^{5}\ \text{m s}^{-1}$$

Exercise 12.5

Based on the information in the previous example, what is the longest wavelength (in nm) that should be able to remove an electron from the surface of cesium metal? What colour is this light?

Amplifier and Meter

The signal emerges from the detector as an electrical current, but these currents are typically quite small, so measurement often requires that the signal be amplified. The amplifier is an electronic device that boosts the very small currents produced in the detector and makes them capable of being displayed on the various display devices used. The amplifier is characterized by a *gain*, which is the multiplier applied to the current from the detector. For example, an amplifier with a gain of 1000 will increase a current of 1 μA to 1 mA. Simple spectrometers may use a current or voltage meter to display the amplified current from the detector. Thus, the meter reading will be directly proportional to the light intensity exiting the cell. As long as the intensity of the light source does not vary with time, any changes in the meter reading will directly reflect changes in the absorption of light in the cell. In most commercial instruments, the meter is replaced by a computer that not only displays the measurement, but also converts it from an intensity to an absorbance, as described in the next section.

12.8 Spectrophotometric Measurements

Now that the instrument used to make spectrophotometric measurements has been examined, consideration must be given to how the measurements are made and what is being measured. It is obvious why the instrument contains a light source, sample compartment, detector, and amplifier. However, why is it necessary to have a monochromator? The probability that a photon will be absorbed, *P*, is a strong function of wavelength, λ. This gives rise to an absorption band that is usually bell shaped. There are wavelengths at which *P* is zero, $\lambda < \lambda_1$ and $\lambda > \lambda_2$ in Figure 12.22. Any light at these wavelengths which falls on the sample is not absorbed at all. *P* is maximum at λ_{max}, and thus absorbance is also maximum at λ_{max}. Thus, if white light is passed through the sample, much of the light will always be transmitted, and the sensitivity will be low. Sensitivity will be maximum if light only at λ_{max} is selected and passed through the sample cell. For this reason, and others to be discussed later, the monochromator is an essential part of the spectrophotometer.

The first step in the use of a spectrophotometer is to set the wavelength selected by the monochromator to λ_{max}. The next step is to properly zero the instrument. One might expect

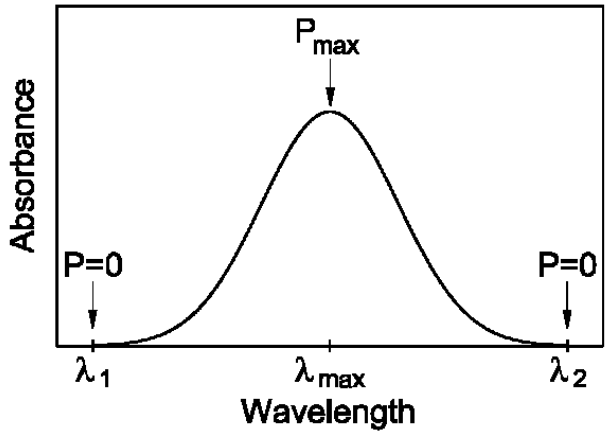


Figure 12.22: For molecules in solution, the probability that a photon will be absorbed varies with the wavelength and the species in solution. The wavelength at which the probability is highest (and absorbance is maximized) is designated as λ_{max}.

that if the light beam were completely blocked, that the meter would read zero (no photons, no detector current). Unfortunately, a small current still flows in the detector circuit even with no light falling on the detector. This current is called the *dark current*. It must be balanced out, so many instruments have a control associated with the amplifier, called the *dark current control*, or *zero*, that adjusts the meter to zero when the light beam is totally blocked. Thus, after adjusting the monochromator, the light beam is blocked and the meter set to zero.

The next step is to place a cell in the light path (with the light beam on). This cell should contain everything in the sample solution *except* the analyte and is called the blank. Under these conditions, for example, say that the meter reads 78.6. Note that the instrument reading is proportional to light intensity. Thus, it can be stated that I_o is equivalent to a reading of 78.6. Why is the blank necessary? Why not just leave the cell out of the beam when establishing I_o? There are two reasons for this:

1) The sample may contain a material that absorbs light in addition to the unknown. If this same material is in the blank, then its absorbance is cancelled out and only the unknown absorbance is measured.
2) The sample cuvette itself reflects a small amount of light (5 to 10%), as shown in Figures 12.15 and 12.16, and this must be compensated.

Referring to Figure 12.23, the light exiting the monochromator is I_o' and that exiting the cuvette is I'. However, the light incident on the sample solution is I_o and that leaving the solution is *I*. I_o is less than I_o' and I' is less than *I* because of reflections at the walls of the cuvette. The true absorbance of the solution is $\log(I_o/I)$. However, if measurements were made without a blank solution, I_o' and I' would be the intensities measured and absorbance would be calculated as $\log(I_o'/I')$, resulting in an error in which the measured absorbance was always greater than the true absorbance.

Referring to Figure 12.24, when a blank is placed in the light beam, the light exiting the sample cell is I_o''. This is taken to represent the light striking the sample solution, and the light exiting the cell when it contains the sample, I', (Figure 12.23) is taken to represent the light exiting the solution. Thus absorbance is calculated as $\log(I_o''/I')$. This does not strictly

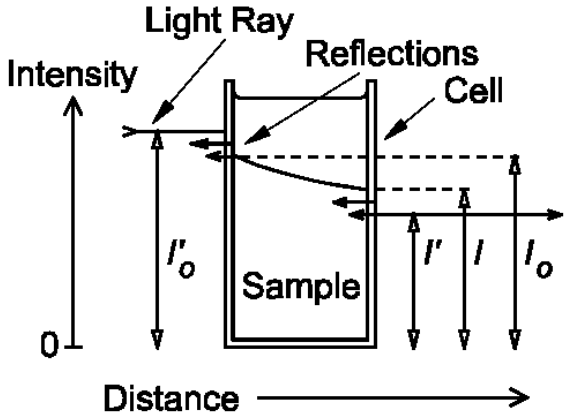


Figure 12.23: Light intensity as it passes through an absorbing sample in a cell. Part of the incident light is reflected at the glass/air interface and the glass/solution interfaces, reducing the amount of light entering and leaving the solution.

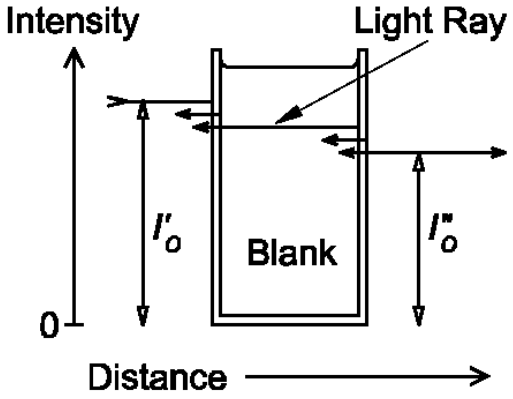


Figure 12.24: Light intensity as it passes through a non-absorbing blank solution.

measure I_o and I, but since $I_o''/I' = I_o/I$, the ratio is correct, and thus the absorbance calculated is also correct. In this way the reflectance of the sample cell is corrected.

The final step in the measurement is to place a cell containing the unknown in the instrument and take a reading. Say that this reading is 35.4. Thus intensity I is equivalent to 35.4. Absorbance can now be calculated.

$$A = \log\left(\frac{I_o}{I}\right) = \log\left(\frac{78.6}{35.4}\right) = 0.346$$

Note that this simple instrument does not read directly in absorbance, it provides two intensities which must be combined to give absorbance. The ratio I/I_o is called the *transmittance* and given the symbol T. Thus

$$T = \frac{I}{I_o} \quad \text{(normally less than unity)} \tag{12.15}$$

and $$A = \log\left(\frac{I_o}{I}\right) = -\log\left(\frac{I}{I_o}\right) = -\log(T) \tag{12.16}$$

The normal procedure with spectrophotometers is to employ a meter that has 100 scale divisions. A second control, which changes the amplification factor of the amplifier, is used when the blank is placed in the instrument to adjust the meter to read full scale (100). Thus, in the example above with the blank in place, the meter is adjusted from 78.6 to 100 with the *100 %T* control. This would cause the sample to read 45.0 instead of 35.4, since the increase in gain would affect both measurements equally. This does not affect either A or T, since

$$T = \frac{35.4}{78.6} = \frac{45.0}{100.} = 0.450$$

It is now convenient to introduce the concept of *percent transmittance*.

$$\%T = 100 \times T = 100 \times \frac{I}{I_o} \tag{12.17}$$

In the example above, the %*T* is 45.0. Note that by adjusting the blank reading to 100, the sample reading (45.0) will automatically be in %*T*. Thus, when set up in the fashion described above, the instrument directly reads the percentage of light transmitted through the sample as compared to the blank. The absorbance is easily calculated from %*T* as follows:

$$A = \log\left(\frac{I_o}{I}\right) = \log\left(\frac{100}{\%T}\right) = 2 - \log(\%T) \qquad (12.18)$$

Many simple spectrophotometers have meters with both *A* and %*T* scales. Since the *A* scale is nonlinear, it is best to measure %*T* from the linear scale and convert mathematically to *A*. Modern instruments often contain computers that calculate absorbance and that perform some of the manual operations described above automatically without operator intervention.

Example 12.8: Transmittance and Absorbance

Imagine that you are making measurements on a simple spectrometer without 0 %T or 100 %T adjustments. With the light beam blocked, the reading is 7.2, while a blank solution gives a reading of 98.8 and a sample solution gives a reading of 36.7. Determine the transmittance, percent transmittance, and absorbance of the sample.

The transmittance is the ratio of the intensity of the light observed for the sample to that observed for the blank, but both of these need to be adjusted for the dark current (when the beam is blocked).

$$T = \frac{I}{I_o} = \frac{36.7 - 7.2}{98.8 - 7.2} = \frac{29.5}{91.6} = 0.322$$

The %*T* is simply 100 times this value, or 32.2%. The absorbance is now calculated as

$$A = -\log(T) = -\log(0.322) = 0.492$$

or $$A = 2 - \log(\%T) = 2 - \log(32.2) = 2.000 - 1.508 = 0.492$$

Exercise 12.6
Would the absorbance calculated in the previous example be higher or lower if the contribution of the dark current were ignored?

Exercise 12.7
What percentage of light passes through a sample cell that has an absorbance of 3.00?

Example 12.9: Transmission of Light through a Cell
With reference to Figures 12.23 and 12.24, imagine you have a spectrometer in which the light intensity incident on the cell, I_o', is exactly 100. The blank solution absorbs no light, and the sample solution has an absorbance exactly equal to 1. Each of the four interfaces (air/glass, glass/solution, solution/glass, glass/air) reflects exactly 2% of the light falling on it. Determine the intensity of light entering the solution (I_o), the intensity of light exiting the cell for the blank (I_o''), the intensity of light exiting the cell for the sample (I'), and the absorbance determined from the last two values.

For the blank solution, 2% of the light will be lost at each interface, or 98% of the light will pass through each interface. Since the light must pass through two interfaces (air/glass, glass/solution) before reaching the solution, the intensity of light reaching the solution will be

$$I_o = 100 \times (0.98) \times (0.98) = 96.04$$

(Note that the values are considered exact, so significant figures are not considered.) Since the blank solution does not absorb any of the light, the same intensity reaches the far side of the cell. The same percentage loss occurs at the two interfaces leaving the cell, so the intensity of light leaving the cell is

$$I_o'' = 96.04 \times (0.98) \times (0.98) = 92.2368$$

For the sample solution, only 10% of the light is transmitted through the solution, since the absorbance is unity and $I/I_o = 10^{-A} = 0.1$. Therefore, the light intensity after passing through the solution will be

$$I = I_o \times 10^{-A} = 96.04 \times (0.1) = 9.604$$

Finally, this light must pass through two interfaces, each with 2% loss, before exiting the cell, so

$$I' = 9.604 \times (0.98) \times (0.98) = 9.22368$$

Based on the observed measurements, the measured absorbance is

$$A = \log\left(\frac{I_o''}{I'}\right) = \log\left(\frac{92.2368}{9.22368}\right) = \log(10) = 1$$

Note that the measured absorbance is exactly the same as the value given and the same as would have been calculated with the true values of I_o (96.04) and I (9.604). Therefore, measurement of the blank is able to account for reflected light.

12.9 Deviations from Beer's Law

Beer's Law, $A = \varepsilon bc$, indicates that the absorbance of a solution is directly proportional to the concentration of a species in solution. Because of this, it can be used indirectly to make methods measurements of concentration by a variety of methods that will be discussed in the next section. While the assumption of linearity (*i.e.* absorbance is directly proportional to concentration) is valid under the ideal conditions assumed in the derivation of Beer's Law, a variety of practical considerations can cause deviations from this ideal linear behaviour. This section examines some of the conditions under which these deviations can occur.

Physical Deviations

One source of deviations from Beer's Law relate to the physics of the interaction of light and matter. Changes in conditions that affect the optics of light measurement can make the linear relationship between concentration and absorbance invalid.

Perhaps the most common example of this is a change in the refractive index of solution. Refractive index is related to the speed of light in a medium, and also influences how much light is reflected when light passes from one medium to another. The greater the difference is in refractive index between two interfaces, then the greater the proportion of light that will be reflected. With reference to Figures 12.23 and 12.24, if there is a change in the refractive index between the blank and the sample, this can change the amount of light reflected at the interfaces and lead to apparent deviations from Beer's Law. In principle, this could happen because refractive index increases with solute concentration, but in practice, the typically low concentrations used in absorbance measurements do not affect refractive index significantly. More likely, refractive index changes would arise from changes in the medium, for example, using distilled water for the blank and measuring the sample in salt water or concentrated acid. For this reason, it is important that the blank matches future samples.

Another potential source of error is the presence of scattering particles in solution, which will obstruct the transmission of light at all wavelengths. In fact, similar measurements are often used to measure the concentration of particulate matter in solution, but the term *optical density* or *turbidity* is normally used in place of absorbance (since the light is scattered and not absorbed), and the term *extinction coefficient* is used in place of molar absorptivity. These methods will not be discussed further here.

Exercise 12.8

Referring to Example 12.9, imagine that the situation was exactly the same except that, for the *sample* solution, the reflected light at the two glass/solution interfaces was 4% due to a higher refractive index in the sample (the reference is exactly the same as in the example). What would be the value of the *measured* absorbance in this case? (Note that the *actual* absorbance of the solution does not change.)

Chemical Deviations

Chemical deviations are those effects that lead to apparent deviations from Beer's Law due to chemical reactions occurring in solution. These occur when the coloured species is involved in a chemical equilibrium that is affected by its concentration and which is unknown to the analyst. An example is probably the best way to illustrate this effect.

Assume that a weak base, B, dissolved in solution is coloured, but its conjugate acid is colourless (the conjugate base of phenolphthalein is an example of this). In principle, the formality of base present in solution could be determined spectrophotometrically. Also assume that $\varepsilon = 10^3\ M^{-1}\ cm^{-1}$, $b = 1$ cm, $K_b = 1\text{x}10^{-5}$, and that the solution is unbuffered. The chemical equilibrium that causes the apparent deviation from Beer's law is

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

The only coloured species in this equilibrium is B. If one can assume that $[OH^-] \gg [H_3O^+]$, then it can be shown that

$$[B] = F_b - [OH^-] \qquad \text{and} \qquad [OH^-] = \frac{-K_b + \sqrt{K_b^2 + 4K_bF_b}}{2}$$

With these equations and Beer's Law, Table 12.3 can be created, providing concentrations and absorbances for different formalities of the base.

Table 12.3. Concentration and absorbance predicted for a hypothetical weak base ($pK_b = 5$) at various formalities. Data are plotted in Figure 12.25.

Formality of base (F)	[B] (M)	Absorbance	Slope ($\Delta A/\Delta F$) (F^{-1})
$1.00\text{x}10^{-4}$	$0.73\text{x}10^{-4}$	0.073	844
$2.00\text{x}10^{-4}$	$1.60\text{x}10^{-4}$	0.160	889
$4.00\text{x}10^{-4}$	$3.42\text{x}10^{-4}$	0.342	921
$7.00\text{x}10^{-4}$	$6.21\text{x}10^{-4}$	0.621	940
$10.00\text{x}10^{-4}$	$9.05\text{x}10^{-4}$	0.905	950
$12.00\text{x}10^{-4}$	$10.95\text{x}10^{-4}$	1.095	954

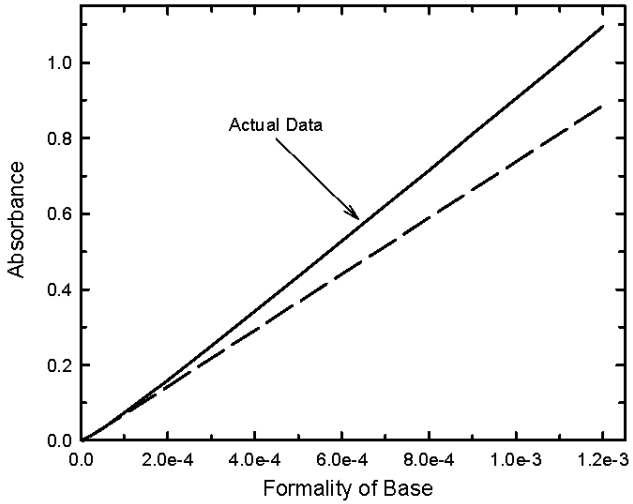


Figure 12.25: Plot of the absorbance of a hypothetical coloured weak base as a function of its formality (solid line). Some data are given in Table 12.3. The dashed line is a linear extrapolation of the data near the intercept. Note the non-linearity and positive deviations at higher base concentrations.

If the analyst were unaware of the chemical equilibrium involved, she/he would assume that [B] was equal to formality and would plot absorbance *vs* formality rather than absorbance *vs*. [B] (which would be unknown). Such a plot is shown in Figure 12.25. In this plot the actual data are represented by a solid line and the tangent to the data at the intercept by a dashed line. Absorbance increases more rapidly than formality (on a relative basis) and the plot is not linear, thus seeming to indicate that Beer's law is not obeyed. Since the slope increases with increasing formality (see Table 12.3) this type of behaviour produces a positive deviation from Beer's law. This positive deviation is due to the fact that the percent dissociation of the base decreases with increasing concentration, meaning that the relative amount of B to BH^+ is increasing as the formality increases. Positive deviations are normally due to chemical problems.

It should be noted that this is only an *apparent* deviation of Beer's Law arising from the assumption that [B] = F_b, since a plot of absorbance *vs* [B] would have been linear. In practice, [B] is normally unknown (unless K_b is known), but Beer's Law provides a way to measure [B] directly if its molar absorptivity can be determined. This can be done by measuring the absorbance in a strong base, where all of the base should be present in its unprotonated form.

When investigating a spectrophotometric method for the first time, the chemist should always be very careful to determine whether any "chemical deviations" from Beer's law are observed. One way to solve the problem of chemical deviations in solutions of weak acids or weak bases is to use a buffer, which forces the ratio of the acid to base to remain constant.

Exercise 12.9

Suppose that, instead of a weak base, the solution measured was a weak acid in which the acid form was coloured and the conjugate base was colourless. Would the deviations from Beer's Law still be positive, as in the discussion above? Explain.

Instrumental Deviations

Deviations from Beer's Law can also arise from the physical limitations of the instrumentation used. There are two major types of such apparent deviations from Beer's Law, (1) those due

to the inability of the monochromator to provide light of a single wavelength, and (2) those due to stray light in the monochromator. These are discussed in more detail below.

With regard to the monochromaticity of light, recall that the probability of photon absorption, *P*, and consequently the molar absorptivity, ε, are a functions of λ. Beer's Law was derived assuming that P was constant, thus Beer's Law is strictly valid for only a single wavelength of light. If the monochromator produced only a single wavelength, there would be no problem. However, no monochromator, no matter how good, can produce only a single wavelength, and the ones used in simple spectrophotometers usually produce a fairly broad band of wavelengths, ranging from a width of 10 to 20 nm at half the band maximum.

This situation is depicted in Figure 12.26, where molar absorptivity, ε, and intensity of light from the monochromator, *I*, are both plotted on the *y*-axis. The band of light from the monochromator is represented as triangular in shape, a reasonable approximation to the actual behaviour. The wavelength value set on the instrument is the wavelength at the peak of the triangle and the bandwidth listed by the manufacturer is the width of the triangle at half the peak height. At wavelength one, the molar absorptivity does not change rapidly with wavelength and the fact that the monochromator produces a small band of wavelengths causes no problem, since the molar absorptivity is approximately the same for all wavelengths exiting the monochromator. This is normally the case at the band maximum. However, at wavelength two, ε varies considerably with λ, and Beer's Law will not be obeyed. This type of deviation from Beer's law will always produce negative deviations, as depicted in Figure 12.27.

Thus there are several advantages to setting the monochromator at the wavelength of maximum absorption - it gives maximum sensitivity and best adherence to Beer's Law, and small variations in the setting from day to day will have a minimum effect.

The second major source of deviations from Beer's Law is stray light. In the case just discussed above, it was pointed out that a monochromator produces not just a single wavelength, but a band of adjacent wavelengths. This is an inherent limitation of monochromators and cannot be avoided. Monochromators also pass some light that is not in this narrow band, and may be far outside the band. This light "should not be there" and could, in theory, be eliminated by careful design. This type of light is called stray light. It causes the same sort of problem as mentioned above, but usually to a larger extent.

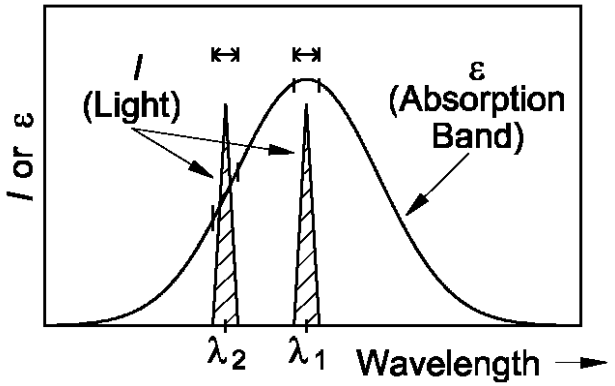


Figure 12.26: Comparison of the absorbance spectrum of a typical solution with the range of light passed by a simple monochromator. At λ_1, which corresponds to λ_{max} for the solution, there is little variation in the molar absorptivity over the range of wavelengths passed by the monochromator. At λ_2, however, ε changes significantly, leading to deviations from Beer's Law.

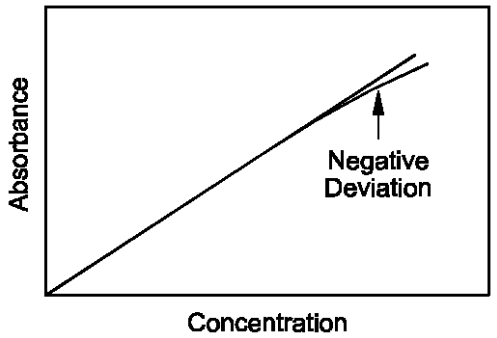


Figure 12.27: Illustration of negative deviations from Beer's Law brought about by non-monochromatic light and stray light.

For example, assume that the monochromator passes 1% stray light at wavelengths that are not absorbed by the sample at all. Thus 1% of the total light will always come through the solution, no matter how concentrated the sample, and the maximum absorbance that can be measured will be $A_{max} = \log(100/1) = 2.00$, regardless of concentration. This also produces a negative deviation from Beer's Law. Stray light usually causes deviations to appear above absorbances of between 1 and 1.5 for inexpensive instruments and is one reason that attempts are made to keep measurements below absorbances of one.

Example 12.10: Stray Light

Imagine a spectrophotometer in which the stray light is 1% of the incident intensity coming from the source at a particular wavelength, and the stray light is not absorbed by the sample. If the apparent absorbance of the sample is 1.000, what is the true absorbance and the percent error in the measured value?

It is perhaps easiest to choose some arbitrary values for the intensities. If we set the observed incident intensity to $I_o^{obs} = 100.0$, then the true incident intensity will be $I_o^{true} = 99.0$, since 1% of the light is stray light and won't be absorbed by the sample. For a solution with an absorbance of $A_{obs} = 1.000$, we know

$$\frac{I^{obs}}{I_o^{obs}} = 10^{-A_{obs}} = 10^{-1.000} = 0.100 \quad \text{or} \quad I^{obs} = (0.100)\, I_o^{obs} = 10.0$$

Since the intensity of stray light is 1.0, we can calculate $I^{true} = I^{obs} - 1.0 = 9.0$. Therefore, the true absorbance can be calculated as

$$A_{true} = -\log\left(\frac{I^{true}}{I_o^{true}}\right) = -\log\left(\frac{9.0}{99.0}\right) = 1.04$$

This gives a percentage error of

$$\%\,\text{error} = \frac{A_{obs} - A_{true}}{A_{true}} \times 100\% = \frac{1.00 - 1.04}{1.04} \times 100\% = -4\%$$

Exercise 12.10
For the conditions given in the preceding example, determine the true absorbance and the percent error for observed absorbance values of 0.500 and 1.500. Where do the largest errors occur?

12.10 Spectrophotometry in Quantitative Analysis

One of the principal uses of Beer's Law is for the indirect measurement of the concentrations of analytes. It applies not only to solutes in liquid solution, but also, for example, to the concentrations of molecules in the atmosphere and (as we will see) atoms in a flame. A variety of techniques can be used, but most rely on the linear relationship between the absorbance and the concentration expressed by Beer's Law. These methods include absolute measurements, calibration, standard addition, multiwavelength methods, and spectrophotometric titrations.

Absolute Method

The simplest method for quantitative analysis would be to assume that Beer's law is valid, measure the percent transmittance (%T), convert it to absorbance (A), look up the value of the molar absorptivity, ε, in a table, and calculate concentration as

$$c = \frac{A}{\varepsilon b} \tag{12.19}$$

This is known as the "absolute" method.

Example 12.11: Absolute Method of Quantitative Analysis
The molar absorptivity of a Lewis base complex of Cu(II) is 24,300 M^{-1} cm^{-1}. When 25.0 mL of sample are mixed with 25.0 mL of the complexing reagent (an excess), the %T of the resulting solution is measured as 46.8% in a 1.00 cm cuvette. What is the copper concentration in the original sample?

The absorbance is first calculated and then used to calculate the concentration of the copper complex in the diluted sample.

$$A = -\log(T) = -\log(0.468) = 0.330$$

$$c_{dil} = \frac{A}{\varepsilon b} = \frac{0.330}{(2.43\times10^{4}\ \mathrm{M^{-1}cm^{-1}})(1.00\,\mathrm{cm})} = 1.3\overline{57}\times10^{-5}\ \mathrm{M}$$

This is the concentration in the diluted solution. For the original sample,

$$c_{orig} = c_{dil}\cdot\frac{V_{dil}}{V_{orig}} = 1.3\overline{57}\times10^{-5}\ \mathrm{M}\cdot\frac{50.0\,\mathrm{mL}}{25.0\,\mathrm{mL}} = 2.71\times10^{-5}\ \mathrm{M}$$

This method is almost never used. There are several reasons for this: (a) there may be no published value of ε, (b) there may be some doubt about the "accuracy" of the published value of ε, (c) the conditions employed when the %T of the unknown is determined may not have been the same as those used when ε was measured, and (d) Beer's Law may not be strictly valid under the conditions used in the experiment (as discussed in the previous section).

Use of a Calibration Curve

Since Beer's law cannot always be trusted, one normally prepares a calibration curve with a set of standards which are as similar to the unknown as possible. The first point on this curve ($A = 0$ at $c = 0$) is determined by the blank. This solution normally contains all reagents used in the analysis but no analyte, and is not simply distilled water. The remaining points are determined from the standards containing known concentrations of analyte, and the unknown is determined from the calibration plot.

Generally, linearity of the calibration curve is assumed. This means that calibration can be carried out with only one standard solution (to estimate the slope, assuming the intercept is zero), or two standard solutions (to estimate the slope and intercept). Usually, multiple calibration standards are strongly preferred, however, since they improve the estimation of calibration parameters and allow the detection of nonlinear deviations from Beer's Law. In fact, multipoint calibration curves can be used to estimate concentrations even when mild nonlinearity is present, as shown in Figure 12.28.

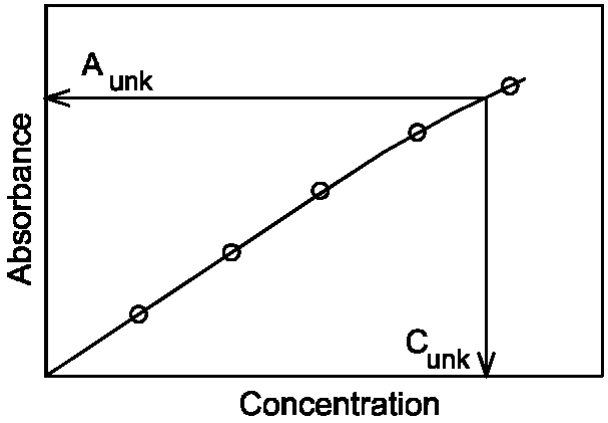


Figure 12.28: A calibration curve with a small amount of nonlinearity. Such curves can still be used to determine the concentration of analyte, as shown, but enough points must be obtained to ensure the nonlinearity is real.

Example 12.12: Absorbance Calibration Curve

A set of standards containing 2.00, 4.00, 6.00, and 8.00x10^{-5} M Co(II) and a colour forming reagent gave a set of absorbance data which, when fit by the method of linear least squares, produced the following values for the calibration curve: slope = 1.344x10^{4} M^{-1}, intercept = 0.0015. If a sample produces an absorbance reading of 0.337, what is the concentration of Co(II) in the sample?

The calibration curve has the form

$$A = 0.0015 + (1.344 \times 10^4\ \text{M}^{-1}) \cdot c$$

or

$$c = \frac{A - 0.0015}{1.344 \times 10^4\ \text{M}^{-1}} = \frac{0.337 - 0.0015}{1.344 \times 10^4\ \text{M}^{-1}} = \frac{0.33\overline{5}5}{1.344 \times 10^4\ \text{M}^{-1}} = 2.50 \times 10^{-5}\ \text{M}$$

In theory the intercept above should be zero. However, indeterminate error in the data points usually gives rise to a small intercept.

Standard addition

The method of standard addition, as explained in topic on Instrumental Methods, can also be employed in spectrophotometry. It is especially useful in cases where certain matrix effects are an important consideration. It should be kept in mind that this method requires that the instrumental response be linear in analyte concentration. Thus Beer's law must be obeyed if standard addition is to be used.

Example 12.13: Standard Addition and Absorbance

The absorbance of a solution containing an unknown amount of Cu(II) and an excess of sodium diethyldithiocarbamate (a colour-forming reagent) is measured as 0.395. A 1.00 mL aliquot of a 5.00 ppm Cu(II) standard is added to 10.00 mL of the sample. The absorbance of this solution is measured as 0.486. What is the Cu(II) concentration (in ppm) in the sample?

Using the information given, we can set up the equations for the two absorbance values assuming that Beer's Law applies.

$$0.395 = \varepsilon b c_u \qquad 0.486 = \varepsilon b\left(\frac{10.00\,\text{mL}}{11.00\,\text{mL}}\cdot c_u + \frac{1.00\,\text{mL}}{11.00\,\text{mL}}\cdot 5.00\,\text{ppm}\right)$$

These can now be solved for c_u by taking the ratio of the second to the first and rearranging.

$$\frac{0.486}{0.395} = \frac{10.00}{11.00} + \frac{5.00\,\text{ppm}}{11.0\,c_u}$$

$$c_u = \left(\frac{5.00\,\text{ppm}}{11.0}\right)\Big/\left(\frac{0.486}{0.395} - \frac{10.00}{11.00}\right) = \frac{0.45\overline{4}5\,\text{ppm}}{(1.2\overline{3}0 - 0.9091)} = \frac{0.45\overline{4}5\,\text{ppm}}{0.3\overline{2}1} = 1.4\ \text{ppm}$$

Exercise 12.11

Phenolphthalein is not only an acid-base indicator, but was also widely used as a laxative until it was suspected to be a carcinogen in high concentrations. In a study on the metabolism of this compound, the phenolphthalein in a 10.00 mL urine sample was extracted into a basic buffer and the percent transmittance at 550 nm was found to be 33.3%. In a separate experiment 1.00 mL of 100. μM phenolphthalein was added to 9.00 mL of the urine, extracted and measured in the same way, with a reading of 18.9%. Determine the concentration of phenolphthalein in the urine.

Multiwavelength Analysis

So far, all of the methods have assumed that the analyte is the only absorbing species in solution. What happens when a solution contains more than one coloured analyte? If the absorption bands of the analytes do not overlap (interfere), then each can be analyzed individually from separate calibration curves as if the other analytes were not present. If a background colour exists in the sample which can be duplicated in the blank, then this

background subtracts out and does not affect the measurement. However, if two or more analytes with overlapping spectra exist in the sample, the situation becomes more complicated.

Individual absorbances are additive and, if Beer's law holds, the problem is readily solved. For a multicomponent mixture (containing components X, Y, *etc.*)

$$A = \log\left(\frac{I_0}{I}\right) = A_X + A_Y + \ldots = \varepsilon_X b c_X + \varepsilon_Y b c_Y + \ldots \quad (12.20)$$

Here A_X and A_Y are the absorbances of analytes X and Y; ε_X and ε_Y are the corresponding molar absorptivities at the wavelength used; and c_X and c_Y are the analyte concentrations.

The individual spectra of a two component mixture and the combined spectrum of the two are shown in Figure 12.29. It is only the combined spectrum that can be measured by the spectrophotometer. One must choose as many wavelengths for measurements as there are analytes in the mixture. These wavelengths are chosen such that the contribution to the absorbance from one component at a particular wavelength is large while the contributions from the other components are small. For a two component mixture, measurements must be made at two different wavelengths. In this case one might choose λ_1 and λ_2 as shown in Figure 12.29. The molar absorptivities for all the different components must be known at all measurement wavelengths. For a two component mixture ε_{1X}, ε_{1Y}, ε_{2X}, and ε_{2Y} must be known. Then the solution absorbances are measured at all selected wavelengths and a set of simultaneous, linear equations is set up and solved for the analyte concentrations. There will be as many equations as there are measurement wavelengths and analytes. For a two component mixture

$$A_1 = \varepsilon_{1X} b [\mathrm{X}] + \varepsilon_{1Y} b [\mathrm{Y}] \quad \text{at } \lambda_1 \quad (12.21)$$

$$A_2 = \varepsilon_{2X} b [\mathrm{X}] + \varepsilon_{2Y} b [\mathrm{Y}] \quad \text{at } \lambda_2 \quad (12.22)$$

The above equations are solved for [X] and [Y]. Note that Beer's Law must be valid in order to get correct results from this method.

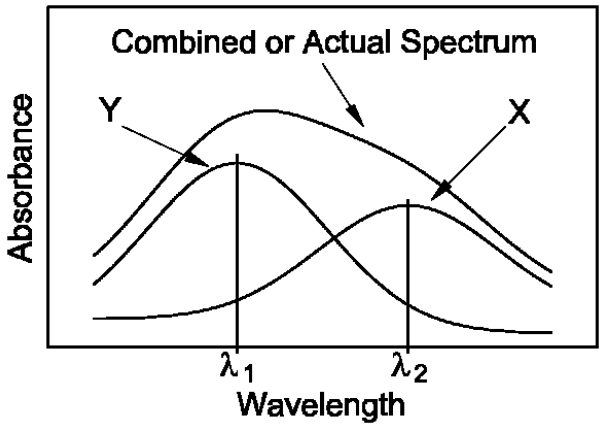


Figure 12.29: Spectra of individual components, X and Y, in a two-component mixture, and the combined spectrum observed by the spectrophotometer. The λ_{max} values of each component are given by λ_1 and λ_2 and would be good choices for a two-wavelength analysis.

Example 12.14: Multiwavelength Analysis

The following data are available: for substance M, $\varepsilon_1 = 3.00\text{x}10^3$, $\varepsilon_2 = 1.00\text{x}10^4$, and for substance N, $\varepsilon_1 = 1.20\text{x}10^4$ and $\varepsilon_2 = 4.00\text{x}10^3$ (all dimensions are $M^{-1}\ cm^{-1}$). The %T values of a mixture of M and N are 10.0% and 18.3% at λ_1 and λ_2, respectively. What are the concentrations of M and N in the sample, assuming a cell path length of 1.00 cm?

First we determine the absorbance values at the two wavelengths.

$$A_1 = -\log(0.100) = 1.000 \quad \text{at } \lambda_1$$

$$A_2 = -\log(0.183) = 0.73\overline{7}5 \quad \text{at } \lambda_2$$

Simultaneous equations can now be set up for each absorbance.

(1)
$$\begin{aligned} 1.000 &= (3.00\times10^3)(1.00)[\text{M}] + (1.20\times10^4)(1.00)[\text{N}] \\ &= 30\overline{0}0\,[\text{M}] + 12\overline{0}00\,[\text{N}] \end{aligned}$$

(2)
$$\begin{aligned} 0.73\overline{7}5 &= (1.00\times10^4)(1.00)[\text{M}] + (4.00\times10^3)(1.00)[\text{N}] \\ &= 10\overline{0}00\,[\text{M}] + 40\overline{0}0\,[\text{N}] \end{aligned}$$

Now we solve the simultaneous equations. From equation (2), we obtain,

$$[\text{M}] = \frac{0.73\overline{7}5 - 40\overline{0}0\,[\text{N}]}{10\overline{0}00} = 7.3\overline{7}5\times10^{-5} - 0.400\,[\text{N}]$$

Substituting this into equation (1) gives

$$\begin{aligned} 1.000 &= 30\overline{0}0\cdot(7.3\overline{7}5\times10^{-5} - 0.400\,[\text{N}]) + 12\overline{0}00\,[\text{N}] \\ &= 0.22\overline{1}3 + (12\overline{0}00 - 12\overline{0}0)[\text{N}] \\ &= 0.22\overline{1}3 + 10\overline{8}00\,[\text{N}] \end{aligned}$$

$$[\text{N}] = \frac{1.000 - 0.22\overline{1}3}{10\overline{8}00} = \frac{0.77\overline{8}7}{10\overline{8}00} = 7.2\overline{1}0\times10^{-5}\ \text{M}$$

Substituting this result back into equation (2) leads to

$$0.73\overline{7}5 = 10\overline{0}00\,[\mathrm{M}] + (40\overline{0}0)(7.2\overline{1}0\times10^{-5})$$
$$= 10\overline{0}00\,[\mathrm{M}] + 0.28\overline{8}4$$
$$[\mathrm{M}] = \frac{0.73\overline{7}5 - 0.28\overline{8}4}{10\overline{0}00} = \frac{0.44\overline{9}1}{10\overline{0}00} = 4.4\overline{9}1\times10^{-5}\ \mathrm{M}$$

Therefore, [M] = 44.9 μM and [N] = 72.1 μM.

Exercise 12.12

Co(II) and Cr(III) form coloured complexes in nitric acid. At 500 nm, the molar absorptivities of the complexes are 1.85x10^3 and 9.90x10^3 M^{-1} cm^{-1} for Co(II) and Cr(III), respectively, and at 600 nm, the values are 5.25x10^3 and 1.95x10^3 M^{-1} cm^{-1}. An unknown mixture of the two ions in nitric acid gives an absorbance of 0.456 at 500 nm and 0.426 at 600 nm. Determine the concentrations of the two ions in the unknown mixture.

Spectrophotometric Titrations

Any instrument that responds to concentration can be used to follow a titration, and spectrophotometers are no exception. These can be used in two ways. In the first one would add a coloured indicator and follow the indicator colour change with the instrument. In this case, the instrument substitutes for the eye in detecting the rapid change in colour at the end point. This method is useful in automated titrations. Since the theory is much the same for visual observation and instrumental observation, this will be discussed no further.

The second method is to use a spectrophotometer to follow a titration in which one or more of the reagents is coloured. An apparatus for carrying out such measurements is shown in Figure 12.30. In this case no indicator is added or needed. Since $A = \varepsilon bc$ (assuming Beer's Law is valid), the calculated response is linear in concentration. This gives rise to a type of titration referred to as a *linear titration*. These are quite general and are observed with many instrumental techniques. Here spectrophotometry will be used as an example of such a titration.

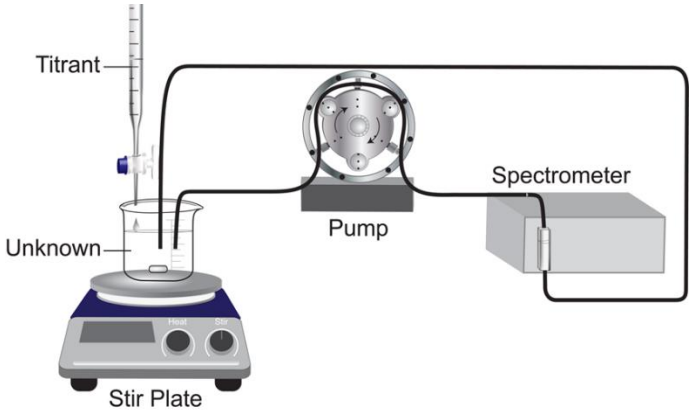


Figure 12.30: Apparatus for carrying out a spectrophotometric titration. The titration mixture is continuously pumped through a flow cell where the absorbance is measured at a selected wavelength.

Assume a general titration reaction of the following type

$$T + U \rightarrow P_1 + P_2$$

where T represents the titrant, U the unknown, and P_1 and P_2 the products. Also assume that only U is coloured. The results derived below apply only to a 1:1 reaction, but other types of reactions can be treated in the same manner.

Before the equivalence point, the titrant, T, is the limiting reagent and it will all be consumed by U. Since the products do not absorb, the absorbance will be determined by the concentration of U.

$$A = \varepsilon_u b\,[\mathrm{U}] = \varepsilon_u b \frac{\text{mol U}}{V} \tag{12.23}$$

$$A = \frac{\varepsilon_u b\,(\text{orig. mol U} - \text{mol T added})}{V_t + V_u} \tag{12.24}$$

$$A = \frac{\varepsilon_u b\,(V_u[\mathrm{U}]_o - V_t[\mathrm{T}]_o)}{V_t + V_u} \tag{12.25}$$

where $[U]_o$ is the original concentration of U before addition of any T ($[U]_o$ is the concentration that is usually determined in the analysis), $[T]_o$ is the concentration of T in the buret, V_t is the volume of titrant added (not the total volume), and V_u is the original sample volume (a constant). If one were to plot A *vs* V_t, the "normal" procedure for a titration curve, the resulting plot would not be linear. The reason for this is that the volume in the titration flask increases as the titration proceeds due to addition of titrant. However, if the measured absorbance is corrected for dilution by multiplying with the inverse of the dilution factor, $(V_t+V_u)/V_u$, then this leads to what is referred to as the *corrected absorbance*, A_{corr}.

$$A_{corr} = A \cdot \frac{(V_t + V_u)}{V_u} \tag{12.26}$$

In most linear titration methods the response, both before and after the equivalence point, must be corrected for dilution of the solution as titrant is added. This correction is always done using an expression similar to Eqn. (12.26). Substitution of this definition into Eqn. (12.25) leads to the following expression.

$$A_{corr} = \varepsilon_u b\,[U]_o - \frac{\varepsilon_u b\,[T]_o}{V_u} V_t \qquad (12.27)$$

Thus a plot of A_{corr} *vs* V_t will be linear with a slope of $-\varepsilon_u b[T]_o/V_u$ and intercept of $-\varepsilon_u b[U]_o$.

After the equivalence point, there is no longer any U present, thus there is no coloured material in solution and the absorbance will be zero.

$$A_{corr} = 0 \qquad (12.28)$$

This is obviously another straight line but with zero slope and zero intercept.

The intersection of the line representing the response before the equivalence point, Eqn. (12.27), and that after the equivalence point, Eqn. (12.28), is obtained by setting the two equations equal to one another.

$$\varepsilon_u b\,[U]_o - \frac{\varepsilon_u b\,[T]_o}{V_u} V_t = 0 \qquad (12.29)$$

or $$[U]_o = \frac{[T]_o V_t}{V_u} \qquad (12.30)$$

or $$\text{orig. mol U} = \text{mol T added} \qquad (12.31)$$

This relationship applies only at the equivalence point, and thus one concludes that the two lines intersect at the equivalence point. The value of V_t in Eqn. (12.30) is that at the intersection, which is the value at the equivalence point, $(V_t)_{ep}$. A graph of the titration curve (the two straight lines) is shown in Figure 12.31.

In this type of titration points are taken throughout the titration, but not at the equivalence point, so there is no need to approach this point carefully. Thus these titrations can be carried out quite rapidly. The equivalence point is determined by extrapolation of the two straight lines. This extrapolation is usually not as accurate as a good indicator colour change. However, this type of titration is free of indicator errors, which appear when the analyte concentration becomes low. Thus, these titrations are most useful for the analysis of dilute solutions, and work quite well, since spectrophotometry is a sensitive technique.

Such titration curves will always be two straight lines, but their exact shape will depend on what species (U, T, P) are coloured, and the magnitude of their molar absorptivities. Two examples are shown in Figure 12.32. The equations for these curves can be derived in the

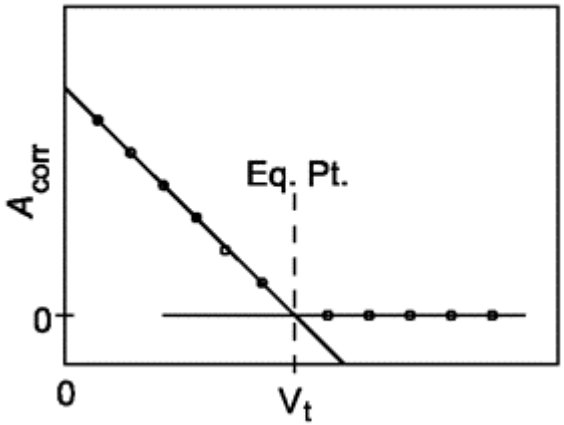


Figure 12.31: Spectrophotometric titration curve showing a plot of the corrected absorbance *vs* the volume of the titrant for a reaction in which only the unknown absorbs. The equivalence point is determined as the intersection of two straight lines.

same fashion as was done above, but it is perhaps more important to develop a qualitative understanding of their general appearance. In Figure 12.32(a), both the unknown, U, and the titrant, T, are coloured, but the products are not. Initially, only U is present in the titration flask, so light will be absorbed. As T is added before the equivalence point, it is totally consumed and so produces no absorbance, but it also reacts with U and therefore decreases its absorbance. At the equivalence point, there is no U and no T, so the absorbance is zero. After the equivalence point, T is still being added, but there is no U to react with it, so the absorbance increases due to increasing amounts of T. Because the slope of the line after the equivalence point is not as steep as that before, we can also tell that the molar absorptivity of T is less than the molar absorptivity of U. In Figure 12.32(b), neither U nor T is coloured, so the initial absorbance is zero. The products are coloured, however, so the absorbance continues to rise as they are generated before the equivalence point. After the equivalence point, there is no change as the reaction is complete.

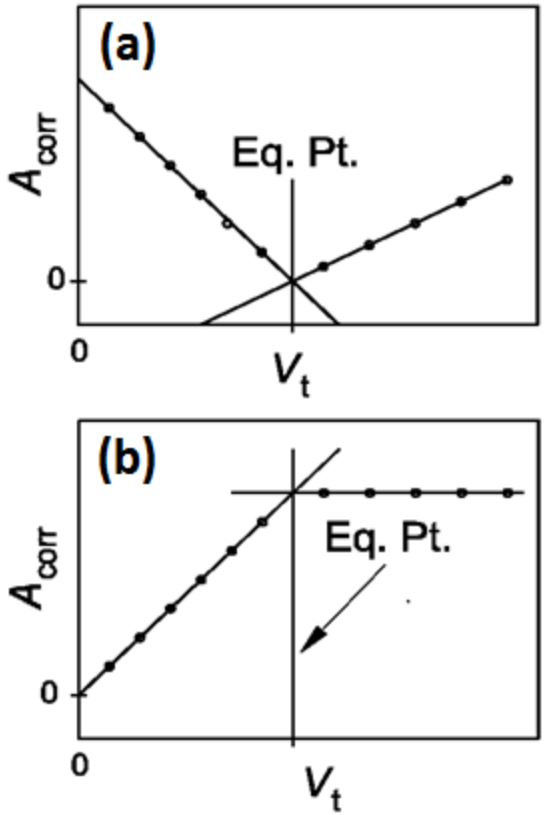


Figure 12.32: Spectrophotometric titration curves under different conditions. (a) Both the unknown, U, and the titrant, T, absorb, but not the products. (b) One or more products, P, absorb, but not the unknown or the titrant.

Example 12.15: Spectrophotometric Titrations

Consider the reaction:

$$2\,T + U \rightarrow 2\,P_1 + P_2$$

Derive equations for the two straight line segments of the linear spectrophotometric titration curve for the case where the only coloured material in solution is P_1. Prove that the equivalence point occurs at the intersection of these two lines. Assume that the cell path length is 1.00 cm.

Let the molar absorptivity of P_1 be represented simply as ε, since it is the only absorbing species in solution. For the segment before the equivalence point, we have:

$$A = \varepsilon\,[P_1] \qquad [P_1] = \frac{\text{mol of T added}}{\text{total volume}} = \frac{V_t\,[T]_o}{V_t + V_u}$$

$$A = \frac{\varepsilon\,V_t\,[T]_o}{V_t + V_u}$$

Correct for dilution by multiplication of both sides by $(V_t+V_u)/V_u$.

$$A\frac{(V_t + V_u)}{V_u} = A_{corr} = \frac{\varepsilon\,[T]_o V_t}{V_u}$$

A plot of A_{corr} *vs* V_t is linear with zero intercept and a slope of $\varepsilon[T]_o/V_u$. For the segment after the equivalence point the only coloured species present is still P_1:

$$A = \varepsilon\,[P_1] \qquad [P_1] = \frac{2 \times (\text{orig. mol U})}{\text{total volume}} = \frac{2\,V_u[U]_o}{V_t + V_u}$$

$$A = \frac{2\,\varepsilon\,V_u[U]_o}{V_t + V_u}$$

After correction for dilution

$$A \cdot \frac{(V_t + V_u)}{V_u} = A_{corr} = 2\varepsilon[U]_o$$

A plot of A_{corr} *vs* V_t will be linear with zero slope and an intercept of $2\varepsilon[U]_o$. At the intersection of these two lines $(A_{corr})_{before} = (A_{corr})_{after}$, or

$$\frac{\varepsilon[T]_o V_t}{V_u} = 2\varepsilon[U]_o$$

$$[T]_o(V_t)_{ep} = 2[U]_o V_u \quad \text{or} \quad \text{mol T} = 2(\text{mol U})$$

which holds only at the equivalence point.

Exercise 12.13

Sketch the general shape of the spectrophotometric titration curve (A_{corr} *vs* V_t) for the following conditions: (a) a reaction where only the titrant absorbs, and (b) a reaction in which both the unknown and one product absorb, and the unknown has a higher molar absorptivity. You may assume 1:1 stoichiometries. Clearly indicate the position relative to zero absorbance, the relative slopes of lines, and the position of the equivalence point.

12.11 Concentration Range and Precision of Absorption Measurements

No discussion of absorbance spectrophotometry would be complete without a discussion of concentration range and accuracy, since these influence the situations under which the method can be used and define the uncertainty in the results. First, regarding the range - what values of concentration are normally measured by this technique? In spectrophotometry (in the visible and UV), ε is normally between 10^3 and $2.5\text{x}10^4$, *b* is normally 1 cm, but is sometimes as high as 10 cm, and *A* usually falls between 0.1 and 1.0. Using the minimum and maximum values above in Beer's law, the concentrations normally measured fall between about 10^{-3} and $4\text{x}10^{-7}$ M. Thus spectrophotometry is considered a trace technique; it is not normally used to measure the main components in a sample (those making up 1% or more of the sample).

What is the precision that one might expect from this technique? The answer to this question comes from the propagation of error formulas that were developed in an earlier topic. In general, we want to relate the uncertainty in concentration to the uncertainty in the transmittance, since that is the quantity that is actually measured. We start with Beer's Law written in terms of transmittance

$$-\log T = \varepsilon b c \tag{12.32}$$

or $$c = -\frac{\log T}{\varepsilon b} \tag{12.33}$$

Recall from the rules for propagation of error that, if $y = \log(a)$, then $s_y = 0.4343 \cdot RSD_a$. Applying this to Eqn. (12.33) leads to an equation for the standard deviation in the concentration.

$$s_c = \frac{0.4343}{\varepsilon b} \cdot RSD_T = \frac{0.4343}{\varepsilon b} \cdot \frac{s_T}{T} \tag{12.34}$$

Note that the negative sign has been dropped. This is because standard deviations are always positive, so we use the absolute value of the propagation of error formula when the result is negative.

Generally, we are interested in the *relative* uncertainty in concentration, since this is a better indication of the quality of the result. To obtain this, we divide both sides of Eqn. (12.34) by *c*.

$$\frac{s_c}{c} = \frac{0.4343}{\varepsilon b} \cdot \frac{s_T}{T} \cdot \frac{1}{c} \tag{12.35}$$

Substituting Eqn. (12.33) into the right hand side of Eqn. (12.35), we obtain

$$\frac{s_c}{c} = \frac{0.4343}{\varepsilon b} \cdot \frac{s_T}{T} \cdot \frac{\varepsilon b}{-\log T} = -\frac{0.4343\, s_T}{T \log T} \tag{12.36}$$

Using the fact that $\log T = 0.4343 \ln T$, we arrive at the final result relating the relative uncertainty in concentration to the uncertainty in transmittance.

$$\mathrm{RSD}(c) = \frac{s_c}{c} = -\frac{s_T}{T \ln T} \tag{12.37}$$

This equation shows that the relative uncertainty in concentration is related to the uncertainty in the transmittance, but also in a complex way to the transmittance of the sample. Note that when $T = 1$ (or 100%T), the logarithm in the denominator goes to zero and the RSD becomes undefined. The same is true when $T = 0$.

Example 12.16: Concentration Errors in Absorption Spectrophotometry

A sample measured on a spectrophotometer gives a percent transmittance of 62.5±0.3%. Estimate the percent relative standard deviation in the concentration obtained from this measurement.

The transmittance value for the sample is 0.625, with a standard deviation of 0.003, so the relative standard deviation in the concentration is

$$\mathrm{RSD}(c) = -\frac{s_T}{T \ln T} = -\frac{0.003}{(0.625)\ln(0.625)} = 0.0\overline{1}02$$

which corresponds to a %RSD in the concentration of 1%.

Exercise 12.14
Estimate the %RSD in concentration if the %T were 91.2±0.3%.

Although Eqn. (12.37) seems straightforward, its application is complicated by the fact that the uncertainty in transmittance, s_T, may also be a function of T. There are two common types of errors that influence the uncertainty in the transmittance. In the simplest case, s_T remains constant regardless of the transmittance, or

$$s_T = K_1 \tag{12.38}$$

where K_1 represents the uncertainty in the transmittance (*e.g.* 0.003 in the previous example). This situation arises from errors in reading the meter and from fluctuations in the amplifier signal (amplifier noise), since both of these should be independent of the transmittance reading. In this case, we can modify Eqn. (12.37) only slightly to give

$$\mathrm{RSD}(c) = -\frac{K_1}{T \ln T} \tag{12.39}$$

It can be readily shown by methods of calculus that, if this is the only type of error present, the relative uncertainty in concentration is a minimum when T = 0.368, or A = 0.434. If, for example, $s_T = K_1$ = 0.005 (a 0.5% error in T), then the minimum RSD in c will be about 1.4% (at T = 0.368). The RSD in c will be less than 2% between T of 0.12 and 0.70 (A = 0.92 and 0.16). In this case, one would attempt to keep the measurements between absorbance values of about 0.1 and 1 to keep the relative uncertainty in c small. The relative uncertainty in c becomes very large at either very low or very high absorbance.

The second type of error is characterized by a standard deviation in T that is directly proportional to the value of T. In other words, the value of T increases (more light is transmitted), so does the uncertainty in T. Mathematically, we write

$$s_T = K_2 T \tag{12.40}$$

The value of K_2 in this equation represents the *relative* uncertainty in the transmittance. For example, if K_2 = 0.005, then T will always have a %RSD of 0.5% regardless of its value. This type of error arises from factors that cause variations in the intensity of light reaching the detector, such as fluctuations in the lamp intensity (called source flicker noise) or variations

in the cell position or the amount of dirt on the windows of the cell. When Eqn. (12.40) is substituted into Eqn. (12.37), we find that

$$\mathrm{RSD}(c) = -\frac{K_2}{\ln T} \tag{12.41}$$

which is somewhat different from Eqn. (12.39). If this type of error predominates, then the relative error in c decreases as T decreases (A increases). For example, if K_2 = 0.005, the relative uncertainty in c will be 2% at T = 0.78 (A = 0.11), 0.2% at T = 0.10 (A = 1), and 0.11% at T = 0.01 (A = 2).

Figure 12.33 demonstrates how these errors vary with T. The plot with the open circles represents the behaviour of constant errors (Type 1) in which s_T = 0.01. Note that the relative error in c increases rapidly at both high and low T (low and high A, low and high concentration). The plot with open squares represents the behaviour of errors proportional to T (Type 2) in which s_T/T = 0.01. In this case, the relative uncertainty in concentration is high only at high T (low A or low concentration).

The more usual case would be some combination of these two types of errors. If both types of errors are present, then they must be combined using the rules for propagation of error, which requires that we add the variances rather than the standard deviations. This means that, in the general case, we have

$$s_T = \sqrt{K_1^2 + K_2^2 T^2} \tag{12.42}$$

Substitution of this into Eqn. (12.37) gives

$$\mathrm{RSD}(c) = \sqrt{\left(\frac{K_1}{T \ln T}\right)^2 + \left(\frac{K_2}{\ln T}\right)^2} \tag{12.43}$$

Based on this general equation, the error will be a minimum at some value of T which will depend on both K_1 and K_2. The plot with open triangles in Figure 12.33 represents the case of random errors in which both types of errors are present at the 1% level. Both types of errors affect the total error at high T (low concentration), but only the errors independent of T affect the total error at low T (high concentration). In this case the minimum relative error in concentration is about 2.9% and occurs at a T of about 0.35. The total error is below 5%

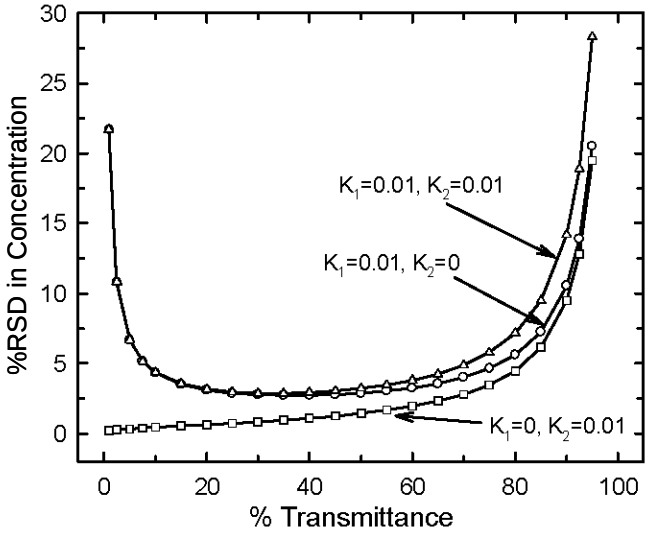


Figure 12.33: Relative uncertainty in concentration as a function of percent transmittance under various conditions of constant and proportional errors in T. Note that the most accurate results are normally obtained in the middle of the %T range.

between T values of 0.08 (A = 1.10) and 0.70 (A = 0.15), again indicating that it would be wise to limit measurements to absorbances between 0.1 and 1.0 if possible. Regardless of the type of error present in the measurement, the relative error in concentration will always be high when measurements are made at low absorbance values.

In summary, spectrophotometry is normally used in trace analysis (concentrations less than about 10^{-3} M) with accuracies approaching 1% when care is taken. Contrast this with titrations which are normally used for major component analysis at accuracies approaching 0.1%. Thus, these different techniques are complementary.

Example 12.17: Spectrophotometric Errors

A sample produces an absorbance reading of 1.58 on a spectrophotometer known to have both constant and proportional errors in transmittance. Those that are independent of T are believed to be about 0.5 %T (absolute standard deviation) and those proportional are 0.7% of T (relative standard deviation). What is the expected percent relative standard deviation in the concentration calculated for the coloured unknown in the sample? What is the dominant source of error in this case?

The specification of errors can be a bit confusing because they are both expressed as percentages even though one is an absolute standard deviation and the other is a RSD. The first error reflects the fact that, if this were the only type of error, every reading of %T would have an uncertainty of ±0.5%, so K_1 = 0.005. The second value indicates that every transmittance reading has a relative uncertainty of s_T/T = 0.007, so K_2 = 0.007. With these values assigned, Eqn. (12.43) can be used to calculate the relative uncertainty in concentration from these measurements.

$$T = 10^{-A} = 10^{-1.58} = 0.026$$

$$\text{RSD}(c) = \sqrt{\left(\frac{K_1}{T \ln T}\right)^2 + \left(\frac{K_2}{\ln T}\right)^2} = \sqrt{\left(\frac{0.005}{(0.026)\ln(0.026)}\right)^2 + \left(\frac{0.007}{\ln(0.026)}\right)^2}$$

$$= \sqrt{(-0.0\bar{5}2)^2 + (-0.00\bar{1}9)^2} = 0.0\bar{5}2$$

Therefore, the relative uncertainty in concentration in this case is 5%. Note that the dominant source of error in this case is the constant component, or that associated with reading the transmittance. This is not surprising, since the amount of light transmitted is very low (2.6%), so the proportional component should be small.

Exercise 12.15

Suppose the sample in the previous example were diluted by a factor of two. What would be the %RSD in the concentration in this case? What is the dominant source of error in this case?

Exercise 12.16

For the conditions given in Example 12.17, at what absorbance value would the constant error and proportional error contribute equally to the concentration uncertainty?

12.12 Molecular Emission Spectroscopy

When a molecule absorbs the energy from a photon in the visible or UV region of the spectrum, it is promoted to a higher energy electronic state. Normally, it will return to the ground electronic state very quickly and lose this energy in the process. The energy can be lost in a number of ways, but most molecules simply convert this absorbed energy to heat (kinetic energy) through collisions with other molecules in solution (processes in the solid or gaseous states will not be discussed). However, some molecules will re-emit the energy as light. This process is described by the equation below.

$$M + h\nu_{abs} \rightarrow M^* \rightarrow M + h\nu_{em}$$

In general, this process is called molecular emission or luminescence. If this process is fast (approximately 10^{-8} s), it is called fluorescence, whereas somewhat slower processes are

referred to as phosphorescence. Which pathway the molecule uses to lose energy, or "relax", from the excited state (collisions, fluorescence, phosphorescence, etc.) depends on a number of factors, including the structure of the molecule, the nature of the excited state, and the chemical and physical environment of the molecule. Fluorescence is the method used most often for molecular emission spectroscopy in solution and the only type that will be discussed here.

In the equation given above, "*h*ν" represents a photon absorbed or emitted. One might expect that the energy absorbed would be equal to the energy emitted so that the frequency and wavelength of the photon emitted are the same as those of the photon absorbed. However, it is almost always true that the emitted photon will have less energy, and therefore a lower frequency ($\nu_{em} < \nu_{abs}$) and longer wavelength ($\lambda_{em} > \lambda_{abs}$), than the absorbed photon. This will turn out to be very convenient for the purposes of analysis. The reason for this phenomenon is shown in the stylized energy level diagram depicted in Figure 12.34.

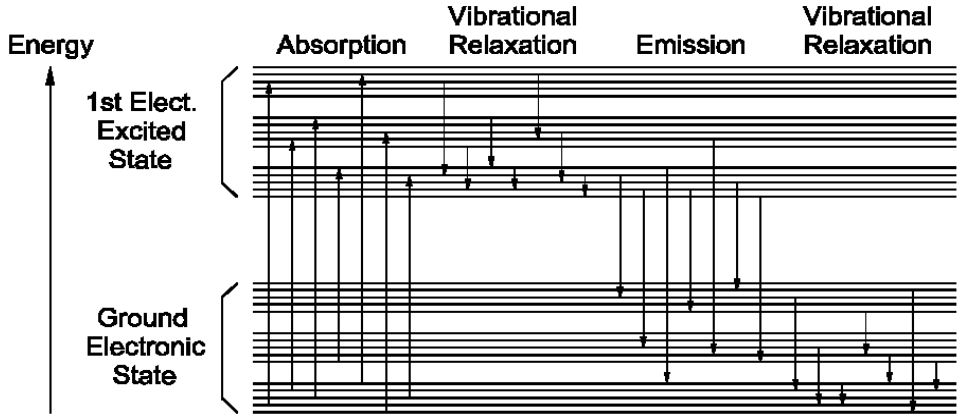


Figure 12.34: Energy level diagram showing the relationship between absorption and fluorescence. Electrons in various vibrational and rotational levels of the ground electronic state are promoted to various levels in the excited electronic state through the absorption of photons of corresponding energy. Electrons in the excited state relax to the lowest vibrational energy through collisions and then return to various levels of the ground electronic state by emitting photons of different energies.

Immediately after absorbing the exciting photon, the molecule will often be in an excited vibrational state (it must be in an excited electronic state). This vibrational energy is converted to kinetic energy very rapidly and the electronically excited molecule falls to its lowest vibrational state. This occurs before re-emission of a photon and is called vibrational relaxation. After the emission of the photon occurs, the molecule is returned to the ground electronic state, but may well be in an excited vibrational state. This extra vibrational energy is again degraded to heat through vibrational relaxation. The net result of this is that some of the energy of the exciting photon is converted to heat by vibrational relaxation, and the re-emitted photon will have a longer wavelength or lower energy than the exciting photon.

If both the absorption spectrum and the emission spectrum are plotted on the same graph, as shown in Figure 12.35, the effect is observed as a shift of the emission spectrum to longer wavelengths than the absorption spectrum. This difference allows the exciting light to be separated from the emitted light. This is absolutely necessary to use this technique in trace chemical analysis.

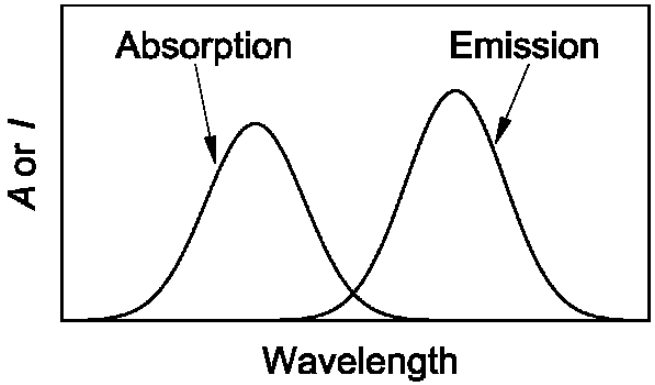


Figure 12.35: Comparison of the absorption spectrum and fluorescence emission spectrum of a typical molecule. The absorption spectrum is a plot of absorbance, *A*, *vs* λ; the emission spectrum is a plot of emission intensity, *I*, *vs* λ. Note that the emission occurs at longer wavelengths (lower energies) than the absorption.

Example 12.18: Fluorescence Emission

Suppose a molecule of chlorophyll-a dissolved in methanol absorbs a UV photon from a nitrogen laser at 337 nm and subsequently emits a photon at 681 nm. How much of the energy from the original photon was lost as heat in the solution?

The amount of energy lost as heat will be the difference between the energy of the photon absorbed and the energy of the photon emitted.

$$\Delta E = E_{abs} - E_{em} = \frac{hc}{\lambda_{abs}} - \frac{hc}{\lambda_{em}}$$

$$= \frac{(6.626\times10^{-34}\ \text{J s})(2.998\times10^{8}\ \text{m s}^{-1})}{337\times10^{-9}\ \text{m}} - \frac{(6.626\times10^{-34}\ \text{J s})(2.998\times10^{8}\ \text{m s}^{-1})}{681\times10^{-9}\ \text{m}}$$

$$= (5.8\overline{9}5\times10^{-19}\ \text{J}) - (2.9\overline{1}7\times10^{-19}\ \text{J}) = 2.98\times10^{-19}\ \text{J}$$

Exercise 12.17

For the example above, imagine that the laser has a power of 4.8 mW (or mJ/s) and that 1.0% of the photons are absorbed by the solution and re-emitted at 681 nm. Assuming that the volume of the solution is 3.0 mL, the specific heat capacity of methanol is 2.53 J/g·K and the density of methanol is 0.787 g/mL, estimate the temperature increase that would be observed after 1.0 minute of exposure.

12.13 Fluorescence Instrumentation

As in absorption spectrophotometry, the instrumentation and the method of making the measurement are discussed first. A schematic diagram of the instrument is shown in Figure 12.36 and is briefly described here, to be followed with a more detailed description of each of the components. The light source provides polychromatic excitation radiation. The excitation monochromator selects the proper wavelength of light for the excitation process and this light passes through the sample cell (from left to right in Figure 12.36), where some of it is absorbed, producing molecules in the excited state. The excited molecules fluoresce, emitting light in all directions. In most instruments, the light emitted at right angles to the exciting radiation is collected and passes through the emission monochromator, which selects a portion of the emitted light to pass to the detector. The detector converts the light signal to an electrical signal which is amplified and output on a meter or computer.

Light Source

In fluorescence one usually needs fairly energetic photons to excite the sample molecules, so tungsten filament lamps are seldom used. Almost all light sources are gas discharge tubes that provide good intensity in the UV region of the spectrum. These may contain H_2 or D_2, as in ordinary UV spectrophotometers, but more often contain either Hg or Xe. Xenon gas discharge lamps have the advantage that they emit both in the uv and the visible.

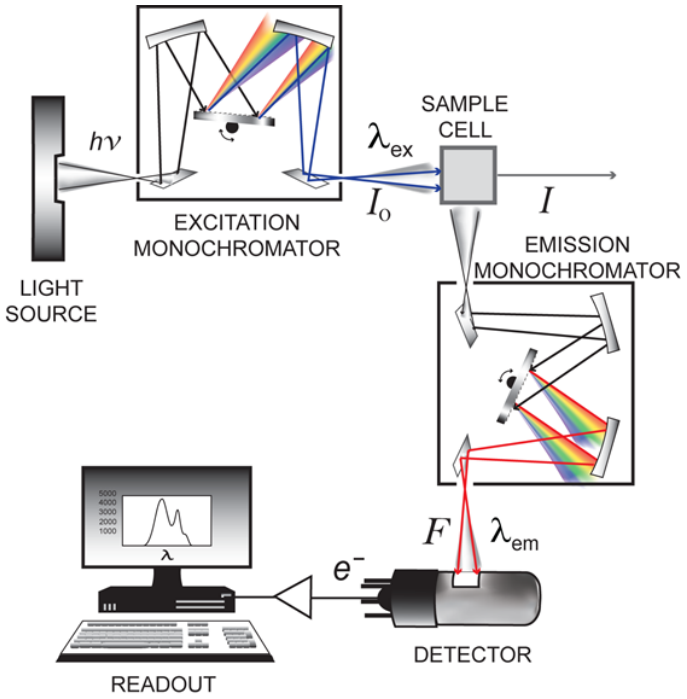


Figure 12.36: Schematic diagram of a fluorescence spectrometer showing the main components.

Monochromators

Unlike spectrophotometers, fluorometers contain two monochromators. The excitation monochromator selects a band of light which is strongly absorbed by the analyte. This light is highly sensitive for exciting the sample molecules. The emission monochromator selects a band of light centered on the emission band, and thus provides high emission sensitivity. These two bands must be completely separate, and the monochromators are set so that this is so, as shown in Figure 12.37. As in Figure 12.35, Figure 12.37 presents both the absorption spectrum and the emission spectrum on the same graph. Only exciting radiation within the excitation bandwidth is allowed to enter the cell. Only fluorescence within the emission bandwidth is allowed to reach the detector. If these two bands overlapped, some of the exciting light, which is present in much higher intensity than the emitted light, might be scattered into the detector and give a false reading.

Often grating monochromators are found on instruments used in fundamental research on fluorescence and photochemistry. However, for simple analytical procedures filters are often used as monochromators. The reason for this is that filters pass much more light than grating monochromators and thus provide more sensitive and simpler instruments. A narrow bandwidth, as provided by a grating monochromator, is not nearly as important in fluorescence as in absorption spectrophotometry.

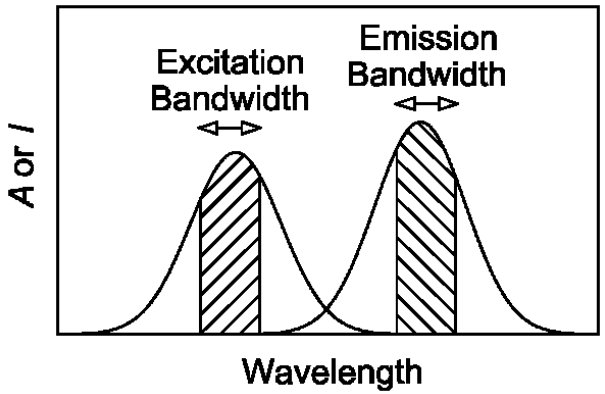


Figure 12.37: Relationship between the absorption (excitation) spectrum and fluorescence (emission) spectrum, and typical wavelength ranges passed by the excitation and emission monochromators. Note that the regions selected do not overlap.

Sample Cell

Square 1.00 cm cuvettes are usually used as sample containers. The difference between those used in fluorescence and absorption measurements is that silica is always used in fluorescence because the exciting radiation is usually in the UV, and all four sides of the cuvette must be of high optical quality, because fluorescence is observed through the side at right angles to the side which passes the excitation radiation. Only two sides of an absorption cuvette need be of high optical quality. Observation of fluorescence at right angles to excitation helps to prevent interference of the excitation radiation with the emitted radiation.

Detector

A device called a photomultiplier tube is used as the detector in fluorescence. These operate on the same principle as vacuum photodiodes, except that they have internal electrodes, called *dynodes* that amplify the small electron signal from the photocathode by a factor of 10^4 to 10^6 (called the *gain*). Thus they provide much larger currents for the same light input than photodiodes. This is needed since the light levels in fluorescence are very low. A schematic representation of a photomultiplier is shown in Figure 12.38.

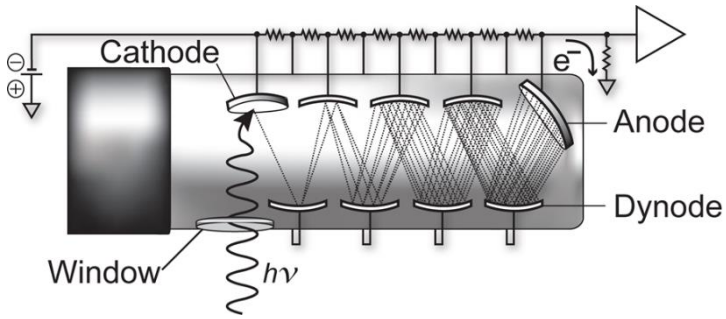


Figure 12.38: Schematic diagram of a photomultiplier tube. A photon ($h\nu$) strikes the photocathode, causing one or more electrons to be ejected. These are accelerated through a positive electric field and strike the first dynode, liberating even more electrons. The process continues, resulting in a multiplication of the original photon signal at the photoanode.

Amplifier and readout

These are basically the same as in absorption spectrophotometry.

Example 12.19: Photomultipliers

If a photomultiplier with a gain of 5.0×10^4 is connected to an amplifier with a gain of 100. to give a current of 2.3 mA, how many photons are reaching the photomultiplier tube per second.

We know that one Ampere (A) is equal to one Coulomb (C) per second, and that each electron has a charge of 1.603×10^{-19} C, so we can work backwards to determine the number of photons.

$$\text{Current at photoanode} = \frac{2.3\times10^{-3}\ \text{A}}{100.} = 2.3\times10^{-5}\ \text{A}$$

$$\text{Number of electrons at photoanode} = \frac{2.3\times10^{-5}\ \text{C s}^{-1}}{1.603\times10^{-19}\ \text{C / electron}} = 1.\overline{43}\times10^{14}\ \text{electrons / s}$$

$$\text{Number of photons} = \frac{1.\overline{43}\times10^{14}\ \text{e}^-\ \text{/ s}}{5.0\times10^{4}\ \text{e}^-\ \text{/ photon}} = 2.9\times10^{9}\ \text{photons / s}$$

Exercise 12.18

In fluorescence, the emitted radiation is uniform (isotropic) in all directions, so normally only a small fraction of the light is collected. Using the results of the previous example and assuming that λ_{ex} = 275 nm, λ_{em} = 348 nm, and that 1.0% of the emitted light is collected, calculate the total energy of photons absorbed in the sample in 1.0 s. You can also assume that each photon absorbed is also emitted.

12.14 Quantitative Fluorescence Measurements

The next subject to be examined is the relationship between the light emitted by the sample in a fluorescence measurement and the concentration of analyte in the sample. The approach taken here will be a bit simpler than is taken in many texts; in other words more simplifying assumptions will be made. At low concentrations, where fluorescence is most useful, the results are the same, regardless of the approach.

One would expect that fluorescence, F, (the intensity of secondary photons emitted) would be proportional to the intensity of primary photons absorbed. Mathematically,

$$F = k(I_o - I) \tag{12.44}$$

where I_o is the incident intensity and I is the intensity of light transmitted through the cell, the difference corresponding to the amount of light absorbed. It will be assumed that the sample molecules do not re-absorb any of the light which they emit, a phenomenon known as *self-absorption* or *secondary absorption*. This is often a very reasonable assumption and when self-absorption does occur, the effect can often be nullified by proper setting of the emission monochromator. It will also be assumed that the entire sample cell is involved in the measurement, not just the centre portion. This will depend on the optics of the instrument. Both assumptions simplify the mathematics.

The proportionality constant, k, in Eqn. (12.44) is a function of the fluorescence efficiency, *i.e.* the number of photons emitted per photon absorbed (called the *quantum efficiency*), and the efficiency of light collection and detection. The value of k is usually between 0.01 and 0.0001, indicating that the detector will see only one photon for between

100 and 10,000 photons absorbed. As will be pointed out below, fluorescence is almost always done at analyte concentrations far below those at which all exciting photons are absorbed. The conclusion one must reach is that usually the detected fluorescence is approximately four to six orders of magnitude or less in intensity than the exciting radiation. If Beer's law is obeyed,

$$I = I_o \cdot 10^{-\varepsilon bc} = I_o \cdot e^{-2.303\,\varepsilon bc} \tag{12.45}$$

$$\begin{aligned} F &= k(I_o - I_o \cdot e^{-2.303\,\varepsilon bc}) = kI_o(1 - e^{-2.303\,\varepsilon bc}) \\ &= F_o(1 - e^{-2.303\,\varepsilon bc}) \end{aligned} \tag{12.46}$$

It is important to note that, in Eqn. (12.46), $F_o = kI_o$ is the *theoretical* fluorescence that would be observed if all of the incident photons were absorbed, and is not normally directly measurable. It is not analogous to I_o, and therefore does *not* represent the fluorescence observed for the blank. In fluorescence, the blank is analogous to the dark current in absorbance measurements, and is subtracted from all other measurements. Eqn. (12.43) can be rearranged to solve for the concentration.

$$\frac{F_o - F}{F_o} = e^{-2.303\,\varepsilon bc} \tag{12.47}$$

or

$$\ln\left(\frac{F_o - F}{F_o}\right) = -2.303\,\varepsilon bc \tag{12.48}$$

or

$$c = \left(\frac{-1}{2.303\,\varepsilon b}\right)\ln\left(\frac{F_o - F}{F_o}\right) \tag{12.49}$$

The net result of this treatment is to demonstrate that, overall, even with certain simplifying assumptions, the relationship between F and c is fairly complex and nonlinear. This is shown in Figure 12.39. Note that F_o is a constant and is the maximum fluorescence which can be obtained from a sample in the absence of self-absorption.

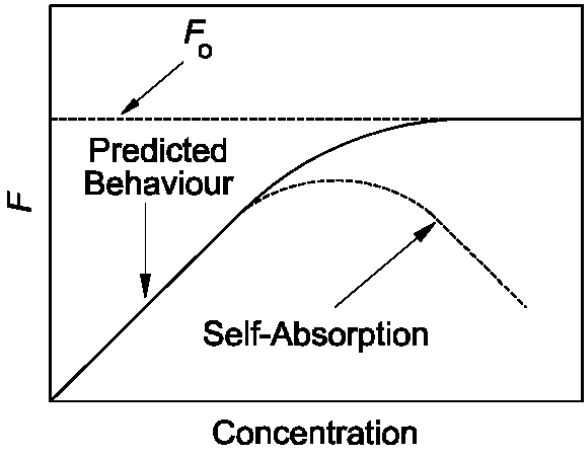


Figure 12.39: Relationship between fluorescence intensity and concentration. At low concentrations, where only a small amount of light is absorbed, the relationship is linear. As more light is absorbed, the non-linear behaviour is observed, until the fluorescence becomes constant when all of the light is absorbed (primary absorbance effect). If self-absorption of the emitted radiation also occurs (secondary absorption), the fluorescence can decrease (dashed line).

Is there a region in which F is linear in c? Yes, and this can be predicted mathematically. Returning to Eqn. (12.46)

$$F = F_o(1 - e^{-2.303\,\varepsilon bc}) \tag{12.46}$$

It is known from mathematics that exponentials can be approximated by the power series given in Eqn. (12.50).

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots \tag{12.50}$$

In this case, $x = -2.303\,\varepsilon bc$. If x is small enough, then the higher order terms can be ignored and $e^x \approx 1 + x$. Substituting these equations into Eqn. (12.46) gives

$$F = F_o\left(1 - 1 + 2.303\,\varepsilon bc - \frac{(2.303\,\varepsilon bc)^2}{2!} + \ldots\right) \tag{12.51}$$

or, if $(2.303\,\varepsilon bc)$ is small enough,

$$F \approx F_o(1 - 1 + 2.303\,\varepsilon bc) = 2.303\,F_o\varepsilon bc = k'c \tag{12.52}$$

The final conclusion is that fluorescence intensity is linear in concentration when the absorbance of the sample is small. Although the molar absorptivity, path length and concentration all contribute to the absorbance, it is usually stated that fluorescence is linear with concentration when the concentration is small. Here "small" means less than the range that would normally be measured by absorbance methods in the same cell.

Can this be explained in a less mathematical fashion? Imagine that you are looking at the sample cell from the same direction as the detector; that is, at right angles to the exciting light (see Figure 12.40). If the concentration of analyte is very low, $c = c_1$, the absorption of light is also low and the exciting light intensity is essentially the same from left to right across the cell. Thus all analyte molecules are subjected to the same excitation intensity and the emission intensity is uniform across the cell. Doubling the analyte concentration will double the fluorescence. However, as the analyte concentration gets higher, $c = c_2$ or c_3, more of the exciting radiation gets absorbed as it crosses the cell. Molecules on the right-hand-side of the cell are subjected to less excitation intensity, and thus emit less than molecules on the left-hand-side of the cell. This gives rise to a negative deviation from the linear equation. As the

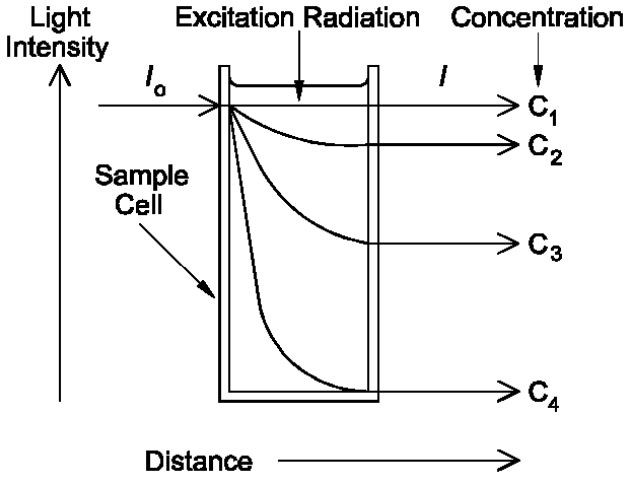


Figure 12.40: Changes in the intensity of the excitation radiation as it passes through the fluorescence cuvette. At low concentrations (c_1), little absorption occurs and the cell receives uniform illumination. As the concentration increases (c_2 to c_4), the right side of the cell receives less light than the left side. When all of the light is absorbed (c_4), the fluorescence intensity is constant.

concentration of analyte increases still more, this effect becomes more serious, until some concentration is reached, $c = c_4$, at which all exciting photons are absorbed in the cell. At this point, molecules on the right wall of the cell see no exciting radiation and emit no fluorescence. From this point on increasing concentration will provide no more fluorescence since all exciting radiation is absorbed.

This line of reasoning leads to the conclusion that the region over which fluorescence is linear in concentration is that in which concentrations are too low to be effectively determined by absorption spectrophotometry. In fact, fluorescence is a much more sensitive technique than absorption spectrophotometry. The question now arises "If fluorescence radiation is four to six orders of magnitude less intense than the exciting radiation (the light that would be used in absorption measurements), how can fluorescence be more sensitive?". The answer will be discussed below.

Example 12.20: Fluorescence Linearity

Imagine a sample that fluoresces has an absorbance of 0.0100. Calculate the percentage difference between the true fluorescence predicted by Eqn. (12.46) and that predicted by the assumption of linearity in Eqn. (12.52). Repeat the calculation for absorbance values of 0.100 and 0.500.

We know that $A = \varepsilon bc = 0.0100$. Therefore, we can calculate the percentage difference as,

$$\%\ \text{difference} = \frac{F_{\text{true}} - F_{\text{pred}}}{F_{\text{true}}} \times 100\% = \frac{F_{\text{o}}(1 - e^{-2.303\,\varepsilon bc}) - F_{\text{o}}(2.303\,\varepsilon bc)}{F_{\text{o}}(1 - e^{-2.303\,\varepsilon bc})} \times 100\%$$

$$= \frac{1 - e^{-2.303\,(0.0100)} - 2.303\,(0.0100)}{1 - e^{-2.303\,(0.0100)}} \times 100\%$$

$$= \frac{1 - 0.9772 - 0.023\overline{0}3}{1 - 0.9772} \times 100\% = \frac{0.0003}{0.0228} \times 100\% = -1\%$$

Similar calculations give −12% error and −68% for $A = 0.100$ and 0.500, respectively.

Exercise 12.19

A sample absorbs 2.00% of the incident radiation and gives a fluorescence reading of 76.3. What is the value of F_o?

Practical Fluorescence Measurements

In practice, fluorescence measurements are made in much the same way as measurements are made in absorption spectrophotometry (except that there is no absolute method). Thus one prepares a blank, one or a set of standards, and the sample. The instrument reading can be set to zero with no sample in the exciting light beam, or it can be set to zero with the blank in the light beam. In the first case the blank fluorescence must be measured and subtracted from the fluorescence of all the standards and the unknown (in some cases the sample and the standards may have different blanks). In the second case the instrument subtracts the blank fluorescence from the sample. A calibration curve is prepared from the standards and used to convert the measured fluorescence of the sample to concentration. The method of standard addition can be used, *if you are sure that fluorescence is linear in concentration*.

The final points to be discussed are concentration range, accuracy, and usefulness. From what has been said it might seem that fluorescence would be almost impossible to use. First, it is linear only when the concentrations are so low that very little of the exciting radiation is absorbed. In other words it is linear when $I \approx I_o$. Second, the fluorescence intensity is very low, requiring a very sensitive instrument. Why not use absorption spectrophotometry instead, since all molecules that fluoresce must also absorb light? (In fact, absorption spectrophotometry *is* used more often than fluorescence.) If one wishes to make measurements at very low concentrations with absorption spectrophotometry, one must measure both I and I_o very accurately and there must be no noise in the instrument, because the absorbance depends on the difference between the logarithms of these two intensities ($A = \log(I_o) - \log(I)$). In fluorescence, even though F is usually very low, the blank is, or can be set to, zero. It is much easier to distinguish between zero and a small intensity and to make accurate measurements of that small intensity than to distinguish small differences between two large intensities and make an accurate measurement of that difference. Moreover, the

signal measured in fluorescence can be increased through an increase in the source intensity (*e.g.* by using a laser), but this does not improve the sensitivity in absorption spectroscopy.

Fluorescence is a very sensitive analytical technique. It is perhaps two orders of magnitude more sensitive than absorption spectrophotometry and is used in the range 10^{-8} to 10^{-5} M. It is more specific than absorption spectrophotometry, since fewer molecules fluoresce than absorb. It is used most often in biochemical analyses for molecules such as drugs and neurotransmitters. Sometimes derivatives that fluoresce can be made from non-fluorescent materials. A good example is the use of a material called dansyl chloride which, when reacted with amino acids, forms products that fluoresce.

Despite its high sensitivity, or perhaps because of it, fluorescence measurements can be prone to problems that require careful attention to sample preparation and measurement. Since it is such a sensitive method, samples are easily contaminated by very small amounts of impurities that fluoresce. Also many real world samples contain more than one fluorescing substance, thus there are often background or matrix problems. Great care must be taken to prevent contamination. The usual accuracy to be expected is between about 2 and 10%.

Example 12.21: Fluorescence Measurements

In a determination of quinine by fluorescence, solutions of 5.0×10^{-7} M and 1.0×10^{-6} M quinine sulfate are prepared. A blank is used to set the fluorometer to zero. The two quinine standards are then read as 39.6 and 79.5 (in arbitrary emission units), respectively. Is fluorescence linear in concentration? A sample of tonic water gives a fluorescence reading of 67.5. What is the concentration of quinine in the tonic water?

Since the second standard concentration is double the first, and since the second intensity is almost also exactly double the first, one would say that fluorescence is linear in concentration. A more elegant method of proving the same thing is as follows. If F is linear in c, then

$$F = k'c \quad \text{or} \quad k' = \frac{F}{c}$$

$$k_1' = \frac{39.6}{5.0\times10^{-7}\ \text{M}} = 7.\overline{9}2\times10^{7}\ \text{M}^{-1} \qquad k_2' = \frac{79.5}{1.0\times10^{-6}\ \text{M}} = 7.\overline{9}5\times10^{7}\ \text{M}^{-1}$$

Since k_1' and k_2' are within 3 parts in 800 of each other, linearity can be assumed. Since there are only two points in the calibration data, the average value of *k*', $k_{avg} = 7.\overline{9}35\times10^{7}\ \text{M}^{-1}$ will be used for the slope.

$$c_{unk} = \frac{F}{k_{avg}} = \frac{67.5}{7.\overline{9}35\times10^{7}\ \text{M}^{-1}} = 8.5\times10^{-7}\ \text{M}$$

Exercise 12.20

A plant extract is to be analyzed for a certain alkaloid as follows: 10.00 mL of the extract are diluted to 20.00 mL with distilled water and produce a reading of 46.3 (arbitrary emission units) on the fluorometer. A 1.00 mL aliquot of a $1.00\text{x}10^{-6}$ M solution of the alkaloid is added to 10.00 mL of extract and diluted to 20.00 mL with distilled water. This solution reads 51.4. Finally 10.00 mL of the extract are mixed with 5 mL of a reagent that destroys the fluorescence of the alkaloid and this is diluted to 20.00 mL with distilled water. This solution reads 20.8. What is the concentration of the alkaloid in the extract? Assume that fluorescence is linear with concentration.

12.15 Atomic Spectroscopy

Thus far, the focus has been on the measurement of absorbance or fluorescence of molecules in solution. Quite often, however, there is a desire to determine elemental concentrations, particularly metals. For example, one might wish to determine the concentration of arsenic or lead in drinking water, or the concentration of manganese in a steel sample that has been dissolved in acid. Such elements exist in solution only as ions. In some cases, the ions may form coloured solutions, as is the case when Cu^{2+} ions dissolve to form a blue colour. If the

absorption is too weak or not present, it may be possible to form a strongly absorbing (or fluorescing) coordination compound by adding a complexing agent, as happens when ammonia is added to Cu^{2+} solutions under the right conditions. In some cases, however, such as with sodium ions, this is not possible. An alternative approach, which will be discussed here, is to convert the ions in solution to atoms in the gas phase and measure their absorption or emission there. How the atoms get into the gas phase will be discussed shortly, but first it is important to understand critical differences between atomic and molecular spectroscopy that affect how the measurements are made.

Atoms absorb and emit light in the same fashion as molecules (in the visible and UV), except that this process is uncomplicated by rotational and vibrational transitions, making it appear much simpler. On absorbing a photon, an atom is promoted to a more energetic electronic state and, on emitting a photon, an atom falls to a less energetic electronic state. Often the ground state is one of the two states involved in these transitions, but not always. These phenomena should therefore be able to be used to perform quantitative analysis for atoms in the same fashion that has been used for molecules. However, in terms of analysis, two major differences exist between molecular and atomic spectroscopy.

First, atomic absorption and emission lines are very narrow compared to the corresponding molecular bands in solution, as explained in Section 12.5. This is both a "problem" and a "feature". It is a feature in that, with such narrow lines, very few lines overlap. If one has many different coloured molecular species present in solution, their absorption bands would certainly overlap and analysis without a prior separation step would not be possible. One can analyze many metals in the presence of each other without any separation step because their lines do not overlap. The narrow lines are also a problem, however, in that it is impossible to make a monochromator good enough to provide light of sufficient purity for Beer's law to be obeyed, since the monochromator bandwidth must be narrow compared to the absorption bandwidth.

The second important difference has already been alluded to - molecules exist readily in solution, *atoms do not*. Thus some method must be devised to convert molecular or ionic species into atoms in order to do the spectroscopy. This will undoubtedly cause drastic changes in the sample. This will be discussed shortly.

There are two main types of atomic spectroscopy, *atomic absorption* and *atomic emission*, and these can be considered to be analogous to their molecular counterparts, although there are some important differences in the principles and instrumentation. The nature of the line spectra observed from atoms will be discussed first, since this is relevant to both types of spectroscopy and the design of the instruments.

Atomic Bandwidth

The problem of bandwidth is examined first. How narrow is an atomic line? Atomic lines have an inherent bandwidth set by the Heisenberg Uncertainty Principle at about 10^{-4} nm (compared to molecular bandwidths in solution of about 100 nm). However, the observed bandwidth is much larger than this for two reasons: Doppler broadening and pressure broadening.

Doppler broadening is a broadening of the absorption line caused by motion of the atoms with regard to the light source (or the direction of the light ray) in atomic absorption (AA) spectroscopy or with regard to the detector in atomic emission spectroscopy. Doppler broadening is a general phenomenon associated with wave motion. The classic example is the change in pitch of a train signal as heard when it approaches a bystander. As the train approaches the observer, the pitch is higher than would be heard by someone on the train. As the train moves away from the observer, the signal pitch is lower. In a similar fashion an atom moving toward a light source (moving in a direction opposite to the direction of the light ray) will experience a frequency higher than an atom at rest. Thus that atom will absorb at a frequency slightly lower (as measured by a stationary observer) than an atom at rest (remember that the atomic energy levels are not affected by translational motion). Likewise an atom moving away from a light source (moving in the same direction as the light ray) will experience a frequency lower than an atom at rest. That atom will absorb at a frequency slightly higher than it would at rest. This behaviour is depicted in Figure 12.41, where ν is the actual frequency of the light ray and ν' is the frequency experienced by the moving atom. Atoms moving at right angles to the light ray will absorb the "correct" frequency. Thus the width of the band of frequencies absorbed by moving atoms is broader than if the atoms were stationary. This type of broadening is temperature dependent, since velocity is a function of temperature.

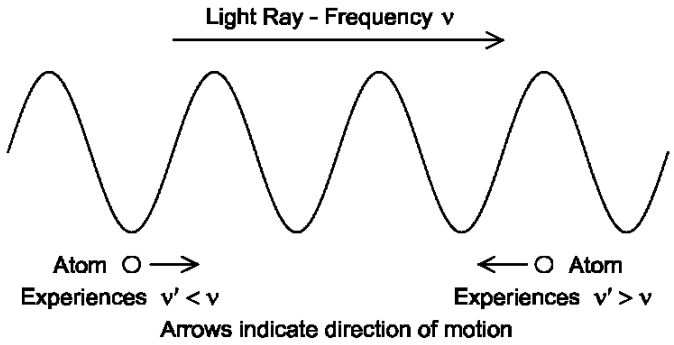


Figure 12.41: Illustration of Doppler broadening. Atoms traveling in the direction of propagation of the radiation will experience a lower frequency of electromagnetic field oscillation, while those traveling in the opposite direction will experience a higher frequency. As a consequence, the atoms will absorb radiation at slightly different wavelengths.

Pressure broadening arises because, although the energy states or levels in atoms are not distorted by translational motion, they are distorted by collisions. This distortion causes these states to be somewhat "fuzzy", not having the expected exact energy values. This in turn affects the energy differences between states and the frequencies of light interacting with these states. This type of broadening is almost directly proportional to pressure.

These two mechanisms combine to produce atomic linewidths in the range of 0.001 to 0.01 nm, which is still about five orders of magnitude lower than molecular bandwidths observed in solution. This will necessitate some special considerations in instrument design.

Example 12.22: Doppler Broadening

A sodium atom absorbs radiation at 589.0 nm. Imagine that the average velocity of a sodium atom is 500. m s^{-1}. Estimate the Doppler broadening that occurs for this absorption line.

Perhaps the easiest way to think of this is to consider one sodium atom moving towards the light source and the other away from it so that the speed of light relative to first atom is (c+v) and that relative to the second atom is (c–v), where v is the velocity of the atom. Using the relation that $\lambda = c/\nu$ (where ν is the frequency, not to be confused with velocity) we can write

$$\Delta\lambda = \lambda_1 - \lambda_2 = \frac{c+v}{\nu} - \frac{c-v}{\nu} = \frac{2v}{\nu} = 2v \cdot \frac{\lambda}{c}$$

$$= 2(500.\ \mathrm{m\,s^{-1}}) \times \frac{589.0\,\mathrm{nm}}{2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}} = 1.96 \times 10^{-3}\ \mathrm{nm}$$

This value is in the range of broadening described above.

12.16 Atomic Absorption Spectroscopy: Instrumentation

Just as in molecular spectroscopy, the topic of atomic absorption (AA) is taken up first. One might guess that the instrument for atomic absorption would be the same as that for molecular absorption - source, monochromator, sample, detector, amplifier, readout. In some respects this is so, but the instrument must somehow be constructed in a manner to take into account the two differences mentioned above, namely the narrow linewidth of atomic absorption lines and the need to get atoms into the gas phase.

Light Source

Beer's Law requires that the absorption of the incident radiation be approximately constant across the wavelengths entering the sample cell, so in molecular absorption spectroscopy, a monochromator is used to select a narrow wavelength range where this will be true. This same approach cannot be used for atomic absorption, however, because even a good quality monochromator will pass a band of wavelengths wider than the absorption line. Moreover, even if it were possible to find such a monochromator, adjustment to exactly the correct wavelength would be quite difficult. How, then, does one obtain light with such a narrow bandwidth in order to make absorption measurements? One must use a special light source that produces a line of exactly the correct wavelength and a very narrow bandwidth. To produce a line of the correct wavelength, the light source must operate with some form of gas discharge and must contain the same element (atom) that is in the sample (the analyte). One such light source is the *hollow cathode lamp* (HCL).

A schematic diagram of a hollow cathode lamp is shown in Figure 12.42. Such lamps usually contain either Ar or Ne gas at a low pressure (0.001 to 0.005 atm). The cathode (the negative electrode) is a hollow cylinder made from or containing the atom of interest, *e.g.* Cu. A gas discharge in the HCL creates inert gas ions (*e.g.* Ne^+) and electrons (e^-) that move toward the cathode and anode, respectively. When the neon ions collide with the cathode, they "sputter" some Cu (or other metal) atoms into the space within the hollow cylinder. These copper atoms can then be excited by collision with Ne^+ or e^- and emit light characteristic of copper.

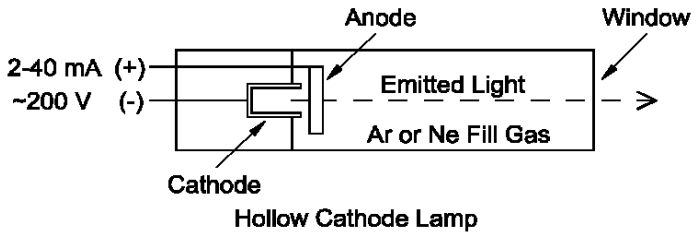


Figure 12.42: Schematic diagram of a hollow cathode lamp (HCL). Positively charged gas atoms strike the negative cathode, which contains atoms of the metals of interest. These atoms are ejected from the surface and undergo collisional excitation to emit radiation of the appropriate wavelength. The light passes through the ring-shaped anode and exits through the window.

$$Cu + Ne^{+*} \text{ (high energy)} \rightarrow Cu^{*} + Ne^{+} \text{ (lower energy)}$$
$$Cu^{*} \rightarrow Cu + h\nu$$

Some collisions are energetic enough to form excited copper ions that can also emit light.

$$Cu + Ne^{+*} \rightarrow Cu^{+*} + Ne^{+}$$
$$Cu^{+*} \rightarrow Cu^{+} + h\nu'$$

In addition to excited copper atoms and ions, there will also be excited neon atoms and ions, and perhaps some other atoms and ions depending on the construction of the HCL. Thus, one will obtain not only the radiation characteristic of copper, the element of interest in the example, but also that radiation characteristic of copper ions, neon atoms and neon ions. This latter radiation is of no use in the atomic absorption spectroscopy of copper atoms. How the problem of this "extra" radiation is solved will be discussed later. Those lines that are of use for the determination of copper are narrow enough that Beer's Law is obeyed reasonably well.

Sample Atomization

The second problem in atomic spectroscopy is to convert the species of interest in the sample into atoms in the gas phase. The solution to the problem is relatively straight forward - one heats the sample sufficiently to destroy the sample matrix (molecules or crystal lattice) and produce atoms. In the process of heating samples to high temperatures, several transformations take place. First, since the sample is usually introduced as a solution, the solvent evaporates. In the second step, most chemical bonds in the sample are broken, liberating the atom of interest. Finally, the atom is vaporized into the gas phase. A consequence of this process is that atomic spectroscopy does not generally distinguish the original form (or *speciation*) of the atom of interest; that is, it does not indicate its ionic or molecular form in the sample or its oxidation state. It should also be mentioned that it is difficult to liberate atoms from some ionic compounds, called *refractory* materials, by this method. This group typically includes certain phosphates and silicates.

The place where atomization takes place in atomic spectroscopy is often called the *atom cell*. This is analogous to the sample cell in molecular spectroscopy, but is not a closed container in which the sample can be held statically. The transformation takes place

dynamically, and the atoms generally only have a transient presence in the atom cell. There are two common methods for atomization in AA, (1) the use of a small oven, usually made of graphite, and (2) the introduction of the sample into a flame. These are discussed in more detail below.

Graphite furnace, or *electrothermal*, atomization involves the use of a small oven, or furnace to atomize the sample. There are several different models of these furnaces available commercially. In the example shown in Figure 12.43, a small sample, usually < 100 μL, is placed on a platform inside a graphite tube. While an inert gas is passed over and through the tube to protect it from oxidation during heating, an electric current is passed through the tube causing the temperature to rise. As the furnace is heated the solvent evaporates, then any organic matrix decomposes ("smoke" may be produced), then the inorganic matrix decomposes and the sample is atomized. These atoms then absorb the light passing through the tube from the hollow cathode lamp while the tube acts as the sample cell. The entire experiment occurs fairly rapidly (under a minute) and the absorbed light appears as a pulse or peak, not a continuous signal, as the atoms generated are swept out of the hollow graphite tube. The peak height of this pulse, when measured as absorbance, is usually proportional to sample concentration. This process is depicted in Figure 12.44. The upper plot indicates the variation of temperature with time in the furnace. The lower plot indicates the variation of measured absorbance with time. The "smoke" caused by matrix decomposition appears as an absorption band earlier in time than the actual absorption band. In fact, the "smoke" may either absorb the light or scatter it, but the result is the same. This peak is ignored in the analysis. This type of atomization is very sensitive and capable of analyzing small samples, 20 μL or less. It is also rather exacting and demands great care and precision. Best results are achieved with automated sampling.

In *flame* atomization, sample solution is first introduced into a *nebulizer* and then passes into a flame. A nebulizer is a device that converts a liquid into a fine spray of droplets in a manner similar to a spray bottle. Several nebulizer designs are used, but a widely used concentric flow nebulizer works by passing a high flow of oxidant gas (usually air) past the tip of a small capillary connected to the sample as shown in Figure 12.45. At the capillary tip the sample is broken into a fine mist. The smallest particles in this mist are carried into the flame by the gas flow, while the largest fall out of the gas stream and eventually exit through

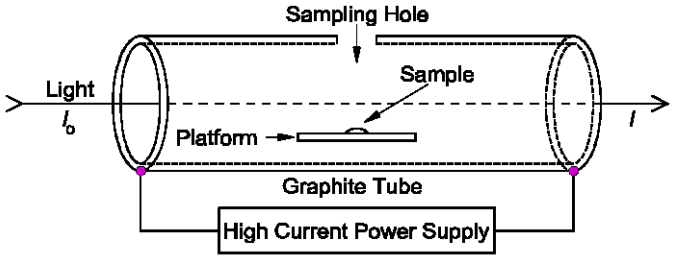


Figure 12.43: Schematic representation of a graphite furnace for electrothermal atomization.

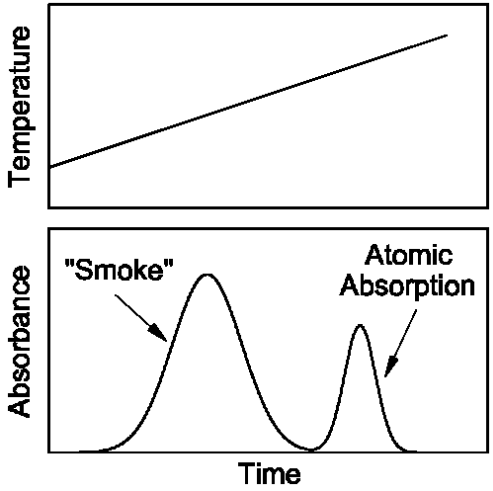


Figure 12.44: Dynamics of electrothermal atomization. The temperature of the graphite furnace increases with time (upper plot). As the temperature increases, the solvent is first removed and then the organic matrix is burned off, leading to scattering of light by particulates in the "smoke". Finally, the atoms are vaporized, leading to absorption of the incident radiation.

the drain. In most such burners, only about 10% of the sample gets into the flame. Fuel gas, usually acetylene (ethyne), is also introduced into the nebulization chamber and mixes with the sample mist and the oxidant. This produces a premixed flame that burns quietly and evenly (the flame on a Bunsen burner is also premixed).

In the flame the solvent in the mist particles evaporates first. Then the solid remaining is atomized (providing that its crystalline form is not too refractory). The atoms thus formed absorb the light passing through the flame from the hollow cathode lamp. Note that the flame used in atomic absorption, is not cylindrical like that from a Bunsen burner, but is extended along one dimension as shown in Figure 12.45. This design, referred to as a *slot burner*, is typically about 10 cm long and is intended to extend the path length to maximize the absorption by the atoms. The aspiration of sample into the flame is continuous and thus the signal produced by the absorption of light is also continuous, in contrast to that produced in the graphite furnace, as long as the flow of sample is not interrupted. In effect, the flame becomes the sample cell.

Flame atomization is not as sensitive as electrothermal atomization and requires much larger amounts of sample (1 - 10 mL), but is simpler and more easily performed manually. For this reason, flame atomization is more widely used for general applications.

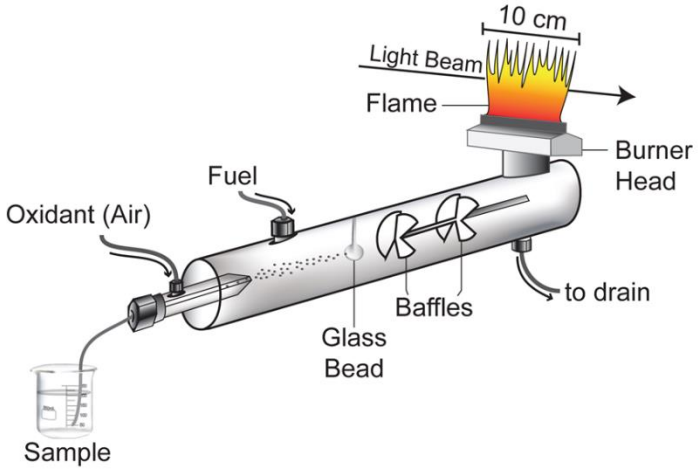


Figure 12.45: Schematic representation of nebulization in flame atomic absorption. Sample solution is drawn in to the nebulizer by a concentric flow of air, which then disperses it as a fine mist. The smallest droplets are mixed with fuel and carried into the slot burner, where they are atomized in the flame. Larger droplets fall and exit through the drain.

Instrument Overview

With this introduction to hollow cathode lamps and atomization, it is now possible to consider the entire instrument used for atomic absorption. A block diagram of a typical AA instrument is shown in Figure 12.46. The detector (usually a photomultiplier tube), amplifier, and meter (readout) are basically the same as those discussed previously. The hollow cathode lamp and the atomizer have already been described. A flame atomizer is depicted in Figure 12.46. If a graphite furnace were to be used in place of the flame, it would go in the same location. However, two features appear in the diagram that have not been introduced or discussed previously. The instrument shown in Figure 12.46 has a device called a *chopper* placed in the light beam, and the monochromator follows the sample rather than preceding it. The reasons for these two modifications are discussed below.

Light Beam Modulation (Chopper)

The need for a chopper (light beam modulation) is discussed first. As an introduction to this topic, note that most spectrophotometers and all fluorometers place the sample cells in light-tight compartments. Under this circumstance room light can have no effect on the measurement. However, it is impossible to place flames and hot graphite tubes in light-tight compartments. Even if this could be done, it would not solve the problem since the flames and graphite furnaces are sources of light themselves. Thus, room light and light given off by the flame or furnace will interfere with the measurement and some method must be found to differentiate such light from the signal light (light from the HCL). This is done by a technique called modulation.

The light from flames and furnaces and much of that found in the laboratory is steady in nature, its intensity does not vary with time. If the light from the HCL is modulated (the light intensity is made to vary with time in a periodic fashion), then light from the HCL and from the interfering sources can be distinguished. The chopper is one type of device that can introduce the modulation. As shown in Figure 12.47, the chopper is similar to a fan whose blades are placed in the HCL light beam. When the chopper rotates, the light is alternately stopped by the blades and passed between the blades. Before the chopper, the light intensity is steady, but after the chopper, the intensity alternates between on (high) and off (low). This alternation is called modulation. The frequency of the modulation depends on the rotation rate of the chopper. The amplifier in an AA spectrometer is special in that it can be exactly "tuned" to the frequency of the light modulation produced by the chopper, much like a radio is tuned to a specific broadcasting station. Thus the amplifier passes only the signal from the HCL and none of the background signal, and in this way gets around the problem of light from sources other than the HCL. This is depicted graphically in Figure 12.48.

Almost all modern research instruments no longer use a chopper. Instead, the power supply to the hollow cathode lamp is pulsed. This also produces pulsed or modulated light from the HCL, and the net result is exactly the same as if a chopper were used.

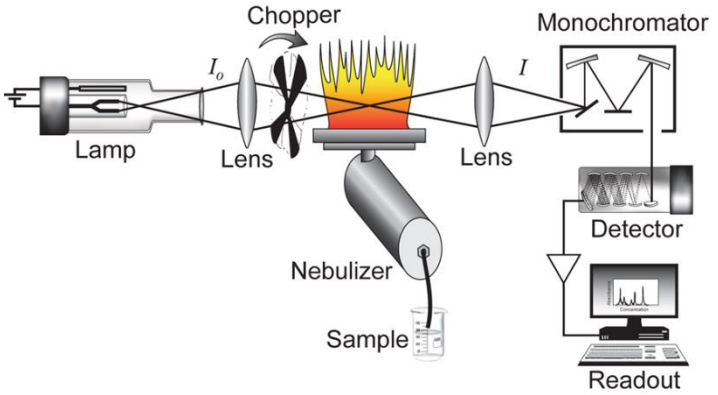


Figure 12.46: Schematic diagram of a typical flame atomic absorption spectrometer. Light from the hollow cathode lamp travels through the flame where the analyte atoms have been atomized. The absorption of light by the atoms is subsequently detected.

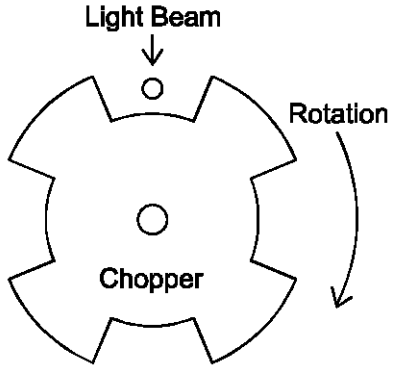


Figure 12.47: Front view of a typical chopper wheel used in atomic absorption spectroscopy.

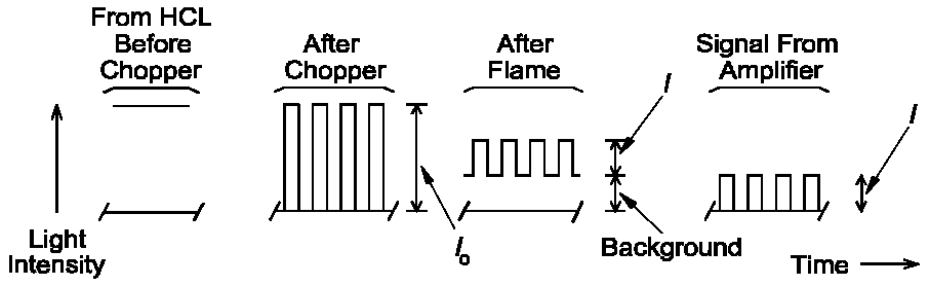


Figure 12.48: Light modulation in AA spectroscopy. Before the chopper, the light from the hollow cathode lamp is constant; after the chopper, it oscillates between zero and a constant level. Atoms in the flame absorb some of this radiation, but the flame also emits a constant background. The amplifier distinguishes the modulated signal from the background and removes the latter.

Monochromator

It has been stated that no monochromator can provide light with a narrow enough bandwidth (less than 10^{-3} nm) to be used in atomic absorption, so a hollow cathode lamp is needed to provide light of the appropriate wavelength with a sufficiently small linewidth. With a hollow cathode lamp as source, it might at first seem that the monochromator that follows the flame in an AA instrument is not needed, since the wavelength has already been selected. However, one difficulty with HCLs, as already mentioned, is that they produce light not only from the element of interest (*e.g.* Cu), but also from ions of this element (Cu^+ or Cu^{2+}) and from atoms and ions of the fill gas (*e.g.* Ne, Ne^+) and any other element that might be present in the cathode. None of this latter radiation can be absorbed by the Cu atoms in the sample, and, if it gets through to the detector, it will cause the sensitivity of the measurement to drop dramatically and Beer's Law to be invalid.

In addition not all of the light from the atoms of the element of interest can be used either. To explain why this is so, consider the hypothetical energy level diagram depicted in Figure

12.49. The arrows on this diagram represent the possible energies of the photons emitted by the HCL from the element of interest. Those lines which terminate in the ground state are called resonance lines. Only the resonance lines and none of the other atomic lines can be absorbed by atoms in the flame or furnace since atoms in the flame or furnace are normally in the ground state before absorbing the light (remember that absorption has the arrows going in the direction opposite that for emission). The final conclusion is that very few of the lines produced by the HCL are useful in atomic absorption spectroscopy.

Some way must be found to select only the one line most useful for the measurement. This is the job of the monochromator in atomic absorption. The monochromator does not make the line emitted by the HCL more monochromatic, it just selects the desired line. This is illustrated by Figure 12.50. When placed after the flame or furnace, the monochromator also helps to remove background light from the sample source and the room.

One question still needs to be answered – why is the emission bandwidth of the HCL narrower than the absorption bandwidth of the sample atoms in the flame or furnace (it must be if Beer's Law is to be valid)? Remember that the atoms absorbing the light are at room pressure and are quite hot (in a flame or furnace). The pressure in the HCL is very low, and thus pressure broadening is not as pronounced as at room pressure. Also the translational temperature of atoms in the HCL is lower than the temperature in the flame or furnace, lessening the effect of Doppler broadening.

Exercise 12.21

Sodium atoms absorb strongly at around 589 nm. Suppose that a monochromator also passes a neon fill gas line at 588.2 nm that has an intensity of 10% of the sodium line when no absorption occurs. What is the absorbance measured on the AA spectrometer when the true absorbance of the sodium is 0.100? When it is 1.00? What is the percent error in each case? Is the problem worse when the absorbance is low or high?

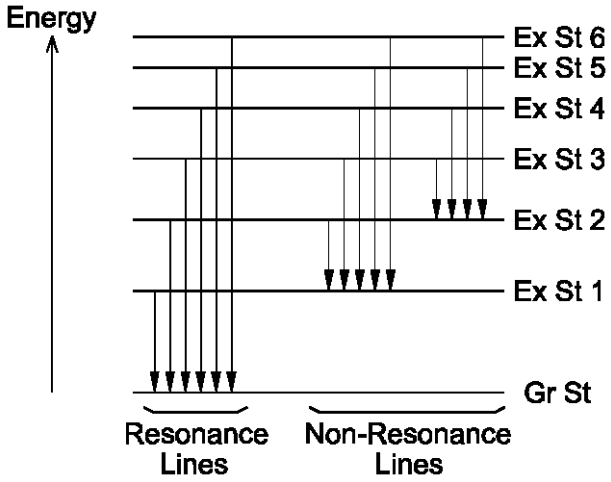


Figure 12.49: Hypothetical energy level diagram showing emission energies for atoms in a hollow cathode lamp. Only resonance lines will be absorbed in the flame.

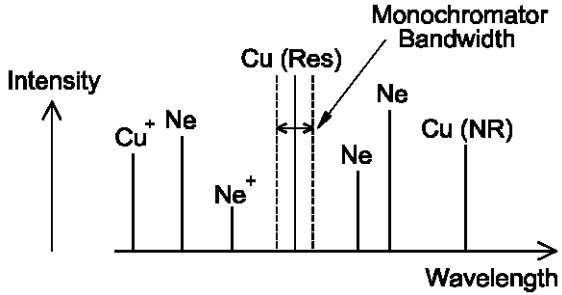


Figure 12.50: Line spectrum of a Cu HCL showing interferences around the resonance line, including fill gas (Ne), ion (Cu^+) and non-resonance (NR) lines.

12.17 Atomic Absorption Spectroscopy: Applications

Absorption measurements in flames and furnaces are made in the same way as those in solution and Beer's Law applie to relate concentration and instrument response. However, absolute calibration cannot be used, since there is no easy way to relate the gas phase concentration of atoms in the flame or furnace to the concentration in solution, as this depends on many physical factors associated with atomization. Calibration curves are normally employed and standard addition can be used. Unfortunately Beer's Law is not as well obeyed in AA as in solution spectrophotometry because: (1) the bandwidth of the light from the HCL is not considerably narrower than that of the atoms in the atom source, and (2) the atom source (flame or furnace) is not a very ideal sample cell. In solution work the boundaries of the cell are very well defined and the sample is uniform throughout the cell. Neither of these circumstances exist in flames or furnaces, and this causes deviations from Beer's Law.

It is obvious that the sample must be destroyed to obtain the atoms for analysis. Therefore AA is useful for what is called elemental analysis, that is the analysis of the elemental content of the sample. Thus, in the case of copper, AA can determine the total amount of copper in a sample, but not how that copper is incorporated in the sample (referred to as *speciation*). Also, AA cannot determine all elements with equal ease because of the difference in the spacing of energy levels for different elements. In general the energy level differences in atoms get larger as one proceeds from the left of the periodic table (the alkali metals) to the right (the halogens) (from metals to non-metals). The alkali metals absorb in the visible region of the spectrum, the halogens in the vacuum (far) ultraviolet. Most metals absorb in the ultraviolet. AA cannot be used in the vacuum ultraviolet (wavelengths below 200 nm) because these wavelengths are absorbed by the atmosphere. Thus AA is not used for the analysis of non-metals.

In terms of the analysis of metals, the sensitivity of absorption (the molar absorptivity) varies from element to element. More important, the ease with which materials can be broken into atoms varies from element to element. The refractory metals form materials, often oxides, that are very hard to break into atoms. The net result of this is that the materials containing these elements leave the flame or the furnace before being broken into atoms, and thus atomic absorption never occurs. Thus, elements like zirconium and tantalum show low sensitivity, whereas elements like copper and cadmium can be determined with high sensitivity.

Since the metals make up about 90% of the elements, AA can be used to determine about 90% of the entries in the periodic table. Like molecular absorption, AA is a trace technique, generally operating in the range of 10^{-5} to 10^{-8} M. Flame AA covers the higher end of this range and graphite furnace AA the lower end. Electrothermal AA is one of the most sensitive techniques available for the determination of many metals. The usual expected accuracy of this technique, when properly applied, is between about 2 and 10%.

As with all analytical techniques, certain problems or characteristics must be taken into account when using atomic absorption. As pointed out above, AA is a destructive technique. The sample cannot be recovered in any form. This also means that no speciation information is available from this technique. Speciation information involves knowledge of the form in which the element exists in the sample. For example, in a sample containing chromium, we might ask "Is the chromium present in the +2, +3 or +6 oxidation state?"; "Is the chromium found as an oxide, a sulfide, or a sulfate?"; "Is the chromium complexed with an organic ligand or is it a simple ion?". These questions cannot be answered by AA. All that AA can reveal is the total chromium present in the sample.

Atomic absorption is affected by certain matrix effects. Many elements show different absorbances depending on the other substances present in the sample. For example, Ca shows different sensitivity in Cl^-, SO_4^{2-}, and PO_4^{3-} solutions. The reason for this is that chlorides, sulfates, and phosphates atomize to different extents, and thus provide different numbers of atoms in the atom source. This type of matrix effect can often be circumvented by adding a material to the sample which will provide the same atomization efficiency regardless of the other materials in the sample. Large organic ligands such as EDTA (ethylenediamine tetraacetic acid), that form strong complexes with metal ions, are often used in this regard. The other approach is to use standard addition, since in standard addition, the same matrix is involved in both the sample and the standard, and the sensitivity does not change drastically between sample and standard.

Metals that are easily ionized also sometimes present problems. The alkali metals are the best examples of such elements. Ionization proceeds as shown below.

$$M(g) \rightleftharpoons M^+(g) + e^- \qquad K = \frac{[M^+][e^-]}{[M]}$$

As the temperature rises, the reaction proceeds more to the right and the value of the equilibrium constant increases. This reaction acts just like the ionization of a weak acid in solution - the percent ionization increases as the total concentration of M decreases. This is in reality a chemical deviation from Beer's Law, which would appear positive if the measured absorbance were plotted *vs* total metal concentration in solution. Another problem is that, since the standards and samples may not contain the same substances, the concentration of electrons in the atom source for the sample and standards may not be the same, leading to different amounts of ionization in the sample and standards. This is analogous to the problem of pH variations in molecular absorption spectroscopy. The problem can be circumvented by adding a large concentration of an easily ionized element (EIE) like potassium to all solutions. In this case the electron concentration, which is established by the large and constant concentration of potassium, is constant. This in turn forces the ratio of $[M^+]/[M]$ to be constant, avoiding both the matrix and deviations from Beer's Law problems. The addition of potassium buffers the electron concentration and acts in a fashion similar to a pH buffer in solution. Of course, the assumption made in this example is that potassium is not one of the elements to be analyzed. If this is not the case, other metals can be used in its place.

Exercise 12.22

The amount of tin in the syrup of canned pineapples was determined by flame AA spectrometry. A 2.00 g sample of the syrup was mixed with 4 mL of nitric acid and 4 mL of hydrochloric acid and heated to digest the organic matter. A 1.2 mL aliquot of 0.25 M potassium chloride was then added as an ionization buffer, along with distilled water to give a total volume of 15.00 mL. The sample was introduced to the AA spectrometer and the percent transmission was measured at 286.3 nm as 81.2%. A second sample was treated in the same way, except that 1.00 mL of a 200. $\mu g\ mL^{-1}$ tin standard was added to the original 2.00 g syrup sample. This gave a percent transmittance reading of 54.3%. Assuming that Beer's Law holds and that the 0%T and 100%T were properly set, determine the concentration of tin in the pineapple syrup in $\mu g/g$.

12.18 Atomic Emission Spectroscopy

As was the case for molecules, if atoms can be promoted to an excited state, then they will return to a lower energy state by radiating light. The wavelength of this light can then be used to identify the emitting element and its intensity can be used to perform quantitative analysis. For molecules, this process was referred to as fluorescence and the energy needed to promote the molecule to the excited state was provided by an intense light source of appropriate wavelength. One might think that a similar method could be used to excite atoms, and it has, but it is generally not the preferred method for two main reasons. First, a light source with a high intensity at the absorption line must be used, limiting the selection to specially designed gas discharge tubes and lasers. Second, unlike molecular fluorescence, in atomic fluorescence, there is no difference in the excitation and emission wavelengths, making it difficult to distinguish fluorescence from scatter.

Instead, in atomic emission spectroscopy, thermal energy (heat) is the method normally used to excite the atoms. This is straightforward, since it is already necessary to heat the sample to destroy the matrix and produce the atoms. Anyone who has seen a fireworks display or placed metal salts in a flame has seen the radiation from atomic emission, which appears in a wide variety of colours, depending on the element. There are two sources of thermal energy normally used in atomic emission, flames and plasmas. The characteristics of these two sources will be described, followed by a discussion of instrumentation and applications of atomic emission (AE) spectroscopy.

Emission from Flames

As was mentioned in discussing AA, most atoms in flames are in the ground state. However, flames produce enough energy to promote some metal atoms, especially those on the left of the periodic table, *e.g.* groups 1 and 2, to excited states. Even the atoms from these elements are mainly in the ground state, but enough are excited so that sufficient light is emitted by the flame to detect these metals at very low concentrations. You can view this energy absorption as arising from multiple infrared photons (heat energy), or (more likely) from the transfer of energy from other excited state species, such as radicals, that result from chemical reactions in the flame.

Atomic emission is one of the oldest spectroscopic techniques, going as far back as Bunsen in the 1800s, whose name is associated with the simple burners still used in laboratories today. However, to obtain maximum emission, the use of hotter flames is preferred, since this will generate the highest concentration of atoms in the excited state. Table 12.4 lists some of the more useful fuel-oxidant mixtures and their flame temperatures. Obviously, it would seem better to use either oxygen or nitrous oxide as oxidant because of the higher temperatures. However, these oxidants, especially oxygen, cannot be used in a premixed burner (such as is used in AA) because the flame burns so rapidly that it would flash back in such a burner. (Nitrous oxide can be used in special premixed burners if precautions are taken.) This is unfortunate, since a premixed flame burns more steadily and quietly and with less background radiation. In general, only the alkali metals are determined in premixed flames with air as oxidant.

A "total consumption" burner is used when the flame components have a high burning rate. Such a burner is shown in Figure 12.51. As with the nebulizers used in AA, the sample is nebulized by passing rapidly moving gases past the tip of a capillary dipping into the sample. The mist produced is introduced directly into the flame. The fuel and oxidant gases are also mixed directly in the flame (no premixing). The term "total consumption" is a bit misleading. It would appear that the entire sample enters the flame, as opposed to only about 10% in the systems used in AA. However, there is strong reason to believe that most of the sample moves through such flames too rapidly to be atomized and thus their performance is no better than the nebulizer-burner systems used in AA. These burners produce hotter flames than premixed burners and can be used to excite more elements, but are seldom used today since plasma emission, described below, is an even better excitation medium.

Emission from Inductively Coupled Plasmas

A plasma is a very hot mixture of molecules, atoms, ions, and electrons in the gas phase. In the inductively coupled plasma (ICP) intense microwave radiation (basically low energy but high intensity heat radiation) heats a gas mixture to temperatures near 10,000 K. This heating is similar to that in a microwave oven but the power levels and temperatures are much higher. Argon is used as the gas which forms the plasma. Liquid sample is introduced into the argon gas stream in the same way as in AA (in a nebulizer system similar to that shown in Figure

Table 12.4. Typical flame temperatures (in °C) for various combinations of fuels and oxidants.

Fuel	Oxidant		
	Air	Oxygen	N_2O
C_2H_2	2400	3140	2800
H_2	2045	2660	2690

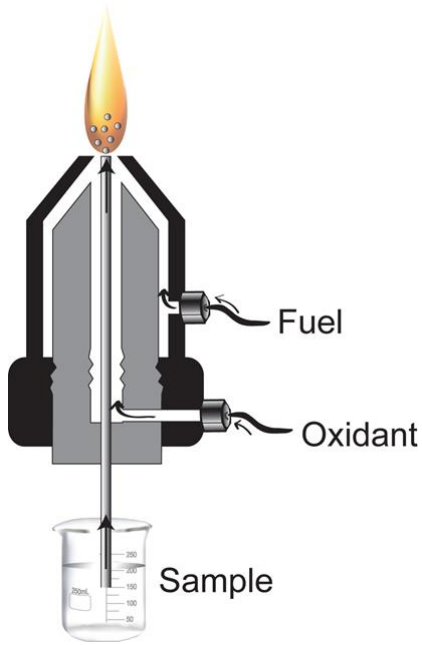


Figure 12.51: Diagram of a total consumption burner in which the entire sample is aspirated into a hot flame.

12.45) and is atomized in the plasma in a device called a plasma torch, shown in Figure 12.52. The high temperature of the plasma has two obvious advantages: (1) it can excite more elements than a flame and it excites each element to a greater degree, thus giving higher sensitivity, and (2) it almost completely destroys the matrix, causing many of the matrix effects observed in flames to disappear. However, many more spectral lines are observed from a plasma emission source and this can cause some spectral overlap and interference among elements. Therefore, the choice of emission line to be observed and the quality of the monochromator (see below) are important considerations. In addition, the instrumentation, as well as the large quantity of argon consumed by the ICP, are more expensive than flame emission spectrometers. Nevertheless, inductively coupled plasmas are the choice of many commercial analytical laboratories involved in elemental analysis.

Instrumentation

As shown in Figure 12.53, the instrument used for atomic emission is very simple, especially if a flame is used as the emission source. The light from the emission source is focused on the monochromator which in turn selects the line of interest and rejects all the other lines from the flame or plasma. The detector, amplifier and readout are similar to those used in the other spectroscopic techniques that have been discussed. In more sophisticated instruments using an ICP, multielement analysis can be performed simultaneously. This is done using a monochromator with several exit slits. These are placed at different positions along the dispersed spectrum and select lines from different elements. For each exit slit and line, there is a detector, amplifier, and readout. Up to about 20 elements can be determined at one time for each sample. This type of analysis is of interest to geologists, mining companies, steel mills, and others who want to know the total metallic composition of samples. The ability to perform multielement analysis is a distinct advantage of ICP atomic emission spectroscopy over AA spectroscopy, where the hollow cathode lamp needs to be changed for each element. Again, however, it is more expensive.

It should be noted that, in modern commercial laboratories, ICP atomic emission spectroscopy has been largely displaced by the combination of ICP with mass spectrometry (ICP-MS). Although the principles of sample introduction and atomization is the same, quantitation of analyte atoms is not performed with optical detection, but rather through the

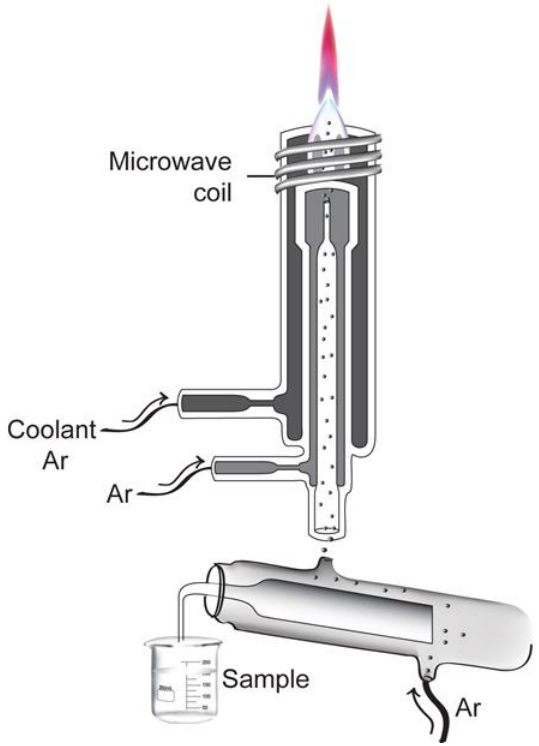


Figure 12.52: Cross-section of an ICP torch, which measures a few cm in diameter. Argon gas flows through concentric quartz tubes. A high frequency (*ca.* 20 MHz) current passes through copper coils that are wrapped around the outer tube. The magnetic field created by this current causes an induction current of ions and electrons within the coils, and the resulting collisions generate high temperatures in a doughnut-shaped region. Emission is measured in a region slightly above the coils.

use of mass spectrometry to measure the concentration of ions produced from the atoms in the plasma. This solves some problems and introduces others, but since ICP-MS is not a spectroscopic technique, it will not be treated in detail here.

Applications of Atomic Emission Spectroscopy

In this type of emission technique (as compared to fluorescence), intensity is usually linear in concentration over many orders of magnitude since there is no excitation radiation to be absorbed and self-absorption is usually small at concentrations present in the flame or plasma.

$$I = kc \tag{12.53}$$

As in all spectroscopic techniques, blanks are used to determine the background signal level, and this level is subtracted from the signal provided by the sample. Usually several standards are employed to prepare a calibration curve (a plot of *I vs c*) and this curve is used to translate the emission intensity of the sample into concentration in the normal manner. Standard addition may also be used in atomic emission analysis. Internal standards, consisting of elements not present in the sample, are also often used to help compensate for changes in flow rates or temperature, or variations in flame or plasma position. As in atomic absorption spectroscopy, ionization buffers, sometimes called *radiation buffers*, are often used to enhance the number of analyte atoms in the flame and reduce the effects of changes in the matrix. Their role can be even more important in atomic emission where higher flame temperatures are likely to increase the number of analyte ions.

The characteristics of atomic emission are very much like those of AA. It is used for the elemental analysis of metals in samples. It is a destructive method and provides, by itself, no information on speciation. It is a trace technique operating down to 10^{-7} M at accuracies of between 2 and 10%. Thus, it might seem to be competitive with AA, and to a large extent it is.

The particular sample often determines which spectroscopic technique is best used. Flame emission instruments are very simple and reliable and are used most often to analyze the alkali metals. Flame AA instruments are also simple and relatively inexpensive and analyze a much wider range of elements than flame emission instruments. These are used when a specific element is to be analyzed and the highest sensitivity is not required. Recall

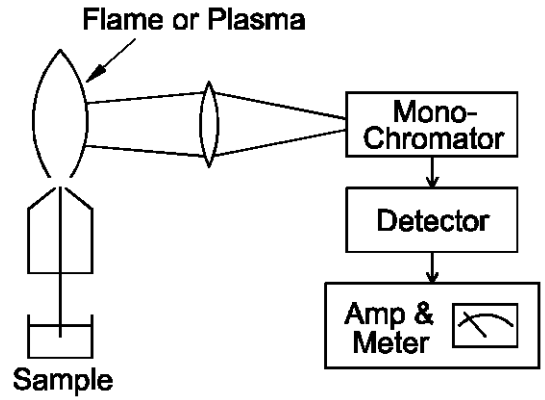


Figure 12.53: Block diagram of a simple atomic emission spectrometer.

that AA instruments usually only analyze one element at a time. For multielement analysis, for higher sensitivity, and for the analysis of refractory elements, ICP atomic emission spectroscopy (ICP-AES) technique is best. Finally for the highest sensitivity (for non-refractory elements), and if sample sizes must be kept small, electrothermal AA is the technique of choice.

Example 12.23: Atomic Emission Spectroscopy

Lithium is often administered as a drug to reduce the symptoms of manic depression. A flame photometer is adjusted to zero (arbitrary units) while aspirating a 0.0001 M KCl (a radiation buffer) solution which contains no lithium. A 1.00 ppm Li^+ solution, also containing 0.0001 M KCl, gives a reading of 86.7 units. A sample, prepared by mixing 10.00 mL of a urine sample with 10.00 mL of 0.0002 M KCl, produces a reading of 36.4 units. What is the lithium concentration in the urine sample?

Note that the concentration of the radiation buffer is the same for all samples. Under these conditions, we assume a linear relationship between concentration and intensity.

$$I = kc$$

Using the standard, we can calculate the proportionality constant.

$$k = \frac{I_{std}}{c_{std}} = \frac{86.7}{1.00\,\text{ppm}} = 86.7\,\text{ppm}^{-1}$$

The concentration of lithium in the diluted urine sample can now be calculated.

$$c_{dil} = \frac{36.4}{86.7\,\text{ppm}^{-1}} = 0.420\,\text{ppm}$$

Correction for the dilution factor gives the concentration in the original sample.

$$c_{orig} = 0.420\,\text{ppm} \times \frac{20.00\,\text{mL}}{10.00\,\text{mL}} = 0.840\,\text{ppm}$$

Exercise 12.23

For the previous example, assume that the uncertainty in the lithium standard is ±0.03 ppm, the uncertainty in the intensity readings is ±0.5, and the uncertainty in the measured volumes is ±0.03 mL. By propagation of error, determine the uncertainty in the original lithium concentration. What is the largest source of uncertainty?

12.19 Summary

Spectroscopy concerns the interaction of light with matter and has widespread application in quantitative analysis, particularly in the visible and UV regions of the spectrum. Methods involve both the absorption and emission of radiation, and are applied to both molecular and atomic species. Molecular absorption spectroscopy is governed by Beer's Law, which defines the amount of light passing through a solution in terms of its molar absorptivity, path length and concentration. Emission from molecular species in solution is referred to as fluorescence. Fluorescence emission is linear at low concentrations and fluorescence measurements are more sensitive than absorbance measurements. Instrumentation includes light sources, monochromators, sample cells and detectors. Atomic spectroscopy also requires a flame or other method to convert a sample to atoms in the gas phase. Atomic absorption measurements use a hollow cathode lamp as a light source and can be used to determine a variety of metals. Atomic emission in flames is applicable mainly to Group 1 and 2 metals, but others can be detected using an inductively coupled plasma.

12.20 Additional Exercises

Exercise 12.24
Calcium atoms absorb and emit light at a wavelength of 422.7 nm (among other wavelengths). What is the frequency and energy (per mole of photons) of this light?

Exercise 12.25
What would be the energy (per photon), wavelength, and frequency of the light emitted when a hydrogen atom falls from the 2nd excited state to the first excited state (see Figure 12.7)?

Exercise 12.26
Assume that the area of a molecule which is responsible for the absorption of a photon is circular with a radius of 75 pm, what is the maximum value for ε for that molecule?

Exercise 12.27
A coloured glass light filter 2.00 mm thick is placed in a spectrophotometer and its %T measured as 8.7. The %T of a piece of glass of the same composition is measured as 79.4 in the same manner. What is the thickness of the glass?

Exercise 12.28
A very simple spectrophotometer (without dark current or 100%T adjustments) is used to measure the concentration of a coloured material in a sample. With the light beam blocked, the meter (which has a linear scale) reads 5.3. With a blank in the light beam the reading is 83.5, with a standard of 5.00×10^{-5} M concentration the reading is 64.4, and with the sample the reading is 31.2. What is the sample concentration, assuming that Beer's Law is obeyed?

Exercise 12.29
If the absorbance of a solution containing 1.00×10^{-5} M of a coloured copper complex is 0.286 in a 1.00 cm cell, what concentration of the coloured complex would be required to absorb exactly half the light that enters the same cell? Assume Beer's law is obeyed.

Exercise 12.30

The %T of a 1.00×10^{-5} M solution of a dye is measured as 28.6 in a 1.00 cm cell. 1.00 L of a 1.00×10^{-2} M solution of the same dye is poured into an irregularly shaped vessel containing clear water and the dye thoroughly mixed. A sample of the resulting solution reads 75.3 %T in the same 1.00 cm cell. What is the volume of the vessel?

Exercise 12.31

The %T of a sample containing a coloured Fe(II) complex (in excess complexing reagent) is measured as 28.6. When 2.00 mL of a 1.00×10^{-4} M Fe(II) standard is mixed with 10.00 mL of the sample, the resulting solution reads 13.8 %T in the same cell. Assuming that Beer's law holds and that the iron complex is the only coloured material in the sample, calculate the concentration of Fe(II) in the original sample.

Exercise 12.32

Benzoic acid, which absorbs in the UV, can be analyzed in water samples by spectrophotometry. A 10.00 mL aliquot of a water sample is diluted to 20.00 mL and reads 56.3 %T in a spectrophotometer. Then 1.00 mL of a 5.00×10^{-5} M solution of benzoic acid is added to 10.00 mL of sample and diluted to 20.00 mL. This solution reads 51.2 %T. What is the concentration of benzoic acid in the sample?

Exercise 12.33

Equilibrium constants can be determined using spectrophotometry. For example, a solution is prepared containing 2.00×10^{-2} F phenolphthalein (an acid-base indicator). Three 1.00 mL portions of this solution are diluted to 100.0 mL with the following three solutions: (a) 0.100 F HCl, (b) 0.100 F NaOH, and (c) a buffer solution of pH 9.35 (where the formalities of both of the buffer components are approximately 0.100). The absorbances of the three solutions as measured in a 1.00 cm cell are:

(a) A = 0.000 (all indicator in the acid form).
(b) A = 0.732 (all indicator in the base form)
(c) A = 0.242

What is the pK_a of the indicator?

Exercise 12.34

If a spectrophotometer exhibits only errors that are independent of T, and if that error is ±1.2 %T, what will be the relative error in concentration made by the instrument at 10 %T, 50 %T, and 90 %T?

Exercise 12.35

Cu(II) and Ni(II) both form coloured complexes with an organic Lewis base reagent. The following data are available: at 450 nm, ε for the Cu(II) complex is 1.53×10^4 M^{-1} cm^{-1} and that of Ni(II) is 3.24×10^3 M^{-1} cm^{-1}; at 530 nm the values are 934 and 7.62×10^3 M^{-1} cm^{-1}, respectively. An unknown containing both metal ions gives a %T of 16.4 at both 450 and 530 nm in a 1.00 cm cell. Calculate the concentrations of the two metal ions in the unknown.

Exercise 12.36

Sometimes colour forming reagents are so highly coloured themselves that they interfere in a spectrophotometric analysis. The reagent dithizone (a deep green colour) can be used in trace metal analysis. It is usually dissolved in a solvent such as dichloromethane and the metal ion reacts with this reagent and is extracted from the aqueous solution into the CH_2Cl_2, changing the colour of that layer. Assume the following:

	ε_{450}	ε_{550}
Coloured reagent	3.24×10^3	1.28×10^4
Coloured metal complex	1.07×10^4	2.44×10^3

If the absorbance of the coloured organic layer is measured as 0.447 at 450 nm and 0.731 at 550 nm, what is the concentration of the metal complex in the CH_2Cl_2 layer? Assume b = 1.00 cm.

Exercise 12.37

The following absorbance data are available for coloured complexes of Co(II) and Cr(III) with an uncoloured reagent in the same cell:

	450 nm	500 nm	550 nm	600 nm
1.00×10^{-4} M Co(II)	0.255	0.183	0.353	0.510
4.00×10^{-5} M Cr(III)	0.042	0.395	0.141	0.083
Mixture of Co(II) + Cr(III)	0.283	0.816	0.532	0.566

What are the concentrations of Co(II) and Cr(III) in the mixture?

Exercise 12.38

Consider a titration of the form: $U + T \rightarrow P1 + P2$. If the titrant (T) is the only coloured species in the reaction at the wavelength of interest, derive equations for the corrected absorbance before and after the equivalence point in the titration. Assume that $\varepsilon_T = 1000\ M^{-1} \cdot cm^{-1}$, $b = 1.00$ cm, $[T]_o = 0.00100$ F, $[U]_o = 0.00100$ F, $V_u = 50.0$ mL. What will be the corrected absorbance (calculated using only the equation you derived for the corrected absorbance after the end point) at 25.0, 50.0, and 75.0 mL of T added?

Exercise 12.39 (Challenge Problem)

This problem calculates the effect of non-monochromatic light on Beer's Law. Assume that a spectrophotometer set to a given wavelength actually passes two separate wavelengths, A and B, each with the same intensity. Second, assume that the sample absorbs both wavelengths, but to different extents. Given $\varepsilon_A = 6.00 \times 10^3$, $\varepsilon_B = 1.00 \times 10^4$, and $b = 1.00$ cm, calculate the actual absorbance measured for $c = 1.00 \times 10^{-4}$ M. Next, assuming in the "ideal" case the molar absorptivity can be taken as the average of the two values, ($\varepsilon_{ideal} = 8.00 \times 10^3$) calculate the "ideal" absorbance of the same solution. What concentration of absorber will produce an actual absorbance of 0.500? What concentration would be needed in the "ideal" case?

Exercise 12.40 (Challenge Problem)

A certain type of spectrophotometer exhibits one type of error which is constant with transmittance and which amounts to 0.25 %T, and a second type which is proportional to transmittance (relative error in *T* is constant) which amounts to 0.20 %. At what value of transmittance will the relative error in concentration be a minimum? To what absorbance does this correspond? What is the relative error in *c* at this point? Between what values of *T* will the relative error in *c* be equal to or less than 1.0 %?

Exercise 12.41

The fluorescence of a 1.00×10^{-7} F quinine sulfate solution was measured as 31.5 with a fluorometer while the background was 4.9. A water sample thought to contain quinine (when treated in the same manner as the standard and the blank) measured 52.9. Assuming that the concentration is low enough for fluorescence to be linear in concentration, calculate the concentration of quinine in the sample.

Exercise 12.42

The oxidized form of riboflavin does not fluoresce. A 10.0 mL sample containing riboflavin is added to 10.0 mL of an oxidizing agent and the fluorescence is measured as 8.7. Next, 10.0 mL of the sample are diluted to 20.0 mL and the fluorescence is measured as 38.6. Finally, 10.0 mL of the sample plus 2.00 mL of a 1.00×10^{-6} F riboflavin solution are diluted to 20.0 mL and the fluorescence measured as 61.3. What is the concentration of riboflavin in the unknown (assuming fluorescence is linear in concentration)?

Exercise 12.43

Assuming that a fluorescent analyte does not absorb any emitted light, that excitation light falls evenly on the entire width of the cell, and that the entire cell width can be "seen" by the detector, derive an equation that predicts the deviation from linearity of fluorescence as a function of *c* and ε, assuming that b = 1.00 cm. (HINT - use the ratio of observed fluorescence to "expected" or "ideal" fluorescence and the series expansion of the exponential retaining both the first and second order

terms in C.) At what concentration will there be a 2% deviation (98% of the expected fluorescence is observed) if $\varepsilon = 1.00 \times 10^4\ M^{-1}\ cm^{-1}$?

Exercise 12.44 (Challenge Problem)
The following data were obtained in a fluorescence analysis:

Solution	Fluorescence
Blank	10.3
5.0×10^{-6} F	43.5
1.0×10^{-5} F	68.8
Unknown	61.3

Assume only that the analyte does not absorb the fluorescent light and that the entire width of the cell is exposed to excitation radiation and is observed by the emission detector. What is the concentration of the analyte in the unknown?

Exercise 12.45
A simple AA spectrometer is used to analyze copper in water samples. The blank provides a reading of 82.6, a 0.100 ppm Cu(II) solution gives a reading of 61.3, a sample gives a reading of 56.5 and the instrument reads 2.1 with the light beam blocked. What is the concentration of Cu(II) in the sample? Assume Beer's Law holds.

Exercise 12.46
Solvent extraction, in which ions are extracted into an organic phase that is insoluble in water (e.g. nitrobenzene), can be used to overcome interferences and pre-concentrate analytes in AA spectroscopy. A 100.0 mL sample of an aqueous solution containing Cd(II) is extracted with 5.00 mL of nitrobenzene containing an extracting reagent and the absorbance of the organic layer is read as 0.341. A sample of nitrobenzene containing 0.200 ppm Cd(II) gives an absorbance of 0.463 under the same conditions. What is the concentration of Cd(II) in the water sample? (Assume Beer's Law is obeyed.)

Exercise 12.47

From the following data determine the concentration of Ba^{2+} in an unknown analyzed by AAS (assume linearity between A and concentration).

Solution	%T
Sample	65.3
8.00 mL of sample + 2.00 mL of 2.00 ppm Ba^{2+}	53.6

Exercise 12.48

The following data are taken on solutions containing both Cu(II) and Ag(I) using an AA spectrometer. These elements are very similar in their behaviour in AA spectroscopy, copper absorbing at 325 nm and silver at 338 nm.

[Cu(II)](M)	[Ag(I)](M)	A_{325}	A_{338}
2.00×10^{-6}	1.00×10^{-6}	0.136	0.193
4.00×10^{-6}	5.00×10^{-7}	0.273	0.098
6.00×10^{-6}	2.00×10^{-6}	0.405	0.388

Is the ratio A_{325}/A_{338} proportional to the ratio [Cu(II)]/[Ag(I)]? A 2.00 mL aliquot of a solution containing 3.00×10^{-5} M Ag(I) are added to 10.0 mL of a sample containing copper but no silver. This solution is then treated in a way that changes the concentrations of its components (but not their ratios) in order to analyze for other elements. Then, the values for A_{325} and A_{338} for this solution are determined to be 0.125 and 0.183 respectively. Using the ratio of these values and the proportionality constant calculate the concentration of Cu(II) in the original sample.

Exercise 12.49

Some materials prevent the atomization of certain metals in the flames normally used in AA spectroscopy. This interference is sometimes so quantitative that it can be used to determine the interferent. An example of such a system is the

interference of phosphate on the atomic absorption of calcium. From the following data determine the concentration of phosphate in the sample.

Solution	A_{423}
2.00×10^{-6} M Ca^{2+}	0.538
2.00×10^{-6} M Ca^{2+} + 1.00×10^{-6} M PO_4^{3-}	0.409
2.00×10^{-6} M Ca^{2+} + 2.00×10^{-6} M PO_4^{3-}	0.280
10.0 mL sample + 10.0 mL 4.00×10^{-6} M Ca^{2+}	0.337

Exercise 12.50

Uranium in well water is to be analyzed by ICP atomic emission at 358.4 nm. A solution of uranyl nitrate ($UO_2(NO_3)_2$) containing 50.0 ppb uranium gives an intensity of 185.3 arbitrary units. The well water sample reads 89.5 units and distilled water reads 20.5 units. What is the concentration of uranium in the well water? Ans: 20.9 ppb.

Exercise 12.51

A saturated solution of CaF_2 (in equilibrium with solid CaF_2) produces an intensity reading of 116.1 on a flame photometer. A 5.00 ppm standard solution of Ca^{2+} ion reads 66.8 and distilled water reads 8.7. From these data, calculate the solubility product of CaF_2.

12.21 Answers to Exercises 12

12.1 green; 2.7×10^{15}, more

12.2 486 nm, blue

12.3 1312 kJ/mol

12.4 5.7×10^{-4} M

12.5 579 nm, yellow

12.6 lower

12.7 0.10%

12.8 1.018

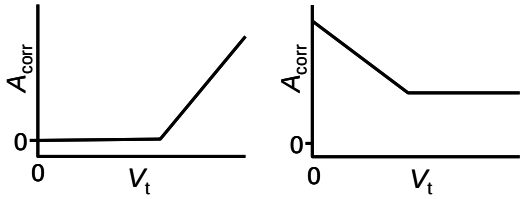
12.9 Yes

12.10 0.510, –1.9%, 1.661, –9.7%

12.11 16 μM

12.12 6.88×10^{-5} M, 3.32×10^{-5} M

12.13 (a) (b)



12.14 4%

12.15 $\overline{1}.7\ \%$, constant

12.16 $0.\overline{1}5$

12.17 0.00024 °C

12.18 2.1×10^{-7} J

12.19 3.81×10^{3}

12.20 5.00×10^{-7} M

12.21 0.090, 0.740, –10.%, –26.0%

12.22 52 μg/g

12.23 $\pm 0.0\overline{2}8$ ppm, the Li concentration

12.24 $7.093 \times 10^{14}\ s^{-1}$, 283.1 kJ/mol

12.25 3.026×10^{-19} J, 656.5 nm, $4.567 \times 10^{14}\ s^{-1}$

12.26 $4.62 \times 10^{4}\ M^{-1} \cdot cm^{-1}$

12.27 0.189 mm

12.28 1.97×10^{-4} M

12.29 1.05×10^{-5} M

12.30 4.41×10^{3} L

12.31 2.23×10^{-5} M

12.32 $3.0_2 \times 10^{-5}$ M

12.33 9.66

12.34 ±5.2%, ±3.5%, ±13%

12.35 [Cu(II)] = 3.03×10^{-5} M, [Ni(II)] = 9.93×10^{-5} M

12.36 2.60×10^{-5} M

12.37 [Co(II)] = 8.37×10^{-5} M, [Cr(III)] = 6.71×10^{-5} M

12.38 –0.500, 0.000, 0.500

12.39 0.755, 0.800, 6.49×10^{-5} M, 6.25×10^{-5} M

12.40 0.341, 0.467, 0.71%, 0.118 to 0.647

12.41 1.80×10^{-7} F

12.42 2.63×10^{-7} F

12.43 1.74×10^{-6} M

12.44 8.4×10^{-6} F

12.45 0.128 ppm

12.46 0.00737 ppm

12.47 0.603 ppm

12.48 1.17×10^{-5} M

12.49 3.12×10^{-6} M

12.50 20.9 ppb

12.51 4.91×10^{-11}

Topic 13

Redox Reactions and Potentiometry

13.1 Contents in Brief

- Oxidation-reduction (redox) reactions
- Electrochemical cells and cell potentials
- Potentiometry with redox and membrane electrodes
- Redox titrations in chemical analysis

13.2 Introduction

Some of the most useful tools for chemical analysis take advantage of the transfer of electrons and the migration of charged species in aqueous solution, most often through oxidation-reduction reactions. In general, these are known as electrochemical or electroanalytical methods and they encompass a wide range of techniques. In this topic we will consider two widely used methods: (1) *oxidation-reduction titrations*, based on classical "wet" chemistry, and (2) *potentiometry*, based on the measurement of electrochemical potential.

13.3 Redox Reactions

An oxidation-reduction, or *redox*, reaction is one which involves the transfer of electrons from one species to another. For example, if we prepare an aqueous solution of Cu^{2+} ions from a salt such as copper sulfate ($CuSO_4$) or copper nitrate ($Cu(NO_3)_2$) and drop in a piece of zinc, as shown in Figure 13.1, then the following reaction will spontaneously occur:

$$\underset{\substack{\text{oxidizing agent}\\(\textit{oxidant})}}{Cu^{2+}(aq)} + \underset{\substack{\text{reducing agent}\\(\textit{reductant})}}{Zn(s)} \rightarrow Cu(s) + Zn^{2+}(aq)$$

In this reaction, two electrons are transferred from the zinc metal atom to the copper ion to form a zinc ion in solution and a copper metal atom. Because the zinc metal loses electrons, it is said to be *oxidized*. Likewise, the copper ion is *reduced* because it gains electrons. Since the Cu^{2+} causes the Zn to be oxidized it is called the *oxidizing agent*, or *oxidant*. Analogously, Zn is the *reducing agent*, or *reductant*. The observed consequence of this reaction is that copper would begin to form on the surface of the zinc metal, and the blue color of the copper solution would begin to diminish as Cu^{2+} ions are replaced by colorless Zn^{2+} ions.

Because a redox reaction can be considered to be composed of two parts, it is sometimes written as two *half-reactions*, as shown below

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \text{reduction half-reaction}$$
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \text{oxidation half-reaction}$$
$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

In this relatively simple example, it is fairly obvious what is oxidized and what is reduced. However, in reactions involving molecules or molecular ions, it may not be so obvious. For example, if dichromate ions ($Cr_2O_7^{2-}$) are mixed with iodide ions, the following reaction can occur:

$$Cr_2O_7^{2-}(aq) + 6I^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3I_2(aq) + 7H_2O(l)$$

In this case, it is not as obvious what is being oxidized or reduced, or even if a redox reaction is occurring. To clarify this, we need to introduce the concept of *oxidation numbers*.

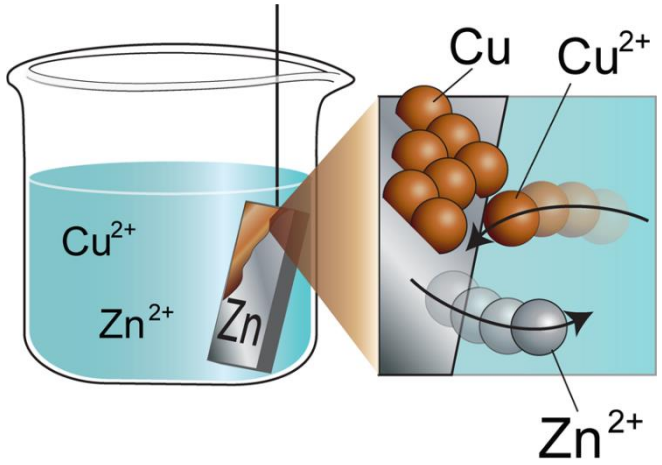


Figure 13.1: Oxidation-reduction (redox) reaction between copper ions and zinc metal.

13.4 Oxidation Numbers

To keep track of the movement of electrons in a redox reaction, chemists have developed the concept of oxidation numbers. For a simple atom or ion, the oxidation number is its charge. For species containing multiple atoms (molecules or molecular ions), *each* atom is assigned an oxidation number (its *oxidation state*) based on certain rules. It is important to remember that these rules are largely a bookkeeping method, but they are intended to reflect how atoms share electrons based on their electronegativities. It is assumed that you are already familiar with rules for calculating oxidation numbers, but the Table 13.1 is included as a review.

The rules given in the table will work for most species as long as there is no more than one type of atom that is not covered in the rules. In some cases, however, the rules may not be sufficient to assign oxidation numbers. For example, in the case of the thiocyanate ion, SCN^-, none of the atoms are mentioned by the rules in the table. In these cases, a more rigorous approach based on the electronegativities of the atoms can be used. This is illustrated with the example in Figure 13.2. Starting with the most stable Lewis structure, each electron is assigned to a specific atom. Lone pair electrons are assigned to the atom they are associated with, and bonding electrons are assigned to the atom in the bond with the higher electronegativity. If the two bonded atoms have exactly the same electronegativity (*e.g.* a C-C bond), half the electrons are assigned to each atom. The number of atoms associated with each atom is then subtracted from its normal valence, resulting in a type of formal charge on the atom that we call the oxidation number.

It should be noted that the application of this second method can lead to different oxidation numbers for different atoms of the same type in the same molecule, whereas all atoms of the same type have the same oxidation number using the rules in Table 13.1. For example, using the rules in the table, both carbon atoms in acetic acid, CH_3COOH have an oxidation number of zero. However, applying the method in Figure 13.2, the methyl carbon has an oxidation number of −3, while the carboxylic acid carbon has an oxidation number of +3, for an average of zero. The latter is more accurate, but the former is more useful in balancing redox reactions.

Table 13.1. Rules for assigning oxidation numbers and some examples.

Rule 0. Apply all the rules in order until there is one type of atom left, then apply Rule 1.

Rule 1. The sum of oxidation numbers of individual atoms must equal the overall charge.

Rule 2. **F** has an oxidation number of **−1**.

Rule 3. Group 1 (except H) = **+1**; Group 2 = **+2**.

Rule 4. **H** has an oxidation number of **+1**.

Rule 5. **O** has an oxidation number of **−2**.

Examples:

H_2O : H = +1, O = −2

ClO_4^- : O = −2, Cl = +7

CH_3COOH : H = +1, O = −2, C = 0

LiH : Li = +1, H = −1

OF_2 : F = −1, O = +2

Exercise 13.1
Determine the oxidation numbers of the atoms in the following molecules or ions.

(a) NaOBr (b) $Cr_2O_7^{2-}$ (c) $CH_3OC_2H_5$ (d) $Ca(MnO_4)_2$ (e) I_3^- (f) CN^- (g) CH_3NH_2

For case (c) above, also determine the oxidation numbers of individual C atoms.

13.5 Balancing Redox Reactions

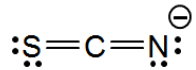
Since redox reactions are ubiquitous in chemistry, including analytical applications, it is important to know how to balance them. It is assumed that you are already familiar with this, but a brief review will be presented here. Two main approaches are presented, referred to as the *oxidation number method* and the *charge balance method*, but there are many variations of these. The charge balance method has the advantage that it is not necessary to know the oxidation numbers, so it is especially useful when these are difficult to determine. However, the oxidation number method has the advantage that it provides a way to check intermediate results.

These two methods will be illustrated using examples. Note that redox reactions typically specify either acidic or basic media simply as a way specify how the hydrogens and oxygens are to be balanced. However, we normally start both methods by balancing the reaction in acidic media, and then adjusting for basic solution at the end if necessary. This step is the same for both techniques.

Example 13.1: Balancing reactions with the Oxidation Number Method
Balance the reaction between oxalic acid and permanganate ion in acidic solution using the oxidation number method.

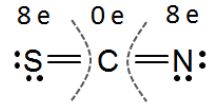
$$H_2C_2O_4(aq) + MnO_4^-(aq) \rightarrow CO_2(g) + Mn^{2+}(aq)$$

(1) Draw Lewis structure and assign electronegativities.



EN(S) = 2.58
EN(C) = 2.55
EN(N) = 3.04

(2) Associate shared electrons with the more electronegative atom and count the total number of electrons assigned to each atom.



(3) Subtract the electron count above from the normal valence of the atom. This will give the oxidation number of the corresponding atom.

S: 6 − 8 = −2
C: 4 − 0 = +4
N: 5 − 8 = −3
Charge: −1

} Oxidation numbers

Figure 13.2: Alternative approach to assigning oxidation numbers based on electronegativities, using the thiocyanate ion as an example.

Step 1. Assign oxidation numbers to determine what is oxidized and reduced.

$$\overset{+1\,+3\,-2}{H_2C_2O_4} + \overset{+7\,-2}{MnO_4^-} \rightarrow \overset{+4\,-2}{CO_2} + \overset{+2}{Mn^{2+}}$$

(Note we have temporarily dropped the phases.) Based on the oxidation numbers, we can see that carbon is oxidized (+3 to +4) and manganese is reduced (+7 to +2).

Step 2. Write the half-reactions with the correct number of electrons based on the oxidation numbers. **Be sure to balance the atoms changing oxidation state.**

$$H_2C_2O_4 \rightarrow \mathbf{2}\ CO_2 + 2e^-$$ (note: need to balance C atoms)

$$MnO_4^- + 5e^- \rightarrow Mn^{2+}$$

Step 3. Multiply the half-reactions by integers to get the lowest common multiple of electrons and combine to cancel electrons.

In this example, the lowest common multiple is 10, obtained by multiplying the first reaction by 5 and the second by 2.

$$5H_2C_2O_4 \rightarrow 10\ CO_2 + \cancel{10e^-}$$
$$2MnO_4^- + \cancel{10e^-} \rightarrow 2Mn^{2+}$$
$$\overline{5H_2C_2O_4 + 2MnO_4^- \rightarrow 10\ CO_2 + 2Mn^{2+}}$$

Step 4. Balance the oxygen atoms using H_2O.

Note that after step 3, the only things that we can add to the reaction are H_2O, H^+ (or H_3O^+) and OH^-. There are 28 oxygen atoms on the left and 20 on the right, so we need 8 more on the right.

$$5H_2C_2O_4 + 2MnO_4^- \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Step 5. Balance the hydrogen atoms using H^+.

There are 10 H on the left and 16 on the right, so we need 6 more on the left.

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10\ CO_2 + 2Mn^{2+} + 8H_2O$$

Note that, at this point, we can do a quick check to see if the charge balance is correct. We see that the charges on the left add up to +10, as do the charges on the right. If these had disagreed, there would be a mistake somewhere and we would need to check our work.

Also note that some cleaning up may be necessary here. If one species (*e.g.* H_2O) appears on both sides, it should be cancelled accordingly.

Step 6. If the reaction is in basic solution, remove H^+ by adding an equal number of OH^- to both sides. React H^+ with OH^- to make H_2O and cancel accordingly.

Since this reaction is not in basic solution, we do not need this step.

Step 7. Write the overall reaction and check the mass balance and charge balance.

$$5\,H_2C_2O_4(aq) + 2\,MnO_4^-(aq) + 6\,H^+(aq) \rightarrow 10\,CO_2(g) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$

Charge balance:	**+4**	**+4**
Mass balance:	16 H, 10 C, 28 O, 2 Mn	10 C, 28 O, 2 Mn, 16 H

If the charge and mass balance are correct, the reaction is balanced. (In rare cases, it may be necessary to adjust the coefficients to get the smallest integer ratios.)

Example 13.2: Balancing reactions with the Oxidation Number Method

Balance the following reaction in basic solution using the charge balance method.

$$CN^-(aq) + AsO_3^-(aq) \rightarrow CNO^-(aq) + As(s)$$

Step 1. Write the half-reactions (without electrons), making sure to balance the atoms changing oxidation state.

An advantage of the charge balance method is that we don't need to know oxidation numbers, but we do need to have an idea of what is oxidized or reduced. In this example, determining the oxidation numbers would require using electronegativities

for CN^- and CNO^-, but it is clear that the oxidation state of C or N changes. We can therefore write the half-reactions as:

$$CN^- \rightarrow CNO^- \qquad AsO_3^- \rightarrow As$$

In this case, the atoms undergoing changes are balanced.

Step 2. Balance the oxygen in each half-reaction with water.

$$CN^- + H_2O \rightarrow CNO^- \qquad AsO_3^- \rightarrow As + 3H_2O$$

Step 3. Balance the hydrogen with H^+ and calculate the charge on each side of each reaction.

$$\underset{\mathbf{-1}}{CN^- + H_2O} \rightarrow \underset{\mathbf{+1}}{CNO^- + 2H^+} \qquad \underset{\mathbf{+5}}{AsO_3^- + 6H^+} \rightarrow \underset{\mathbf{0}}{As} + 3H_2O$$

Step 4. Balance the charges for each half-reaction by adding electrons.

$$CN^- + H_2O \rightarrow CNO^- + 2H^+ + 2e^- \qquad \text{(both sides now } -1\text{)}$$
$$AsO_3^- + 6H^+ + 5e^- \rightarrow As + 3H_2O \qquad \text{(both sides now 0)}$$

Note that, after this step, the electrons should be on opposite sides for the two half-reactions, or else something is wrong.

Step 5. Multiply the half-reactions by integers to get the lowest common multiple of electrons and combine to cancel electrons, as well as H^+ and H_2O.

The lowest common multiple here is 10, obtained by multiplying the first reaction by 5 and the second by 2.

$$5CN^- + \mathbf{5}H_2O \rightarrow 5CNO^- + \mathbf{10}H^+ + \cancel{10e^-}$$
$$2AsO_3^- + \mathbf{12}H^+ + \cancel{10e^-} \rightarrow 2As + \mathbf{6}H_2O$$
$$\overline{5CN^- + 2AsO_3^- + 2H^+ \rightarrow 5CNO^- + 2As + H_2O}$$

The reaction should now be balanced in acid solution.

Step 6. If the reaction is in basic solution, remove H^+ by adding an equal number of OH^- to both sides. React H^+ with OH^- to make H_2O and cancel accordingly.

$$5\,CN^- + 2\,AsO_3^- + \overset{2\,H_2O}{\boxed{2\,H^+ + \mathbf{2\,OH^-}}} \rightarrow 5\,CNO^- + 2\,As + H_2O + \mathbf{2\,OH^-}$$

$$5\,CN^- + 2\,AsO_3^- + H_2O \rightarrow 5\,CNO^- + 2\,As + 2\,OH^-$$

Step 7. Write the overall reaction and check the mass balance and charge balance.

$$5\,CN^-(aq) + 2\,AsO_3^-(aq) + H_2O(l) \rightarrow 5\,CNO^-(aq) + 2\,As(s) + 2\,OH^-(aq)$$

Charge: **−7** **−7**

Mass: 5 C, 5 N, 2 As, 7 O, 2 H 5 C, 5 N, 7 O, 2 As, 2 H

Since the charge and mass balances are confirmed, the reaction is balanced.

You should be able to balance redox reactions in both acidic and basic solution. Either the oxidation number or charge balance method can be used, but it is useful to know both in case problems come up with one or the other.

Exercise 13.2

Balance the following redox reactions as specified.

(a) $NO_3^-(aq) + I_2(aq) \rightarrow IO_3^-(aq) + NO_2(g)$ (in acid)

(b) $O_2(g) + As(s) \rightarrow HAsO_2(aq)$ (inacid)

(c) $Al(s) + NO_2^-(aq) \rightarrow AlO_2^-(aq) + NH_3(aq)$ (in base)

(d) $NO_3^-(aq) \rightarrow N_2O(g) + O_2(g)$ (in base)

13.6 Electrochemical Cells

In an earlier example, it was stated that copper(II) ions would react spontaneously with zinc metal in a redox reaction.

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

The reaction occurs spontaneously under standard conditions because the standard Gibbs energy change, ΔG^{o}, is negative. The energy from this reaction is released in solution as heat as a result of the direct transfer of electrons from zinc to the copper ions. However, if we could somehow separate the two half-reactions, we could force the electrons to travel through an external solution and extract electrical energy. One way to do this is as shown in Figure 13.3, where a copper electrode, isolated in a compartment with the Cu^{2+} ions, is electrically connected with a compartment containing a zinc electrode and Zn^{2+} ions. Electrons are now forced to travel through an external circuit from the from the Zn electrode to the Cu electrode.

Although the device in Figure 13.3 seems like it will work in principle, no continuous current will flow. The problem is that the solutions are composed of both cations (Cu^{2+} and Zn^{2+}) and corresponding anions (*e.g.* SO_4^{2-}) so that they are electrically neutral (equal positive and negative charges). As soon as the redox reaction is initiated, Zn^{2+} ions will be generated in the zinc compartment, and Cu^{2+} ions will be converted to Cu in the copper compartment. This will result in an excess positive charge in the zinc solution and an excess negative charge in the copper solution so that the solutions are no longer electrically neutral. The excess charges in the solution quickly counteract the driving forces of the reaction, and it is no longer able to proceed. This was not a problem when the reactants were combined directly, since each Cu^{2+} ion consumed was replaced by a Zn^{2+} ion generated.

The solution to this problem is to allow a limited movement of charged species between the two compartments. It does not matter what ions are used to maintain the electroneutrality, but the copper and zinc ions should not be readily exchanged. One approach is to use a *salt bridge*. A classical salt bridge consists of KCl (or other unreactive salt) dissolved in an agar gel (a polysaccharide gel often used to culture bacteria) as shown in Figure 13.4. The gel allows limited mobility of the K^+ and Cl^- ions which can enter each compartment to balance the charged species in solution. This now permits current to flow in the external circuit.

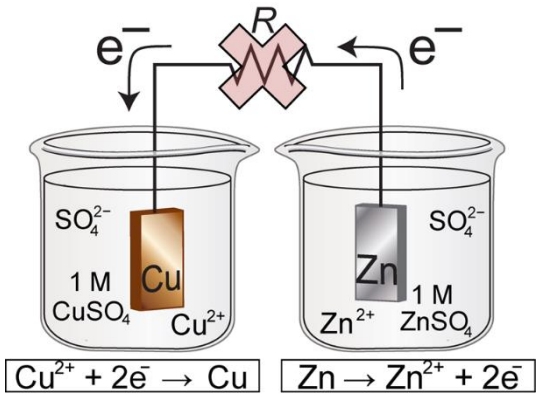


Figure 13.3: Separation of redox half-reactions. No current flows through the resistance, *R*, in this arrangement because of charge build up in each compartment.

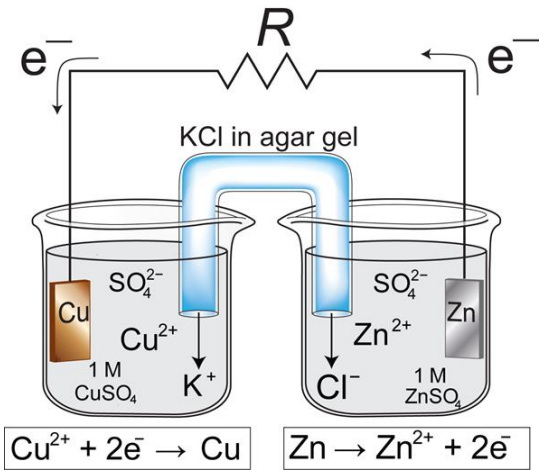


Figure 13.4: An electrochemical cell with a salt bridge which allows the flow of current in the external circuit.

The configuration shown in Figure 13.4 is a classical electrochemical cell. The KCl/agar salt bridge is an effective way to maintain charge balance in the cell compartments, but it is by no means the only method that can be used. In modern electrochemical cells, a much simpler arrangement consisting of a porous glass frit is often employed, as shown in Figure 13.5. Because of its shape, this arrangement is sometimes called an "H-cell". The pores in the glass frit allow the slow diffusion of sulfate ions (or other anions) from the left side, where they are in excess, to the right side, where there is an excess of Zn^{2+}, thereby balancing the solution charges. This kind of solution contact is more generally called a liquid junction, which includes both the salt bridge and the frit.

You might wonder why the positive Zn^{2+} ions don't travel through the porous frit to the left side of the cell. In fact, nothing prevents this, but the diffusion of ions through the frit is very slow under normal conditions and is not likely to affect the zinc concentration. It should also be noted that such solutions are often prepared in the presence of an inert salt (supporting electrolyte) such as KCl, and the flow of these ions between the two compartments can maintain solution electroneutrality.

Drawing an electrochemical cell, as shown in Figure 13.5, or describing it in words can be awkward. As an alternative, a shorthand notation is sometimes used to efficiently represent the components of the cell. An example of such a representation is shown in Figure 13.6. The notation begins with the composition of the left electrode, followed by a vertical line representing the phase boundary between the solid electrode and solution in the left compartment. All of the relevant solution components (those involved in the redox reaction), are then given, followed by a double vertical line to represent the salt bridge or equivalent component (e.g. frit). This is followed by the solution components in the right compartment, a phase boundary, and then the right electrode.

There are many variations on this basic scheme. Concentrations may or may not be specified, but typically the phase is given if they are not. Solutions may also be represented showing only the relevant ions (i.e. those involved in the reaction). Finally, while some protocols specify which electrode should be on the left (e.g. based on the direction of current flow), we will make no such specifications and the assignment of left and right are entirely arbitrary. Therefore, all of the shorthand representations of the cell shown in Figure 13.7 would be acceptable.

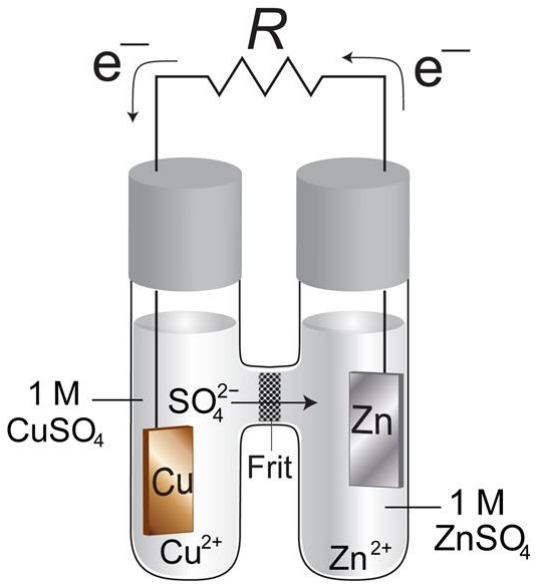


Figure 13.5: An H-cell in which a porous glass frit substitutes for the salt bridge.

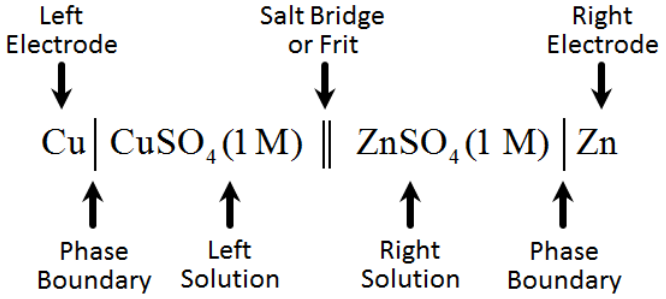


Figure 13.6: Shorthand notation for the electrochemical cell shown in Figure 13.5.

A metal electrode is an essential part of an electrochemical cell because it facilitates the transfer of electrons to or from the solution to the external circuit, but it does not have to participate directly in the reactions. Figure 13.8 shows an electrochemical cell composed of a Ce^{4+}/Ce^{3+} redox couple on the left and with an Fe^{2+}/Fe^{3+} redox couple on the right. In this case, the half-reactions (shown below) occur at a platinum electrode.

$$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq) \quad \text{left compartment}$$
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \quad \text{right compartment}$$
$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq) \quad \text{overall reaction}$$

The platinum electrode is often chosen to facilitate such reactions because it is relatively inert and won't be easily oxidized or reduced. Other electrodes, such as gold or graphite, are also sometimes used. The figure also shows the shorthand notation for this cell. Note that all reactive species (Ce^{4+}, Ce^{3+}, Fe^{2+}, Fe^{3+}) are shown even though some (Ce^{3+}, Fe^{3+}) may not be present initially. The choice of cerium (Ce) ions for a redox reaction may seem unusual, but Ce^{4+} is commonly used in electrochemistry since it is a strong oxidizing agent.

The use of inert metal electrodes facilitates the construction of many different types of electrochemical cells involving different half-reactions (redox couples). However, not all redox couples are suitable for electrochemical cells, since they may occur too slowly to give a stable current. Reactions that are sufficiently fast to be used in a cell are said to be *reversible*.

Example 13.2: Representing electrochemical cells in shorthand notation

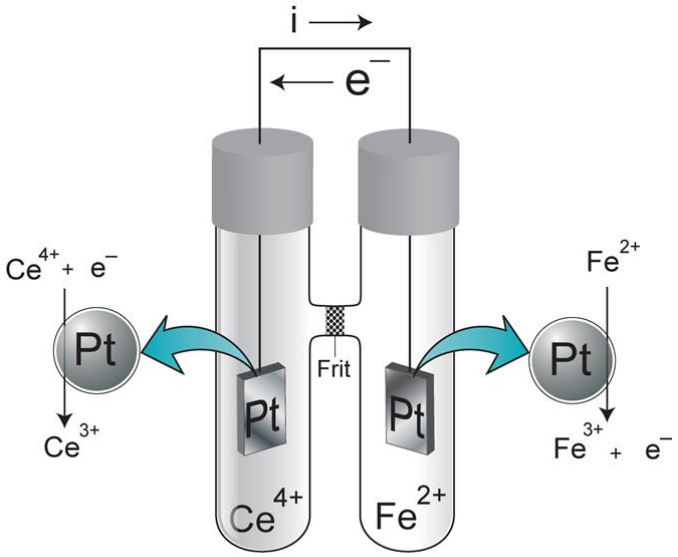
Give shorthand representations of the electrochemical cells described below.

(a) The left compartment of a cell consists of a solution of tin(II) at a concentration of 0.010 M which is oxidized at a platinum electrode to tin(IV), present at a concentration of 0.0020 M. The right compartment contains a silver wire coated with a solution solid silver chloride. The AgCl is reduced to Ag in a solution of 0.10 F KCl.

(b) The half-reactions involved in the discharge of a lead acid battery used in cars (pictured in Figure 13.9) are:

$$Cu \,|\, CuSO_4(aq) \,\|\, ZnSO_4(aq) \,|\, Zn$$
$$Cu \,|\, Cu^{2+}(aq) \,\|\, Zn^{2+}(aq) \,|\, Zn$$
$$Zn \,|\, Zn^{2+}(1\ M) \,\|\, Cu^{2+}(1\ M) \,|\, Cu$$

Figure 13.7: Alternative shorthand representations of the copper-zinc electrochemical cell.



$$Pt \,|\, Ce^{4+}(aq), Ce^{3+}(aq) \,\|\, Fe^{2+}(aq), Fe^{3+}(aq) \,|\, Pt$$

Figure 13.8: An electrochemical cell using platinum electrodes and its shorthand representation.

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$
$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

Both reactions occur at lead electrodes in aqueous sulfuric acid.

(a) The half-reactions are $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ and $AgCl + e^- \rightarrow Ag + Cl^-$, leading to the representation below.

$$Pt \left| Sn^{2+}(0.010\,M), Sn^{4+}(0.0020\,M) \right\| Cl^-(0.10\,M) \left| AgCl(s) \right| Ag$$

Note that something different about this electrode from the ones we have seen so far is the presence of two phase boundaries on the right due to the presence of solid silver chloride.

(b) One shorthand representation of the battery is:

$$Pb \left| PbSO_4(s) \right| H_2SO_4(aq) \left\| H_2SO_4(aq) \right| PbO_2(s) \left| PbSO_4(s) \right| Pb$$

Although this is technically correct, the actual cell is simpler than this. Since none of the redox species is present in solution and the reactions share a common electrolyte, there is no need for a salt bridge, so it is more accurate to write:

$$Pb \left| PbSO_4(s) \right| H_2SO_4(aq) \left| PbO_2(s) \right| PbSO_4(s) \left| Pb \right.$$

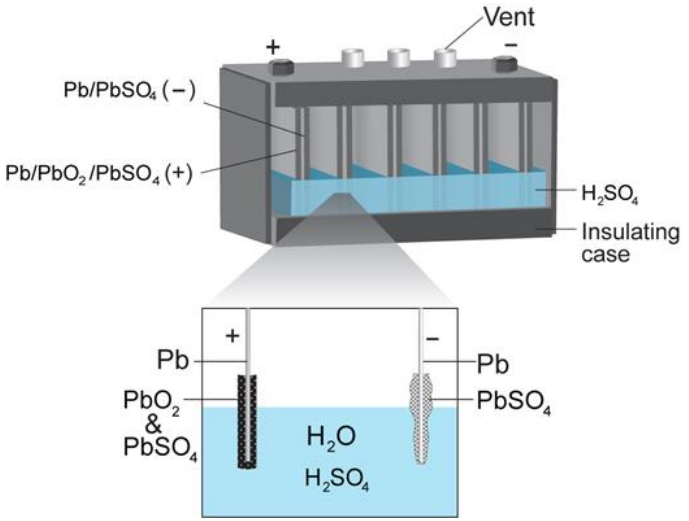


Figure 13.9: Composition of a lead-acid battery containing six individual cells (connected in series). One lead electrode has a deposit of PbO_2 and $PbSO_4$ on the surface, while is coated with $PbSO_4$. Separators of individual cells are not shown.

Exercise 13.3

An electrochemical cell is constructed based on the following two half-reactions:

$$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

The first reaction occurs at a cadmium electrode and the second occurs at a gold electrode. Write the shorthand notation for the cell.

13.7 Standard Potentials

Separating the two half-reactions in a redox reaction allows the electrons to be directed through an external circuit to do work. This movement of electrons requires a difference in electrical potential between the two electrodes, which drives the electrons from the more negative electrode to the more positive electrode. (Electrical current is normally defined to flow in the opposite direction- positive to negative.) Therefore, it is important to be able to determine the potential difference between the two electrodes, also known as the *cell potential* or *cell voltage*. The potential will depend on the reactions involved and the concentrations of the chemical species. If we could determine the potential of each compartment of the cell, we could subtract them and this would give us the cell voltage.

Unfortunately, it is impossible to define the potential of a single electrode or half-reaction, since a point of reference is always needed. As an analogy, consider the water flowing over a waterfall to represent electron flow in a circuit, as shown in Figure 13.10. The distance the water falls is analogous to the cell potential. To obtain this distance, we could subtract the height (elevation) at the bottom of the waterfall from that at the top, but this raises the question of how we measure the elevations. Usually, we consider a standard reference point, such as sea level. The reference point chosen really doesn't matter (sea level or Mt. Everest), since everything is relative, but we need to agree on it. The same is true with electrochemical cells.

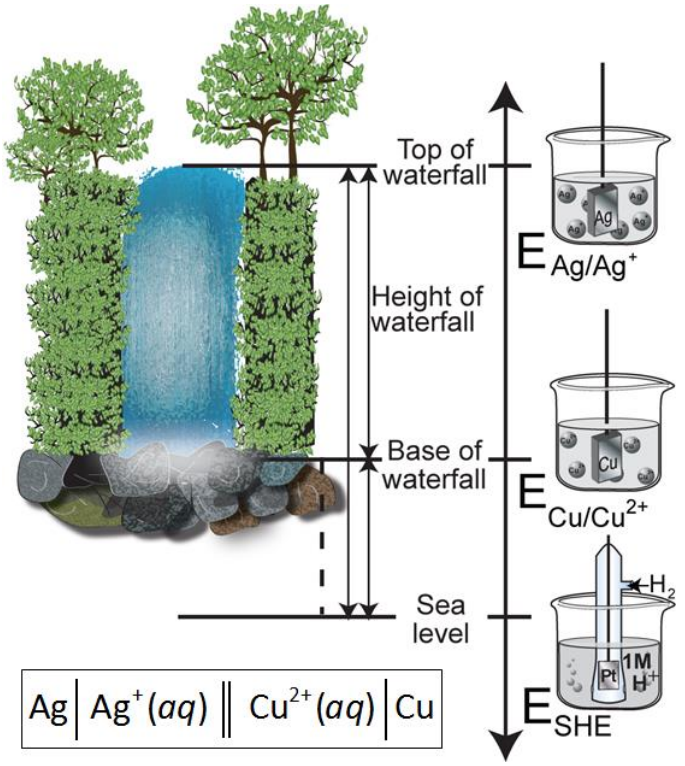


Figure 13.10: Measuring cell potentials with respect to the standard hydrogen electrode is analogous to measuring heights with respect to sea level. By using a common reference point, the potential difference between any two half-reactions can be determined.

The Standard Hydrogen Electrode (SHE)

In electrochemistry, the common reference point for measuring half-cell potentials is the standard hydrogen electrode (SHE), analogous to sea level in measuring elevation. The choice of this electrode is arbitrary, but is partly based on the simplicity of the chemical constituents in the half-reaction, shown here as a reduction.

$$2\,H^+(aq) + 2\,e^- \rightarrow 2\,H_2(g)$$

The reaction is carried out under standard conditions, which means that the concentration (or more accurately, the activity) of H^+ (more accurately, H_3O^+) is 1 M and the pressure of hydrogen gas above the solution (P_{H2}) is 1 atm. Whether the reaction proceeds as a reduction or an oxidation depends on the other electrode. For example, if the hydrogen electrode is part

of a half-cell with the Zn/Zn^{2+} redox couple at standard conditions ($[Zn^{2+}]$ = 1 M) as shown in Figure 13.11, the zinc will be oxidized and the overall reaction is as shown below.

$$Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad E_{cell} = 0.763\ V$$

In this case, the oxidation at the zinc electrode provides the electrons that flow to the platinum electrode to reduce H^+. Therefore, the Zn electrode has a lower (negative) potential relative to the Pt electrode. The negative electrode is called the *anode* and is always where the oxidation occurs. Conversely, the more positive electrode is the *cathode*, where the reduction occurs. The shorthand notation for the cell is:

$$Zn\,|\,Zn^{2+}(1\ M)\,\|\,\underbrace{H^+(1\ M)\,|\,H_2(1\ atm)\,|\,Pt}_{SHE}$$

Alternatively, to simplify the representation of the SHE, it is often represented simply as:

$$Zn\,|\,Zn^{2+}(1\ M)\,\|\,SHE$$

In practice, the SHE is not a very convenient electrode to use as it involves bubbling flammable hydrogen gas through a solution over an expensive electrode material. However, practicality is not a major concern since it is only a reference. By analogy, sea level is not a very convenient reference point for elevation if you are a long distance from the ocean, but it is still used.

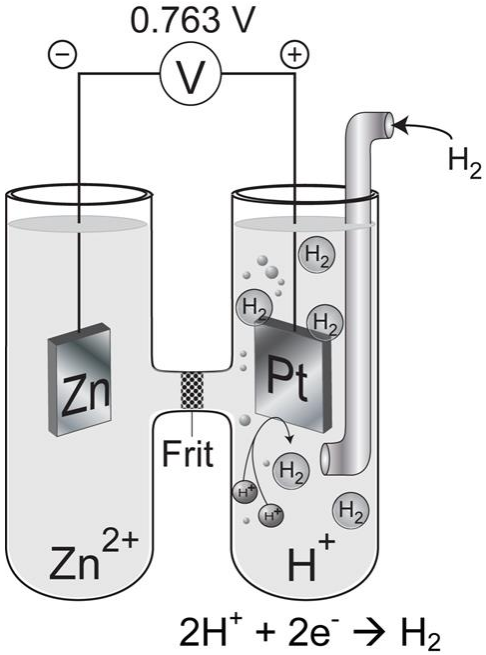


Figure 13.11: An electrochemical cell that could be used to measure the standard potential for the Zn/Zn^{2+} reaction.

Cell Potential and Thermodynamics

Recall that, for a reaction to be spontaneous, the Gibb's energy change, ΔG, must be negative. The relationship between ΔG for a redox reaction and the potential of a cell composed of the corresponding half-reactions, E, is given by:

$$\Delta G_{rxn} = -nF\mathrm{E}_{rxn} \qquad (13.1)$$

where ΔG is the Gibbs energy change for the redox reaction (J/mol), n is the number of electrons transferred, and F is Faraday's constant, which is the charge on 1 mol of electrons, or 9.6485×10^4 coulombs/mol. If the reaction takes place under standard conditions, we write:

$$\Delta G^{o}_{rxn} = -nF\mathrm{E}^{o}_{rxn} \qquad (13.2)$$

It follows that, for a reaction to be spontaneous, E must be positive so that ΔG is negative. A cell in which the reaction occurs spontaneously is called a *galvanic cell* (as opposed to an *electrolytic cell*, in which the reaction is driven by an external circuit). In a galvanic cell, the potential is always given as a positive value.

Example 13.3: Calculating the Gibbs energy change

Calculate the value of ΔG^o for the cell depicted in Figure 13.11.

Under standard conditions, it was already noted that the spontaneous reaction is:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad E = 0.763\ V$$

By definition, $E = E^o$ at standard conditions. Using eqn 13.2,

$$\Delta G^o_{rxn} = -nFE^o_{rxn} = -(2)(96,485\,C/mol)(0.763\,V) = -147,236\ C\cdot V/mol$$
$$= -147\,kJ/mol$$

In this calculation, it is noted that two electrons are transferred in the reaction as written, and the identity CxV = J was used.

By extension of the above example, it will be noted that the reverse reaction will be non-spontaneous, and this is reflected by a change in the signs of both ΔG and E.

$$Zn^{2+}(aq) + H_2(g) \rightarrow Zn(s) + 2H^+(aq) \qquad E^o_{rxn} = -0.763\ V$$
$$\Delta G^o_{rxn} = +147\ kJ$$

Therefore, the reduction of Zn^{2+} by H_2 is not spontaneous at standard conditions.

Standard Reduction Potentials

For the cell pictured in Figure 13.11, if we used a voltmeter to measure the cell voltage, we would find a value of 0.763 V, with the Zn electrode more negative than the Pt electrode. The cell voltage itself does not tell us about the direction of the reaction unless we specify the sign

in a consistent way. For this reason the **standard reduction potential**, E^o, for a half-reaction is always defined as the potential observed when *reduction* occurs at that electrode and oxidation occurs at the SHE. For the Zn/Zn^{2+} redox couple, this means that we would write:

$$Zn^{2+}(aq) + H_2(g) \rightarrow Zn(s) + 2\,H^+(aq) \qquad E^o = -0.763\,V$$

where all species are at standard conditions. Of course, this reaction is not spontaneous, so we can't measure it directly, but we can measure the reverse reaction and change the signs. In practice, this means that, for the arrangement in Figure 13.11, we would simply measure the potential of the zinc electrode (the test electrode in this case) relative to the SHE.

$$E^o = E_{test} - E_{SHE} \quad \text{(at standard conditions)} \qquad (13.3)$$

If we were to construct a similar cell with a copper electrode, as shown below,

$$Cu\,|\,Cu^{2+}(1\,M)\,\|\,H^+(1\,M)\,|\,H_2(1\,atm)\,|\,Pt$$

we would find that the Cu electrode was more positive than the Pt electrode by 0.337 V, meaning that the reduction of Cu^{2+} occurs spontaneously in this case. The standard reduction potential is given by,

$$Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2\,H^+(aq) \qquad E^o = +0.337\,V$$

In a similar way, we could write reactions that define the standard reduction potentials for other half-reactions, as shown in Table 13.1. However, the inclusion of the H_2/H^+ redox couple in these equations is unnecessary, since it is implied by the definition of a standard reduction potential. Therefore, in most tables, only the half-reaction of interest is shown, as illustrated in Table 13.2. Unfortunately, this representation implies that the electrode potential can be measured independently, but this is not the case. Note that the H^+/H_2 redox couple is also included in the tables and, by definition, has a standard reduction potential of zero.

For convenience, a more complete listing of standard reduction potentials is given in Table 13.3, and an even more extensive list can be found in Appendix A.8. It should be noted that "standard" does not imply a temperature, but such tables are normally specified at 25 °C, since potentials are temperature dependent.

Table 13.1. Standard reduction potentials for selected redox couples showing the overall cell reaction.

Reaction	E^o(V)
$Zn^{2+} + \mathbf{H_2} \rightarrow Zn + 2\mathbf{H^+}$	−0.763
$Cr^{3+} + \frac{1}{2}\mathbf{H_2} \rightarrow Cr^{2+} + \mathbf{H^+}$	−0.41
$2H^+ + \mathbf{H_2} \rightarrow H_2 + 2\mathbf{H^+}$	0.0000
$AgCl + \frac{1}{2}\mathbf{H_2} \rightarrow Ag + Cl^- + 2\mathbf{H^+}$	+0.222
$Cu^{2+} + \mathbf{H_2} \rightarrow Cu + 2\mathbf{H^+}$	+0.337

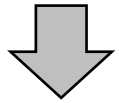


Table 13.2. Standard reduction potentials for selected redox couples showing only the reduction half-reaction.

Reaction	E^o(V)
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	−0.763
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$2H^+ + 2e^- \rightarrow H_2$	0.0000
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.222
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.622

Standard Cell Potentials

In principle, any pair of half-reactions could be combined into an electrochemical cell. If the cell is constructed under standard conditions (concentrations = 1 M, gas pressures = 1 atm, solids and liquids in pure form) the measured potential is the **standard cell potential**. In this course, this will be always be taken to be positive, since the spontaneous reaction is assumed to occur. The steps in determining the standard cell are as follows.

(1) Based on the cell, identify the reduction half-reactions and their E° values.
(2) Write the more negative half-reaction as an oxidation and change the sign of E°.
(3) Combine the half-reactions to obtain the overall cell reaction, multiplying by the necessary coefficients to eliminate electrons. Do not multiply the E° values.
(4) Add the E° values to obtain the standard cell potential.

An example will be used to illustrate this calculation.

Example 13.4: Calculating a standard cell potential

Calculate the standard cell potential and identify the anode and cathode for the cell given below.

$$Zn\left|\, Zn^{2+}(1M) \right\| Cr_2O_7^{2-}(1M), Cr^{3+}(1M), H^{+}(1M) \,\left|\, Pt\right.$$

Note that the concentrations are redundant, since we have specified standard conditions. The reduction half-reactions and their standard reduction potentials from Table 13.3 are:

$Zn^{2+} + 2e^- \rightarrow Zn$ $\quad E° = -0.763$ V

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $\quad E° = +1.33$ V

Since the zinc half-reaction has the more negative potential, it will occur as the oxidation in the spontaneous cell reaction. To combine the reactions, we need to multiply the first reaction by 3 to cancel the electrons.

Table 13.3. Standard reduction potentials for selected half-reactions at 25 °C.

Reaction	E^o (V)
$Ag^+ + e^- \rightarrow Ag$	+0.799
$AgBr(s) + e^- \rightarrow \rightarrow Ag + Br^-$	+0.071
$AgCl(s) + e^- \rightarrow Ag + Cl^-$	+0.222
(satd KCl)	+0.197
$Ca^{2+} + 2\,e^- \rightarrow Ca$	−2.868
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	+0.741
$Cr_2O_7^- + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$	+1.33
$Cu^{2+} + 2\,e^- \rightarrow Cu$	+0.337
$Fe^{2+} + 2\,e^- \rightarrow Fe$	−0.440
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
$2\,H^+ + 2\,e^- \rightarrow H_2(g)$	0.0000
$Hg_2^{2+} + 2\,e^- \rightarrow 2\,Hg(l)$	+0.792
$Hg_2Cl_2\,(s) + 2\,e^- \rightarrow 2\,Hg\,(l) + 2\,Cl^-$	+0.268
(satd KCl) (SCE)	+0.242
$I_2 + 2\,e^- \rightarrow 2\,I^-$	+0.622
$IO_3^- + 6\,H^+ + 5\,e^- \longrightarrow ½\,I_2 + 3\,H_2O$	+1.178
$MnO_4^- + 8\,H^+ + 5\,e \rightarrow^- Mn^{2+} + 4\,H_2O$	+1.51
$NO_3^- + 3\,H^+ + 2\,e^- \rightarrow HNO_2 + H_2O$	+0.940
$NO_3^- + 4\,H^+ + 3\,e^- \rightarrow NO(g) + 2\,H_2O$	+0.955
$Pb^{2+} + 2\,e^- \rightarrow Pb$	−0.126
$PbSO_4 + 2\,e^- \rightarrow Pb + SO_4^{2-}$	−0.355
$PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \rightarrow PbSO_4 + 2\,H_2O$	+1.685
$Zn^{2+} + 2\,e^- \rightarrow Zn$	−0.763

$$3Zn \rightarrow 3Zn^{2+} + \cancel{6e^-} \qquad E^o_{ox} = +0.763\,V$$

$$Cr_2O_7^{2-} + 14H^+ + \cancel{6e^-} \rightarrow 2Cr^{3+} + 7H_2O \qquad E^o_{red} = +1.33\,V$$

$$3Zn + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Zn^{2+} + 2Cr^{3+} + 7H_2O \qquad E^o_{cell} = +2.0\overline{9}3\,V$$

Thus the standard cell potential is 2.09 V, with the zinc electrode acting as the anode (oxidation) and the platinum electrode acting as the cathode (reduction).

Note that the sign of the Zn/Zn^{2+} potential was reversed when the direction was changed, but it was not multiplied by the factor of 3. Also note that the solution uses the subscripts "ox", "red" and "cell" to distinguish the E^o values from the standard reduction potentials in the table.

The calculations above are carried out as if we can measure the half-reaction potentials directly, but we are actually measuring each electrode potential against an imaginary SHE, as pictured in Figure 13.12. Therefore, a more accurate (although unnecessary) representation of the calculation would be:

$$3Zn + 6H^+ \rightarrow 3Zn^{2+} + 3H_2 \qquad E^o_{LHS} = +0.763\ V$$

$$Cr_2O_7^{2-} + 3H_2 + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O \qquad E^o_{RHS} = +1.33\ V$$

$$3Zn + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Zn^{2+} + 2Cr^{3+} + 7H_2O \qquad E^o_{cell} = +2.0\overline{9}3\ V$$

It should also be apparent that, if we don't need the overall cell reaction, the standard cell potential can be calculated by simply subtracting the standard reduction potential of the anode from that of the cathode once these have been identified.

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} \qquad (13.3)$$

For the current example, this gives:

$$E^o_{cell} = E^o(Cr_2O_7^{2-}/Cr^{3+}) - E^o(Zn^{2+}/Zn) = 1.33\ V - (-0.763\ V) = 2.0\overline{9}3\ V$$

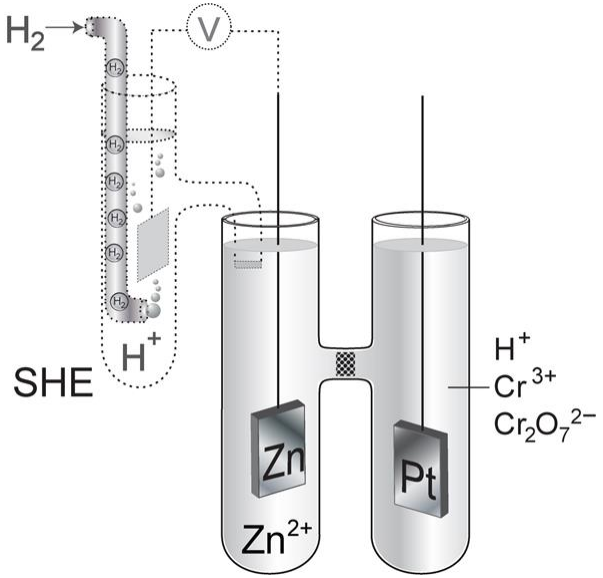


Figure 13.12: Example electrochemical cell showing the half-cell potential measured against an imaginary SHE.

Exercise 13.4

Calculate the standard cell potential for a cell in the lead acid battery given in an earlier example. Also, give the overall cell reaction and identify the anode and cathode.

$$\mathrm{Pb}\left|\mathrm{PbSO_4}(s)\right|\mathrm{SO_4^{2-}}(1\mathrm{M})\left\|\mathrm{H^+}(1\mathrm{M}),\mathrm{SO_4^{2-}}(1\mathrm{M})\right|\mathrm{PbO_2}(s)\left|\mathrm{PbSO_4}(s)\right|\mathrm{Pb}$$

Standard Reaction Potentials

Not all redox half-reactions can be configured into a practical electrochemical cell, but it still may be possible to determine their standard reduction potentials, often indirectly. The availability of this information is extremely useful, since it facilitates the calculation of thermodynamic quantities associated with redox reactions. We have already seen the relationship in Eqn. (13.2) between the Gibbs energy change, ΔG°, and the standard potential, E°, for a reaction, but you should also recall that ΔG° is related to the equilibrium constant for a reaction, leading to the three-way relationship in Equation (13.4).

$$\Delta G^{\circ}_{rxn} = -nF\mathrm{E}^{\circ}_{rxn} = -RT\ln K \qquad (13.4)$$

Eqn. (13.4) implies that if we can determine the potential of a reaction under standard conditions, called the **standard reaction potential**, then we can determine ΔG° and K for the reaction.

The difference between the standard *cell* potential and the standard *reaction* potential is that the latter is calculated for the reaction as written, which may not be spontaneous, and therefore the sign of E° may be positive or negative. This calculation can be performed even if no cell can actually be constructed. Eqn. (13.3) can still be employed, but the anode in this case is defined by the oxidation half-reaction. An example will illustrate this.

Example 13.5: Calculating a standard reaction potential

Calculate the standard reaction potential for the redox reaction below. Also, calculate ΔG^{o} and K at 25 °C for the reaction. Will copper deposit at a silver electrode under standard conditions?

$$2\,Ag(s) + Cu^{2+}(aq) \rightarrow 2\,Ag^{+}(aq) + Cu(s)$$

In this reaction, the silver is being oxidized and the copper ions reduced, representing the anode and cathode, respectively. The standard reduction potentials (Table 13.3) for Ag^{+} and Cu^{2+} are +0.799 V and +0.337 V, respectively. Combining these:

$2\,Ag \rightarrow 2\,Ag^{+} + 2\,e^{-}$	$E^{o}_{ox} = -0.799\,V$
$Cu^{2+} + 2\,e^{-} \rightarrow Cu$	$E^{o}_{red} = +0.337\,V$
$2\,Ag + Cu^{2+} \rightarrow 2\,Ag^{+} + Cu$	$E^{o}_{rxn} = -0.462\,V$

Note that the sign of the reduction potential has been reversed for the oxidation half-reaction. We could also have used a variation Eqn. (13.3) instead:

$$E^{o}_{rxn} = E^{o}_{cathode} - E^{o}_{anode} = E^{o}_{Cu^{2+}/Cu} - E^{o}_{Ag^{+}/Ag}$$
$$= +0.337\,V - (+0.799\,V) = -0.462\,V$$

We can now calculate the thermodynamic quantities.

$$\Delta G^{o}_{rxn} = -nFE^{o}_{rxn} = -(2)(96,485\,C/mol)(-0.462\,V)$$
$$= +89,152\,J/mol = +89.2\,kJ/mol$$

$$K = \exp\left(-\frac{\Delta G^{o}_{rxn}}{RT}\right) = \exp\left(\frac{nF}{RT}E^{o}_{rxn}\right)$$
$$= \exp\left(\frac{(2)(96,485\,C\cdot mol^{-1})}{(8.3145\,J\cdot mol^{-1}\cdot K^{-1})(298.15\,K)}(-0.462\,V)\right) = e^{-35.\overline{963}} = \overline{2}.4\times10^{-16}$$

In the second equation, we made the substitution $\Delta G^o = -nFE^o$ and used the identity $C \cdot V = J$ to cancel units. Note that, because the exponent has only one significant decimal place, we should only retain one significant digit in the answer.

Clearly, since E^o is negative, ΔG^o is positive, and K is extremely small, this means that the reaction should not be spontaneous at standard conditions. In other words, copper should deposit on a silver wire placed in a solution which is 1 M in both Ag^+ and Cu^{2+}.

Exercise 13.5

Use the information in Table 13.3 to predict if nitrous acid should spontaneously decompose to nitrate and nitric oxide gas by the reaction below under standard conditions at 25 °C. Calculate E^o, ΔG^o and K for the reaction to support your answer.

$$3\,HNO_2(aq) \rightarrow NO_3^-(aq) + 2\,NO(g) + H^+(aq) + H_2O(l)$$

13.8 The Nernst Equation

All of the cells examined so far have been at standard conditions (concentrations = 1 M, pressures = 1 atm), but it is necessary to be able to calculate cell potentials under other conditions. The *Nernst equation* facilitates these calculations and is easily derived by recalling the equation for ΔG away from standard conditions.

$$\Delta G = \Delta G^o + RT \ln Q = -nFE^o + RT \ln Q \qquad (13.5)$$

In this equation, Q is the reaction quotient, calculated in the same way as the equilibrium constant, but not requiring the reaction to be at equilibrium (where $Q = K$). Combining this with Eqn. (13.1) ($\Delta G = -nFE$) leads to one form of the Nernst equation:

$$E_{rxn} = E^o_{rxn} - \frac{RT}{nF} \ln Q \qquad (13.6)$$

In this representation, E_{rxn}, E^{o}_{rxn} and Q refer to the reaction *as written* (anode defined by the oxidation) and the potentials can be positive or negative. However, we are usually using this equation to determine the cell potential rather than the reaction potential. Essentially the same equation is used, but in this case, E_{cell} is always positive and corresponds to the *spontaneous* reaction for the cell.

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\ln Q \qquad (13.7)$$

In a more useful variation of this equation that will be applied in this course, the constants are combined at 25 ºC and it is converted to a base 10 logarithm, which leads to the following form,

$$E_{cell} = E^{o}_{cell} - \frac{0.05916\ \text{V}}{n}\log Q \qquad (13.8)$$

where 0.05916 = (*RT/F*)ln10 at 25 ºC.

The implementation of Eqn. (13.8) poses some practical problems because it applies to the *spontaneous* cell reaction. Since this depends on both the E^{o} values for the half-reactions and the concentrations, it may be difficult to predict the spontaneous reaction in advance. Also, the application of this equation to the overall cell reaction is tricky in the case of *concentration cells*, where both cell compartments have the same half-reactions, but different concentrations of reactants. For these reasons, we will apply the **half-reaction method** to calculate cell potentials in this course.

The Half-Reaction Method for Calculating Cell Potentials

The half-reaction method for calculating cell potentials treats each half-cell independently, calculating the reduction potential using only that half-reaction. The steps are as follows:

(1) Based on the cell, identify the reduction half-reactions and their E^{o} values.

(2) Calculate E_{red} for each half-reaction using the Nernst equation as given below.

$$E_{red} = E^{o} - \frac{0.05916\ \text{V}}{n}\log Q \qquad (13.9)$$

Note that the electrons are ignored in the expression for *Q*.

(3) The more negative potential is assigned to E_{anode} and the more positive to $E_{cathode}$. The cell potential is then calculated as:

$$E_{cell} = E_{cathode} - E_{anode} \quad (13.10)$$

For the overall cell reaction, the oxidation occurs at the anode.

It appears here that we are calculating single electrode potentials, but what we are really doing is calculating the reaction potential vs. a SHE. An example will be used to illustrate this calculation.

Example 13.6: Calculating a cell potential using the half-reaction method

Calculate the potential of the following cell at 25 °C. Which compartment is the anode?

$$Pt\left|\, KI(1.50\,F), I_2(0.00100\,F) \right\| HCl(0.100\,F), Cr(NO_3)_3(0.0100\,F), Na_2Cr_2O_7(0.0100\,F) \,\right| Pt$$

This cell appears slightly different than some of the ones we have seen in that it shows the compounds used to prepare the cell rather than just the ions. This makes it a little harder to identify the half-reactions, but once the species that have been oxidized and reduced have been identified, the counter-ions can be ignored. The reduction half reactions in this case are:

$I_2 + 2e^- \rightarrow 2I^-$ $\quad E^o = +0.622$ V

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $\quad E^o = +1.33$ V

From the standard reduction potentials, we can guess that the left-hand-side (LHS) will be the anode (more negative), but we can't be sure until we consider the concentrations. The next step is to calculate the individual reduction potentials using the Nernst equation.

$$E_{LHS} = E^{o}_{I_2/I^-} - \frac{0.05916\ V}{n}\log Q = +0.622\ V - \frac{0.05916\ V}{2}\log\left(\frac{[I^-]^2}{[I_2]}\right)$$

$$= +0.622\ V - \frac{0.05916\ V}{2}\log\left(\frac{(1.50\ F)^2}{0.00100\ F}\right) = +0.622\ V - \frac{0.05916\ V}{2}\log(22\overline{5}0)$$

$$= +0.622\ V - \frac{0.05916\ V}{2}(3.352) = +0.622\ V - 0.09915\ V = +0.523\ V$$

$$E_{RHS} = E^{o}_{Cr_2O_7^{2-}/Cr^{3+}} - \frac{0.05916\ V}{n}\log Q = +1.33\ V - \frac{0.05916\ V}{6}\log\left(\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}\right)$$

$$= +1.33\ V - \frac{0.05916\ V}{6}\log\left(\frac{(0.0100\ F)^2}{(0.0100\ F)(0.100\ F)^{14}}\right) = +1.33\ V - \frac{0.05916\ V}{6}\log(1.00\times10^{12})$$

$$= +1.33\ V - \frac{0.05916\ V}{6}(12.000) = +1.33\ V - 0.1183\ V = +1.2\overline{1}2\ V$$

From these results, it is clear that the LHS is the anode (oxidation reaction), so

$$E_{cell} = E_{cathode} - E_{anode} = 1.2\overline{1}2\ V - 0.523\ V = \underline{\underline{0.69\ V}}$$

There are several points that should be noted from this example.

- Although it appears that we are calculating the potentials of each half-reaction in isolation, we are actually performing each calculation with respect to the SHE, as shown in Figure 13.13. We can ignore $[H^+]$ and P_{H2} in Q because they are equal to unity.
- The number of electrons do not need to be equalized in the two half-reactions to calculate the cell potential. This is only necessary in writing the overall reaction.
- Although concentration units were shown in the log term, these actually represent activities, so they are dimensionless and don't need to cancel.
- Because of the logarithm, Q needs to be very large or very small to alter the potential significantly from its value under standard conditions.

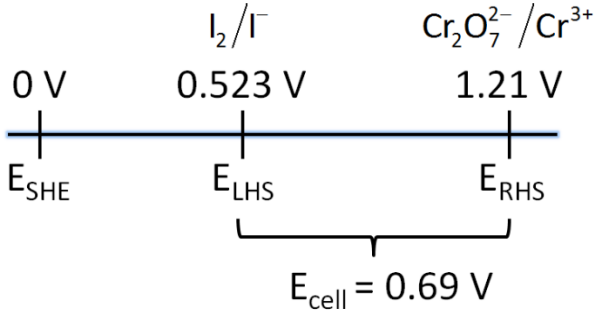


Figure 13.13: In the half-reaction method, the potential of each half-reaction is calculated vs. the SHE.

Exercise 13.6

Calculate the potential of the following electrochemical cell and identify the anode.

$$\mathrm{Zn}\left|\,\mathrm{Zn(NO_3)_2(0.00500\,F)}\right\|\mathrm{NaCl(2.00\,F)}\left|\,\mathrm{AgCl}(s)\,\right|\mathrm{Ag}$$

Exercise 13.7

The lead acid battery (see Figure 13.9, Example 13.2b, Exercise 13.4) actually has no liquid junction (salt bridge or frit) for an individual cell compartment, so a more accurate representation of the cell might be as shown below.

$$\mathrm{Pb}\left|\,\mathrm{PbSO_4}(s)\,\right|\mathrm{H_2SO_4}(aq)\left|\,\mathrm{PbO_2}(s)\,\right|\mathrm{PbSO_4}(s)\left|\,\mathrm{Pb}\right.$$

Calculate the cell potential if the concentration of sulfuric acid is 1.00 F (assume complete dissociation). What would be the potential if the concentration were 0.100 F? 10.0 F?

Exercise 13.8

Calculate the potential of the following cell. On which side does the reduction occur?

$$\mathrm{Cu}\left|\,\mathrm{Cu^{2+}(0.500\,M)}\,\right\|\,\mathrm{Cu^{2+}(1.00\times10^{-5}\,M)}\left|\,\mathrm{Cu}\right.$$

13.9 Reference Electrodes

Often in electrochemical measurements we are only interested in the changes in one of the cell compartments and the other cell compartment serves as a fixed reference point. This second compartment is referred to as a **reference electrode**, while the compartment we are interested in is referred to as the **test electrode** or **working electrode**. In principle, any half-reaction could be used as a reference electrode as long as the concentrations of the reactants remains fixed. The SHE would be a natural choice, since it is the reference for standard

reduction potentials. In practice, however, the SHE is not very safe or convenient since it requires a source of hydrogen gas maintained at a constant pressure. It also does not give a very stable potential since other reactions can occur at the platinum electrode.

The ideal reference electrode should be relatively simple to employ and provide a stable potential that is not prone to interferences. Because the potential depends on reactant concentrations, electrodes that involve few species in solution are advantages, since these involve minimal adjustment of concentrations. There are two widely used reference electrodes, the **silver/silver chloride electrode** and the **saturated calomel electrode**.

Silver/Silver Chloride Electrode (Ag/AgCl)

The Ag/AgCl is perhaps the simplest reference electrode to construct, since it consists simply of a silver wire with a thin coating of silver chloride in a solution of chloride ions (usually from KCl). As shown in Figure 13.14, the internal solution is separated from the test solution by a small glass frit, which acts as the liquid junction. Because both the silver and silver chloride are in solid form, the potential depends only on the concentration (or, more accurately, the activity) of the chloride ion. Typically, either a 1 M or saturated KCl solution (~4 F) is used, with potentials of 0.222 V and 0.197 V, respectively, relative to the SHE.

The main advantages of the Ag/AgCl electrode are that it is stable, inexpensive, easy to prepare, and compact. The coating of AgCl is typically made by electrochemical deposition and therefore is much thinner than that depicted in the figure. The small size means that the electrode can be used in many applications where space is restricted.

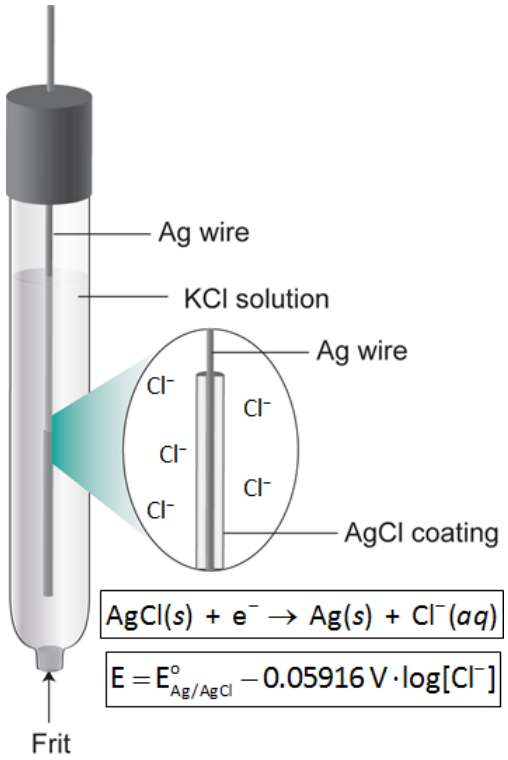


Figure 13.14: A silver/silver chloride reference electrode. The potential (vs. SHE) depends on the KCl concentration, which is typically 1 M (+0.222 V) or saturated (+0.197 V).

Saturated Calomel Electrode (SCE)

The SCE is based on the reduction of mercury in mercury(I) chloride (Hg_2Cl_2, historically given the common name "calomel") to elemental mercury and chloride. Figure 13.15 shows the construction of the SCE and gives the half-reaction. A platinum wire is in contact with liquid mercury, solid Hg_2Cl_2 and a saturated solution of KCl that enters through the porous plug. A liquid junction facilitates electrical contact with the test solution. As with the Ag/AgCl electrode, the potential depends only on the concentration of chloride ion, which is kept saturated in the SCE, giving rise to a potential of 0.242 V (see Table 13.3 and Appendix).

The SCE has been widely used as a reference electrode and is sometimes regarded as more robust than the Ag/AgCl electrode in terms of interfering reactions, but it is more cumbersome and has the added disadvantage of containing toxic mercury compounds, which is why it has been used less frequently in recent years.

Example 13.7: Calculating cell potential with a reference electrode

Calculate the potential of the following electrochemical cell and write the overall cell reaction.

$$Cu\left|\, Cu^{2+}(0.00146\,M)\right\| SCE$$

Note that an abbreviated notation has been used for the saturated calomel electrode to simplify the cell representation, where SCE = KCl(sat'd) | $Hg_2Cl_2(s)$ | Hg(*l*) | Pt. To calculate the cell potential, we use the half-reaction method.

LHS: $Cu^{2+} + 2e^- \rightarrow Cu$ $\quad E^o = +0.337\ V$

$$E_{LHS} = 0.337\,V - \frac{0.05916\,V}{2}\log\left(\frac{1}{0.00146\,M}\right) = 0.337\,V - (0.02958\,V)(2.836)$$

$$= 0.337\,V - 0.08387\,V = 0.253\,V$$

RHS: $E_{RHS} = E_{SCE} = 0.242\ V$

We see that the RHS is the anode so

$$E_{cell} = E_{cathode} - E_{anode} = 0.253\,V - 0.242\,V = \underline{\underline{0.011\,V}}$$

and the overall cell reaction is

$$Cu^{2+}(aq) + 2Hg(l) + 2Cl^-(aq) \rightarrow Cu(s) + Hg_2Cl_2(s)$$

Note that simply reporting that the cell potential is 0.011 V does not indicate which electrode is the anode and which is the cathode. The same cell potential would be obtained if the

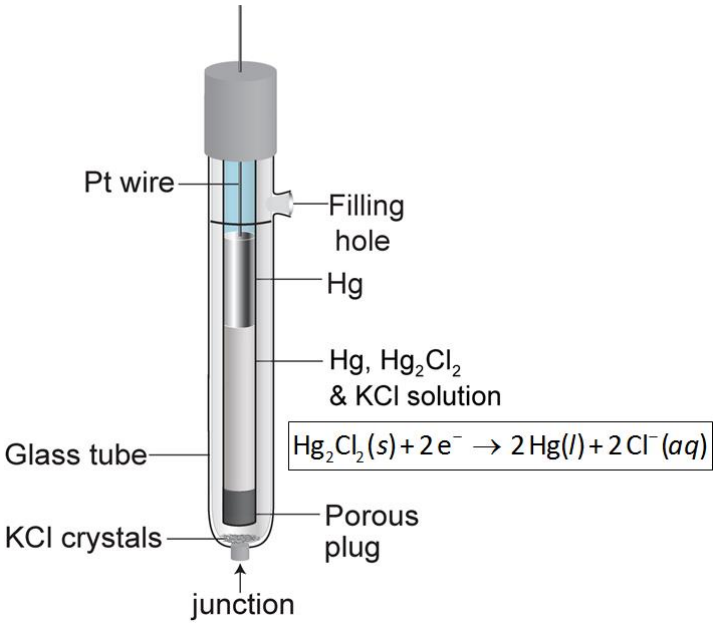


Figure 13.15: A saturated calomel reference electrode.

concentration of Cu^{2+} were 2.61×10^{-4} M, but the Cu electrode would now be the anode. Therefore, it is more accurate to say that the potential of the Cu electrode is +0.011 V relative to the SCE. This will become an important concept when we discuss potentiometry.

Exercise 13.9

With a different copper solution, the potential of the Cu electrode in the previous example is found to be +0.045 V relative to the SCE, as shown in Figure 13.16. What is the concentration of Cu^{2+} in the solution?

Exercise 13.10

The potential of the Ag/AgCl reference electrode (vs. SHE) is 0.197 V in a saturated KCl solution. Use this and the information in Table 13.3 to estimate the solubility of KCl (in mol/L) at 25 °C. Why do you think this is lower than the value given in the text (about 4 mol/L)?

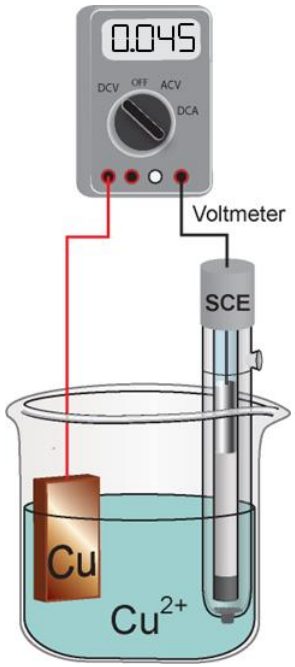


Figure 13.16: Device to measure copper concentration in Example 13.9.

13.10 Analytical Applications of Electrochemistry

From the exercises in the previous section, it should be evident that the measurement of voltage in electrochemical cells allows the determination of solution concentrations. Analytical methods based on this principle are referred to as **potentiometric methods** since they involve the measurement of electrical potential (voltage). These techniques are widely used in analytical laboratories. Another use of redox reactions for chemical analysis is through **redox titrations**. Both of these techniques will be discussed in the following sections.

Potentiometric methods are based on galvanic cells, in which the spontaneous reaction occurs. Other analytical methods are based on electrolytic cells in which an external potential is applied and the current is measured as a function of voltage (voltammetry), or the total charge delivered is recorded (coulometry). These methods will not be treated in this course.

13.11 Potentiometry: Electrodes

The term *potentiometry* refers to the application of potentiometric methods, where the concentration of an analyte is determined from cell potential. The application of these methods involves two distinct types of electrodes, **redox electrodes** and **membrane electrodes**. While the calculations carried out with these two kinds of electrodes are similar, they operate by distinctly different mechanisms. These are discussed in this section.

Redox Electrodes

A redox electrode is simply an electrode at which a redox reaction occurs. We have already seen a number of these. For the purpose of potentiometric measurements of concentrations, these electrodes can be placed into two groups.

(1) **Electrodes of the First Kind.** These are electrodes where the analyte to be measured is oxidized or reduced. The simplest example is a metal ion measured using a metal electrode of the same element, as in the earlier example of a copper electrode used to measure Cu^{2+} ions (see Figure 13.16).

(2) **Electrodes of the Second Kind.** With these electrodes, the analyte to be measured is oxidized or reduced, but is involved in the reaction so that it appears in the Nernst equation. These electrodes are most often used to measure the concentration of anions of insoluble metal salts coated on the metal. For example, an Ag/AgCl electrode can be used to measure the concentration of chloride ions even though it is the Ag and not the Cl that is undergoing a change in oxidation number (see Figure 13.17).

There are also "Electrodes of the Third Kind", which make use of a secondary equilibrium to make measurements on a species that is not redox-active, but these will not be treated here.

In general, it is desirable for the redox electrode to depend on the concentration of only one ion. While it is possible, for example, to measure the concentration of Fe^{2+} (or Fe^{3+}) by making measurements of the Fe^{2+}/Fe^{3+} potential at a Pt electrode where the concentration of one of the ions is fixed and the other is unknown, this is not very practical. The same could be said of using a hydrogen electrode (Pt | H_2 | H^+) to measure [H^+] or P_{H2}. Therefore, electrodes of the first kind are usually limited to the analyte metal (*e.g.* Zn, Cu, Ag, Pb),

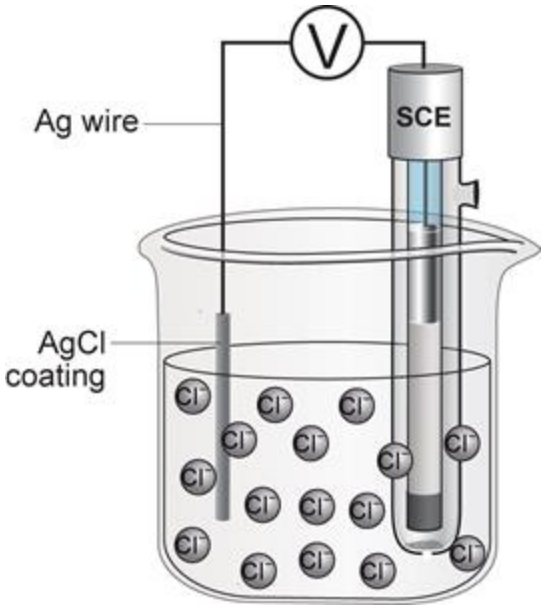


Figure 13.17: A redox electrode of the second kind, used to measure the concentration of chloride.

although not all metals can be used in this way (*e.g.* Fe). Likewise, electrodes of the second kind normally consist of a metal coated with its insoluble salt to measure the anion (*e.g.* Ag/AgBr to measure Br^-, $Pb/PbSO_4$ to measure SO_4^{2-}). Consequently, electrodes of the first kind are normally used to measure metal cations and electrodes of the second kind are normally used to measure anions. Examples of how to make measurements of analyte concentrations are presented in the next section.

Redox electrodes are simple, inexpensive and usually easy to prepare. In practice, however, they have a somewhat limited utility because they are prone to interfering redox reactions that can occur at the metal surface, thereby changing the potential. Therefore, they are normally only used in applications where the likelihood of interfering reactions is small (*i.e.* when the analyte ion is the dominant species present). For other applications, membrane electrodes are usually a better choice.

Membrane Electrodes (Ion Selective Electrodes)

Membrane electrodes, also known as **ion selective electrodes** (ISEs) are much more widely used for potentiometric measurements than redox electrodes because they are less prone to interferences and can be designed for ions that do not undergo reversible redox reactions in solution, such as Na^+. If you have measured pH electronically in the laboratory, you would have used glass pH electrode rather than a hydrogen electrode. This glass electrode is one type of membrane electrode.

Membrane electrodes work on a principle entirely different from that of redox electrodes, although the final results in terms of the calculations are essentially the same. The mechanism that establishes the voltage changes in a membrane electrode does *not* involve a redox reaction, although redox electrodes are necessary to make the measurements. The equation that describes the behavior of the membrane electrode has the same form as the Nernst equation, even though there are no standard potentials for a membrane electrode. To explain how the membrane electrode works, we will develop a simple model. However, it is important to note that, while the model is useful, it does not necessarily reflect how a particular membrane electrode *actually* works.

The model of the membrane electrode is represented in Figure 13.18. In this model, the membrane is a thin material that separates two solutions, the *test solution* on the left and the

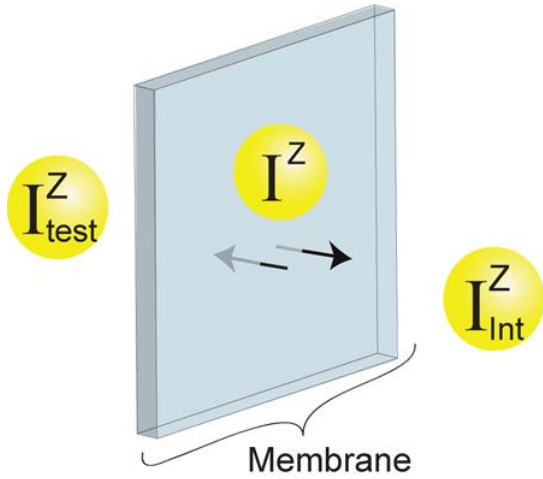


Figure 13.18: A model for a membrane electrode in which the membrane allows for the selective transport of only one type of ion, I^z, between a test solution and an internal solution.

internal solution on the right. The key feature of the membrane is that it is *selective* for the passage of one type of ion, $\mathbf{I^z}$ (*e.g.* Ca^{2+}, F^-), from one side to the other. In other words, the membrane acts as a kind of border guard that, because of its design, allows for the passage of only one type of ion, excluding all of the others. Thermodynamics dictates that the net movement of these ions will be from the side with the higher concentration to the side with lower concentration. However, because only ions of one type of charge can move, this will lead to an excess of positive charges on one side and negative charges on the other, resulting in an electrical potential across the membrane. This potential will push the ions in the opposite direction to the original flow, and when it is large enough, the two effects will cancel each other so that there is no net flow across the membrane. At this point, the system is in *electrochemical equilibrium*, where the effects of chemical diffusion and electrical potential balance each other.

To illustrate, consider that a positive ion, M^+, has a higher concentration in the test solution than in the internal solution, as shown in Figure 13.19. The M^+ ions will move from the left to the right, leaving an excess of negative counterions on the left and an excess of positive ions on the right, resulting in an electrical potential across the membrane, E_{mem}. Since the right side is more positive, at some point it will repel the transport of additional positive M^+ ions and equilibrium will be established. If the concentration of M^+ ions were higher in the internal solution, the ion flow would be in the opposite direction and the sign of E_{mem} would be reversed. The same arguments apply for negative ions, except that a higher concentration of ions in the test solution would result in the right side of the membrane having a more negative potential.

Although it will not be derived here, it can be shown through thermodynamics that the membrane potential exhibits Nernstian type of behavior, given by,

$$E_{mem} = E_{int} - E_{test} = \frac{RT}{zF}\ln\frac{a_{test}}{a_{int}} \approx \frac{RT}{zF}\ln\frac{C_{test}}{C_{int}} \qquad (13.11)$$

In this equation, z is the charge on the ion *including the sign*, a_{test} and a_{int} are the activities of the ion in the test and internal solutions, and C_{test} and C_{int} are the corresponding concentrations. As with all applications of the Nernst equation, we should employ activities rather than concentrations, but for our purposes we will assume that the two are equal. If we also assume

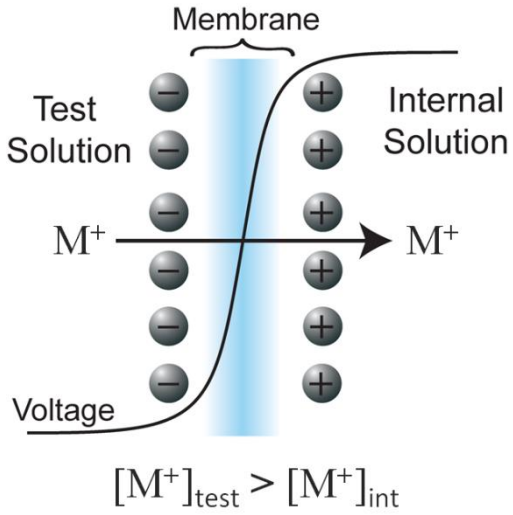


Figure 13.19: The establishment of electrochemical equilibrium across a selective membrane. The higher concentration of M^+ ions on the left results in diffusion across the membrane until it is counterbalanced by the build-up of excess positive charges.

that measurements are made at 25 ºC and convert the equation to a base 10 logarithm, it can be written as:

$$E_{mem} = \frac{0.05916\ V}{z} \log \frac{C_{test}}{C_{int}} \qquad (13.12)$$

In principle, this equation gives us a way to relate the concentration of ions in the test solution to the membrane potential if C_{int} is known. In practice, however, there is no way to measure the membrane potential directly. Instead, we need to measure it indirectly using redox reference electrodes.

As a practical example to illustrate how these measurements are performed, we will use a glass pH electrode, pictured in Figure 13.20. The thin glass membrane on the right separates an internal solution with a fixed concentration of H^+ ions, $[H^+]_{int}$, and a test solution with an unknown concentration of H^+ ions, $[H^+]_{test}$. On each side of the membrane is a reference electrode. The *internal* reference electrode in this case is an Ag/AgCl electrode (we will assume $[Cl^-] = 1$ M) and the *external* reference electrode is a SCE. The type of reference electrodes used is not important, as long as they are compatible with the ions present, and the same type of electrode for both. The reference electrodes allow us to measure the membrane potential indirectly, and therefore determine $[H^+]_{test}$.

Figure 13.21 presents another view of this measurement, showing a cross-section of each electrochemical interface and the changes in potential (note: since absolute potentials are unknown, only relative changes can be shown). In order to resolve the ambiguity of sign in measuring cell potentials, **in potentiometry, the potential of the test electrode is always measured relative to the reference electrode**. The "reference electrode" refers to the external reference (on the left) and the "test electrode" includes the internal reference (on the right). Therefore, we can write an equation for the measured potential, E_{meas}.

$$\begin{aligned} E_{meas} &= E_{test} - E_{ref} = E_{Ag/AgCl} + E_{mem} - E_{SCE} \\ &= E_{Ag/AgCl} + \frac{0.05916\ V}{+1} \log \frac{[H^+]_{test}}{[H^+]_{int}} - E_{SCE} \\ &= E_{Ag/AgCl} + (0.05916\ V) \log [H^+]_{test} - (0.05916\ V) \log [H^+]_{int} - E_{SCE} \end{aligned}$$

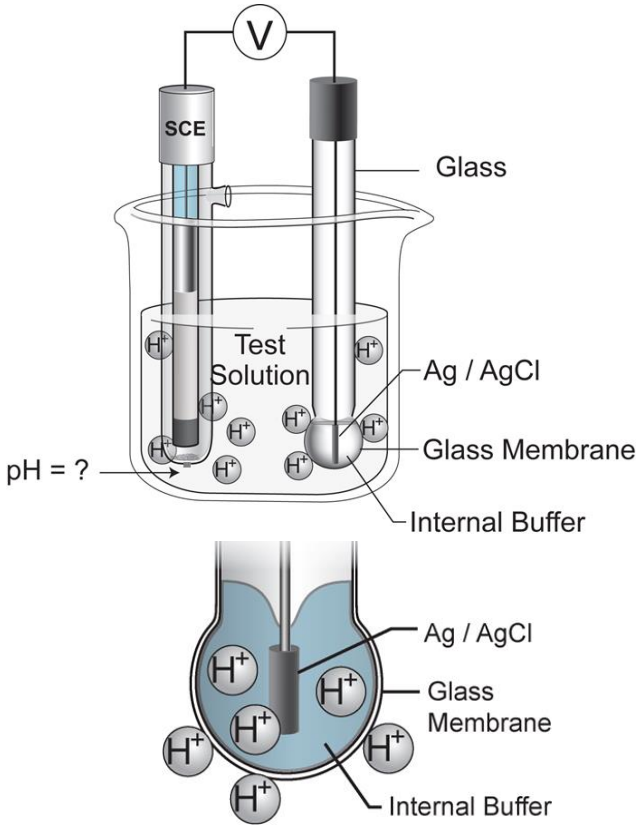


Figure 13.20: pH measurement using a glass electrode, with an expanded view of the glass membrane electrode. Note that an external reference electrode (SCE) and an internal reference electrode (Ag/AgCl) are used to allow measurement of the membrane potential.

The substitution for E_{mem} comes from Eqn. (13.12). Since the reference potentials and $[H^+]$ are constants, we can group these together into a single constant, *K*.

$$E_{meas} = \overbrace{E_{Ag/AgCl} - (0.05916\ V)\log[H^+]_{int} - E_{SCE}}^{K} + (0.05916\ V)\log[H^+]_{test}$$
$$= K + (0.05916\ V)\log[H^+]_{test} = K - (0.05916\ V)\cdot pH$$

This allows us to determine the pH of the solution directly. For example, if we assume $[H^+]_{int} = 1.00$ M, then $K = (0.222V - 0.000\ V - 0.242\ V) = -0.020$ V. If the measured potential were −0.200 V, the pH would be calculated as:

$$pH = -\frac{E_{meas} - K}{0.05916\ V} = -\frac{(-0.200\ V) - (-0.020\ V)}{0.05916\ V} = 3.04$$

This corresponds to $[H^+]_{test} = 9.1x10^{-4}$ M and $E_{mem} = -0.180$ V, indicating that the membrane potential is more positive on the test side, as expected from our earlier model.

It should be emphasized that pH is **not** actually calculated in this manner in practice because the non-ideal behavior of the electrodes and interfaces means that *K* cannot be determined without calibration. The purpose here was simply to illustrate how membrane electrodes follow the Nernst equation even though they do not involve a redox reaction. It should also be mentioned that many modern pH electrodes incorporate the reference electrode into the same probe as the test electrode, so it may appear as though there is only one electrode.

Although our model of the membrane was based on selective transfer of an ion through the membrane, in practice, it is sufficient for the ion to bind selectively to the surface. This is what happens in a glass electrode, where the positively charged H^+ ions interact with Si-O functionalities in the hydrated glass layer.

This same general principle applies to all membrane electrodes, although the designs of the electrodes can vary substantially. Membrane electrodes are usually placed in one of three broad categories, as listed below.

(1) **Glass membrane electrodes.** These electrodes, of which the pH electrode is by far the most widely used, consist of a thin membrane of specially formulated glass as already described. In addition to H^+, these electrodes can also respond to other small, singly

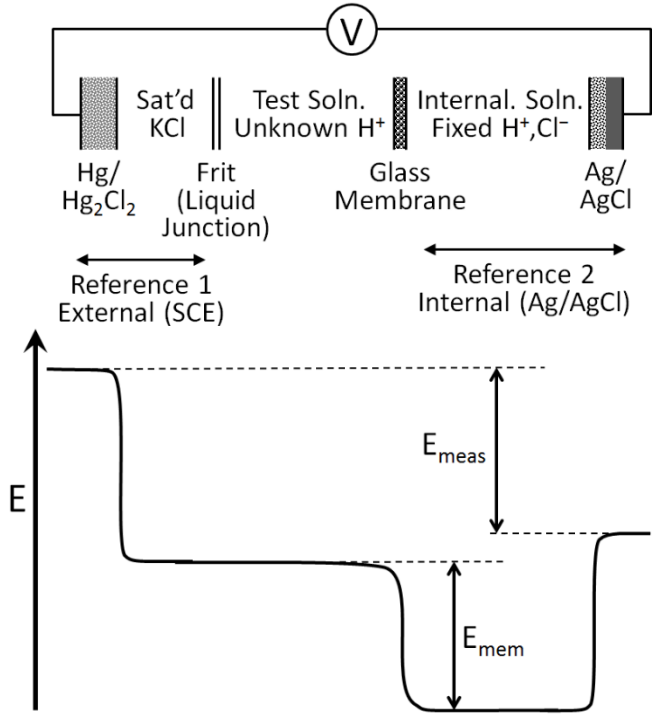


Figure 13.21: A simplified view of the interfaces and potential variations in a glass pH electrode.

charged ions, such as Na^+, K^+, Ag^+ and Tl^+. The differences in these electrodes are largely in the composition of the glass, which contains additives such as Na and Ca. The composition is optimized to respond mainly to the ion of interest.

(2) **Liquid membrane electrodes.** These electrodes consist of a porous organic polymer membrane (*e.g.* polyvinylchloride, PVC) whose pores are filled with an organic solvent which is immiscible with water. An ion exchange compound or complexing agent, capable of binding with the ion of interest is dissolved in the organic solvent. This is illustrated in Figure 13.22 for a calcium ISE. Ca^{2+} ions (internal or test solution) can bind to the ion exchanger to facilitate transport across the membrane and thus establish the membrane potential. A Ag/AgCl electrode is used as the internal reference and a reservoir of the solvent surrounding the electrode ensures that the membrane is replenished. Electrodes of this type have been designed to measure ions such as Ca^{2+}, Mg^{2+}, K^+, Rb^+, Cs^+, NO_3^-, ClO_4^- and BF_4^-.

(3) **Solid state membranes.** The membrane in these electrodes is usually either a single crystal or an insoluble precipitate (normally silver salts) which exhibits ionic conductance. The crystal may be doped to promote ion transport through vacancies within the crystalline lattice. Figure 13.23 shows the design of such an electrode based on doped LaF_3 crystal for the measurement of fluoride ions. Interactions at the surfaces of the crystal allow for the exchange of F^- ions, allowing the development of the membrane potential. Solid state electrodes have been fabricated for ions such as F^-, Cl^-, Br^-, I^-, SCN^-, S^{2-}, Ag^+ and Pb^{2+}.

Membrane electrodes have a number of important advantages over redox electrodes. Because they do not rely on redox reactions, ions that cannot normally be measured at a redox electrode (*e.g.* Na^+, Ca^{2+}, F^-) can be determined. Also, although they can be prone to interferences like redox electrodes, these interferences are normally due to ions of a similar size and charge rather than competing redox reactions, and therefore the effects are more predictable. For these reasons, most potentiometric measurements today are made with membrane electrodes.

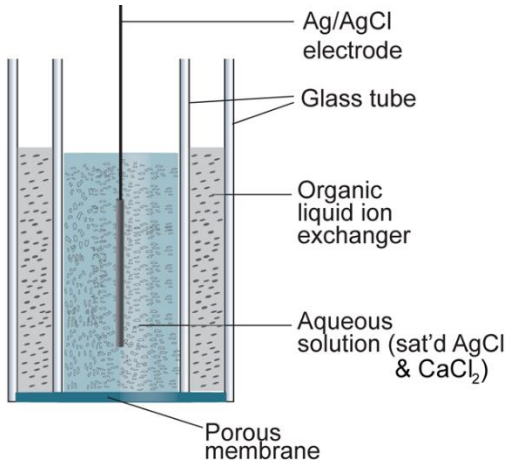


Figure 13.22: A liquid membrane electrode for the measurement of Ca^{2+} ions.

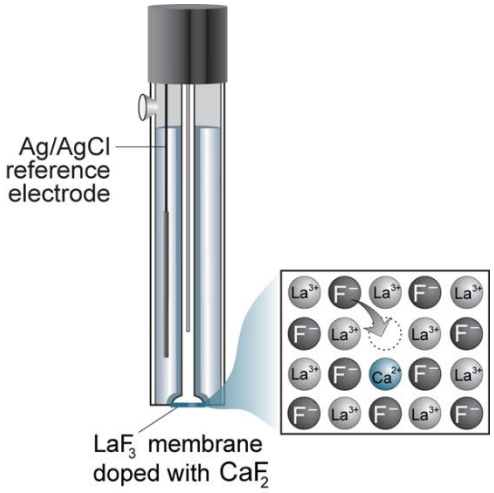


Figure 13.23: A solid state electrode for the measurement of fluoride ions.

13.12 Potentiometry: Concentration Measurements

From an analytical perspective, the objective of making potentiometric measurements is to determine the concentration of an analyte in an unknown solution. Regardless of whether redox or membrane electrodes are used, the same general equation can usually be applied to describe the measured potential.

$$E_{meas} = E_{test} - E_{ref} = K_1 + K_2 \cdot \log C \qquad (13.13)$$

There are some important aspects to note in the application of this equation.

- In potentiometry, the voltage is always measured **with respect to the reference electrode** (*i.e.* $E_{test} - E_{meas}$) so, unlike E_{cell} which was always taken to be positive, E_{meas} can be **positive or negative**.
- Unlike most analytical relationships which are linear in concentration, potentiometric measurements are linear in the **logarithm** of the concentration (or more accurately, the activity). This extends the concentration range of measurements over other techniques, but also contributes to reduced precision (fewer significant digits). It also affects how certain methods, such as standard addition, are applied.
- The constants K_1 and K_2 depend on the particular electrode system under study. Unlike other linear calibrations where the intercept term is sometimes ignored, ***K*₁ can never be assumed to be zero**. It depends on factors like the reference electrodes used and may be positive or negative. On the other hand, if a "**Nernstian response**" is assumed (*i.e.* ideal behavior), then the slope term, K_2, can be taken to have the value it has in the Nernst equation.

  $$K_2(\text{ideal}) = \frac{2.303 \cdot RT}{zF} = \frac{0.05916\ \text{V}}{z} \quad (\text{at } 25\ ^\circ\text{C}) \qquad (13.14)$$

  Notice that, instead of "*n*", this equation uses "*z*", which is the charge on the analyte ion, **including the sign**. Therefore, K_2 can be positive or negative. If Nernstian behavior cannot be assumed, then K_2 must be determined from calibration.

The methods for employing Eqn. (13.13) to determine concentration are similar to other analytical techniques and include absolute calibration, one-point calibration, two-point

calibration, multipoint calibration and standard addition. However, there are some important differences in potentiometry that arise from the logarithmic form of Eqn. (13.13) and its origins in the Nernst equation. These are discussed in more detail below.

Absolute Calibration

The first, and simplest, method of calibration is "absolute" potentiometry. In this type of measurement, the values of K_1 and K_2 can, in principle, be determined from the Nernst equation and the standard potentials of the test and reference electrodes. It is important to recognize that absolute calibration **can only be applied to redox electrodes** and not to membrane electrodes, since standard potentials are not available. It is also required that the reference electrode be identified.

With the absolute method, only one measurement is needed to determine concentration. Since the objective is to calculate an unknown concentration from a known cell voltage, the calculations are opposite to those used to calculate a cell voltage from known concentrations.

Example 13.7: Absolute Calibration

The voltage of a silver electrode coated with insoluble silver bromide is measured as +0.194 V vs SCE when placed in a cell containing bromide ion. Determine the concentration of the bromide ion in the test electrode compartment.

The reaction at the test electrode is $AgBr(s) + e^- \rightarrow Ag(s) + Br^-$ $E° = +0.071$ V

Therefore, using the Nernst equation, we can write:

$$\begin{aligned} E_{meas} &= E_{test} - E_{ref} = E^{o}_{Ag/AgBr} - \frac{0.05916\ V}{1}\log[Br^-] - E_{SCE} \\ &= (0.222\ V - 0.242\ V) - (0.05916\ V)\cdot\log[Br^-] \\ &= -0.020\ V - (0.05916\ V)\cdot\log[Br^-] \end{aligned}$$

This is consistent with Eqns. (13.13) and (13.14), where $K_1 = -0.020$ V and $K_2 = -0.05916$ V (note that absolute calibration assumes a Nernstian response). Based on this, we can solve for the unknown concentration.

$$\log[Br^-] = \frac{0.194\ V + 0.020\ V}{-0.05916\ V} = \frac{0.214\ V}{-0.05916\ V} = -3.6\bar{1}73$$

$$[Br^-] = 10^{-3.6\bar{1}73} = \underline{\underline{2.4 \times 10^{-4}\ M}}$$

Some notes are in order regarding this example. First, be careful of the signs in the calculations. It is easy to make an error, so if the answer does not make sense (particularly if it is a very high concentration) check your calculations. Second, students often wonder about where the concentration units come from, since the logarithm is dimensionless. The answer is that the Nernst equation actually calculates activities, which are technically dimensionless, but referenced to a value of 1 M. We have made the assumption that the concentration is equal to activity. Thus, the absolute method always gives concentrations in moles per liter. Finally, note that although the potential was measured with three significant figures, the rules for logarithms only allow us to keep two significant digits in the final answer, since that is the number of significant decimal places in the antilogarithm. This apparent reduction in precision is common with potentiometric measurements.

Although the absolute method is simple, it depends on the accuracy of the values found in the tables, and more importantly, on the ability of the experimental system to follow the expected theoretical predictions. The voltage of a SCE, in theory, is 0.242 V *vs*. SHE. However, this value can vary by over 10 mV from electrode to electrode, depending on age and method of preparation. Variations of a few mV can cause large changes in calculated concentrations because of the logarithmic relationship. For this reason absolute potentiometry is seldom used in practice.

Exercise 13.11

The voltage of a lead electrode in a solution of Pb(II) was measured as –0.432 V with respect to a saturated Ag/AgCl reference electrode. What is the concentration of Pb(II) in the solution? What are the values of K_1 and K_2 in this cell?

One-Point Calibration

For a one-point calibration with a linear relationship, a zero intercept is assumed and one standard is used to estimate the slope of the calibration curve. In potentiometry, however, the intercept term, K_1 in Eqn. (13.13), is almost never zero. It is also difficult to estimate due to variations in reference cell potentials and other factors. On the other hand, the slope, K_2 in Eqn. (13.13) can be predicted from the Nernst equation, as long as the cell can be assumed to exhibit a *Nernstian response*. Thus, in a one-point calibration, the value of K_1 is calculated from the calibration standard and K_2 is obtained from Eqn. (13.14).

Example 13.7: One-point Calibration

The voltage of a sulfate ion selective electrode placed in a 1.00×10^{-4} F Na_2SO_4 solution is +0.031 V vs. a SCE reference electrode. When the same electrode is placed in a solution containing an unknown amount of sulfate, the voltage reading is −0.051 vs. the SCE. What is the sulfate concentration in the unknown?

Since we are using a membrane electrode (ISE) we *cannot* use absolute calibration since we don't know the internal reference electrode or the internal sulfate concentration. Since we only have one calibration solution, we must assume a Nernstian response, so the equation for the response is:

$$E_{meas} = K_1 + K_2 \cdot \log[SO_4^{2-}] = K_1 + \frac{0.05916\ V}{-2}\log[SO_4^{2-}] = K_1 - (0.02958\ V)\log[SO_4^{2-}]$$

We can use the standard solution to calculate K_1.

$$K_1 = E_{unk} - (0.02958\ V)\cdot\log(1.00\times10^{-4}\ M) = 0.031\ V - (-0.11832\ V) = -0.08732\ V$$

This can now be used to calculate the unknown concentration.

$$\log[SO_4^{2-}]_{unk} = \frac{E_{unk} - K_1}{K_2} = \frac{-0.051\ V - (-0.08732\ V)}{-0.02958\ V} = -\frac{0.03632\ V}{0.02958\ V} = -1.\overline{2}28$$

$$[SO_4^{2-}]_{unk} = 10^{-1.\overline{2}28} = \underline{\underline{0.05\overline{9}\ M}}$$

Some comments should be made about the units used in these calculations at this point.

- In some cases, voltages may be expressed in mV rather than V. The calculations can be performed without converting the measured voltages, but if this is done the multiplier in the Nernst equation needs to be adjusted accordingly (59.16 mV instead of 0.05916 V) and, for the absolute method, the corresponding E^o values also need to be converted.
- The calculations can also be performed if the concentration units are not in mol/L. This will not affect the value of K_2 (slope term), but modifying the concentration units will change the value of K_1. This is only a problem for the absolute method, where K_1 is obtained directly from E^o values, so it is often best to work in mol/L.

Exercise 13.12

A 1000. ppm Zn^{2+} solution is placed in a cell containing a 1 M Ag/AgCl reference electrode and a solid zinc electrode and the voltage of the zinc electrode is measured as −1.024 V *vs*. the reference. A solution containing an unknown concentration of zinc is then measured in the same way and the voltage of the zinc electrode is measured as −1.067 V. Calculate the concentration of the zinc in the unknown (in ppm) using both the absolute method and one-point calibration. Also give the value of K_1 for each method.

Two-Point Calibration

For the one-point calibration, a Nernstian response was assumed so that $K_2 = \pm 2.303\ RT/nF$. In some cases, however, the voltage may still be log-linear in the concentration, but the slope term, K_2, may not exactly match the value predicted by the Nernst equation. This can happen for a variety of reasons related to non-ideal behavior of the electrode. Under these circumstances, two standard solutions can be used to solve for the two unknowns, K_1 and K_2, in Eqn. (13.13). These values can then be employed to determine the concentration in the unknown, as illustrated in the following example.

Example 13.8: Two-Point Calibration

A membrane electrode sensitive to nitrate ion is used to test for this ion in agricultural runoff. In a 50.0 ppm nitrate solution the voltage of the ISE (*vs.* the reference) is −13.5 mV and in a 5.00 ppm nitrate solution it is 43.6 mV. What is the nitrate concentration (in both ppm and mol/L) in a sample that reads 85.4 mV?

We start from Eqn. (13.13) which describes the potentials measured for the two standards, E_{s1} and E_{s2}.

$$E_{s1} = K_1 + K_2 \log C_{s1} = -13.5 \text{ mV} \qquad E_{s2} = K_1 + K_2 \log C_{s2} = +43.6 \text{ mV}$$

Taking the difference of these equations, we can solve for the slope.

$$E_{s1} - E_{s2} = K_2(\log C_{s1} - \log C_{s2}) = K_2 \log \frac{C_{s1}}{C_{s2}}$$

$$K_2 = \frac{E_{s1} - E_{s2}}{\log\left(C_{s1}/C_{s2}\right)} = \frac{(-13.5\,\text{mV}) - (43.6\,\text{mV})}{\log\left(50.0\,\text{ppm}/5.00\,\text{ppm}\right)} = \frac{-57.1\,\text{mV}}{1.00} = -57.1 \text{ mV}$$

Note that this is negative, as we expect from the charge on the ion, and close to what we would anticipate from the Nernst equation (59.16 mV) for a singly charged ion. This can now be used to calculate the value of K_1 from either of the standards.

$$\begin{aligned} K_1 &= E_{s1} - K_2 \log C_{s1} = -13.5\,\text{mV} - (-57.1\,\text{mV})\log(50.0\,\text{ppm}) \\ &= -13.5\,\text{mV} + (57.1\,\text{mV})(1.69\overline{8}97) = -13.5\,\text{mV} + 97.\overline{0}11\,\text{mV} \\ &= 83.\overline{5}11 \text{ mV} \end{aligned}$$

Now we can solve for the concentration in the unknown.

$$\log C_u = \frac{E_u - K_1}{K_2} = \frac{85.4\,\text{mV} - 83.\overline{5}11\,\text{mV}}{-57.1\,\text{mV}} = \frac{1.\overline{8}89\,\text{mV}}{-57.1\,\text{mV}} = -0.03\overline{3}08$$

$$C_u = 10^{-0.03\overline{3}08} = \underline{\underline{0.927 \text{ ppm}}}$$

$$C_u \text{ (in mol/L)} = 0.927\,\text{mg/L} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol } NO_3^-}{62.005 \text{ g}} = \underline{\underline{1.49 \times 10^{-5}\,\text{M}}}$$

Exercise 13.13

A liquid membrane electrode sensitive to Sr^{2+} give a potential of 7.6 mV when pSr = 5.00 and 72.3 mV when pSr = 3.00 (note: pSr = −log[Sr^{2+}]). Calculate the concentration (in mol/L) of strontium in a solution which gives a reading of 34.7 mV.

Multipoint Calibration

Multipoint calibration, or the calibration curve method, makes no assumptions as to either the slope or linearity of response of the electrode, but requires the largest number of standard solutions. The voltage of the test electrode with respect to the reference electrode is measured for a set of standard solutions and the voltage is plotted *vs. logarithm* of the concentration. The voltage for the unknown is then measured and the calibration graph is used to determine the unknown concentration from this voltage, as shown in Figure 13.19. This is usually the most accurate method since the use of multiple standards reduces errors, allows the detection of outliers, and permits nonlinear plots to be used. When preparing standard solutions with this method, the logarithmic concentration scale should be kept in mind and concentrations should be constant multiples of one another (*e.g.* 2, 4, 8, 16, 32 ppm) to ensure even spacing.

Example 13.8: Multipoint Calibration

The following data were collected for an iodide ISE for a series of standards.

Iodide conc. (μM)	0.01	0.1	1	10	100	1000
Voltage (mV)	−72.8	−108.3	−167.1	−229.9	−294.2	−349.5

A urine sample, pretreated to remove interfering chloride ions, gives a potential reading of −265.1 mV. Estimate the concentration of iodide in the sample.

Since we have multiple measurements, we use a calibration curve. We begin by plotting the measured electrode potential against logC, as shown in Figure 13.24. We notice that the lowest concentration appears to be an outlier, and so it is excluded from the remaining calculations. Curvature at low concentrations is not

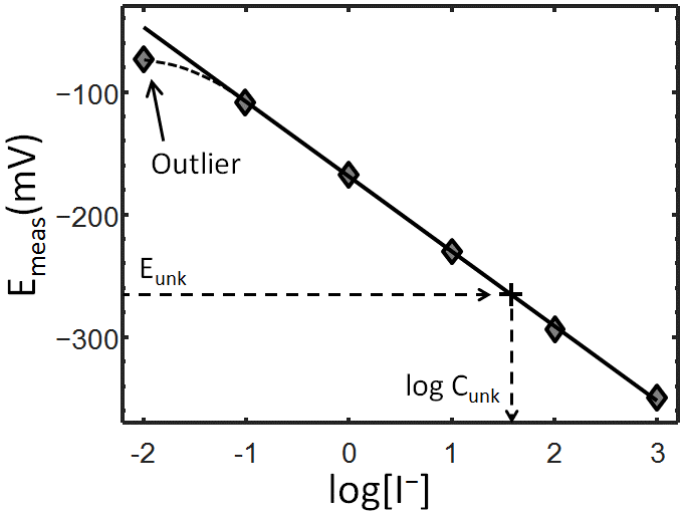


Figure 13.24: Multipoint calibration for potentiometric measurements in Example 13.8.

unusual in potentiometry due to interferences from other ions, and curvature at high concentrations is also observed for other reasons. (These data are taken from real experimental measurements.) This ability to detect non-ideal behavior is one of the main advantages of multipoint calibration.

Using the remaining five measurements, the slope and intercept are calculated using linear regression, which gives

$$\text{intercept} = -168.85\,\text{mV} = K_1 \qquad \text{slope} = -60.95\,\text{mV} = K_2$$

Note that the slope is near the expected value of −59.16 mV. Using these values we can solve for the unknown.

$$\log C_{\text{unk}} = \frac{\text{E}_{\text{unk}} - K_1}{K_2} = \frac{-265.1\,\text{mV} - (-168.85\,\text{mV})}{-60.95\,\text{mV}} = \frac{-96.\overline{2}5\,\text{mV}}{-60.95\,\text{mV}} = 1.5\overline{79}$$

$$C_{\text{unk}} = 10^{1.5\overline{79}} = \underline{\underline{38\,\mu\text{M}}}$$

Standard Addition

As discussed earlier in this course, the use of standard addition and internal standards can help reduce the influence of the sample matrix in analytical methods. Because each test electrode measures only one ion, it is not possible to use internal standards in potentiometry, but the standard addition method can be employed. This approach can be used, for example to compensate for differences in the ionic strength between the unknown and the standard.

When applied to potentiometry, the standard addition method *assumes a Nernstian response* ($K_2 = (2.303)RT/zF$), or that K_2 is known from independent measurements. Because the concentration terms occur in the logarithm for potentiometry, there is no multipoint standard addition method. Standard addition is usually performed by making measurements on two solutions, typically the unknown and the unknown spiked with a known amount of standard. This provides two equations for two unknowns, the constant K_1 in Eqn. (13.13) and the concentration of the sample. Although the principle is the same as for other analytical methods, the math is a bit different because of the logarithmic term, as illustrated below.

Example 13.9: Standard Addition in Potentiometry

The voltage for an ISE sensitive to F^- was measured as +0.105 V *vs*. the external reference electrode in a sample of tap water. A second sample, consisting of 20.0 mL of tap water and 2.00 mL of 0.00100 M F^-, gave a voltage of 0.067 V. Calculate the concentration of fluoride ion in the tap water. Assume a Nernstian response.

The response of the ion selective electrode is

$$\mathrm{E} = K_1 + \frac{0.0592\,\mathrm{V}}{-1}\log[\mathrm{F}^-] = K_1 - (0.0592\,\mathrm{V})\cdot\log[\mathrm{F}^-]$$

Recognizing that the problem is a standard addition, two equations can be written based on the two potentiometric responses.

$$0.105\,\mathrm{V} = K_1 - (0.0592\,\mathrm{V})\cdot\log[\mathrm{F}^-]_\mathrm{u}$$

$$0.067\,\mathrm{V} = K_1 - (0.0592\,\mathrm{V})\cdot\log\left(\frac{20.0\,\mathrm{mL}}{22.0\,\mathrm{mL}}\cdot[\mathrm{F}^-]_\mathrm{u} + \frac{2.00\,\mathrm{mL}}{22.0\,\mathrm{mL}}\cdot(0.00100\,\mathrm{M})\right)$$

K_1 can be cancelled by subtraction, leading to

$$0.105\,\mathrm{V} - 0.067\,\mathrm{V} = (0.0592\,\mathrm{V})\left[\log\left(\frac{20.0\,\mathrm{mL}}{22.0\,\mathrm{mL}}[\mathrm{F}^-]_\mathrm{u} + \frac{2.00\,\mathrm{mL}}{22.0\,\mathrm{mL}}(0.00100\,\mathrm{M})\right) - \log[\mathrm{F}^-]_\mathrm{u}\right]$$

or

$$\frac{0.038\,\mathrm{V}}{0.0592\,\mathrm{V}} = \log\left(\frac{20.0}{22.0}\cdot\frac{[\mathrm{F}^-]_\mathrm{u}}{[\mathrm{F}^-]_\mathrm{u}} + \frac{2.00}{22.0}\cdot\frac{(0.00100\,\mathrm{M})}{[\mathrm{F}^-]_\mathrm{u}}\right)$$

By taking the antilogarithm of both sides, we can then rearrange to solve for the concentration of the unknown.

$$10^{0.6\bar{4}19} = 4.3\bar{8}4 = \frac{20.0}{22.0} + \frac{2.00}{22.0}\cdot\frac{(0.00100\,\mathrm{M})}{[\mathrm{F}^-]_\mathrm{u}}$$

$$[F^-]_u = \frac{(2.00/22.0)\cdot(0.00100\,M)}{4.3\overline{8}4-(20.0/22.0)} = \frac{9.0\overline{9}09\times10^{-5}\,M}{4.3\overline{8}4-0.90\overline{9}09}$$

$$= \frac{9.0\overline{9}09\times10^{-5}\,M}{3.3\overline{4}7} = \underline{\underline{2.62\times10^{-5}\,M}}$$

Exercise 13.14

The electrode in Example 13.8 is used to measure the concentration of iodide in a urine sample by the method of standard addition. Measurement of the urine sample gives a potential of −221.5 mV. A second solution is prepared by adding 5.00 mL of a 1.00 mM iodide standard to 45.00 mL of the urine sample, giving a reading of −277.4 mV. What is the concentration of iodide in the unknown? (Use the value of K_2 given in Example 13.8 rather than the Nernstian slope.)

13.13 Potentiometry: Practical Considerations

At first glance, potentiometry appears to be the ideal analytical method – simply place the electrode in the solution of interest and obtain the concentration. The technique is rapid and direct, and can often be used to measure concentration changes in real-time. In practice, however, there are other limitations that affect both redox and membrane electrodes. Some of these are discussed in this section.

Concentration vs. Activity

An important consideration that has been ignored in most of the discussion so far is that potential measurements respond to *activity* rather than concentration. This presents a problem, since we are usually interested in concentration in a chemical analysis. You will recall that the activity of an ion, X, is related to the concentration through its activity

coefficient, γ: $a_X = \gamma_X[X]$. In a non-ideal solution where γ<1, this means the activity is lower than the concentration. Replacing concentration with activity in Eqn. (13.13), we can write:

$$\begin{aligned} E_{meas} &= K_1 + K_2 \cdot \log a_X = K_1 + K_2 \cdot \log(\gamma_X \cdot [X]) \\ &= K_1 + K_2 \cdot \log \gamma_X + K_2 \cdot \log[X] \end{aligned} \qquad (13.15)$$

This equation indicates that measurements will still be linear in concentration as long as γ *is constant for all of the measurements made*. This would result in simple adjustment of K_1 to $K_1' = K_1 + K_2 \log \gamma_X$.

Since γ depends only on the ionic strength of the solution, a simple way to ensure that it remains constant is to use a **total ionic strength adjustment buffer** (TISAB) to ensure that approximately the same ionic strength is used for all measurements. This buffer contains a high enough concentration of non-interfering electrolyte (*e.g.* KCl) to ensure that the ionic strength in the samples and standards remains essentially constant.

Liquid Junction Potentials

Whenever two solutions are in contact through a liquid junction, such as a glass frit, ions can move between the two solutions. Although the diffusion may be slow, if the rates of ion transport are different for different ions, a potential difference can build up. To illustrate, consider the case shown in Figure 13.25 where a glass frit separates HCl and KCl solutions of equal concentration. There should be no net movement of Cl^- ions, which are equal on both sides, but there will be a net movement of H^+ ions to the right and K^+ ions to the left. However, because they are smaller, the H^+ ions move about six times as the K^+ ions, resulting in an excess of positive charges on the right and consequently a potential across the frit. This is called the liquid junction potential, E_{LJ}, and can be added to Eqn. (13.13).

$$E_{meas} = K_1 + E_{LJ} + K_2 \cdot \log C \qquad (13.16)$$

As with the effect of activity, as long as E_{LJ} is constant, it will only result in a change to the constant K_1 and not affect the linear response. The use of a TISAB in this case will help to keep E_{LJ} constant. KCl is often favored for this, since K^+ and Cl^- have similar mobilities.

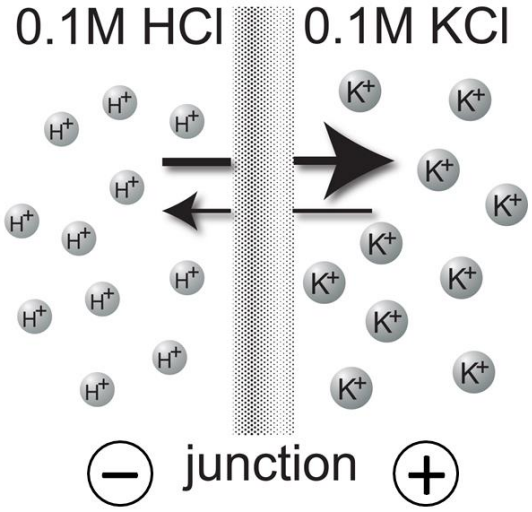


Figure 13.25: A liquid junction (frit) separating solutions of HCl and KCl of the same concentration. Migration of H^+ ions across the frit is faster than K^+ ions.

Interferences

An interference is any substance present in a sample that can affect the correct measurement of the analyte by potentiometry. There are a variety of mechanisms by which this can occur, as discussed below.

(1) **Chemical Equilibria.** In general, potentiometric measurements respond to the concentration of the *free* ion in the solution. Therefore, any equilibria that reduce the concentration of the ion in solution will affect the measurement. For example, since HF is a weak acid, the concentration of fluoride ions will be reduced in acidic solutions, as shown in the equilibrium in Figure 13.26. Likewise, the presence of ammonia in solution can reduce the amount of free Cu^{2+} in solution through complex formation. Ions can also bind to other species in solution, especially those involving biological fluids. In some cases, the measurement of free ions may be desired, but in cases where the total concentration is the objective, these limitations need to be recognized.

(2) **Redox Interferences.** For redox electrodes, an important source of interference is other redox reactions that can occur at the metal electrode. Just as a Pt electrode can facilitate different redox reactions (*e.g.* H_2/H^+, Fe^{2+}/Fe^{3+}), other metal electrodes can serve to catalyze redox reactions other than the one of interest. These other redox couples can modify the potentials in unpredictable ways, leading to erroneous results. Membrane electrodes are not susceptible to this type of interference, which is one of the reasons they are more widely used.

(3) **Membrane Interferences.** While membrane electrodes are not susceptible to redox interferences, they are prone to interferences from ions which have similar properties to the intended analyte. Membrane electrodes are *selective* but not *specific*, which means that, while they have been designed to maximize the response from a particular analyte, other ions can still elicit some response. A list of some analyte ions and typical interferents for ion selective electrodes is presented as Table 13.4, which also lists other typical specifications, such as concentration range and ionic buffers (TISABs) used. (Note the actual specifications for a particular electrode depend on its design – this table is only intended to give you a sense of these characteristics.)

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$$

Figure 13.26: Chemical equilibria that could affect the measurement of fluoride and copper ions in solution.

The extent to which an ion interferes with the determination of an analyte ion is given by its *selectivity* coefficient, which is specific for a given ion and electrode design. For the determination of ion "I" with charge *z*, the effect of interfering ions "J" and "L", with charges *x* and *y*, is given by the Nicolsky-Eisenman equation:

$$E = K_1 + \frac{0.05916\ V}{z}\log\left([I^z] + k_J[J^x]^{z/x} + k_L[L^y]^{z/y} + ...\right) \quad (13.17)$$

The quantities k_J and k_L are the selectivity coefficients for ions J and L. For example, suppose a potassium ISE has selectivity coefficients $k_{Na} = 0.0003$, $k_{Rb} = 0.1$, $k_{Cs} = 0.004$, and $k_{NH4} = 0.007$. This would mean that if the sample solution had equal concentrations of K^+ and Rb^+, the calculated potassium concentration would be 10% higher than it actually is, whereas the other ions would have to have a much higher concentration before they had the same effect. These types of interferences cannot be mitigated through standard addition, so it is important to know the nature of the matrix in which the measurement is made.

Exercise 13.15

Blood plasma has been estimated to contain sodium ions at a concentration of 140 mM and potassium ions at a concentration of 4 mM. If $[K^+]$ is determined with the potassium ISE described above, what will be the percentage error due to the sodium interference?

Range

A unique feature of potentiometric measurements is a very large measurement range, which can extend over several orders of magnitude. This is a consequence of the log-linear response, and typical ISEs have a range that can extend from 10^{-6} to 1 M, or even wider (*e.g.* glass pH electrode), which makes them useful for both trace analysis and major components. In practice, the lower limit of an ISE depends on interfering ions and there selectivity coefficients. The presence of interfering ions will cause the calibration curve to become flat at the low end because it is responding only to the interfering ion and not the analyte. This is illustrated in Figure 13.27, which shows the response of a hypothetical sodium ISE in the

Table 13.4. Typical specifications for ion selective electrodes.

Analyte Ion	Conc. Range (M)	pH Range	Main Inter-ferences	Ionic Buffer
Cl^-	10^{-6}- 1	1-12	I^-, Br^-, CN^-, S^{2-}	KNO_3
Br^-	10^{-5}- 1	1-12	I^-, CN^-, S^{2-}	KNO_3
Ca^{2+}	10^{-6}- 0.1	4-11	Ba^{2+}, Al^{3+}, Sr^{2+}	KCl
NH_4^+	10^{-5}- 0.1	1-9	K^+, Na^+	CH_3COOH
Cu^{2+}	10^{-7}- 1	2-7	Hg^{2+}, Ag^+, S^{2-}, Cl^-, Br^-	KNO_3
Cd^{2+}	10^{-5}- 0.1	3-7	Hg^{2+}, Ag^+, Cu^{2+}, Pb^{2+}, Fe^{3+}	KNO_3

presence of interfering potassium ions, where the selectivity coefficient for K^+ is 0.01. As the concentration of K^+ becomes higher, the useful range of the electrode shrinks at low concentrations. At high concentrations, the linear response can be limited by activity effects or solubility limitations.

The most well-known example of interference effects is the "alkaline error", which is observed for high pH measurements using a glass electrode. This arises because the common glass electrode shows some response to Na^+ and K^+ in addition to H^+. At a pH of 12 or higher, the concentration of H^+ is very low, while the interfering ions (typically from NaOH or KOH) are abundant, causing the pH to be underestimated.

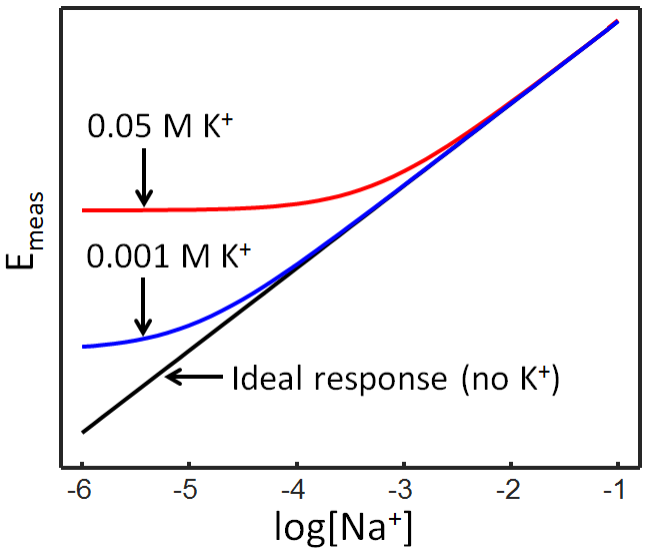


Figure 13.27: Effect of an interfering ion (K^+) on the response of a sodium ion selective electrode.

Precision

The wide linear range of potentiometric methods is counterbalanced by the fact that they are somewhat less precise than other analytical methods, with relative uncertainties in concentration typically on the order of 10%. Working from Eqn. (13.13), we can express the logarithm of the concentration as

$$\log C = \frac{(E - K_1)}{K_2} = \frac{E}{K_2} - \frac{K_1}{K_2} \qquad (13.18)$$

If we assume that K_2 = (0.05916 V)/z and that the only source of imprecision is in the voltage measurement (which is not necessarily the case), it can be shown by propagation of error that the relative error in the concentration is:

$$RSD_C = \frac{s_C}{C} = \frac{2.303 \cdot |z|}{0.05916\ \text{V}} \cdot s_\text{E} = (38.9\ \text{V}^{-1})|z| \cdot s_\text{E} \qquad (13.19)$$

Here s_E is the absolute standard deviation in the voltage measurement, usually about 2 mV under normal conditions. Thus, the relative standard deviation in the concentration is (38.9)(1)(0.002) = 0.078, or about 8%. For z = ±2, the error becomes about 15%. Thus, concentrations determined by potentiometry are normally not reliable to more than two significant figures. However, it should also be kept in mind that other sources of error, such as liquid junction potentials and interferences, can also limit the accuracy of the result.

13.14 Redox Titrations

Titrations are an important class of methods for quantitative analysis that are based on a controlled chemical reaction. Although acid-base titrations are perhaps the most familiar to you, titrations based on other types of reactions, such as complexation or redox reactions are also widely used. Redox titrations form the basis of many standard analytical methods, such as the Winkler method, which is used to determine dissolved oxygen in water, and the Karl Fischer titration, used to determine the amount of water in organic solvents.

In the same way that acid-base titrations are based on acid-base reactions, redox titrations are based on redox reactions. Calculations are carried out in the same way, using volumes and stoichiometric ratios to determine the moles or concentration of unknown. For a redox reaction to be useful, it should be rapid and go to completion. A typical example is the use of potassium permanganate (the titrant) to determine the concentration of Fe^{2+} (the titrand).

$$MnO_4^-(aq) + 5\ Fe^{2+}(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{2+}(aq) + 4\ H_2O(l)$$

To carry out calculations for any redox titration, it is essential to have a balanced chemical equation. A quantity of the unknown (an oxidant or a reductant) is titrated against a known quantity of titrant (the reductant or oxidant) until the endpoint is reached.

Although there are similarities in the calculations for any titration method, there are some important practical differences between acid-base titrations and redox titrations.

(1) Stoichiometry for redox titrations is often not 1:1.
(2) Instead of a strong acid or a strong base, the titrant in redox titrations is a strong oxidant or a strong reductant.
(3) Instead of acid-base indicators, redox titrations use a variety of methods, including color changes, redox indicators and redox electrodes.
(4) Because many redox reactions are slow, back titrations are more common.

For acid-base titrations, the endpoint is normally detected through the use of an acid-base indicator, although a pH electrode can also be used. For redox titrations, the endpoint can be detected in one of three ways.

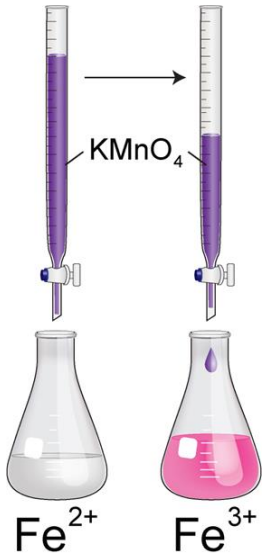


Figure 13.28: Redox titration of potassium permanganate with iron(II). In this case, the end point is signaled by the pink color of excess MnO_4^-.

(1) Monitoring of the appearance of a coloured product or the disappearance of a coloured reactant. Unlike most acids and bases, many redox reagents absorb in the visible region and can be monitored either through a spectrophotometric titration or, if they absorb strongly enough, by direct visualization. An example of this would involve the reaction of potassium permanganate ($KMnO_4$), a strong oxidizing agent, with a reductant such as Fe^{2+}, as shown in Figure 13.28. The permanganate ion has a deep purple colour, so the endpoint in the titration can be determined by watching the disappearance of this colour.

(2) Following the cell potential over the course of the titration. Just as extreme changes in pH take place at the equivalence point in an acid-base titration, changes in the electroactive species present in the titration flask during a redox titration lead to large changes in the electrochemical potential of the solution at the equivalence point. This change in potential can be monitored with electrodes in a *potentiometric titration*, as illustrated in Figure 13.29, which shows the apparatus that could be used to follow the oxidation of Fe^{2+} by a standard Ce^{4+} solution, a strong oxidizing agent. The cell potential of a platinum electrode is measured with respect to a reference electrode and shows a rapid change at the equivalence point, as illustrated in Figure 13.30.

(3) Use of redox indicators. Acid-base indicators are weak acids which change colour depending on pH. Likewise, redox indicators are compounds that can undergo a redox reaction and have different colors in the oxidized and reduced form. Several redox indicators are available and, just as the selection of acid-base indicators depends on the pH at the equivalence point, the selection of a redox indicator depends on the electrochemical potential in the titration flask at the equivalence point, which in turn, depends on the species involved in the titration and their concentrations.

(4) Use of starch indicator. For titrations involving iodine, known as *iodometric titrations*, a soluble starch is widely used as an indicator, since it forms a deep blue complex with I_2 in solution.

Just as acid-base titrations use strong acids and bases as the titrant, redox titrations use strong oxidants or reductants. Cerium(IV) is the strongest commonly used oxidant (E^o = 1.70 V in perchloric acid), but MnO_4^- (E^o = 1.51 V) is often favored because of its deep purple color, which allows easy endpoint detection. Potassium dichromate ($K_2Cr_2O_7$) and

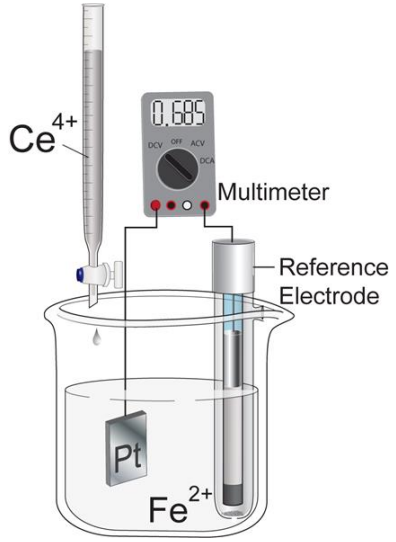


Figure 13.29: Apparatus for the potentiometric titration of iron(II) with cerium (IV).

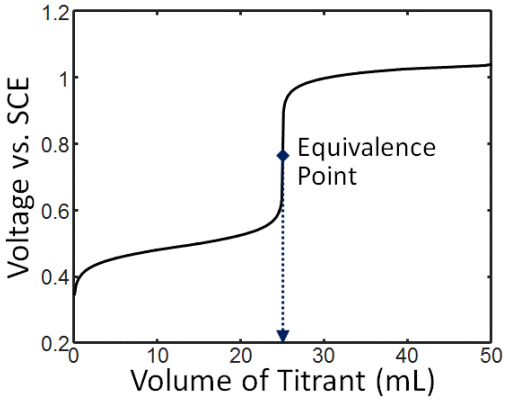


Figure 13.30: Theoretical titration curve for the potentiometric titration of 25 mL of 0.1 M Fe^{2+} with 0.1 M Ce^{4+} in 1 M HCl.

potassium iodate (KIO_3) are weaker oxidants (E^o = 1.33 V and 1.18 V), but are available as primary standards, so they don't need to be standardized. To standardize oxidant solutions, typically ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ as a source of Fe^{2+}) or oxalic acid ($H_2C_2O_4$, oxidized to CO_2) are used as primary standards. Strong reducing agents are not commonly used as titrants since they are readily oxidized by O_2 in air and therefore unstable.

A special class of redox titrations known as *iodometric methods* use iodine as an oxidizing agent. Although not a strong oxidizer, iodine has the advantage of being easily detected with a starch indicator. Since molecular iodine (I_2) is not very soluble, the tiiiodide ion, I_3^-, is typically used instead. When reduced, this yields iodide ions:

$$I_3^-(aq) + 2\,e^- \rightarrow 3\,I^-(aq) \qquad E^o = +0.536\ V$$

To prepare a standard triiodide solution, a known amount of primary standard KIO_3 is usually reacted with an excess of iodide ion by the reaction:

$$IO_3^-(aq) + 8\,I^-(aq) + 6\,H^+(aq) \rightarrow 3\,I_3^-(aq) + 3\,H_2O(l)$$

In some cases, I^- is used to determine an oxidizing agent. Excess iodide is added and the triodide formed is back-titrated with thiosulfate ion, $S_2O_3^{2-}$.

Exercise 13.16

The amount of ethanol (C_2H_5OH, MW = 46.068 g/mol, density = 0.7873 g/mL) in wine can be determined by back titration after an excess of potassium dichromate is used to convert the alcohol to acetic acid (CH_3COOH) in acidic solution. A 20.00 mL sample of wine is first diluted to 100.0 mL with distilled water. A 5.00 mL aliquot of this solution is then mixed with 25.00 mL of 0.1148 F $K_2Cr_2O_7$ in 6 M sulfuric acid and heated for 30 min to complete the oxidation of ethanol. After cooling, the excess dichromate in the solution is titrated with 0.3443 F ferrous ammonium sulfate:

$$6\,Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\,H^+(aq) \rightarrow 6\,Fe^{3+}(aq) + 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

The volume of titrant required is 27.24 mL. If the wine has a density of 0.9819 g/mL, calculate the percentage of alcohol by weight (%w/w) and volume (%v/v) in the wine.

13.15 Summary

Oxidation-reduction reactions form the basis of several important analytical techniques, such as redox titrations and potentiometry, and others not covered here. Redox reactions involve the transfer of electrons and can be balanced through appropriate techniques. The electrochemical potential of a redox reaction, calculated by the half-reaction method, can be used to determine its Gibbs energy change and equilibrium constant, and hence its spontaneity. The Nernst equation allows the voltage of an electrochemical cell to be calculated with a knowledge of reactant concentrations and standard cell potentials. It forms the basis of potentiometric methods that can be used to determine analyte concentration based on a logarithmic relationship with voltage. Both redox electrodes and membrane electrodes can be used. Membrane electrodes, also called ion selective electrodes, are not based on redox reactions and are more widely used because they are less prone to electrochemical interferences. This includes the commonly used pH electrode. In general, potentiometry is a simple, sensitive, and reasonably selective technique that covers a wide concentration range, but it is subject to certain matrix effects and is not applicable to all analytes.

13.16 Additional Exercises

Exercise 13.17

Balance the following redox equations:

In acid:

$Zn(s) + NO_3^- \rightarrow Zn^{2+} + NH_4^+$

$CH_3CH=CHCH_3 + MnO_4^- \rightarrow CH_3COOH + Mn^{2+}$

$Cr_2O_7^{2-} + H_2O_2 \rightarrow Cr^{3+} + O_2(g)$

$Cr_2O_7^{2-} + CH_3CH_2OH \rightarrow Cr^{3+} + CH_3COOH$

$PbS(s) + NO_3^- \rightarrow Pb^{2+} + NO + S(s)$

In base:

$Cr(OH)_4^- + HO_2^- \rightarrow CrO_4^{2-}$

$SeCN^- + BrO^- \rightarrow SeO_3^{2-} + OCN^- + Br^-$

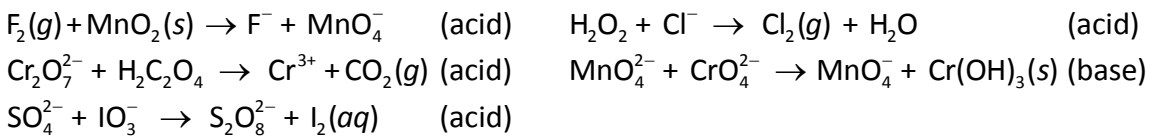
$Zn(s) + OH^- \rightarrow Zn(OH)_4^{2-} + H_2(g)$

$ClO_3^- \rightarrow Cl^- + ClO_4^-$

$CN^- + AsO_3^- \rightarrow CNO^- + As(s)$

Exercise 13.18

Balance the following reactions. In each case, give the value of *n* and the standard *reaction* potential, and indicate if the reaction is spontaneous.



Exercise 13.19

One compartment of an electrochemical cell contains a silver electrode in an Ag^+ solution. The other compartment contains a platinum electrode in a solution of iodate ion, iodine, and H^+. Write the short-hand notation for the cell. Determine the standard cell potential and write the spontaneous reaction under standard conditions. Calculate ΔG^o and K for the reaction as written at 25 ^oC.

Exercise 13.20

For each of the following cells, calculate the cell potential and answer the questions.

(a) $Cu|Cu^{2+}(0.0100\,M) \,||\, Fe^{3+}(0.100\,M), Fe^{2+}(0.0250\,M)|Pt$
Which electrode is more positive?

(b) $Zn|Zn^{2+}(0.0500\,M) \,||\, Br^-(0.0100\,M), Br_2(0.0100\,M)|Au$
Which electrode is the cathode?

(c) $Pt|Fe^{2+}(0.0550\,M), Fe^{3+}(0.00850\,M), HCl(1.00\,F) \,||\, HCl(1.00\,F), Sn^{2+}(0.115\,M), Sn^{4+}(0.0350\,M)|Pt$
What is the potential of the right electrode with respect to the left electrode?

(d) $Pt|IO_3^-(0.0100\,M), I_2(0.00100\,M), H^+(0.100\,M) \,||\, I_3^-(0.00100\,M), I^-(0.100\,M)|Pt$
Which electrode is the anode?

(e) $Au|Cr^{2+}(0.0550\,M), Cr^{3+}(0.00730\,M) \,||\, H^+(0.00500\,M), Cr^{3+}(0.135\,M), Cr_2O_7^{2-}(0.0250\,M)|Au$

(f) $Pt|IO_3^-(0.0100\,M), I_2(0.00200\,M), H^+(0.100\,M) \,||\, H^+(1.00\,M), Cr^{3+}(0.0200\,M), Cr_2O_7^{2-}(0.0100\,M)|Pt$
Which compartment contains the cathode?

Exercise 13.21
The voltage of a silver electrode in a solution of Ag^+ was measured as 0.389 V with respect to a SCE reference electrode. What is the concentration of Ag^+ in the solution?

Exercise 13.22
A lead electrode coated with insoluble lead sulfate is used to determine the sulfate concentration in waste water samples. The voltage of the lead electrode measured *vs.* a saturated silver/silver chloride reference electrode is −0.508 V. What is the sulfate concentration in the sample?

Exercise 13.23
The voltage of a zinc electrode in a 0.100 M Zn(II) solution was measured as −1.231 V *vs* a reference electrode. That same electrode gave a voltage of −1.256 V with an unknown. What is the concentration of Zn(II) in the unknown?

Exercise 13.24
The voltage of an electrochemical cell with a test electrode sensitive to $[H^+]$ and a reference electrode is measured as 0.173 V when a standard solution of pH 7.00 is in the cell. The same cell gives a reading of 0.301 V with a 0.0100 F solution of a weak acid in the cell. Assuming a Nernstian response, calculate the K_a of the weak acid.

Exercise 13.25
The voltage of a hydrogen electrode at 25°C was measured as −0.575 V *vs* an SCE reference electrode while immersed in a 0.00100 F solution of a weak acid. At this electrode, H_2 was bubbled through the solution into the open atmosphere. Atmospheric pressure was measured as 748.0 mm Hg. The vapor pressure of water at 25°C is 23.8 mm Hg. (Remember that one standard atmosphere is 760.0 mm Hg pressure.) Calculate the pK_a of the weak acid.

Exercise 13.26
The voltage of a Cu(II) membrane electrode (vs SCE) is +0.031 V in a 0.00100 M Cu^{2+} solution. The electrode voltage is −0.042 V in an unknown. What is the pCu in the unknown? Assume that the cell response is ideal.

Exercise 13.27

An electrochemical cell consisting of a Ca^{2+} ion selective electrode and an SCE reference electrode is used to measure [Ca^{2+}] in liquid samples. The voltage of the Ca^{2+} sensitive electrode *vs* the SCE is +0.015 V in a 0.0100 M calcium solution. The same measurement gives a voltage of −0.038 V for an unknown. What is the [Ca^{2+}] in the unknown assuming the electrode response is Nernstian?

Exercise 13.28

A membrane electrode responsive to cyanide ion produces the following voltages when measured *vs* a reference electrode:

1.00×10^{-3} M CN^-	+338 mV
1.00×10^{-4} M CN^-	+390 mV
Unknown	+412 mV

What is the concentration of cyanide ion in the unknown?

Exercise 13.29

A sample containing bromide ion was placed in a cell containing a bromide ISE and the voltage of the ISE was measured as −0.139 V *vs* the reference electrode. A 10.0 mL aliquot of the sample was mixed with 1.00 mL of a 0.00100 M bromide-containing solution and the voltage of the ISE in this solution was −0.154 V. What is the concentration of Br^- in the sample? Assume Nernstian electrode response.

Exercise 13.30

A potassium liquid membrane electrode is calibrated using two standard solutions with the following measurements: E_{ISE} = 0.1131 V in 0.00800 M KCl, E_{ISE} = 0.0824 V in 0.00200 M KCl. An unknown solution gives a reading of 0.0237 V. When the electrode is placed in a mixture of 10.00 mL of an unknown and 5.00 mL of the 0.00200 M KCl standard is 0.0318 V. Determine the concentration of K^+ in the unknown using: (a) a two point calibration, (b) standard addition assuming a Nernstian slope, and (c) standard addition using the measured slope. What kinds of errors will standard addition compensate for?

Exercise 13.31

Suppose the response of a sodium ISE vs SCE is given by: $E = K + (0.05916\,V)\cdot\log(a_{Na^+})$ where K = −0.045 V. Calculate the potential in solutions where the activity of Na^+ is 0.100 M and 0.00100 M, and also in solutions with 0.100 F NaCl and 0.00100 F NaCl. For the latter, you will have to calculate activities using the Debye-Hückel equation.

Exercise 13.32

Measurement of fluoride ion using a fluoride ISE is complicated by equilibrium with HF at low pH, interference from hydroxide at high pH, and complex ion formation with ions like Fe^{3+} and Al^{3+}. If the total amount of F^- in a solution is fixed, predict the effect on the potential (more positive, more negative) when: (a) the pH is increased, (b) the pH is decreased, and (c) Fe^{3+} ions are added.

Exercise 13.33

Nitrite ion (NO_2^-) can be determined in basic solution by titration with standard potassium permanganate ($KMnO_4$), producing nitrate ion (NO_3^-) and manganese dioxide ($MnO_2(s)$). If 50.0 mL of sample are titrated with 0.02000 M $KMnO_4$, requiring 37.4 mL of titrant, determine the concentration of nitrite in the sample.

Exercise 13.34

Dissolved SO_2 can be determined in basic solution (as sulfite) by titration with chromate ($SO_3^{2-} + CrO_4^{2-} \rightarrow SO_4^{2-} + Cr(OH)_3$ - unbalanced). If 50.0 mL of a sample are titrated with 0.0300 M K_2CrO_4, requiring 43.8 mL of titrant, determine the concentration of sulfite ion in the original sample.

Exercise 13.35

Nitrous acid (HNO_2) can be determined in acidic solution with permanganate (MnO_4^-), the products being NO_3^- and Mn^{2+}. 50.0 mL of a 0.0200 F solution of MnO_4^- are added to 50.0 mL of a solution of nitrous acid and allowed to react for 15 min. (for complete oxidation). 40.0 mL of 0.0200 F Fe^{2+} are required to titrate the excess MnO_4^- (products Mn^{2+}, Fe^{3+}). What is the formality of HNO_2 in the sample solution?

Exercise 13.36

A solution of potassium permanganate ($KMnO_4$) is to be used to determine the uranium content of an ore by oxidizing U^{4+} to UO_2^{2+}. The MnO_4^- is standardized by titration with a standard solution of Fe^{2+}, where 50.00 mL of permanganate requires 39.42 mL of 0.03871 F Fe^{2+} (the Fe^{2+} is oxidized to Fe^{3+}). A 0.4931 g sample of ore is dissolved, the uranium converted entirely to U^{4+}, and diluted to 50 mL. This solution requires 36.91 mL of permanganate for titration. In both titrations the MnO_4^- was reduced to Mn^{2+} and the pH was 0.00. What is the %U in the sample?

Exercise 13.37

Vitamin C (ascorbic acid, $C_6H_8O_6$) can be determined by a redox titration with iodate in the presence of excess iodide. During the titration, the iodate reacts with iodide to produce the triiodide ion which then reacts with ascorbic acid to form dehydroascorbic acid ($C_6H_6O_6$) according to the following *unbalanced* reactions.

$$IO_3^- + I^- \rightarrow I_3^-$$
$$I_3^- + C_6H_8O_6 \rightarrow C_6H_6O_6 + I^- \qquad \text{(unbalanced)}$$

A standard solution of iodate is prepared by first dissolving 0.1573 g of primary standard KIO_3 in water and diluting to 1000.0 mL. A 10.00 mL aliquot of this solution is then mixed with 10 mL of 1 M HCl and diluted to 100.0 mL to form the titrant. An unknown sample is prepared by adding 5.00 mL of apple juice to 50 mL of 0.1 M HCl containing 1 g of KI and starch indicator. The titration requires 17.22 mL of the iodate to reach the deep blue end point. Calculate the number of mg of vitamin C in 250. mL of the apple juice.

13.17 Answers to Exercises 13

13.1 (a) Na = +1, O = −2, Br = +1
(b) O = −2, Cr = +6
(c) H = +1, O = −2, C = −2
(C_1 = −2, C_2 = −1, C_3 = −3)
(d) Ca = +2, O = −2, Mn = +7
(e) I = −1/3
(f) C = +2, N = −3
(g) C = −2, N = −3, H = +1

13.2 Check mass and charge balance.

13.3 $Cd \mid Cd^{2+}(aq) \parallel Cr_2O_7^{2-}(aq), Cr^{3+}(aq), H^+(aq) \mid Au$

13.4 2.040 V, anode = $Pb/PbSO_4$
$Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$

13.5 Yes. $E^o = 0.015$ V, $\Delta G^o = -8.\overline{6}8$ kJ/mol, $K = \overline{3}3$

13.6 1.035 V, Zn

13.7 2.076 V, 1.898 V, 2.253 V

13.8 0.139 V, LHS

13.9 $0.0\overline{2}0$ M

13.10 2.6 mol/L

13.11 2.1×10^{-4} M, $K_1 = -0.323$ V, $K_2 = +0.02958$ V

13.12 Absolute: $K_1 = -0.985$ V, $C_{unk} = \overline{1}11$ ppm
One-pt.: $K_1 = -0.970$ V, $C_{unk} = \overline{3}5$ ppm

13.13 6.9×10^{-5} M

13.14 13.6 μM

13.15 +1%

13.16 9.19_7 %(w/w), 11.4_7 %(v/v)

13.17 Check mass and charge balance

13.18 6, 1.18 V, yes; 6, 1.82 V, yes;
10, −0.83 V, no; 2, 0.381 V, yes;
3, −0.69 V, no

13.19 $Ag \mid Ag^+(aq) \parallel H^+(aq), IO_3^-(aq), I_2(aq) \mid Pt$
$IO_3^- + 5\,Ag + 6\,H^+ \rightarrow \frac{1}{2}\,I_2 + 5\,Ag^+ + 6\,H_2O$
0.379 V, −183 kJ/mol, $1._1 \times 10^{32}$

13.20 (a) 0.529 V, Pt; (b) 1.948 V, Au;
(c) 0.559 V, –0.559 V; (d) 0.565 V, right;
(e) 1.48 V; (f) 0.24 V, right

13.21 $1.4_5 \times 10^{-3}$ M

13.22 0.03_3 M

13.23 0.0143 M

13.24 2.1×10^{-8}

13.25 8.28

13.26 5.47

13.27 $1.6_2 \times 10^{-4}$ M

13.28 $3.7_8 \times 10^{-5}$ M

13.29 $1._0 \times 10^{-4}$ M

13.30 (a) $1.4_1 \times 10^{-4}$ M; (b) $9._5 \times 10^{-4}$ M;
(c) $8._6 \times 10^{-4}$ M

13.31 −0.104 V, −0.222 V, −0.111 V, −0.223 V,

13.32 (a) more –ve; (b) more +ve; (c) more +ve

13.33 0.0224 M

13.34 0.0394 M

13.35 0.0420 F

13.36 27.19%

13.37 33.44 mg/250 mL

Topic 14

Chromatography

14.1 Contents in Brief

- Partitioning and sample extraction
- The theory of chromatography
- Plate theory (peak separation)
- Rate theory (peak shape)
- Types of chromatography

14.2 Introduction

In nature, samples rarely exist as single components. Analytes are often present in very complex mixtures (think seawater, plant extracts, or blood). For proper characterization, most detection strategies require some type of separation before analysis. This separation step allows analytes to be introduced to a detector being free of matrix interferences, providing a more accurate profiling of the sample. This topic discusses one of the most powerful forms of separation available, chromatography.

14.3 Phase Separation

Several strategies exist to separate sample components. Most involve transferring components from one phase to the next, *e.g.* distillation, which involves transfer of sample from liquid to gas. Consider now the analysis of a pesticide, initially present in a soil sample. Since most instruments cannot directly analyze the unprocessed soil sample, the pesticide must be separated from the sample matrix. Let's suppose the pesticide is soluble in non-polar solvents such as hexane, while the remaining soil components are not. The analyte (*i.e.* the pesticide) can be separated from the soil by mixing the soil with some hexane, allowing the pesticide to dissolve, and filtering the remaining solids. This process of transferring analyte from one phase to the next is called *extraction*, and is a frequent first step in sample processing before detection. Several factors are important in the extraction, including the efficiency of extraction (*i.e.* recovery of the analyte), as well its purity.

Consider yet another two-phase system. Our pesticide has now moved into lake water (being sparingly soluble in water). The pesticide will again extract into hexane, as a preferred solvent to dissolve the compound. Figure 14.1 shows a quantity of this lake water added to a separatory funnel, along with a quantity of hexane. As the liquids are shaken, the analyte, *S*, will *partition*, or distribute, between the two phases, according to an equilibrium process. This can be described as follows:

$$S_{aq} \rightleftharpoons S_{org}$$

The expression below characterizes the partitioning of analyte between the two phases:

$$K = \frac{[S]_{org}}{[S]_{aq}} \qquad (14.1)$$

This equilibrium constant, *K*, is known as a *partition coefficient*. Since the pesticide favours the hexane layer in our example, we can say that $K > 1$. The relative concentration of analyte in each phase is calculated from the magnitude of *K*. The amount (*i.e.* the moles) in each phase can only be determined if the relative volume of the two phases is also known.

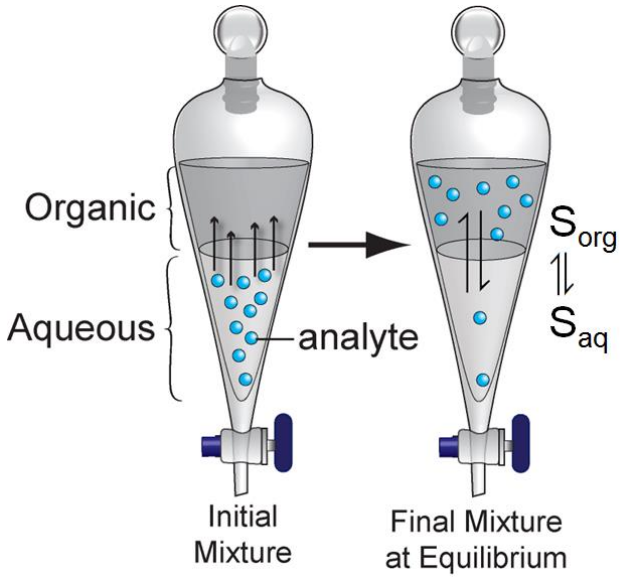


Figure 14.1: Partitioning of a sample, S, between two immiscible solvents. An equilibrium is established as S distributes between the two layers.

Example 14.1: Extraction efficiency

Suppose *K* for the pesticide in a hexane/water system is 80. For equal volumes of water and hexane, what percentage of the pesticide is extracted into the hexane?

Beginning from the expression for *K*:

$$K = \frac{[S]_{org}}{[S]_{aq}} = \frac{\text{mol } S_{org} / V_{org}}{\text{mol } S_{aq} / V_{aq}} = \left(\frac{\text{mol } S_{org}}{\text{mol } S_{aq}}\right)\left(\frac{V_{aq}}{V_{org}}\right)$$

Rearranging the equation above, the following is obtained:

$$\frac{\text{mol } S_{org}}{\text{mol } S_{aq}} = K\left(\frac{V_{org}}{V_{aq}}\right)$$

For equal volumes of each phase, (V_{org} / V_{aq}) cancels, and the concentration ratio is equal to the mole ratio. The percent extracted is calculated as follows:

$$\%\,\text{extracted} = \frac{\text{mol } S_{org}}{\text{total mol } S} \times 100\% = \frac{\text{mol } S_{org}}{\text{mol } S_{org} + \text{mol } S_{aq}} \times 100\%$$

and we also know from above that

$$\text{mol } S_{org} = K\left(\text{mol } S_{aq}\right)$$

These two equations can be combined into the following:

$$\%\,\text{extracted} = \frac{K\left(\text{mol } S_{aq}\right)}{K\left(\text{mol } S_{aq}\right) + \left(\text{mol } S_{aq}\right)} \times 100\% = 100\%\left(\frac{K}{1+K}\right)\left(\frac{\cancel{\text{mol } S_{aq}}}{\cancel{\text{mol } S_{aq}}}\right)$$

$$\%\,\text{extracted} = 100\%\left(\frac{80.}{1+80.}\right) = 9\overline{8}.8\%$$

Exercise 14.1
For the pesticide described in Example 14.1, what percent is extracted if the volume ratio of water/hexane is 10/1?

Exercise 14.2
Suppose another compound was added to the water layer. If 80.% of this compound extracted into the hexane, what is the partition coefficient of this compound? Assume a 10:1 volume ratio of water to hexane.

Solvent extraction is a simple strategy to separate one substance from the remainder of the sample, but is only effective if the compound of interest has a high K (allowing high extraction efficiency), while all other substance have small K's (allowing improved separation). Unfortunately, few systems satisfy both requirements.

Example 14.2: Purification efficiency
Consider the separation of analyte, A, from an interfering compound, B. Both substances begin in water at equal molar concentration. If K_A = 10.0, and K_B = 0.100, calculate the mole ratio of A to B in the hexane layer after extraction. Assume equal volumes of water and hexane.

From Example 14.1, we solved for the following expression:

$$\%\,\text{extracted} = \frac{K}{1+K} \times 100\%$$

For compound A:

$$\%\,\text{extracted} = 100\%\left(\frac{10.0}{1+10.0}\right) = 100\%\left(0.90\overline{9}1\right) = 90.9\%$$

For compound B:

$$\%\,\text{extracted} = 100\%\left(\frac{0.100}{1+0.100}\right) = 100\%\left(0.090\overline{9}1\right) = 9.09\%$$

Since we started with equal moles of A and B in the water layer, the relative extraction efficiency is equivalent to the mole ratio in the hexane layer:

$$\left(\frac{\text{mol } A_o}{\text{mol } B_o}\right) = \left(\frac{90.9}{9.09}\right) = \frac{10}{1}$$

The separation described in Example 14.2 increased the purity of A from 50% to over 90%. Such purification is far from spectacular, even though the partition coefficients differ by a factor of 100. Real world samples might contain hundreds, if not thousands of similar compounds, having similar partition coefficients. Therefore, to be useful, it will be necessary to find a way to improve this separation. The solution is to repeat this extraction process many times, as described in the section that follows.

14.4 Countercurrent Extraction

Hold on – how will multiple extractions improve the separation? One would assume multiple extractions would simply result in the complete extraction of compounds A and B (*i.e.* high yield, but low purity). This would be true, if one simply re-extracted the remaining water with more hexane, and combined the resulting hexane extracts. But the true answer to improve separation, without sacrificing yield, lies in the fashion in which the extractions are performed. The strategy begins with an arrangement of test tubes as shown in Figure 14.2.

Suppose the aqueous sample contains two similar components (A and B, with $K_A > K_B$). The mixture is placed in test tube 0, and an organic solvent (say hexane) is added. As seen in Figure 14.2, A and B partition between the solvents, and since A has the higher partition coefficient, it will have a greater concentration in the organic layer. Nonetheless, some of A and B remain in the water layer.

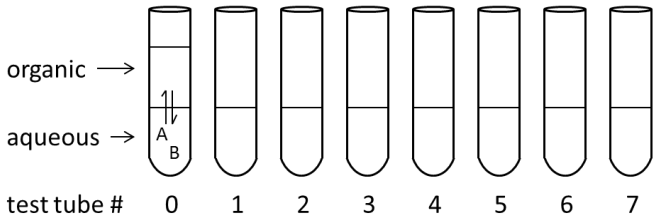


Figure 14.2: A series of test tubes is primed to perform a countercurrent extraction. Compounds A and B are initially in the water phase of test tube 0, and are extracted with an organic solvent such as hexane.

It is here that the experiment takes a twist. The organic layer from test tube 0 is transferred to test tube 1, which contains fresh aqueous solvent. Also, fresh organic solvent is added to test tube 0. In doing so, A and B will partition between the aqueous and organic layers within each test tube. Compound A remains highest in concentration in the organic layer of both test tubes.

In the next step, he organic layers from both test tubes are transferred one tube forward (*i.e.* 1 moves to 2; 0 moves to 1, and fresh solvent is added to 0). The extractions are repeated in all test tubes. This is seen in Figure 14.3. The process continues in this fashion, moving the organic layers one tube forward and continuing the extractions. In doing so, the organic layer behaves as a "moving" phase and, while traveling down the test tubes, carries with it a portion of sample A and B. The velocity at which A and B move down the line of test tubes is directly proportional to the fraction of the sample in the moving phase. In brief, the higher the partition coefficient, the greater the affinity towards the "moving" solvent phase, and the faster the compound travels down the line of test tubes. If the process is repeated enough times, compound A will move ahead of B (Figure 14.3). Despite having similar partition coefficients, the resulting purity of A can be extremely high, so long as there are enough extraction events. It is also seen in Figure 14.3 that the process will result in distributing the components among multiple test tubes. This *broadening* effect will be discussed later.

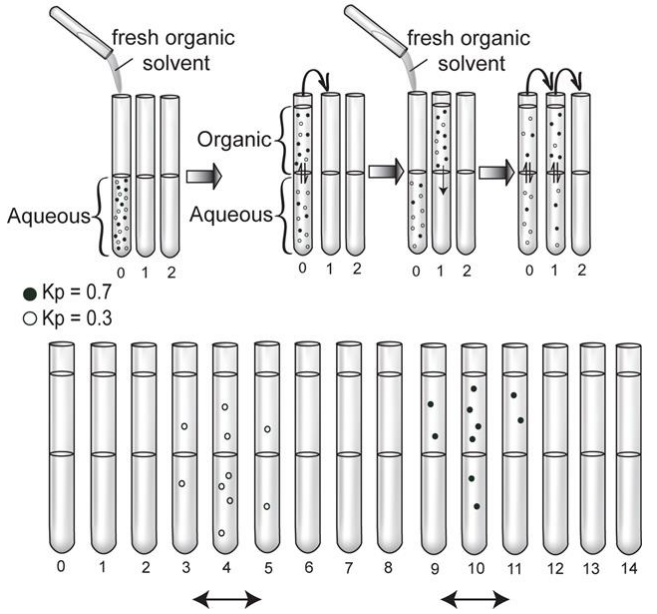


Figure 14.3: Countercurrent extraction. As the extraction even continue, compound A moves ahead of B. To finish this experiment, one would simply combined test tubes #9-11 to obtain A in high purity and with high yield.

14.5 Chromatography

The successive strategy for extraction described above is known as a countercurrent extraction. The benefits of performing multiple extractions in this way are clear in terms of providing high purity separations on similar compounds. Nonetheless, the experiment is cumbersome (think 100+ test tubes!). Fortunately, the strategy was replaced by a much simpler one - *chromatography*.

In chromatography, what was once a set of discrete extractions (*i.e.* test tubes) is replaced with the configuration shown in Figure 14.4. Here, a long tube carries a flow of liquid, while the inner surface of the tube is coated with an immiscible liquid. The tube, including the stationary contents, is called the *column*. Sample components are initially present in the moving phase, and enter the tube (from the left side in Figure 14.4). As the moving layer,

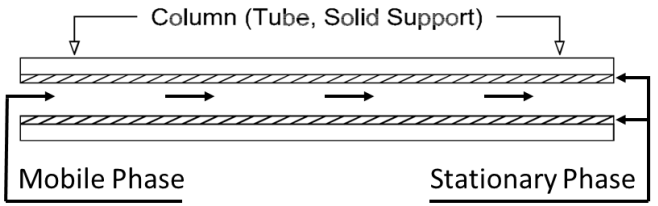


Figure 14.4: The column used in chromatography, containing stationary and mobile phase, which flows from left to right through the column.

referred more properly as the *mobile phase*, makes contact with the *stationary phase* of the column, sample components will partition according to their respective values of *K*. Mobile phase continues to bring fresh solvent to the stationary phase, and in much the same way as the countercurrent experiment, enables a continuous extraction of the sample components. The column can be thought of as an incremental series of test tubes, where each segment allow another extraction event. These extractions, together with the traveling mobile phase, force components A and B to be carried down the length of the tube at different rates, dependent on their affinity for the mobile and stationary phase (*i.e.* on *K*).

In the countercurrent extraction process, the organic phase could be considered to be the mobile phase, since it was moved continuously from one tube to the next while the water in each tube remained stationary. In column chromatography, when the stationary phase is more polar than the mobile phase, this is referred to as *normal phase chromatography*. However, the opposite situation can be employed as well, such that the mobile phase is more polar than the stationary phase, and this is referred to as *reversed phase chromatography*. Which approach is used depends on the situation and this topic will be revisited later.

As with countercurrent extraction, the movement of solutes down the column will result in a 'band' of sample, rather than an infinitely thin line. Sample concentration will be highest at the band's center, as seen in Figure 14.5. As mobile phase moves forward, a non-equilibrium situation arises in which the sample must re-partition between mobile and stationary phase. At the band's front, the higher concentration in the mobile phase causes solute to move into the stationary phase. At the trailing edge, sample in the stationary phase moves back into the mobile phase.

In general, solutes partition between the mobile (*m*) and stationary (*s*) phases according to:

$$S_m \rightleftharpoons S_s$$

Since sample is introduced to the column by way of the mobile phase, it is customary to write the equilibrium expression in this direction. Now the partition coefficient is defined as

$$K = \frac{[S]_s}{[S]_m} \tag{14.2}$$

Note that the stationary phase is in the numerator, according to the equilibrium above.

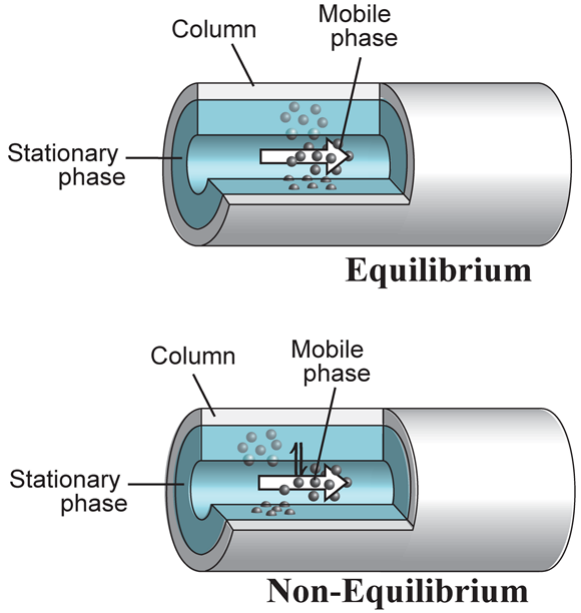


Figure 14.5: As mobile phase travels down the column, sample in the stationary phase lags behind the moving band front. This non-equilibrium causes the sample to re-partition in (or out) of the stationary phase.

The first chromatographic separations were done with coloured materials using packed, glass columns, allowing the separations to be observed visually. This gave rise to the name "chromatography", which comes from the Greek meaning to write with colour.

Exercise 14.3

In the column system described above, imagine there are two compounds, A and B, that are to be separated. Assuming $K_A > K_B$, which compound reaches the end of the column first? Explain.

Exercise 14.4

Suppose a compound has no affinity for the stationary phase. What will be its value for K? How fast will it travel through the column? What other parameters dictate how long it will take to make its way through the column

14.6 Classifying Various Modes of Chromatography

At this point a brief introduction to the most common forms of chromatography is warranted. There are many ways to classify different types of chromatography. One is according to the state of the stationary phase, being either solid or liquid. We've already seen an example of a liquid stationary phase, which coats the inner surface of the tube. Samples can partition into the bulk of this phase, and the term used to describe this type is *partition chromatography*. If the stationary phase is solid, however, analytes can no longer partition into this layer. Instead, its surface is active and material can be attracted to and adsorb on that surface. *Adsorption chromatography* is the term used to describe this form of chromatography.

The mobile phase can also vary, giving rise to another mode of classification. Thus, one makes reference to *liquid chromatography* (LC) or to *gas chromatography* (GC), depending on the composition of the mobile phase (it is understood in GC and LC that we are referring

to the state of the mobile phase). Considering the various combinations of state of mobile and stationary phase, there are actually four varieties of chromatography according to this classification: *gas-liquid chromatography* (GLC), *gas-solid chromatography* (GSC), *liquid-liquid chromatography* (LLC), and *liquid-solid chromatography* (LSC). The example shown in Figure 14.4 depicts LLC.

One can also classify chromatography according to the column format. Figure 14.4 describes an *open tubular column*. Open tubular columns must have very small internal diameters (<1000 μm), in order to keep the distance an analyte has to travel between the two phases to a minimum (more on this a bit later in this topic). A column with such a small inner diameter is normally referred to as a *capillary column*. The other type of column in common use is the *packed column*. Such a column still has an inert outer tube (*e.g.* glass or stainless steel), but the stationary phase is no longer coated on the tube. Instead it is coated on small, inert particles, being usually spherical and of approximately uniform size. These particles are packed into the tube and form a "bed", as pictured in Figure 14.6. If the stationary phase is a solid, the particles themselves act as the stationary phase. Mobile phase passes through the space between the particles as solutes partition between the mobile and stationary phases. The mechanism of separation is the same in both packed and open tubular columns. The great advantage of packed columns is that they can be made very large in diameter and thus can accommodate larger sample quantities (proportional to the column surface area). Capillary columns usually separate more efficiently, but can only accommodate very small samples. The amount of material that can be placed at the beginning of a column without degrading the separation quality is called the *loading capacity*. Columns that are designed to purify products from synthetic reactions are called *preparative columns* and need to have large loading capacities. On the other hand, *analytical columns* are designed to separate compounds for analysis and do not need such large capacities.

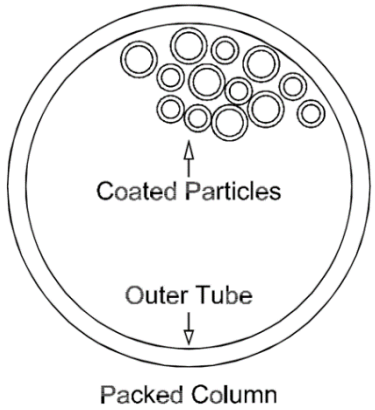


Figure 14.6: A packed column used in gas chromatography. The particles completely fill the inner tube of the column. The gas (mobile phase) flows through the space between the coated particles.

Example 14.3: Column capacity

A packed capillary column used in liquid chromatography has an inner diameter of 300 microns. The loading capacity for effective separation on such a column is only 5 μg. What would be the loading capacity on an 'analytical' column (inner diameter 2.1 mm), packed in an identical format with the same packing material?

The loading capacity of a column is proportional to the cross-sectional area of the column. Thus we must calculate the ratio of surface areas for each column:

$$\text{Area of circle} = \pi r^2 = \pi\left(d/2\right)^2$$

Taking the ratio of two circles, the constants cancel to give:

$$\text{Column Loading Ratio} = \text{Area Ratio} = \left(\frac{d_{2.1\,\text{mm}}}{d_{300\,\text{microns}}}\right)^2$$

$$\frac{x}{5\,\mu\text{g}} = \left(\frac{2.1\,\text{mm}}{0.300\,\text{mm}}\right)^2 = 49$$

$$x = 49 \times 5\,\mu\text{g} = \overline{2}45\,\mu\text{g}$$

In Example 14.3, the larger diameter column can accommodate almost 50 times more sample than the capillary column. Even larger columns exist, some up to a meter in diameter, and are used for the preparative purification of compounds on a commercial scale. Note that the column length does not factor into the column capacity.

14.7 The Chromatogram

In the countercurrent experiment, it was stated that the velocity at which samples move down the line of test tubes depends on the relative distribution of the components between mobile and stationary phases. The same relation holds true for column chromatography. More specifically, the speed at which a band of solute moves through the column depends on the proportion of time the solute spends in the mobile phase. If a compound partitions fully into the stationary phase, it will never arrive at the other end of the column. Likewise, compounds having no affinity for the stationary phase ($K = 0$) will spend all of their time in the mobile phase, and have a velocity equal to the velocity of the mobile phase. Thus, band velocity will depend on the value of K.

Consider a chromatographic experiment in which two components enter a column as a mixture. Compound A has no affinity for the stationary phase (K= 0), and thus exits the column first, while compound B partitions between mobile and stationary phase, exiting the column at some later point in time. A detector can be placed at the end of the column, to monitor the concentration of compounds as they exit the column. As discussed earlier, a spectrophotometer would make a good detector, particularly when a flow cell is used. Most chromatographic instruments (called *chromatographs*) include this or other types of detectors. Now if one were to plot the detector response as a function of time, the resulting trace, called a *chromatogram*, might look like the one shown in Figure 14.7.

The time at which the components are detected (*i.e.* the time they exit the column) is evident from the chromatogram. *Elution* is the term used to describe the emergence of components from a chromatographic column. The time when compounds elute is usually referred to as *retention time*, t_r. It is taken as the time of the maximum intensity of the detected peak, which for an ideal peak will correspond to the center of the band (more on peak shape later). Thus compound B has a retention time t_r = 7 min. In this particular example, the early eluting peak (t_r = 2 min) corresponds to a non-retained component. The characteristic elution time of a non-retained compound is given the symbol t_m (m = mobile phase)

Exercise 14.5

Compound A in Figure 14.7 is a non-retained component, and its retention time (2 min) is given the symbol t_m. Why do you suppose "m" an appropriate symbol? Must the first compound observed in a chromatogram have $t_r = t_m$? Why or why not?

It should not come as a surprise that $t_m \neq 0$, since this component must still make its way through the column. The magnitude of t_m is defined according to two parameters: (1) The mobile phase flow rate, F; and (2) the dimensions of the column, or more specifically, the volume of the column occupied by the mobile phase, or V_m. The volume of the mobile phase is sometimes referred to as the column's dead space volume, representing the space in between the stationary phase of the column.

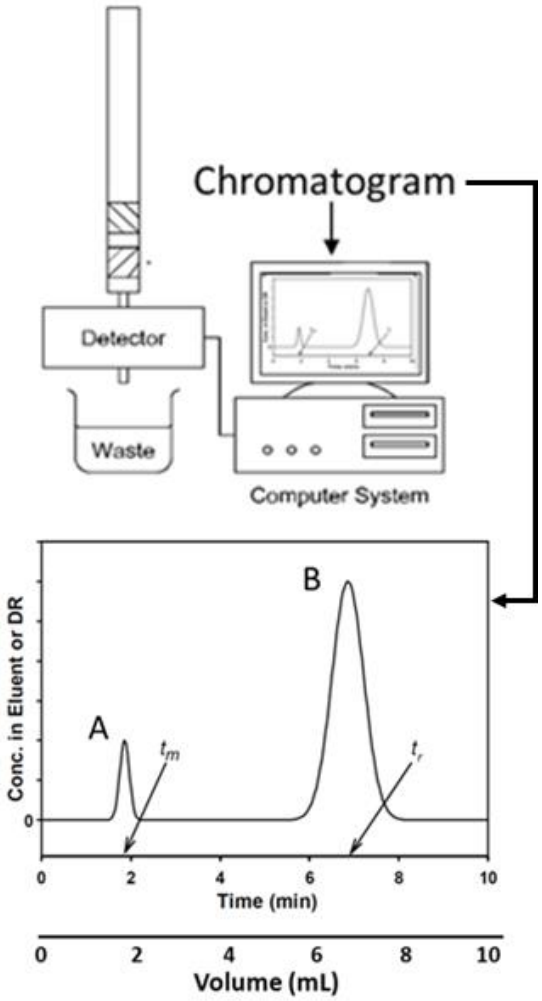


Figure 14.7: A chromatogram, generated by a chromatograph, by monitoring sample components as they exit the column. The x axis can be labeled in units of time, or volume.

Chromatographic experiments typically take place under constant mobile phase flow rate. For this reason, the characteristic point of elution of sample components can be expressed in units of volume, rather than time. In Figure 14.7, the *x* axis is also labeled in units of mL, thus referring to the volume of mobile phase which passes through the column before the components elute. The relation between retention time, t_r, and retention volume, V_r, is easily derived from dimensional analysis:

$$(\text{mL})_{volume} = (\text{min})_{time} \times \left(\frac{\text{mL}}{\text{min}} \right)_{flow\ rate}$$

$$V_r = t_r F \tag{14.3}$$

where F (flow rate) might be expressed in units of mL/min, and t_r in minutes. The volume of the mobile phase is often referred to as the *column volume*, and so one can express the retention of components in terms of the number of column volumes.

Exercise 14.6

From Figure 14.7, express the retention volume of compounds A & B as the number of 'column volumes' required to elute the components.

Exercise 14.7

From Figure 14.7, how much time does compound B spend in the mobile phase? How much time does B spend in the stationary phase? Can you generalize a relationship about all compounds eluting from a column?

14.8 Band Velocity

As described above, sample components travel through a chromatographic column and, depending on their affinity for the column's stationary phase, exit the column at different times (or volumes). A theory must now be developed to relate the characteristic retention

time (or volume), with the fundamental equilibrium processes which are responsible for the separation (*i.e.* the partition coefficient, *K*). It is noted here that differences exist between the mathematical expressions governing adsorption chromatography and partition chromatography. Only the expressions defining partition chromatography will be presented.

Sample molecules move down the column only when they are in the mobile phase. It can be stated that sample velocity, ν, will equal the mobile phase velocity, ν_m, multiplied by the fraction of time spent in the mobile phase. Furthermore, the fraction of time spent in the mobile phase is equal to the fraction of molecules (or mols), f_m, of substance in the mobile phase. Thus

$$\nu = \nu_m f_m \tag{14.4}$$

The fraction of solute in the mobile phase is determined as follows:

$$f_m = \frac{\text{mol}_m}{\text{mol}_{total}} = \frac{V_m[S]_m}{V_m[S]_m + V_s[S]_s} \tag{14.5}$$

where *V* represents the volume of a particular phase. Dividing numerator and denominator by $[S]_m$ and making use of Eqn. (14.2) leads to:

$$f_m = \frac{V_m}{V_m + KV_s} \tag{14.6}$$

Thus by substituting Eqn. (14.6) into (14.4) the velocity of the sample band is given by

$$\nu = \frac{\nu_m V_m}{V_m + KV_s} \tag{14.7}$$

Sample velocity describes the motion of sample components in units of distance over time (*e.g.* $\text{cm}\cdot\text{sec}^{-1}$). This is not the most practical way of defining a chromatographic separation. An expression relating retention time to sample velocity is easily described:

$$t_r = \frac{L}{\nu} \tag{14.8}$$

where L is the column length (in cm). Thus substituting (14.7) into (14.8)

$$t_r = \frac{L(V_m + KV_s)}{\nu_m V_m} \tag{14.9}$$

The eluent velocity, ν_m, is not easily measured, but is related to the mobile phase area, A_m, (in cm^2) and the flow rate by

$$\nu_m = \frac{F}{A_m} \tag{14.10}$$

The mobile phase area, A_m, can be obtained from the volume of the mobile phase and column length:

$$A_m = V_m / L \tag{14.11}$$

Substituting (14.13) and (14.14) into (14.12) leads to

$$t_r = \frac{A_m L(V_m + KV_s)}{FV_m} = \frac{V_m + KV_s}{F} \tag{14.12}$$

The retention volume, V_r, is also easily obtained, combining (14.3) with (14.12).

$$V_r = t_r F = (V_m + KV_s) \tag{14.13}$$

The flow rate, F, is easily measured experimentally, as is V_m (V_r for a non-retained material). The stationary phase volume, V_s, may or may not be known to the chemist but is usually known if the column is self-packed, or alternatively is provided by the manufacturer of the column.

Example 14.4: Retention time and Volume

Calculate t_r and V_r for a compound with a K of 10.0 when it passes through a chromatography column 30.0 cm in length with a mobile phase flow rate of 0.100 mL/min. A non-retained compound elutes from the column after 1.86 min. A stationary phase volume of 0.0500 mL was used to prepare the column.

We have V_s = 0.0500 cm^3 and F = 0.100 cm^3/min, and t_m is the retention time (t_r) for the unretained compound, so this gives:

$$V_m = Ft_m = (0.100\ \text{cm}^3\ \text{min}^{-1})(1.86\,\text{min}) = 0.186\ \text{cm}^3$$

$$V_r = V_m + KV_s = (0.186\ \text{cm}^3) + (10.0)(0.0500\ \text{cm}^3) = 0.686\ \text{cm}^3 \text{ or } 0.686\ \text{mL}$$

$$t_r = \frac{V_r}{F} = \frac{0.686\ \text{cm}^3}{0.100\ \text{cm}^3\ \text{min}^{-1}} = 6.86\,\text{min}$$

A second, slightly different treatment for band velocity is often employed. The *capacity factor*, *k′*, is defined as the ratio of time spent in the stationary phase to that spent in the mobile phase:

$$k' = \frac{\text{time}_s}{\text{time}_m} = \frac{\text{mol}_s}{\text{mol}_m} \tag{14.14}$$

The ratio of time in the stationary phase to that in the mobile phase is equal to the ratio of moles in the stationary phase to moles in the mobile phase at any point in time. Thus as *k′* increases, analytes spend more time in the stationary phase, and band velocity decreases. Retention time and retention volume consequently increase. The relation between *k′* and *K* is easily solved:

$$k' = \frac{\text{mol}_s}{\text{mol}_m} = \frac{C_s V_s}{C_m V_m} = \frac{KV_s}{V_m}$$

or

$$K = \frac{k' V_m}{V_s} \tag{14.15}$$

When this expression is substituted into Eqn. (14.15), we arrive at a relation between retention time and k':

$$t_r = \frac{V_m + KV_s}{F} = \frac{V_m + V_s k' V_m / V_s}{F} = \frac{V_m(1+k')}{F} \tag{14.16}$$

We see that the time at which compounds elute depends on the flow rate, the column dimension, and of course, the partitioning of sample between mobile and stationary phase (expressed through *k′*). To obtain the equivalent relationship involving retention volume, note

that V_m/F equals the time for eluent (or a non-retained material) to travel through the column. If this is represented by t_m, then

$$t_r = t_m(1+k') \tag{14.17}$$

and $$V_r = F \cdot t_r = F \cdot t_m(1+k') = V_m(1+k') \tag{14.18}$$

Example 14.5: Capacity factor

Calculate the capacity factor for a material that elutes from a column in 6.85 min. A non-retained substance elutes in 45 s.

Substituting the quantities into Eqn. 14.18 and converting the units accordingly,

$$6.85\ \text{min} = \left(\frac{45\ \text{s}}{60\,\text{s}\cdot\text{min}^{-1}}\right)(1+k') = (0.75\ \text{min})(1+k')$$

$$k' = \frac{6.85\ \text{min}}{0.75\ \text{min}} - 1 = 8.1$$

Exercise 14.8

Rearrange Equation 14.17 to obtain the expression for *k′* as a function of retention time. What is *k′* for compounds A and B in Figure 14.7?

In comparing the two approaches, note that both *K* and *k′* are dimensionless constants, but *k′ is not an equilibrium constant*. *K* depends only on the materials involved, that is the solute and the mobile and stationary phases, and is independent of how the column is constructed (which would change the volumes of stationary and mobile phase). Thus *K* will be the same from column to column as long as the same materials are used in each column. *k′* depends not only on the substances used, but also on the column dimensions, and thus will vary with each new column. On the other hand *k′* has the clear advantage of being easily determined experimentally without exact knowledge of the method of column preparation.

14.9 Resolution

To this point, it was simply accepted as fact that components will elute from a chromatographic column as a band, producing the detected peak shapes shown in Figure 14.7. The actual shape of a band of solute must now be considered. Peak shape has obvious implications in the ability to separate components. Consider the example below

Example 14.6: Retention time and capacity factors

A sample contains two compounds (K_1 = 10.0 and K_2 = 12.0). If this sample is passed through a column with V_s = 0.0500 cm^3, V_m = 0.186 cm^3, and F = 0.100 mL/min, what will be the retention time for each compound? Will they separate?

Conveniently, the retention time for compound 1 was already calculated, as these parameters are identical to those in Example 14.4. This gave t_{r1} = 6.86 min.

For compound 2:

$$t_{r2} = \frac{(0.186\ \text{cm}^3) + (12.0)(0.0500\ \text{cm}^3)}{0.100\ \text{cm}^3\ \text{min}^{-1}} = 7.86\ \text{min}$$

The difference in retention time is therefore exactly 1.00 min.

Will they separate? Strangely, the correct answer is "we don't know"!

The reason why the question in Example 14.6 cannot be answered, wherein two compounds of differing retention times may or may not separate, is related to the bandwidth; to this point peak width is not yet known. Figure 14.8 illustrates the dilemma. For both the upper and lower chromatogram if Figure 14.8, the retention times of the two peaks are identical, and correspond to those times described in Example 14.8 (*i.e.* 6.86 and 7.86 min). The only difference is the peak width, being three times larger in the upper chromatogram than the lower one. Each peak contains the same area, and so the peak height in the lower chromatogram is also a factor of three greater than the signals above.

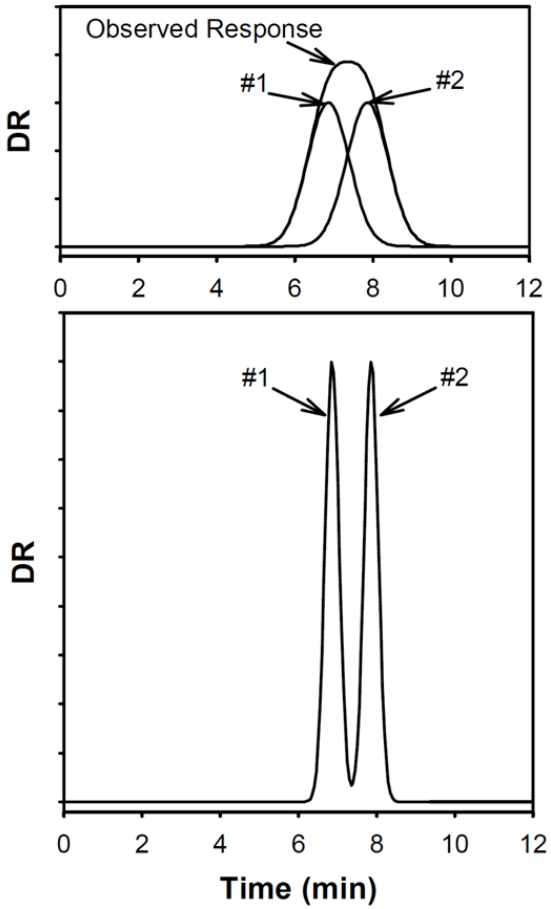


Figure 14.8: The influence of peak width on the quality of separation. Peaks #1 and #2 are always separated by 1 min, but the peaks in the upper chromatogram are three times wider than in the lower chromatogram.

In the upper chromatogram, the peak widths cause the two bands to overlap considerably. If the detector is unable to distinguish compound 1 from compound 2, then the observed response will be displayed as the sum of both of peaks (Figure 14.8). This response looks like a single peak and might be mistaken for just the one. In the bottom chromatogram of Figure 14.8, the summed detector response displays two clear peaks with very little overlap. It is obvious that if peak width can be kept narrow, very similar compounds can be separated, despite minimal time between them. Thus, good peak shape (*i.e.* narrow peak width) is as important to good separations as is difference in retention time.

As you may have noticed, the ideal peak shape is symmetrical and bell shaped. It can most accurately be described mathematically as a Gaussian distribution:

$$\text{Detector Response} = \text{DR} = h \cdot \exp\left(\frac{-(t - t_r)^2}{2s^2}\right) \qquad (14.19)$$

where h is the peak height, t is time, t_r is the retention time, and s is the standard deviation of the peak width, in time units. Note that Detector Response = h when $t = t_r$, and that response decreases both before and after t_r. The Gaussian peak shape observed by a detector is related to the distribution of substances as they travel through the column. Molecules of each substance have an associated average velocity, v. More molecules travel at this velocity than any other. However, some molecules travel faster (or slower) than average and exit the column before (or after) the band maximum. This is one factor that gives rise to the bell-shape of the peaks.

From the discussions above it is obvious that the ability to separate two compounds will depend on both the difference in retention times (or volumes) and the bandwidths of the two compounds. The question "Do compounds separate" is rather arbitrary, since it is realized that two compounds can never be separated with "absolute" purity (though we can get pretty close!). To quantify the degree of separation, a method often used is to determine the *resolution*. Referring to Figure 14.9, the resolution, R, between compounds A and B is defined as:

$$R = \frac{\text{peak separation}}{\text{peak width}}$$

or $$R = \frac{(t_r)_B - (t_r)_A}{0.5\left[(t_w)_A + (t_w)_B\right]} \quad (14.20)$$

where *A* and *B* represent the two materials being separated and t_w is the peak width in time. t_w is the width of the peak at the baseline, as shown in Figure 14.9.

What is the width of the peak at its base? Recall from the discussion of statistics that, for a Gaussian curve, 68.3% of the area of the peak lies between $\pm 1s$, 95.5% lies between $\pm 2s$, and 99.7% lies between $\pm 3s$. In Eqn. 14.20, peak width is taken as $4s$. Visually, this width can be seen in Figure 14.9 (labelled *w*), and can be found approximately by drawing tangent lines to the peak.

The peak width at base is sometimes difficult to discern. A preferred way to determine resolution is to measure the peak width at a constant point along the peak. This point is most often taken as the half width, being the points in time which intersect the peak at half of its maximum height (Figure 14.9). We can show this mathematically as

$$\frac{\mathrm{DR}}{h} = 0.500 = \exp\left[\frac{-(t - t_r)^2}{2s^2}\right] \quad (14.21)$$

Taking the logarithm of both sides provides

$$0.639 = \frac{(t - t_r)^2}{2s^2} \quad (14.22)$$

or $$\frac{(t - t_r)}{2s} = \sqrt{1.386} = \pm 1.177 \quad (14.23)$$

Thus the width of an ideal peak, $w_{1/2}$, at half of its height, $h_{1/2}$, is $2(1.177s)$.

$$w_{1/2} = 2(1.77s) = 2.35s \quad (14.24)$$

The peak width at half height is also referred to as the Full Width at Half Maximum, or *FWHM*. When $w_{1/2}$ (*aka FWHM*) is used for peak width, the equation to be used for calculating resolution is as follows:

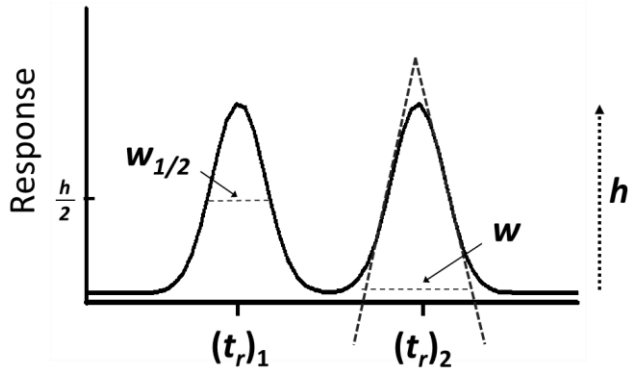


Figure 14.9: Illustation of the measurement of the resolution between two peaks. The half width ($w_{1/2}$) is also known as the *Full Width at Half Maximum* (FWHM), and is a more reliable point to use than the base peak width (w).

$$R = \frac{0.589\Delta t_r}{\left(w_{1/2}\right)_{avg}} \qquad (14.25)$$

The constant, 0.589, indicates that the peak width at half height is not quite half that of the peak at base (determined by drawing tangent lines).

So how large does R have to be to conclude that two peaks are indeed separated? This definition is again arbitrary, as one must define the degree of purity to say that two compounds are separated. Technically speaking, there will always be some degree of impurity resulting from a chromatographic separation (though it might be too small to observe). If two peaks contain equal amounts of material (peak areas are equal, assuming equal detector response), and if two fractions can be collected which divide the two peaks exactly half way between the peak maxima, then one could calculate the relative abundance of each sample component in each fraction.

Looking into the numbers, at a resolution R = 0.5, each fraction will contain 84.1% of the major component and 15.9% of the minor component. At a higher value of R, the composition of the major constituent will increase, while that of the minor component will decrease. Table 14.1 lists these split values for several values of resolution. From Table 14.1, it is seen that any separation in which R is > 1.0 is good and that any separation in which R is > 1.5 can be taken as a quantitative separation.

Figure 14.10 shows graphically how changes in resolution affect the shape of the chromatogram for the conditions described above. At R = 1.5, the separation is almost "baseline". If R = 1.0, the separation is not complete, but it is obvious that two compounds are present. At R = 0.5, only one peak is actually observed, albeit a distorted one, indicating that the peak is made up of more than one component.

Example 14.7: Resolution

Determine the resolution and associated uncertainty for compounds A and B in the chromatogram below.

Table 14.1. The peak overlap, as indicated by split ratio (%), at various levels of resolution.

Resolution	$\Delta t_r(s_t)$	Split(%)
0.50	2.0	84.1 to 15.9
0.75	3.0	93.3 to 6.7
1.00	4.0	97.7 to 2.3
1.50	6.0	99.9 to 0.1
2.00	8.0	99.99 to 0.01

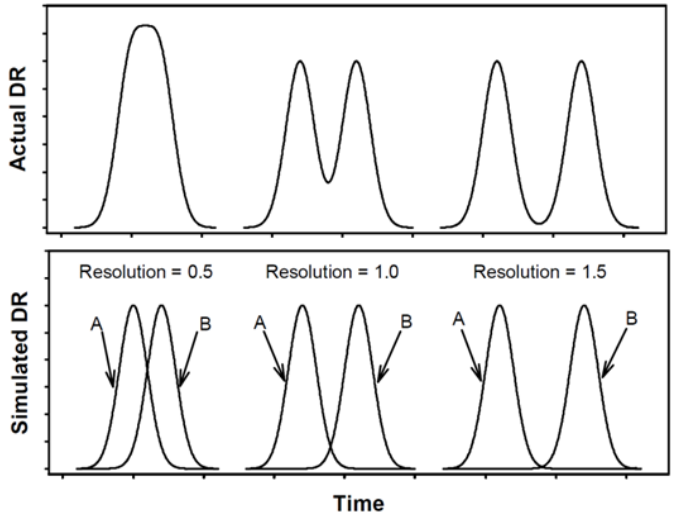
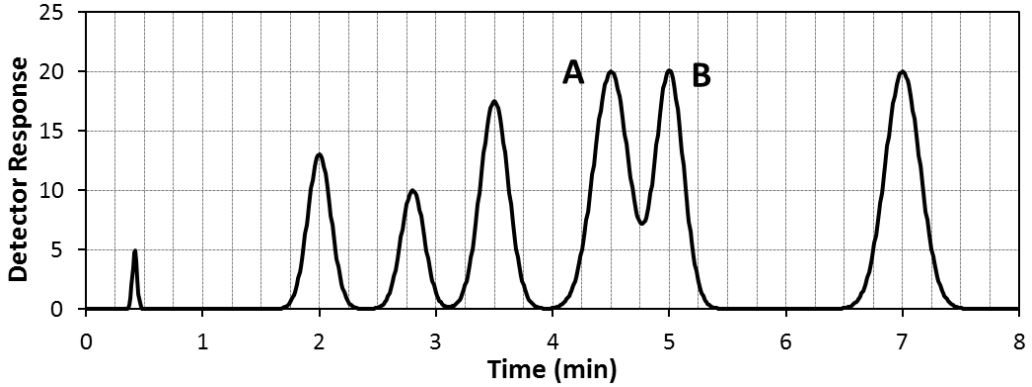


Figure 14.10: Peak separation at varying values of R. The actual detector response (upper traces) represents the sum of the two peaks in the lower traces.



There are two equations for resolution, though it is advised to use Eqn. 14.25, which employs half-widths. To determine half-width, one reads where the peak intersects a response of 10, using the gridlines to assist in reading. Note that there are 4 divisions per minute, so each gridline = 0.25 min.

Peak A appears to intersect at about 1.3 ($\pm$0.1) gridlines beyond the 4 min mark, and again at 2.8 ($\pm$0.1) gridlines, thus the half width is:

$$(w_{1/2})_{\text{gridlines}} = (2.8 \pm 0.1) - (1.3 \pm 0.1) = 1.5 \pm \sqrt{2 \times (0.1)^2}$$

or $$(w_{1/2})_{\text{time}} = (0.25 \text{ min/gridline}) \times (1.5 \pm 0.14 \text{ gridlines})$$

$$w_{1/2} = 0.375 \pm 0.035 \text{ min}$$

Similarly for peak B:

$$w_{1/2} = (0.25 \text{ min/grideline})(1.2 \pm 0.14 \text{ gridlines})$$

$$w_{1/2} = 0.30 \pm 0.035 \text{ min}$$

Retention times for peaks A and B are easily read, as 4.50 min and 5.00 min, respectively, and Δt_r = 0.50 min, again with an uncertainty of 0.035 min. Plugging into Eqn. 14.25

$$R = \frac{0.589\left(0.50 \pm 0.035 \text{ min}\right)}{0.5 \times \left[\left(0.375 \pm 0.035 \text{ min}\right) + \left(0.3 \pm 0.035 \text{ min}\right)\right]}$$

Based on the rules of error propagation discussed earlier, we have,

$$R = 0.9 \pm 0.1$$

The error propagation illustrates that the uncertainty in reading the graph translates into an uncertainty in the final result. Reporting the resolution as 0.8, or 1.0 would therefore be perfectly acceptable.

Exercise 14.9

What is the half width for the peak with t_r = 7 min, in the chromatogram shown in Example 14.7? What is *your* uncertainty in this reading?

Resolution is a fundamental concern in chromatography, with the rule of thumb being *the higher the better*! Considerable effort (and money) can go into improving the resolution between compounds. Strategies to improve resolution include finding the right combination of mobile and stationary phase to maximize differences in retention between compounds. But, as you have surely realized by now, good chromatography is about more than large differences in retention, it's also about peak shape (narrow peak width = better chromatography). The theory of separation presented thus far does not address peak width. Thus a different theory must be developed. In other words, the reasons as to why bands broaden as they move through a column will have to be investigated.

14.10 Plate Theory

Plate theory was the first theory developed to explain the shape of chromatographic peaks and was modelled on the theory of distillation columns. Distillation columns were divided into regions called plates in which an equilibrium was considered to exist (analogous to our earlier extraction system involving test tubes). In chromatographic plate theory the column is

considered to be "divided" into small regions, again called *plates*, in which equilibrium was considered to exist (sound familiar?). As we have already seen, the column is not truly divided, but can think of it as a series of very small extraction tubes linked together, as shown in Figure 14.11, where one tube = one plate. More plates would therefore give rise to a better separation. While this is not a particularly accurate description of a chromatographic column, the theory has survived the test of time.

None of the derivations involved in plate theory will be presented, just the important results. As one might guess, more plates results in narrower bands, giving rise to improved separation. For a fixed column length, more plates translate into a smaller length of the column per plate. One very important parameter that came from plate theory is the concept of the length of a plate, or the *height equivalent to a theoretical plate*, HETP. This is very often used in chromatography to describe the quality of a column. If N is the number of plates in the column, then

$$\text{HETP} = L/N \tag{14.26}$$

where L is the column length. Note that HETP has units of length, while N has no units. Plate theory also provided an expression for the shape of a chromatographic band or peak. Recall Eqn. 14.19:

$$\text{Detector Response} = \text{DR} = h \cdot \exp\left(\frac{-(t-t_r)^2}{2s^2}\right)$$

Plate theory not only predicts that bandwidths go down as N increases, but more specifically that

$$\sigma = \sqrt{N} \tag{14.27}$$

where σ is the bandwidth or standard deviation in terms of *the number of plates*. In this text the symbol, σ, will be used for this particular bandwidth or standard deviation, which has no units.

Exactly what is a bandwidth in terms of the number of plates? We have already seen the standard deviation of a peak, as measured in units of time. The difference here is that we are talking about bandwidth inside the column. Assume that a column has 100 plates (shown in Figure 14.12). Plate theory states that $\sigma = 100^{1/2} = 10$. Remembering a Gaussian distribution,

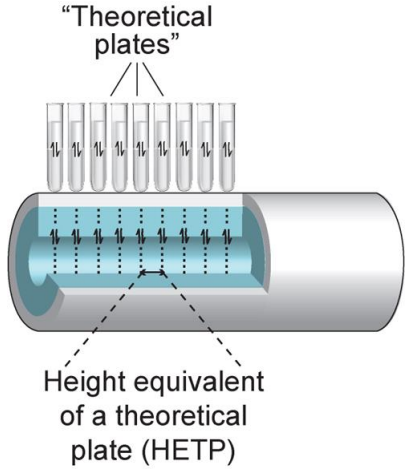


Figure 14.11: Conceptual illustration of a theoretical plate.

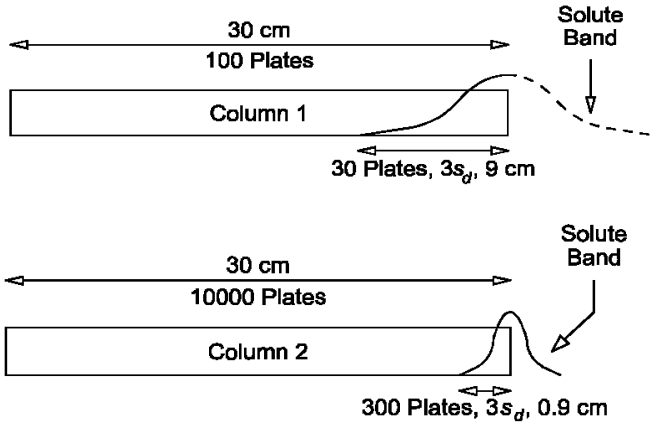


Figure 14.12: Comparison of columns of equal length. The column with more plates will result in narrower bands.

this means that for a chromatographic band centered at the end of the column (*i.e.* half of the band has already left the column), 49.8% will occupy the last 30 plates. The number of plates in a column thus predicts the bandwidth of the peak, both in terms of plates and in terms of width or distance in the column.

It may seem strange that plate theory predicts that σ increases as N increases, yet at the same time predicts that as N increases, bandwidth decreases. What is decreasing is not bandwidth in terms of plates, it is bandwidth, s_d, in terms of the width or length of a band in the column. Confused? Consider the example below.

Example 14.8: Plate numbers and HETP

Assume that two columns are to be compared, both 30 cm in length. Column #1 has 100 plates, column #2 has 10000. What is the HETP for each column?

For column #1: HETP = L/N = 30cm/100 = 0.30 cm

For column #2: HETP = 30cm/10000 = 0.0030 cm

For columns of equal length, a higher number of plates means that the plates effectively get smaller (HETP decreases). Thus, from Figure 14.12, while the band in column 2 occupies more plates than the band in column 1 (300 *vs* 30 plates), the reduced size per plate more than makes up for the increase in σ. When the band maximum reaches the end of column #1, $3s_d$ = 9.0 cm (30 plates × 0.30 cm/plate). When a band maximum reaches the end of column #2, $3s_d$ = 0.90 cm (300 plates × 0.003 cm/plate). In summary, as N increases (or HETP decreases), the physical bandwidths (inside the column) decrease and separations get better. Bandwidth is a function of the square root of either N or HETP.

Since N (or HETP) is such an important parameter, a method must be devised to determine its value. This could hypothetically be done if one could look into a column and measure the actual width of a band. The relationship between σ and s_d is as follows:

$$s_d = \sigma(\text{HETP}) = \sqrt{N}\,(\text{HETP}) \qquad (14.28)$$

Also, from Eqn. 14.24, s_d is related to the peak width:

$$\frac{(w_{1/2})_d}{2.35} = \sqrt{N}(\text{HETP}) \tag{14.29}$$

Rearranging and substituting (14.26) into (14.29) gives

$$N = \left(\frac{(w_{1/2})_d}{2.35(\text{HETP})} \right)^2 = \frac{(w_{1/2})_d^2 N^2}{5.55L^2} \tag{14.30}$$

Solving for N provides the result

$$N = \frac{5.55L^2}{(w_{1/2})_d^2} \tag{14.31}$$

Here, $(w_{1/2})_d$ refers to the distance a band occupies inside the column (not the half-width observed in time units in a chromatogram). This value is not typically known. Fortunately, the relationship also holds true in a chromatogram. Here, retention time is directly proportional to the column length and peak width (in time) is directly proportional to the band width (in distance). The proportionality constant is simply the band velocity, v.

$$L = vt_r \tag{14.32}$$

and $$(w_{1/2})_d = v(w_{1/2})_t \tag{14.33}$$

Substituting (14.32) and (14.33) into (14.31) gives

$$N = \frac{5.55(vt_r)^2}{[v(w_{1/2})_t]^2} = \frac{5.55t_r^{\,2}}{(w_{1/2})_t^{\,2}} \tag{14.34}$$

providing a simple relationship between N, t_r, and $w_{1/2}$. There are other, similar methods for measuring N.

Example 14.9: Plate numbers, HETP and retention time

A hydrocarbon elutes from a 2.00 m packed CG column with t_r = 9.65 min. The times when the detector response is ½ the peak height are 9.40 and 9.89 min. What are the values of N and HETP for this column?

The data provided can be used to calculate $(w_{1/2})_t$, which can then be used to calculate the other parameters.

$$(w_{1/2})_t = (9.89\ \text{min}) - (9.40\ \text{min}) = 0.49\ \text{min}$$

$$N = \frac{5.55(9.65\ \text{min})^2}{(0.49\,\text{min})^2} = 2.15\times10^3$$

$$\text{HETP} = \frac{2.00\ \text{m}}{2.15\times10^3} = 9.3\times10^{-4}\ \text{m} = 0.93\ \text{mm}$$

The parameter, *N*, provides a method of comparing columns in terms of their efficiency of separation. Unfortunately plate theory does not provide a model that explains the factors that influence HETP. Thus, it gives no clue as to how to design a column to provide better separations. A better theory is still needed.

14.11 Rate Theory

One way to study the causes of band broadening is to vary different parameters and to observe the effect on HETP or *N*. The parameter that is most often varied is the velocity of the mobile phase, v_m (measure in distance per unit time), or the flow rate, *F* (measured as volume per unit time). The behaviour shown in Figure 14.13 is observed if HETP is measured and plotted as a function of v_m. It was pointed out by van Deemter that this behaviour could be fit by a function of the following form:

$$\text{HETP} = A + \frac{B}{v_m} + Cv_m \qquad (14.35)$$

where *A*, *B*, and *C* are constants. This equation is often referred to as the van Deemter equation. It is strictly an empirical equation - in other words it seems to fit the data well, but it does not come *directly* from theory. At low v_m the Cv_m term goes to zero and the B/v_m term controls HETP. Likewise at high v_m, the B/v_m term goes to zero and HETP is controlled by

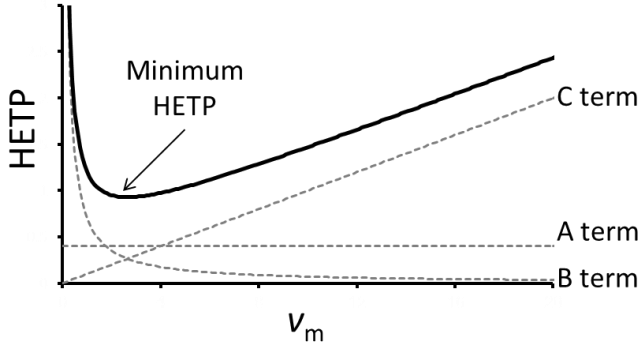


Figure 14.13: HETP as a function of mobile phase velocity. The curve represents a contribution of three terms. The ideal flow rate to operate the column is the one producing the minimum HETP.

the Cv_m term. Often the *A* term is quite small and may not be particularly important in influencing the overall behaviour.

An attempt must now be made to explain how this type of behaviour could arise. Keep in mind that an increase in HETP means a decrease in *N*, the number of plates, and an increase in bandwidth. As HETP increases, separation efficiency decreases. Thus there is an optimum flow rate for the best separations, as shown in Figure 14.13. Considering the van Deemter equation, there are three parameters that contribute to the magnitude of HETP, two of which are dependent on the mobile phase velocity (*B* & *C* terms), and one of which is not (the *A* term). A discussion is provided for each of these three terms below.

The *A* term: Column Packing

What effects could give rise to a contribution to bandwidth which is independent of flow rate? First of all, bands must start with a finite size - you cannot make the initial bandwidth infinitely narrow. This will contribute to the *A* term. There is a finite spread in molecular velocity (as explained above some molecules will move faster than the average, some slower) which will cause the band to broaden a fixed amount, independent of flow rate. Finally for packed columns, if the column is not well packed, channels may develop in the bed (obviously not a problem with open tubular capillary columns), causing the molecules to travel vastly different path lengths. Anytime path lengths of differing sizes are available to the sample, molecules will traverse the column in different times (some molecules will travel longer distances and as a result take more time than others) and the bands will broaden. If the column is well packed and if the initial sample size is small (the initial bandwidth is small), the *A* term is usually also very small and is sometimes neglected in discussing band broadening.

The *B* term: Longitudinal Diffusion

For the B/v_m term, we see that HETP increases as v_m decreases, or in other words, bands broaden as the mobile phase velocity becomes low. *Why?* The answer is related to diffusion, wherein there is a "natural desire" of the molecules in the high concentration band centre to diffuse toward lower concentrations. This type of diffusion is referred to as *longitudinal diffusion*, or diffusion along the length of the column, and is depicted in Figure 14.14. This is "bad" diffusion, as it causes the band to broaden out over time. At very low flow rates (low

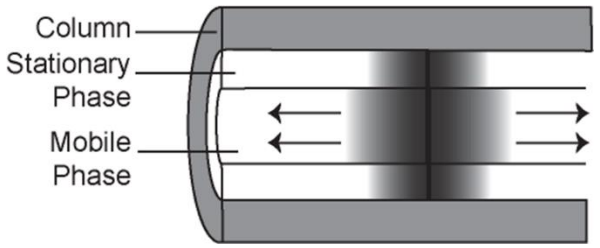


Figure 14.14: Longitudinal diffusion contributes to band broadening.

v_m) all bands move through the column more slowly and have more time to broaden under the influence of this type of diffusion. As v_m increases, all bands move through the column more rapidly and have less time to broaden due to longitudinal diffusion. Thus, if this were the only term to consider, then fast flow rates would improve separation. Unfortunately, there is another competing term which forces a limit on how fast the separation can be carried out..

The *C* term: Transverse Diffusion

The final term, Cv_m, is again related to diffusion. Recall the *B* term where the goal was to minimize diffusion by increasing flow rate. Here, diffusion becomes a desirable property, and is needed to improve separation. How can this be? The type of diffusion that we are referring to is *transverse diffusion*. This is diffusion perpendicular to the direction of flow of the mobile phase, and is needed to achieve equilibrium between mobile and stationary phase.

As was shown before, bands will partition between mobile and stationary phase. The moving mobile phase forces a non-equilibrium condition which causes bands to broaden. Any delay in re-establishing the equilibrium will further contribute to band broadening. At a low flow rate, the slow kinetics involved in the equilibrium do not factor in significantly, as the sample has sufficient time to equilibrate between mobile and stationary phase. When the mobile phase velocity increases, the solute does not have sufficient time to allow for equilibration and the band in the mobile phase tends to get ahead of that in the stationary phase. This is illustrated in Figure 14.15.

So how does diffusion play into this equilibrium? First, in order for any partitioning to take place, the solute must physically move to the phase boundary between mobile and stationary phase. While in the mobile phase, solutes are moving down the column, away from the band in the stationary phase. Diffusion must bring the solute from the bulk of the mobile phase to the phase boundary. Thus, a slower mobile phase velocity would permit more time for such diffusion to occur. Another solution to this problem is to make the distances travelled in the mobile phase as short as possible. In a packed column this requires the use of very small particles, in a capillary column, the use of a very small diameter tube.

One also considers transverse diffusion in the *stationary phase* (this does not apply when the stationary phase is a solid surface). This is the same effect as above, except the phase is different. During the time it takes sample molecules to diffuse up to the phase boundary to

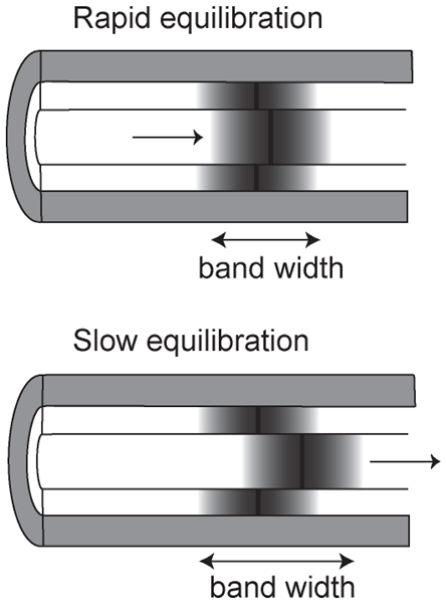


Figure 14.15: Slow equilibration between the mobile and stationary phase leads to greater peak broadening.

re-enter the mobile phase the band in the mobile phase is moving down the column, as illustrated in Figure 14.16. The solution in this case is to use a "light liquid loading", in other words keep the layer of stationary phase thin so that molecules do not have to travel very far to get to the mobile phase. This means that sample size must be kept small in order not to overload the stationary phase. When overloading occurs, band shape degrades markedly.

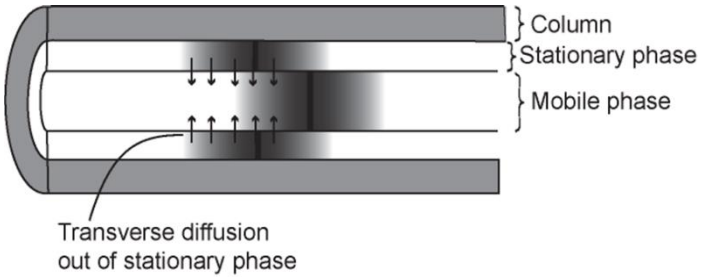


Figure 14.16: Slow diffusion out of the stationary phase will result in band broadening.

One can summarize the above to obtain a set of guidelines for obtaining the best separations:

1) Operate at minimum HETP (optimum v_m).
2) Use a small sample size (small initial bandwidth).
3) Load sample on the column evenly (again small initial bandwidth).
4) Pack the column evenly - avoid channels (for packed columns).
5) Use a small diameter solid support (for better packing).
6) Use a solid support of uniform diameter (keeps path lengths even for packed columns).
7) For liquid stationary phases, use a small amount of liquid..
8) For solid stationary phases, use a solid with a uniform surface.

14.12 Gas Chromatography

In gas chromatography the mobile phase is always a gas, usually H_2, He, or N_2. The stationary phase can be either a liquid or a solid. However, solids are seldom used in practice (although there are certain applications where a solid must be used, *e.g.* analysis of gas mixtures) and the term "gas chromatography" is invariably taken to mean "gas-liquid chromatography". Only GLC will be discussed in this text. In this type of chromatography the stationary phase is a liquid, usually very high boiling, which is either coated on the solid support or chemically bonded to it. The best way to proceed may be to describe the instrument, called a *gas chromatograph*. A block diagram of a gas chromatograph is shown in Figure 14.17. The mobile phase, called the *carrier gas*, is usually stored in a large metal cylinder under high pressure. The carrier gas should be light and inert. Thus He, H_2, and N_2 are usually used in this regard. Helium is the most inert and probably the best all-around choice, but also the most expensive. Hydrogen is the lightest, which has certain advantages, but is the least inert.

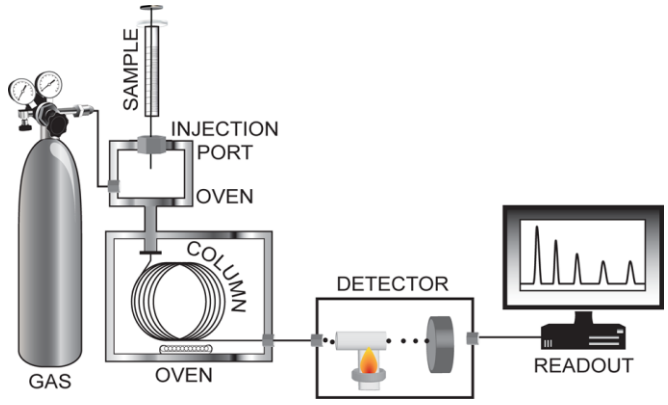


Figure 14.17: A block diagram of a gas chromatograph.

A regulating valve is used to reduce the tank pressure to about 1-2 atm above ambient for use in the column.

In GC, the sample is usually measured in a glass syringe of about 1 to 10 μL capacity. Thus samples are not large and some sampling error results when trying to accurately deliver such small sample sizes. To place a sample on the column, the syringe needle pierces a rubber membrane called a septum and the sample is rapidly injected into a small, hot chamber called an injection port. The sample then volatilizes rapidly and is carried onto the column in the mobile phase. The injection port oven is usually maintained at a higher temperature than the column. The injection port must not be so hot as to pyrolyze the sample and must not react with the sample. Sample injection is somewhat of an art in gas chromatography.

The column has its own oven, the temperature of which can be changed quite rapidly. During an experiment the temperatures of the injection port and detector ovens are held constant, but the column oven, and thus the column, often change temperature. The need for this will be explained later. As mentioned previously, two types of columns are used, packed and capillary. Packed columns are typically 1 to 3 m in length and 3 to 6 mm in internal diameter with 1000 to 10000 plates. The inert support upon which the stationary phase is coated is usually the skeletons of one-celled plants called diatoms. This material is made of silica (SiO_2), is hollow, and has a diameter of about 0.15 mm. Capillary columns are small silica tubes, 0.1 to 0.5 mm in internal diameter and 10 to 100 m in length with 10000 to 250,000 plates. The stationary phase is usually bonded to their walls. These have become very popular in recent years and provide the best separations of all types of chromatography (they have the largest number of plates). Capillary columns require very small sample sizes and special injection ports.

Several types of detectors are in use, too many to describe each one individually. In order to keep the sample molecules in the gas phase, all detectors are also mounted in ovens, which are usually maintained at a higher temperature than the column. One of the most popular detectors is the *flame ionization detector* (FID), which is diagrammed in Figure 14.18. In this detector some or all of the effluent from the column is mixed with hydrogen gas and burned in an H_2/air flame. Molecules that contain C-H bonds produce ions and electrons in such a flame. These ions and electrons are collected by polarized plates placed on either side of the flame. The small current from these ions is amplified by the amplifier and displayed by some

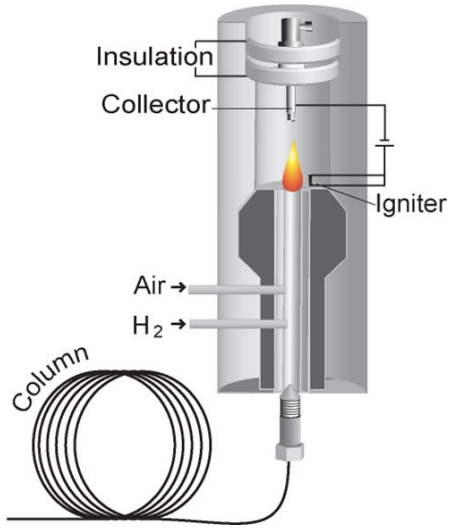


Figure 14.18: A flame ionization detector, used for gas chromatography.

type of recording device or computer. This detector does not respond well to materials which contain no C-H bonds. Thus it is useful mainly for organic molecules, but since very few other substances are volatile enough to get through a gas chromatograph, this detector is almost a universal gas chromatographic detector.

If more information about the sample is required, the detector of choice for gas chromatographs is a *mass spectrometer*. The acronym GC-MS is often used to describe the instrumental coupling of gas chromatography with mass spectrometry. Mass spectrometers possess the considerable advantage over flame ionization detectors in that they are able to provide chemical information about the sample. Specifically, they can often determine the compound's molecular weight. In addition, the chemical composition and structure of a molecule can sometimes be discerned through the generation and detection of fragment ions. Under specific conditions, the fragmentation pattern of a molecule reads like a chemical fingerprint, and thus can be used to identify unknown molecules as they are separated and detected by the *GC-MS* instrument.

The carrier gas in gas chromatography is ideal, and therefore does not interact with the sample molecules. Thus the type of carrier gas used has very little effect on the separations. The factors which are most important in determining the preference of the sample for either the mobile or the stationary phase are the temperature and the polarity of the liquid (stationary) phase. The higher the temperature, the greater the vapour pressure of the sample components, and the greater the affinity for the mobile phase. Thus gas chromatography separates mainly based on sample boiling point (or vapour pressure). Components with higher boiling points (lower vapour pressures) will move more slowly through the column, and thus will have higher retention times.

If two sample components have the same vapour pressures, separations can usually be achieved if the molecules have different polarities. A non-polar molecule will prefer to dissolve in a non-polar stationary phase, likewise a polar molecule prefers polar stationary phases (like prefers like). Thus if two components have the same vapour pressure and are chromatographed on a column with a polar stationary phase, the more polar of the components will have the longer retention time and *vice versa*. Many different liquid phases of various polarities are available. These are selected, often by trial and error, to fit the separation at hand. They must be stable and non-volatile at the temperatures used. This places an upper

limit of about 250 - 300°C on the use of gas chromatography. Above this temperature most liquid phases either begin to decompose or to bleed from the column.

What will occur if a sample contains a mixture of components with a wide boiling range? If the column temperature is held constant (termed *isothermal* operation) those components with low boiling points will come through the column almost immediately, all bunched together, those with intermediate boiling points will separate well, and those with high boiling points, while still separating well, will take a very long time to come through the column and will exit as very broad, small peaks which may not even be recognized as peaks. No single temperature can be found to separate all components of such a sample well and quickly. Figure 14.19 demonstrates this behaviour.

At first glance this might seem contradictory. Since N should be a constant for a column, all sample components should have the same σ and s_d. This is indeed the case (for similar sample components). However, the longer the retention time, the lower the sample velocity, v, and the longer it will take a component to come from the column. Thus s_t increases as t_r increases, even though s_d does not. Put a different way, $s_t = s_d/v$, and s_t, which is related to the peak width on the chromatogram, increases as v decreases while s_d remains constant. Thus for peaks of constant area, the peak height decreases and the peak width increases as t_r increases. The first peaks in a chromatogram are typically tall and narrow, and the last peaks are short and wide.

The solution to this dilemma is to change the column temperature during the experiment. This is called *temperature programming*. The temperature is initially held low so that the volatile sample components come through slowly enough to separate well. Then the temperature is raised so that the higher boiling components will come through more quickly while still separating well. Thus all peaks are fairly tall and narrow and the experiment can be done more rapidly. This is the reason that the column oven must be able to change temperature rapidly. Figure 14.20 shows a chromatogram of the same sample as shown in Figure 14.19 (run isothermally), but now run under temperature programming conditions. Note the difference in time scales with that of Figure 14.19.

Normally in temperature programming the temperature is increased linearly at a rate of about 3 to 20°C/min. Sometimes the temperature is held constant for a short period of time before starting the program and often it is also held constant at the end of a run. More

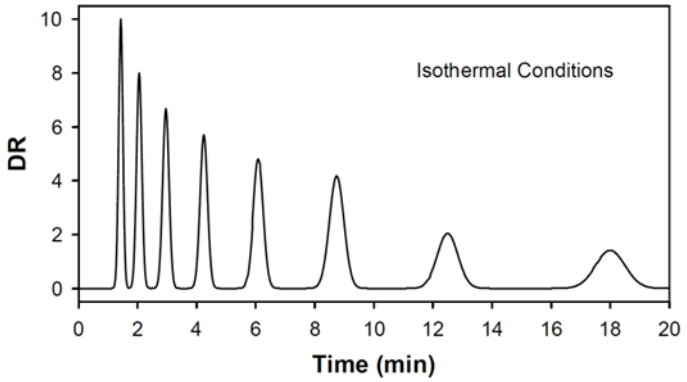


Figure 14.19: A GC separation of a homologous series of compounds, conducted at constant temperature.

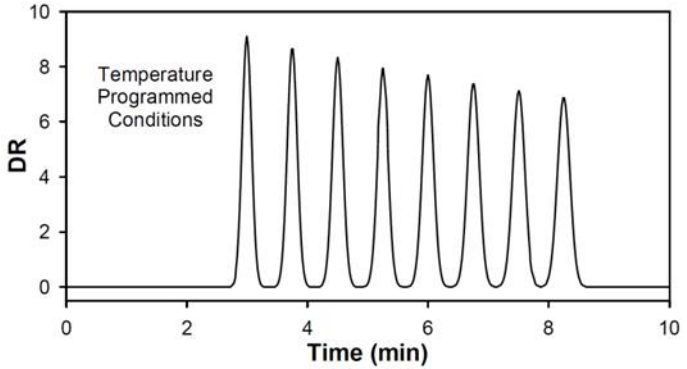


Figure 14.20: The same series of compounds shown in Figure 14.19 are now separated using a temperature-programmed GC run. Not only does peak shape improve, but the entire separation is completed in much shorter time.

sophisticated chromatographs allow periods during the run when the temperature can be held constant. Note that the partition coefficient, *K*, and the capacity factor, *k′*, are both a function of temperature and will change during a temperature programmed run. Thus all equations derived above which assume that these parameters are constant are invalid for temperature programmed experiments.

Gas chromatography is probably the most *ideal* type of chromatography. It has available to it many sensitive detectors, the theory is well developed, most samples are well-behaved, and columns with large numbers of plates are readily available. Unfortunately sample components must be volatile at temperatures of 300°C or less (a sample component must have a minimum vapour pressure of about 2 mm Hg) and thermally stable at temperatures where they are volatile. This excludes many organic compounds, most compounds of biochemical interest (unless they are broken into smaller molecules and/or derivatized), and almost all inorganic materials. Thus gas chromatography is best used for simpler organic molecules. For example, it finds wide use in the petroleum and chemical manufacturing industries.

14.13 Liquid Chromatography

Obviously liquid chromatography uses a liquid as the mobile phase. Today most analytical liquid chromatography is referred to as *HPLC*, which means either high pressure liquid chromatography or high performance liquid chromatography. This leads to an interesting bit of history regarding chromatography. The first type of chromatography was liquid chromatography. The columns used were large, open, had few plates, and were used mainly in preparatory work. This was the situation for many years before gas chromatography was developed. Rate theory was evolved by gas chromatographers, high-plate columns were developed, and liquid chromatography fell into disuse. Then liquid chromatographers read gas chromatographic theory and decided to make more ideal solid supports - more inert, more uniform, and much smaller in particle size. When this happened the number of plates in their columns increased dramatically (thus the “high performance”), but since the particle size was so small, the pressures needed to drive the mobile phase through the columns also increased dramatically (thus the “high pressure”). Liquid chromatography now approaches gas chromatography in its separation power and research in liquid chromatography has undergone

a renaissance. Gas chromatography has certainly not fallen into disuse, but it is no longer at the forefront of chromatographic technology.

As was done with gas chromatography, the discussion will start with the instrument. In many respects the instrument is very similar to a gas chromatograph; however, there are significant differences. A block diagram of a liquid chromatograph is shown in Figure 14.21. The mobile phase or eluent is usually placed in a simple container such as a flask or bottle. This phase can be water, an organic solvent, or mixtures of different solvents. In fact mixtures are the most common eluents.

The pressures required for modern HPLC work usually range from about 100 atm to about 500 atm. Thus the next component in line after the solvent reservoir is a pump capable of providing these high pressures with a constant flow. In many of the more versatile liquid chromatographs two or more solvent reservoirs are provided and the pump is actually capable of mixing two or more solvents in any ratio. This ratio can be changed during an experiment.

Due to the high pressures involved, one cannot inject a sample onto the column directly with a syringe, as is done in gas chromatography. Instead a sampling valve is used. This valve contains a sample loop which has a fixed volume. Sample is loaded into this loop with a syringe, and then the valve is turned in order to inject the loop's contents into the HPLC mobile phase. The advantage of this arrangement is that a constant amount of sample can be placed on the column with each injection (unless air is somehow placed in the sample loop) without great difficulty. However, one cannot vary the sample size easily with an injection valve; one must change the sample loop to do so.

The columns themselves are usually stainless steel tubes packed with very small particles. The tube length normally varies between 3 and 25 cm, the inner diameter between 0.075 and 4 mm, and the particle size between 2 and 10 μm. The plate height (HETP) in liquid chromatography is smaller than in gas chromatography, but the columns are also much shorter because it would take tremendous pressures to drive solvents through long columns. Liquid chromatographic columns typically have between 2000 and 20000 plates.

The detectors available for use in liquid chromatography are far different from those used in gas chromatography. Spectrophotometers and fluorometers are two types of detectors commonly used in liquid chromatography. In these detectors a flow cell replaces the normal spectrophotometric cuvette. It is often the same length (1 cm). Obviously to use such detectors

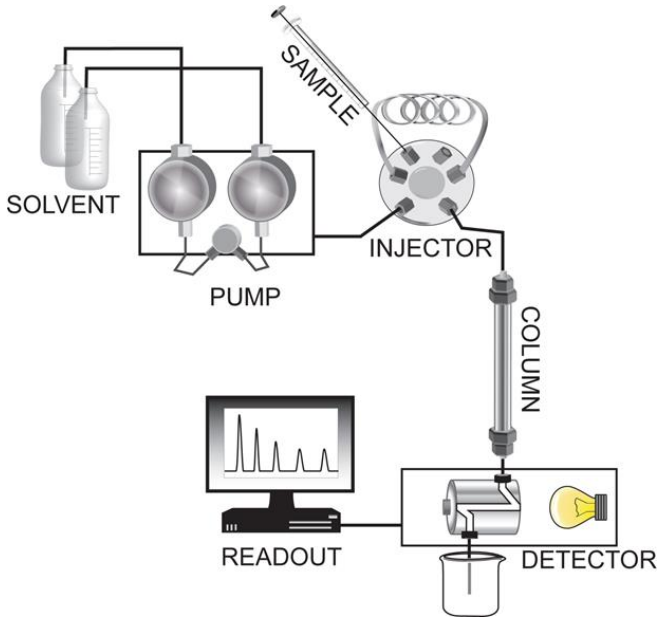


Figure 14.21: A block diagram of a liquid chromatograph.

the sample must absorb light or fluoresce and the eluent must not. Not all samples absorb light and even fewer fluoresce, while some solvents do absorb light, especially in the ultraviolet. The coupling of mass spectrometers to liquid chromatography (*a.k.a.* LC-MS) has traditionally been more difficult than GC-MS. The reason is that the liquid eluent caused problems as it was brought into the vacuum region which defines a mass spectrometer. This is no longer a concern, as new strategies have been developed to overcome this problem, and such detectors are now common.

The actual mechanism of separation in liquid chromatography is somewhat different than in gas chromatography. In GC the mobile phase is ideal, it does not interact with the sample molecules, and thus the particular gas used is not important. Volatility differences between molecules are very important in determining whether good separations are achieved. In liquid chromatography the mobile phase is not ideal, it interacts strongly with the sample molecules, and thus it plays a very important role in the separations. On the other hand temperature is relatively unimportant, which is the reason many liquid chromatographs do not have ovens and are not thermostated. In liquid chromatography polarity, including sample, eluent, and stationary phase polarity, are the most important factors in determining whether good separations can be achieved.

In adsorption chromatography the "solid support" is not coated with anything. Its surface acts as the second phase for the separation, the place where the sample molecules reside when not in the mobile phase. The most common solid used in adsorption chromatography is silica (SiO_2), but alumina (Al_2O_3) is also often used. These can be obtained with various types of surfaces, depending on pretreatment. In general the mobile phases used in adsorption chromatography are relatively non-polar organic solvents such as hydrocarbons and chlorinated hydrocarbons. The more polar a sample molecule, the more it will prefer the silica surface to the liquid phase. Thus, as the polarities of the sample molecules increase, so do the retention times, and separations are based on polarity. If it is desired to move polar samples more rapidly through a column, then the mobile phase is made more polar itself, either by changing the solvent completely (*e.g.* from hexane to methylene chloride or acetone) or mixing a more polar solvent with the original non-polar solvent.

In partition chromatography the solid support is coated with the stationary phase. With most modern HPLC stationary phases, the liquid phase is actually chemically bonded to the

solid support. This prevents the stationary phase from slowly leaching from the column. If one uses a non-bonded stationary phase, then one should saturate the mobile phase with molecules of the stationary phase before passing it through the column in order to slow down the leaching.

The most common solid support for bonded phases is silica. At first it might seem that bonding a liquid phase to a silica surface would be difficult, but it is easier than one might guess. The silica surface contains many -SiOH groups (silanol groups) that are relatively active. When these are reacted with a chloroorganosilane the following reaction occurs:

$$\text{-Si-OH} + \text{ClSiR}_3 \rightarrow \text{-Si-O-SiR}_3 + \text{HCl}$$

The "R" groups connected to the second silicon atom on the right make up the liquid phase. These are commonly either 8 or 18 carbon atoms in length and are hydrocarbons. When one refers to a "C18 bonded phase" one is speaking about the above type of stationary phase where the R groups are 18 carbons in length. The bonding of multiple C18 chains to a silica support is shown in Figure 14.22.

Variations in the stationary phase are achieved in several ways. One can change the length of the R group, *e.g.* from 4 to 8 to 18 carbons. One can add polar substituents to the R group such as -OH and $-NH_2$. Finally one can pack the surface with different amounts of stationary phase.

Although variety can be obtained with bonded phases as explained above, these phases are typically rather non-polar and the eluents used with them are usually polar, often involving solvents such as water, methanol, or acetonitrile (CH_3CN). On these types of columns the non-polar sample molecules prefer the stationary phase; the lower the sample polarity, the greater the retention time. To bring a nonpolar sample through the column faster, one uses a less polar eluent or mixes a less polar component into the eluent. In terms of polarity, this behaviour is the reverse of that in adsorption chromatography (which was the first type of liquid chromatography employed). For this reason adsorption chromatography or any partition chromatography in which polar samples are more tightly held by the stationary phase and in which eluent polarity is increased during an experiment is called *normal phase chromatography*. Partition chromatography in which non-polar compounds are more tightly

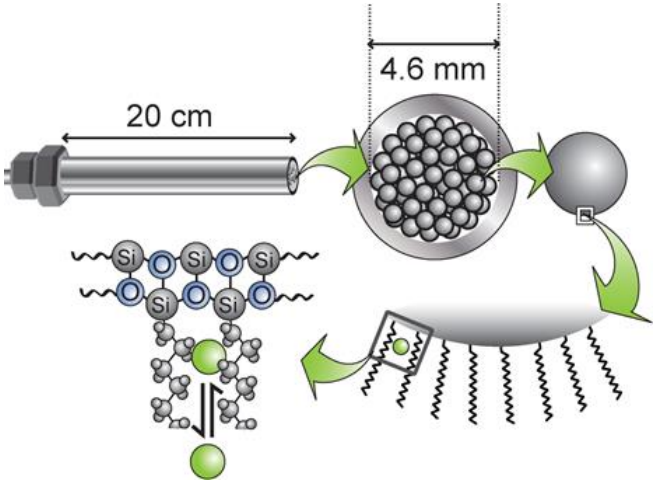


Figure 14.22: In HPLC, the stationary phase is typically chemically bonded to the solid support. C18-coated silica particles are commonly employed as the packing material for LC columns.

held by the stationary phase and in which eluent polarity is decreased during an experiment is called *reversed phase chromatography*.

If one has a sample of many components which have a variety of polarities, it will be difficult to select an eluent with a polarity that will separate all the components well. Analogous to temperature programming in GC, in LC one can change the composition of the mobile phase during the experiment. This is done by using two or more solvents of differing polarity and continuously changing the proportion of these in the mixture. This is termed *solvent programming* and is the reason why the more sophisticated liquid chromatographs have pumps with this mixing capability. An LC experiment in which the solvent composition is constant is termed *isocratic*.

The exact type of system that works best with a particular sample must often be decided by trial and error. If a sample can be separated by GC, it is perhaps the simpler choice. But not all compounds are suitable for GC; liquid chromatography finds use in separating temperature sensitive and non-volatile substances, which include many of the materials with which scientists deal.

14.14 Other Types of Chromatography

There are several types of chromatography which do not easily fit into the above classifications. Two types, all forms of liquid chromatography are discussed below.

Gel permeation chromatography

Gel permeation or *size exclusion* chromatography uses a completely inert, porous solid phase. Thus, ideally, there is no direct interaction (adsorption or partitioning) between the analyte and the stationary phase. The behaviour of sample molecules toward the stationary phase will depend on the size of the sample molecules. If sample molecules are too large to enter the pores of the stationary phase, there will be no retention and these compounds move through the column with the mobile phase, as shown in Figure 14.23. On the other hand, smaller molecules can fit inside the pores. The liquid filling these pores can be thought of as the stationary phase, seeing as how the space is shielded from the moving liquid phase. Small molecules diffuse in and out of these pores, and thus spend a longer period of time in the

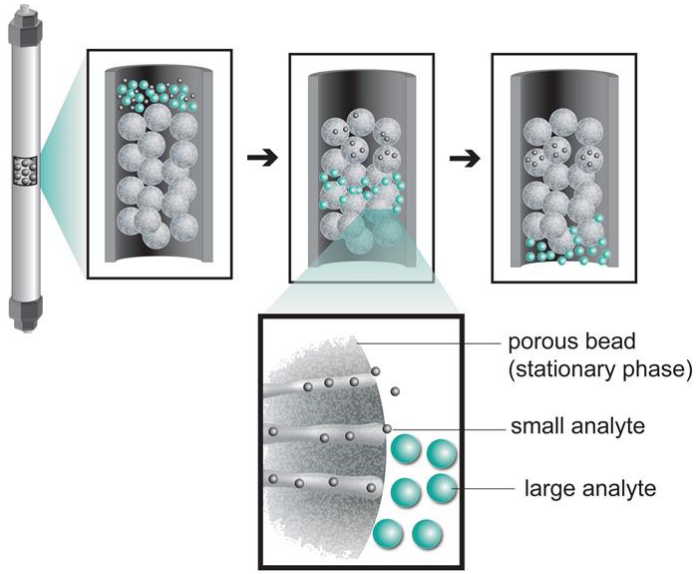


Figure 14.23: Mechanism of gel permeation chromatography. Smaller molecules spend more time in the pores of the stationary phase and take longer to elute.

column. Molecules of intermediate size also spend some time inside the pores. But considering that the pores of the stationary phase will have a distribution of sizes, not all pores will be available to these intermediate molecules. Thus they will spend some time in the stationary phase, but not as much time as the small molecules.

Stationary phases are available with different pore size ranges. Thus, a given size exclusion column can be designed to separate compound over a given mass range. Compounds with molecular weights above and below the optimum range are separated poorly or not at all. This type of chromatography is particularly useful to biochemists and polymer chemists, both of which work with large molecules, and molecules with a large range of sizes.

Example 14.10: Gel Permeation Chromatography

Often in GPC a linear relationship exists between log(molecular weight) (logMW) and t_r. A standard with MW of 35,000 Da has a retention time of 7.52 min and a standard of 62,000 Da has t_r of 4.21 min. What is the approximate MW of a material with a retention time of 5.13 min?

For a linear relationship, $\log(MW) = a + bt_r$

$$b = \frac{\left(\log(35{,}000) - \log(62{,}000)\right)}{\left(7.53 - 4.21\right)\ \text{min}} = -0.0748\ \text{min}^{-1}$$

$$a = \log(35{,}000) + (0.0748\ \text{min}^{-1})(7.52\ \text{min}) = 5.11$$

$$\log(MW_u) = 5.11 - (0.0748\ \text{min}^{-1})(5.13\ \text{min}) = 4.72$$

$$MW = 53{,}000\ \text{Da}$$

Ion exchange chromatography

In *ion exchange chromatography* the stationary phase is usually an organic polymer which contains groups that can ionize. One of the most common polymers used for the stationary phase is polystyrene, made from a cross-linked structure of styrene (also named vinylbenzene

or phenylethene). To act as an ion exchange medium, ionizable groups must be added to the matrix. One way to do this is to sulfonate the benzene rings in the polymer, which results in the structure shown in Figure 14.24. The sulfonate group is permanently attached to the polymer backbone, but the hydrogen ion associated with it can be replaced by any other cation, *e.g.* sodium or calcium.

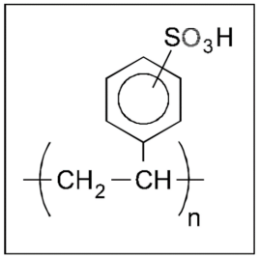


Figure 14.24 Derivatization of a polystyrene support.

The polymer backbone is usually represented simply as "R", so the material which has been used in this example would be RSO_3H or $RSO_3^-H^+$. This is called a *strong acid cation exchanger* because the proton can be exchanged at any pH (it acts like a strong acid) and because it exchanges cations. If the sulfonate group were replaced with a carboxylate group, giving RCOOH, a weak acid cation exchanger would result. Similarly, strong or weak anion exchangers are available, resulting when an amine group or quaternary ammonium group is substituted for the sulfonate group. Thus, $RNH_3^+OH^-$ is a weak base anion exchange resin while $RN(CH_3)_3^+OH^-$ is a strong base anion exchanger.

In ion exchange, the mobile phase is almost always an aqueous solution, also containing added ionic materials. Before placing a sample on the column, all of the ionisable groups on the resin are coupled with the same ion on purpose. The strong acid cation exchange resin will continue to be used as the example. For this type of material, the hydrogen ion usually is employed. The resin is converted to the hydrogen form by passing a solution of concentrated acid through the column. The result is that each RSO_3^- group has associated with it a hydrogen ion.

Now imagine that a sample is placed on the column, and that the sample contains two or more types of ions, other than H^+, which are to be separated. These might be Na^+ and K^+. What happens? The sodium ion and the potassium ion can exchange with the hydrogen ion.

$$RSO_3^-H^+ + Na^+ \rightarrow RSO_3^-Na^+ + H^+$$

$$RSO_3^-H^+ + K^+ \rightarrow RSO_3^-K^+ + H^+$$

Thus a sodium or potassium ion from the solution replaces a hydrogen ion on the resin and the hydrogen ion goes into solution. While the sodium and potassium ions are on the resin associated with the RSO_3^- groups, they do not move. At some later time another hydrogen ion from solution will exchange with the sodium or potassium ions, allowing the latter to go back into solution. Thus the bands of these ions move down the column, continuously

exchanging with hydrogen ion. If one of these ions is more attracted to the resin than the other, it will move more slowly, and separation will be achieved. This process is illustrated in Figure 14.25. Anion exchange chromatography works in exactly the same way, except that anions are continuously moving back and forth between the mobile and stationary phases. These again can separate on the basis of differences in affinity between ions for the stationary phase. Note that the mobile phase or eluent *must* contain the ion that is associated with the resin in the beginning, H^+ in the example above. If it did not, the Na^+ and K^+ would go onto the stationary phase, but would never come off, since there would be no ions in solution with which to exchange.

Ion exchange chromatography is very useful in separating inorganic materials, both cations and anions. However, one cannot normally separate both the anions and cations in a sample in one experiment. Ion exchange chromatography, for example, is very useful for identifying the ionic components in acid rain and other polluted natural water samples. However, this type of chromatography also works well with organic ions. There are types of amino acid analyzers which use ion exchange columns to separate the amino acids in a sample one from another. Ion exchange resins are also used in water purification. "Deionized" water results when ordinary water is passed through a mixture of a cation exchange resin in the hydrogen form and an anion resin in the hydroxide form. All cations are exchanged for H^+ and all anions for OH^-. These two ions react with each other to produce water. Thus no ions remain in the water (except for the residual hydrogen and hydroxide ions). This is a better way of removing ions from water than distillation.

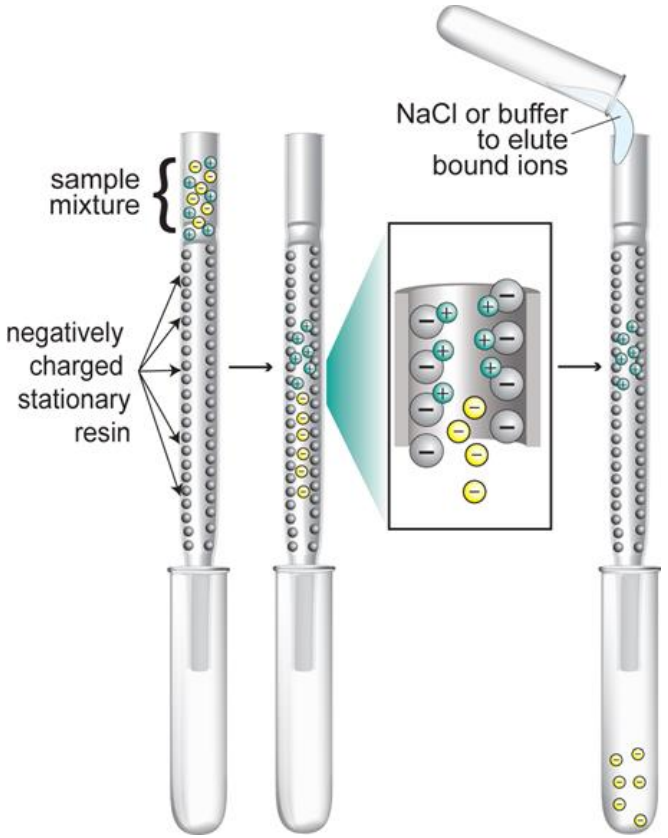


Figure 14.25: Illustration of ion-exchange chromatography with a cation exchanger.

14.15 Qualitative Analysis

On a given column, any specific sample component will always have the same retention time, and thus retention time can be used to identify sample components. What is usually done is to pass standards (known substances) through the chromatograph and measure the various t_r values. Such standards must be run on each new column because t_r will change from column to column, even though the same materials are used for all columns. Column characteristics also change somewhat with time, so it is wise to re-measure the standards from time to time on the same column. Then the sample is run and if a peak in the sample occurs at the same t_r

as one of the standard peaks, that component in the unknown is assumed to be the same as the standard.

This is not foolproof and cannot be taken as absolute proof of identity. Whereas it is true that a given component will always have the same retention time from run to run (provided that the column has not aged to any extent), it may also happen that another substance in the sample will have the same retention time. Thus to positively identify a substance, information additional to the retention time will be necessary. However, often in routine analysis when a series of well characterized samples is being analyzed, retention time alone is considered sufficient to identify the presence of a specific component.

Sometimes a sample whose characteristics are less well established is analyzed and component peaks need to be identified. If no standards are available which correspond to the suspected unknowns, can anything be done? One can still go to the literature to see if another chemist has analyzed a similar sample. However, one cannot directly use t_r or V_r values from the literature for identification, even if your column is packed with the same materials as that in the literature. The reason is that your column will almost certainly have a different V_m and V_s than the one in the literature. k' for your column will also be different from that of the literature column. However, if you use the same conditions (same stationary and mobile phases, same temperature or solvent composition) as those used in the literature, the value of K, the partition coefficient, will be the same for both systems. Is there any way this can be used? Proceed as follows:

$$V_r = t_r F = (V_m + KV_s)$$

or $$V_r - V_m = KV_s$$

Now assume that you add a material to your sample which is not originally in the sample, but which must also have been in the samples described in the literature. This is essentially an internal standard. Its peak must not interfere with any of the other peaks in your sample. One uses the internal standard peak to calculate a parameter called the *relative retention ratio* (*RRR*) as follows:

$$RRR = \frac{(V_r - V_m)_{unk}}{(V_r - V_m)_{std}} = \frac{K_{unk}V_s}{K_{std}V_s} = \frac{K_{unk}}{K_{std}} \tag{14.36}$$

Since the *K*'s are the same for both columns, the relative retention ratios will also be the same, regardless of how the column is packed (provided the same materials are used). The values of relative retention ratios should be the same from lab to lab. Thus, if the *RRR* for your peak matches one from the literature, this can be taken as tentative identification, keeping in mind that more than one compound can have the same *RRR*. Retention times can be used to calculate *RRR* values as well as retention volumes.

$$RRR = \frac{(V_r - V_m)_{unk}}{(V_r - V_m)_{std}} = \frac{(t_r - t_m)_{unk}}{(t_r - t_m)_{std}} \tag{14.37}$$

Since the use of *RRR* assumes that the *K*'s are constant, this method of qualitative analysis cannot be used with temperature programming in gas chromatography or solvent programming in liquid chromatography.

Example 14.11: Relative Retention Ratios

You are in the middle of a series of analyses for chlorinated hydrocarbons using GC and you must replace the column in your chromatograph with one made by a different manufacturer. The new column is made from the same materials as the old column. You do not have time to run all the standards, so you run chlorobenzene through the new column and calculate the retention times for all the other compounds from the chlorobenzene data. On the old column the retention times are as follows: "air" peak (non-retained peak) - 0.57 min, chlorobenzene - 5.23 min, *m*-dichlorobenzene - 8.46 min. For the new column the retention times are: "air" peak - 0.82 min, chlorobenzene - 4.96 min. What should the retention time of *m*-dichlorobenzene be on the new column?

Let chlorobenzene be the standard and *m*-dichlorobenzene be the unknown. For the old column:

$$RRR = \frac{(8.46\,\text{min} - 0.57\,\text{min})}{(5.23\,\text{min} - 0.57\,\text{min})} = 1.693$$

For the new column:

$$1.693 = \frac{(t_r - 0.82\,\text{min})}{(4.96\,\text{min} - 0.82\,\text{min})}$$

$$t_r = 1.693(4.96\,\text{min} - 0.82\,\text{min}) + 0.82\,\text{min} = 7.83\,\text{min}$$

14.16 Quantitative Analysis

The chromatogram also contains quantitative information. If the detector response is linear in concentration (and it usually is) then the peak area is directly proportional to concentration.

$$A = kC \tag{14.38}$$

where A is peak area, C is sample concentration and k is the proportionality constant. Thus the measurement of concentration becomes a problem in the measurement of the area of a peak. This can be done in several ways. Assume that peak height, h, is proportional to area. Thus

$$A = k_1 h \tag{14.39}$$

and

$$h = k_2 C \tag{14.40}$$

Since h is easily measured, this should be a simple way to do quantitative analysis if the assumption holds. Why might h not be proportional to area? Peak height depends on sampling technique - the narrower the starting band of the sample, the larger all peak heights will be, all other parameters being constant. Thus peak height will not necessarily always be proportional to area.

It is easiest to use this approximation for the first peaks in a chromatogram, those that come through the column most rapidly. Why? The longer the retention time of a peak, the greater the width of a peak (t_w or s_t). For this reason, peak height is most easily and accurately measured on the tall, narrow peaks at the start of a chromatogram.

Approximate the area using the peak height and width taken from the chromatogram. There are two common ways of doing this. One can measure h and $w_{1/2}$ and assume that

$$A = hw_{1/2} = k_3 C \tag{14.41}$$

The area calculated this way will always be 93.9% of the actual area of an ideal peak. Alternatively, one can draw tangents to the inflection points on the peak. This forms a triangle, the base of which is w (4s) and the height of which is h'. The area of this triangle, which approximates the area of the peak, is $h'w/2$. Thus one assumes that

$$A = \frac{h'w}{2} = k_4 C \tag{14.42}$$

The area calculated in this way should be 96.8% of the actual area of an ideal peak.

Peak areas may also be integrated by a computer, noting here that variations in the position of the baseline must be taken into consideration. Nonetheless, once one has established a method for measuring peak area, then one runs a standard to determine the proportionality constant between area and concentration, or better, one prepares a calibration curve using several standards, and then runs the sample. Using the calibration curve or the constant, one then determines the unknown concentration in the usual fashion. If area is directly proportional to concentration, then the method of standard addition can be used.

Example 14.12: Quantifying Compounds in Chromatography

Continuing with your analysis of chlorinated compounds (see the example above), a standard solution containing 0.0100 mol/L of chlorobenzene when chromatographed gave a peak height of 8.41 cm and a width (at half-height) of 33 s from a 5.0 µL injection. An unknown produced a peak height of 5.36 cm and a half-width of 31 s from a 2.0 µL injection. What is the concentration of chlorobenzene in the unknown?

Since the volumes injected are not equal, you must work with moles, since more fundamentally area is proportional to moles (only to concentration when the injected volumes are equal).

$$A_{std} = (8.41\,cm)(33\,s) = 2\bar{7}8\ cm \cdot s = K \cdot mol_{std}$$

$$A_{unk} = (5.36\,cm)(31\,s) = 1\bar{6}6\,cm \cdot s = K \cdot mol_{unk}$$

$$mol_{unk} = \frac{A_{unk}}{A_{std}} \cdot mol_{std} = \frac{1\bar{6}6\,cm \cdot s}{2\bar{7}8\,cm \cdot s} \cdot (5.0 \times 10^{-6}\,L)(0.0100\,M) = 2.\bar{9}9 \times 10^{-8}\,mol$$

$$C_{unk} = \frac{2.\bar{9}9 \times 10^{-8}\,mol}{2.0 \times 10^{-6}\,L} = 0.015\,mol\ L^{-1}$$

14.17 Internal Standards

One problem with regard to sampling with a syringe was mentioned above - the difficulty of reproducing or accurately measuring injection volumes with such a small syringe. Such injection is normally precise to no better than 10%. If more precision is needed, one can use an internal standard as described earlier in the introduction to instrumental methods. Recall that the internal standard is a substance that is not normally found in the sample, but has characteristics similar to the analyte and does not interfere with its determination (*i.e.* it has a different retention time). The same amount of internal standard is normally added to all standards and samples, and usually the same volume of solution is injected for all solutions. One then measures the areas of the analyte and the internal standard peaks in all experiments and calculates the ratio of the areas of analyte to internal standard, A_{unk}/A_{std}, for each component and each experiment. The calibration curve, as shown in Figure 14.26, is prepared by plotting the area ratio *vs.* the analyte concentration for the standards. The ratio depends on the accuracy with which you prepared the standard solutions, not on the volume injected. If the injection volume should increase by 10%, both areas, the internal standard and the analyte, would also increase by 10%, but the ratio would remain constant. Thus, variations in injected volume do not affect the quantitative result. The final results are obtained from the area ratios of the unknowns and the calibration curve in the usual manner.

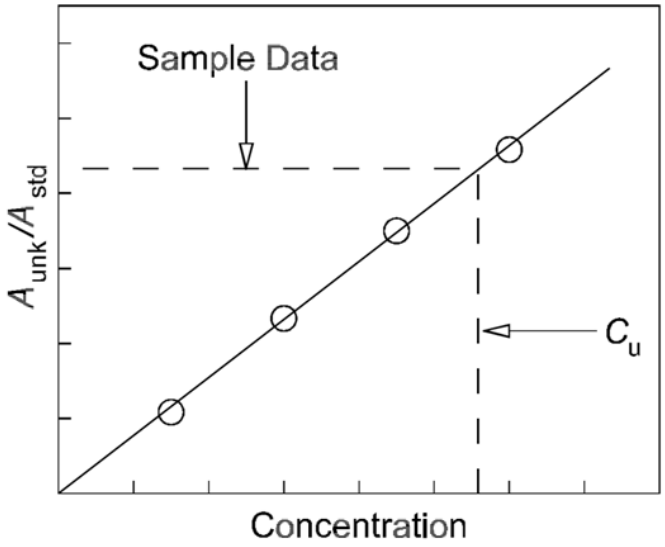


Figure 14.26: The formation of a calibration curve, using the method of internal standards.

Example 14.13: Internal Standards

You are using GC for the analysis of fats (lipids). One of the main components of saturated fats is palmitic acid (hexadecanoic acid, $C_{15}H_{31}COOH$). Large carboxylic acids are difficult to chromatograph using GC (their volatility is low), but their esters are not. Thus the acids are often esterified prior to analysis by GC. 2.0 µL of a standard solution of 0.0100 M methyl palmitate and 0.0100 M methyl undecanoate (internal standard) produced areas of 386 and 291 units respectively on an electronic integrator. When 1.00 mL of 0.100 M methyl undecanoate is added to 9.00 mL of a sample and this is analyzed in the same way, areas of 186 and 268 units for the unknown and the internal standard respectively, are obtained. What is the concentration of methyl palmitate in the unknown?

Assume $\frac{A_u}{A_s} = \frac{kC_u}{C_s}$ or $k = \frac{A_u C_s}{A_s C_u}$

$$k = \frac{386(0.0100 \text{ mol L}^{-1})}{291(0.0100 \text{ mol L}^{-1})} = 1.326$$

$$C_u = \frac{A_u C_s}{A_s k} = \frac{186(0.100 \text{ mol L}^{-1})\left(\frac{1.00 \text{ mL}}{10.00 \text{ mL}}\right)}{268(1.326)}$$

$$C_u = 0.00523 \text{ mol} \cdot \text{L}^{-1}$$

However, the unknown was diluted with the standard. Thus

$$\text{Original } C_u = \left(0.00523 \text{ mol L}^{-1}\right)\left(\frac{10.00 \text{ mL}}{9.00 \text{ mL}}\right) = 0.00581 \text{ mol L}^{-1}$$

14.18 Summary

Real world samples often consist of complex mixtures that require separation of the components before the analyte can be determined. Chromatography is a technique where analytes are selectively partitioned between a mobile phase and stationary phase in a continuous fashion, permitting their separation. The degree of separation depends on the nature of the analytes and the separation technique, and is characterized by the resolution. The resolution capability of a column depends on the number of theoretical plates and varies in accordance with the van Deemter equation. Chromatographic methods are broadly classified according to their mobile phase as gas or liquid chromatography. Both qualitative and quantitative analysis is possible.

14.19 Additional Exercises

Exercise 14.10

5.00 g of CCl_4 (d = 1.60 g/mL), the stationary phase, are loaded onto a KelF support (a polymer of C, Cl, and F), slurried with water, the mobile phase, and packed into a column. A solute which does not dissolve in CCl_4 (*e.g*. NaCl) has a V_r of 18.3 mL. A high molecular weight alcohol has a V_r of 52.1 mL on the same column. Calculate the partition coefficient for the alcohol.

Exercise 14.11

Determine V_r for the column of Exercise 14.10 for alcohols with K = 8.61 and 12.82.

Exercise 14.12

A typical GC capillary column (open column) has a bore (inner diameter) of 0.250 mm and a length of 50.0 m. The column walls are coated to a thickness of 0.0100 mm. Calculate V_r for such a column for a compound with a K of 50.0.

Exercise 14.13

The following are typical values in gas chromatography: F = 30.0 mL/min, t_m = 30 s, t_r = 300 s, wt% of the stationary phase with respect to the total column packing =

5.0%, weight of the column packing = 2.00 g, density of the liquid stationary phase = 0.90 g/mL. Calculate typical values for *K* and *k'*.

Exercise 14.14

A 0.125 inch o.d. (outside diameter) GC column is packed as follows: 10.00g of inert support are mixed with a solution containing 1.000 g of stationary phase and the solvent is evaporated. The stationary phase density is 0.917 g/mL. As much coated support as possible is packed into the column; that remaining unpacked weighed 8.58 g. When operated at a flow rate of 20.0 mL/min of He, the "air" peak (non-retained) emerged at 26.5 s and a sample peak at 138.1 s. What are the values of *K* and *k'* for the sample?

Exercise 14.15

The following data were taken in a GC experiment: t_r of air (non-retained) = 33 s, t_r of benzene = 275 s, t_r of toluene = 342 s. From the literature it is known that the partition coefficient of benzene for the stationary phase in your column and at your column temperature is 650. Calculate K for toluene.

Exercise 14.16

The column of Exercise 14.10 would have to have 558 plates to separate the alcohols of Exercise 14.11 with baseline resolution. If the plate height were 0.80 mm, how long a column would be necessary for such a separation?

Exercise 14.17

A packed GC column with 4000 plates is a very good column. What is the half peak width for a peak with a retention time of 432 s on such a column?

Exercise 14.18

The bandwidth in chromatography could be defined as the width (distance) between the two inflection points on the peak (the points at which the slope is the steepest). Assuming an ideal peak (Gaussian), show mathematically what this bandwidth would be in terms of *s*. At what height would this bandwidth be measured?

Exercise 14.19

The flow rate for the column in Problem 14.12 is 2.00 mL/min and the half width of the peak is 6.22 s. How many plates does the column contain? What is HETP?

Exercise 14.20

Typical values for the column length, the number of plates, the flow rate of eluent, and the mobile phase volume are shown below for LC, packed column GC, and capillary column GC.

	LC	Packed GC	Capillary GC
L	10 cm	2 m	50 m
N	10,000	5,000	100,000
F	1 mL/min	20 mL/min	2 mL/min
V_m	0.400 mL	12.00 mL	2.00 mL

Compare these types of chromatography by calculating HETP, the half width (in time) of a peak for a component with k' = 10.0, and the k' for a component that is separated by two half widths from the peak for k' = 10 (this separation is quantitative).

Exercise 14.21

The following data were taken on a 3.00 metre GC column using nitrogen gas as the carrier (mobile phase) and dibutyl phthalate as the stationary phase:

# of plates	Gas velocity (cm/sec)	# of plates	Gas velocity (cm/sec)
364	1	1875	20.0
850	2.5	1550	30.0
1460	5.0	1250	40.0
2000	10.0	1050	50.0
2030	15.0		

Plot the above data and determine (approximately) the coefficients (*A*, *B*, and *C*) of the van Deemter equation. Assuming that V_m is 20.0 mL, determine the optimum flow rate. If 3.45 mL of the stationary liquid phase were used, determine the

retention volume and retention time (under optimum conditions) for a substance with a *K* value of 50.0.

Exercise 14.22

The van Deemter equation is usually written in terms of the velocity of the mobile phase, but it can also be written in terms of the flow rate of the mobile phase since flow rate is directly proportional to velocity. Thus one could write HETP = $A + B/F + CF$. A 3.00 m packed column is prepared using a solid support loaded with 1.89 mL of stationary phase. At a flow rate of 10.0 mL/min a non-retained substance exhibits a t_r of 2.83 min. A series of experiments determines that A = 0.0554 cm, B = 0.1682 cm·mL/min, and C = 0.00481 cm·min/mL. Determine the best flow rate, the minimum value for HETP and the maximum number of plates for this column. For a compound with a *K* of 30.0, determine the retention times for flow rates of 5.00, 10.0, and 20.0 mL/min.

Exercise 14.23

Many commercial chemicals are not pure compounds but isomeric mixtures. Polychlorinated biphenyls, reputed by some to be very dangerous substances, are good examples. There are six isomers alone of the dichlorobiphenyls (DCBs) (where the chlorines are on different rings). A commercial testing laboratory reports the following data:

Compound	V_r	Compound	V_r
"air"	4.3 mL	2,2'-dichlorobiphenyl	52.4 mL
2-bromobiphenyl	48.2	3,4'-DCB	53.2
2,3'-DCB	49.6	3,3'-DCB	53.9
2,4'-DCB	50.3	4,4'-DCB	54.6

and you observe the following values run on an unknown containing 2-bromobiphenyl as internal standard:

"air"	9.5 mL	Unknown #2	45.5 mL
2-bromobiphenyl	42.4	Unknown #3	47.1
Unknown #1	44.0		

Assuming that the temperature and column materials are the same for the two data sets, determine which components are in the sample.

Exercise 14.24

A mixture containing pentane (internal standard) and all the isomers of hexane was chromatographed (GLC) giving the following retention volumes: "air", 11.5 mL; pentane, 23.3 mL; 2,2-dimethylbutane, 37.2 mL; 2,3-dimethylbutane, 45.6 mL; 2-methylpentane, 47.1 mL; 3-methylpentane, 49.8 mL; and hexane 54.0 mL. Irv Gratch, an infamous undergraduate student, then used the chromatograph and from that moment on no further peaks were obtained from the instrument. A new column was packed (same materials as the first) and an unknown hexane sample (with pentane added) was run at the same temperature as the above mixture with the following results (V_r): "air" 5.7 mL; pentane, 27.2 mL; Unk #1, 67.8 mL; Unk #2, 75.6 mL; Unk #3, 83.1 mL. What isomers of hexane are in the sample?

Exercise 14.25

An electronic integrator provides the following data for a set of standards and an unknown analyzed by GLC:

Sample	Reading(C_6H_{12})	Reading(C_6H_6)
0.00100 mol C_6H_{12} + 0.000100 mol C_6H_6	937	83
0.00100 mol C_6H_{12} + 0.000250 mol C_6H_6	1042	231
0.00100 mol C_6H_{12} + 0.000500 mol C_6H_6	868	384
0.00100 mol C_6H_{12} + 0.001000 mol C_6H_6	945	836
0.00100 mol C_6H_{12} + 1.00 mL of Unknown	998	291

The cyclohexane is used as an internal standard. All samples are diluted to 10.0 mL with a suitable solvent. Show whether the instrument response is linear in concentration. Compute the concentration of benzene in the original sample.

Exercise 14.26

The composition of various oils used in cooking is of great concern since saturated oils have been linked to heart disease. These oils are the triesters of glycerol ($CH_2OHCHOHCH_2OH$) and long chain fatty acids. One method of analysis is to saponify the oil (the triglycerides), remove the glycerol, prepare the methyl esters of the acids, and analyze the methyl esters by GC. The fatty acids usually contain 16 or 18 carbons and are saturated or contain one or two double bonds. The chromatogram of Figure A-1 was taken from the literature and shows the following peaks: A - $C_{15}H_{29}COOCH_3$, B - $C_{15}H_{31}COOCH_3$, C - $C_{17}H_{31}COOCH_3$, D - $C_{17}H_{33}COOCH_3$, E - $C_{17}H_{35}COOCH_3$, and F - $C_{17}H_{35}COOC_2H_5$, added as internal standard. The chromatogram in Figure A-2 was taken on a column made from the same materials and run at the same temperature in an analysis laboratory. What compounds are contained in the sample from the second chromatogram?

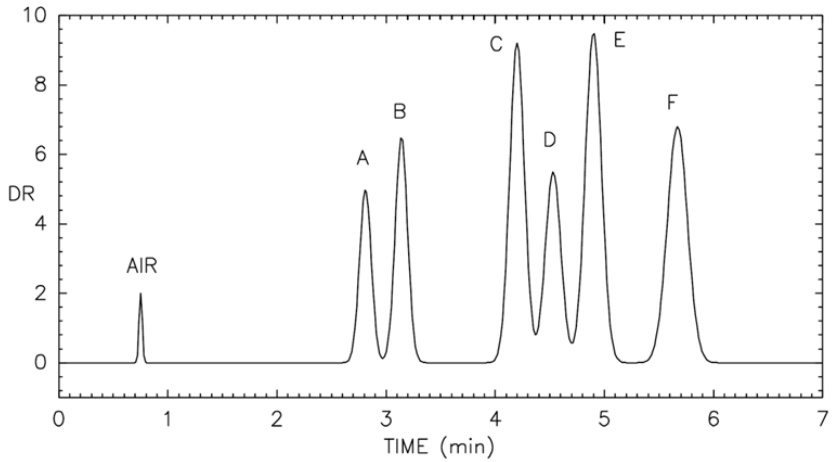


Figure A-1

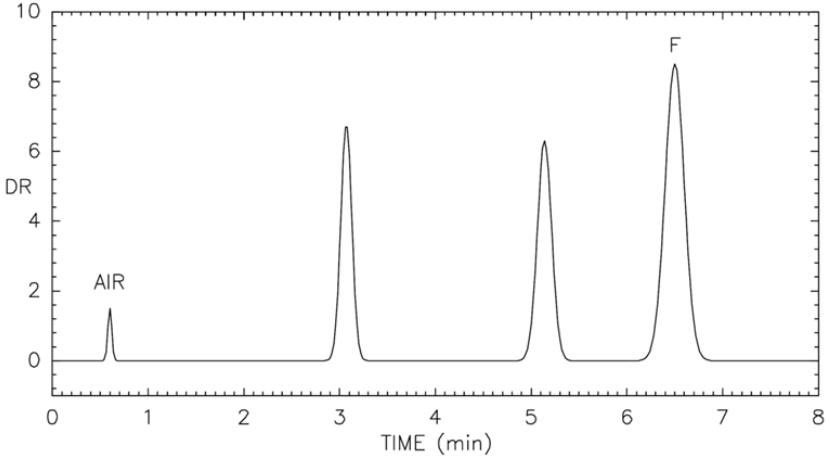


Figure A-2

Exercise 14.27

To analyze caffeine in urine you prepare a 1.00×10^{-4} M solution of caffeine in methanol, inject 20.0 µL of this into a liquid chromatograph which uses a spectrophotometric detector operating at 254 nm and obtain the chromatogram shown in Figure A-3. You then obtain a urine sample, remove some of the sample components by extraction (not changing the sample volume) and inject 20.0 µL of this sample into the same column, obtaining the chromatogram shown in Figure A-4. Assuming that area is directly proportional to concentration, determine the concentration of caffeine in the urine sample.

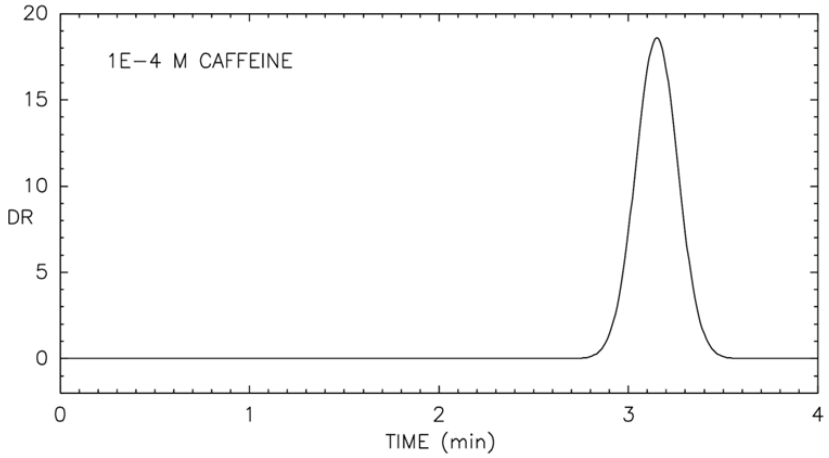


Figure A-3

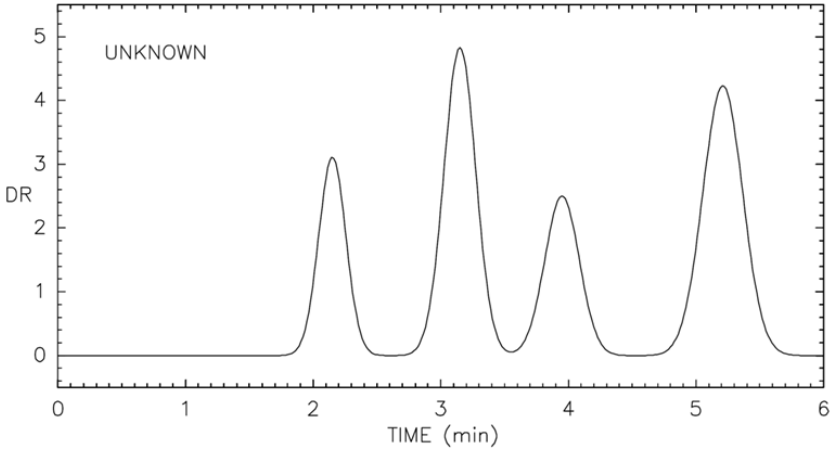


Figure A-4

Exercise 14.28

An internal standard is to be used for quantitative analysis in LC. 0.50 mL of 1.00×10^{-3} M internal standard is added to 4.50 mL of sample, giving mixture one. A 20 µL injection of mixture one produces areas of 35.4 (arbitrary units) for the internal standard and 15.5 for the unknown. 1.00 mL of the internal standard is added to 9.00 mL of a 1.00×10^{-2} M solution of the unknown to form mixture two. 0.20 mL of mixture two are added to 1.00 mL of mixture one to form mixture three. A 20 µL injection of mixture three produces areas of 31.9 for the internal standard and 42.6 for the unknown. What is the concentration of unknown in the original sample?

14.20 Answers to Exercises 14

14.1 89%

14.2 40

14.3 B

14.4 K=0; it travels with the same velocity as the mobile phase

14.5 This is the time it takes the mobile phase to move through the column. No.

14.6 A = 1, B ≅ 3.5

14.7 2 min, 5min; all eluting compounds spend the same time in the mobile phase (t_m)

14.8 $k'=(t_r - t_m) / t_m$; $k_A' = 0$, $k_B' = 2.5$

14.9 0.35 min ± ? (depends on your confidence in reading the graph)

14.10 10.8

14.11 45.2 and 58.4 mL

14.12 20.9 mL

14.13 1.22×10^3, 9.00

14.14 155 and 4.21

14.15 830

14.16 45 cm

14.17 16.1 s

14.18 2*s*, DR = 0.607*h*

14.19 5.65×10^4, 0.0884 cm

14.20 0.0010 cm, 0.040 cm, 0.050 cm, 6.22 s, 13.2 s, 4.92 s, 10.52, 10.73, and 10.16

14.21 A = 0.0202 cm, B = 0.799 cm^2/sec, C = 0.00498 sec, F = 50.7 mL/min, V_r = 192.5 mL, and t_r = 3.80 min

14.22 5.91 mL/min, 0.112 cm, 2670, 17.0 min, 8.50 min, 4.25 min

14.23 2,2'-, 2,4'-, and 4,4'-DCB

14.24 2,3-DMB, 3-MP, and H

14.25 0.329 mol/L

14.26 A, D

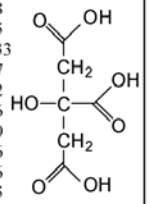
14.27 2.90×10^{-5} M

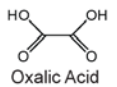
14.28 7.52×10^{-4} M

Table of Acid Dissociation Constants

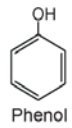
Acid	Formula	pK_a
Acetic acid	CH_3COOH	4.76
Arsenic acid	H_3AsO_4	2.22
		6.98
		11.50
Arsenious acid	H_3AsO_3	9.29
Benzoic acid	C_6H_5COOH	4.21
Butanoic acid	C_3H_7COOH	4.98
Carbonic acid	H_2CO_3	6.35
		10.33
Chloroacetic acid	$ClCH_2COOH$	2.87
Citric acid	$C_3H_5O(COOH)_3$	3.12
		4.76
		6.40
Cyanic acid	HOCN	3.66
Dichloroacetic acid	$Cl_2CHCOOH$	1.26
Formic acid	HCOOH	3.75
Hydrazoic acid	HN_3	4.73
Hydrocyanic acid	HCN	9.21
Hydrofluoric acid	HF	3.17
Hydrogen peroxide	HOOH	11.65
Hydrogen sulfide	H_2S	7.02
		13.9
Hypobromous acid	HOBr	8.60
Hypochlorous acid	HOCl	7.53
Hypoiodous acid	HOI	10.64
Maleic acid	HOOCCH=CHCOOH	1.92
		6.22
Malonic acid	$HOOCCH_2COOH$	2.85
		5.70
Nitrous acid	HNO_2	3.29
Oxalic acid	HOOCCOOH	1.27
		4.27


Benzoic Acid


Citric Acid


Oxalic Acid

Phenol	C_6H_5OH	9.98
Phosphoric acid	H_3PO_4	2.15
		7.20
		12.15
Propanoic acid	CH_3CH_2COOH	4.87
Succinic acid	$HOOCCH_2CH_2COOH$	4.21
		5.64
Sulfuric acid	H_2SO_4	∞
		1.99
Tartaric acid	HOOCCH(OH)CH(OH)COOH	3.04
Trichloroacetic acid	Cl_3CCOOH	0.66


Phenol

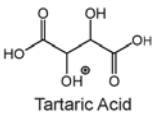
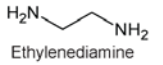
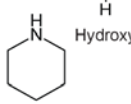

Tartaric Acid

Table of Base Dissociation Constants

Base	Formula	pK_b
Ammonia	NH_3	4.76
Aniline	$C_6H_5NH_2$	9.40
Cyclohexylamine	$C_6H_{11}NH_2$	3.36
Dimethylamine	$(CH_3)_2NH$	3.23
Ethylamine	$C_2H_5NH_2$	3.37
Ethylenediamine	$NH_2CH_2CH_2NH_2$	4.07
		7.15
Hydrazine	H_2NNH_2	5.77
Hydroxylamine	$HONH_2$	8.04
Methylamine	CH_3NH_2	3.38
Piperidine	$C_5H_{10}NH$	2.88
Propylamine	$C_3H_7NH_2$	3.43
Pyridine	C_5H_5N	8.78
Pyrrolidine	C_4H_8NH	2.69
Triethanolamine	$(HOC_2H_4)_3N$	6.24
Trimethylamine	$(CH_3)_3N$	4.20


Ethylenediamine


Hydroxylamine


Piperidine

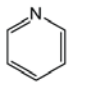

Pyridine

Table of t-values for Various Confidence Intervals and Degrees of Freedom (Two-Tailed)

Degrees of Freedom	Confidence Interval 80%	90%	95%	98%	99%
1	3.078	6.314	12.706	31.821	63.657
2	1.886	2.920	4.303	6.965	9.925
3	1.638	2.353	3.182	4.541	5.841
4	1.533	2.132	2.776	3.747	4.604
5	1.476	2.015	2.571	3.365	4.032
6	1.440	1.943	2.447	3.143	3.707
7	1.415	1.895	2.365	2.998	3.499
8	1.397	1.860	2.306	2.896	3.355
9	1.383	1.833	2.262	2.821	3.250
10	1.372	1.812	2.228	2.764	3.169
∞	1.282	1.645	1.960	2.326	2.576

Table of Critical Values for *Q* and Grubbs' Tests

Number of Observations	Q_{crit} 90%	95%	99%	G_{crit} 90%	95%	99%
3	0.941	0.970	0.994	1.153	1.154	1.155
4	0.765	0.829	0.926	1.463	1.481	1.496
5	0.642	0.710	0.821	1.671	1.715	1.764
6	0.560	0.625	0.740	1.822	1.887	1.973
7	0.507	0.568	0.680	1.938	2.020	2.139
8	0.468	0.526	0.634	2.032	2.127	2.274
9	0.437	0.493	0.598	2.110	2.215	2.387
10	0.412	0.466	0.568	2.176	2.290	2.482

Table of Standard Reduction Potentials

Half-Reaction	Standard Potential (V)
$Ag^+ + e^- \rightarrow Ag$	+0.799
$AgBr(s) + e^- \rightarrow Ag + Br^-$	+0.071
$AgCl(s) + e^- \rightarrow Ag + Cl^-$	+0.222
	+0.197 (sat'd KCl)
$AgI(s) + e^- \rightarrow Ag + I^-$	−0.152
$H_3AsO_4 + 2\,H^+ + 2\,e^- \rightarrow H_3AsO_3 + H_2O$	+0.559
$H_3AsO_3 + 3\,H^+ + 3\,e^- \rightarrow As + 3\,H_2O$	+0.248
$BiO^+ + 2\,H^+ + 3\,e^- \rightarrow Bi + H_2O$	+0.32
$BiOCl(s) + 2\,H^+ + 3\,e^- \rightarrow Bi + H_2O + Cl^-$	+0.160
$Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-$	+1.087
$Br_2^- + 2\,e^- \rightarrow 3\,Br^-$	+1.051
$BrO^- + H_2O + 2\,e^- \rightarrow Br^- + 2\,OH^-$	+0.76
$2\,CO_2(g) + 2\,H^+ + 2\,e^- \rightarrow H_2C_2O_4$	−0.49
$Cd^{2+} + 2\,e^- \rightarrow Cd$	−0.402
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.70 (1 F $HClO_4$)
	+1.60 (1 F HNO_3)
	+1.44 (1 F H_2SO_4)
	+1.28 (1 F HCl)
$Cl_2(aq) + 2\,e^- \rightarrow 2\,Cl^-$	+1.395
$HClO + H^+ + e^- \rightarrow \frac{1}{2}\,Cl_2(g) + H_2O$	+1.63
$Co^{2+} + 2\,e^- \rightarrow Co$	−0.277
$Cr^{3+} + 2\,e^- \rightarrow Cr^{2+}$	−0.91
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$CrO_4^{2-} + 4\,H_2O + 3\,e^- \rightarrow Cr(OH)_3(s) + 5\,OH^-$	−0.13
$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$	+1.33
$Cu^{2+} + 2\,e^- \rightarrow Cu$	+0.337
$Cu^+ + e^- \rightarrow Cu$	+0.518
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.159
$F_2 + 2\,e^- \rightarrow 2\,F^-$	+2.87
$Fe^{2+} + 2\,e^- \rightarrow Fe$	−0.440
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
	+0.732 (1 F HCl)
	+0.68 (1 F H_2SO_4)
$2\,H^+ + 2\,e^- \rightarrow H_2$	+0.0000
$Hg^{2+} + 2\,e^- \rightarrow Hg$	+0.854
$Hg_2^{2+} + 2\,e^- \rightarrow 2\,Hg$	+0.792
$2\,Hg^{2+} + 2\,e^- \rightarrow Hg_2^{2+}$	+0.907
$Hg_2Br_2(s) + 2\,e^- \rightarrow 2\,Hg + 2\,Br^-$	+0.139
$Hg_2Cl_2(s) + 2\,e^- \rightarrow 2\,Hg + 2\,Cl^-$	+0.268
	+0.242 (sat'd KCl)
$Hg_2I_2(s) + 2\,e^- \rightarrow 2\,Hg + 2\,I^-$	−0.040
$Hg_2SO_4(s) + 2\,e^- \rightarrow 2\,Hg + SO_4^{2-}$	+0.614
$I_2(aq) + 2\,e^- \rightarrow 2\,I^-$	+0.622
$I_3^- + 2\,e^- \rightarrow 3\,I^-$	+0.536
$HOI + H^+ + 2\,e^- \rightarrow I^- + H_2O$	+0.99
$IO_3^- + 6\,H^+ + 5\,e^- \rightarrow \frac{1}{2}\,I_2 + 3\,H_2O$	+1.178
$Mn^{2+} + 2\,e^- \rightarrow Mn$	−1.182
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.542
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.558
$MnO_4^- + 4\,H^+ + 3\,e^- \rightarrow MnO_2(s) + 2\,H_2O$	+1.69
$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$	+1.51
$MoO_4^{2-} + 4\,H_2O + 6\,e^- \rightarrow Mo + 8\,OH^-$	−1.05
$N_2(g) + 2\,H_2O + 4\,H^+ + 2\,e^- \rightarrow 2\,NH_3OH^+$	−1.87
$N_2H_5^+ + 3\,H^+ + 2\,e^- \rightarrow 2\,NH_4^+$	+1.275
$NO_3^- + 3\,H^+ + 2\,e^- \rightarrow HNO_2 + H_2O$	+0.94
$NO_3^- + 4\,H^+ + 3\,e^- \rightarrow NO(g) + 2\,H_2O$	+0.96
$HNO_2 + H^+ + e^- \rightarrow NO(g) + H_2O$	+1.00
$Ni^{2+} + 2\,e^- \rightarrow Ni$	−0.231
$O_2(g) + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$	+0.682
$O_2(g) + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$	+1.229
$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$	+1.776
$OsO_4(s) + 8\,H^+ + 8\,e^- \rightarrow Os + 4\,H_2O$	+0.85
$Pb^{2+} + 2\,e^- \rightarrow Pb$	−0.126
$PbSO_4(s) + 2\,e^- \rightarrow Pb + SO_4^{2-}$	−0.355
$PbO_2(s) + SO_4^{2-} + 4\,H^+ + 2\,e^- \rightarrow PbSO_4(s) + 2\,H_2O$	+1.685
$S(s) + 2\,H^+ + 2\,e^- \rightarrow H_2S(aq)$	+0.141
$SO_4^{2-} + 4\,H^+ + 2\,e^- \rightarrow SO_2(g) + 2\,H_2O$	+0.17
$SO_4^{2-} + H_2O + 2\,e^- \rightarrow SO_3^{2-} + 2\,OH^-$	−0.93
$S_4O_6^{2-} + 2\,e^- \rightarrow 2\,S_2O_3^{2-}$	+0.09
$SbO_3^- + H_2O + 2\,e^- \rightarrow SbO_2^- + 2\,OH^-$	−0.589 (10 F NaOH)
$H_3SbO_4 + 2\,H^+ + 2\,e^- \rightarrow H_3SbO_3 + H_2O$	+0.75
$SbO_2^- + 2\,H_2O + 3\,e^- \rightarrow Sb + 4\,OH^-$	+0.675 (10 F NaOH)
$SbO^+ + 2\,H^+ + 3\,e^- \rightarrow Sb + H_2O$	+0.212
$Sn^{2+} + 2\,e^- \rightarrow Sn$	−0.136
$Sn^{4+} + 2\,e^- \rightarrow Sn^{2+}$	+0.154
	+0.140 (1 F HCl)
$Ti^{2+} + 2\,e^- \rightarrow Ti$	−1.630
$Ti^{3+} + e^- \rightarrow Ti^{2+}$	−0.368
$TiO^{2+} + 2\,H^+ + e^- \rightarrow Ti^{3+} + H_2O$	+0.100
$Tl^+ + e^- \rightarrow Tl$	−0.336
$Tl^{3+} + 2\,e^- \rightarrow Tl^+$	+1.28
$TlCl(s) + e^- \rightarrow Tl + Cl^-$	−0.557
$U^{3+} + 3\,e^- \rightarrow U$	−1.80
$U^{4+} + e^- \rightarrow U^{3+}$	−0.61
$UO_2^{2+} + 4\,H^+ + 2\,e^- \rightarrow U^{4+} + 2\,H_2O$	+0.334
$V^{2+} + 2\,e^- \rightarrow V$	−1.18
$V^{3+} + e^- \rightarrow V^{2+}$	−0.255
$VO^{2+} + 2\,H^+ + e^- \rightarrow V^{3+} + H_2O$	+0.337
$VO_2^+ + 2\,H^+ + e^- \rightarrow VO^{2+} + H_2O$	+1.000
$Zn^{2+} + 2\,e^- \rightarrow Zn$	−0.763