LECTURE – 1

Introduction to Analytical Chemistry

1.1 Types of analytical chemistry & their uses .
1.2 Classifying Analytical Techniques.
1.3 Quantitative Analysis Methods.
1.4 Applications of Analytical Chemistry.
1.5 Units For Expressing Concentration of Solutions.
1.6 P - Functions.
1.7 Stoichiometric Calculation.
1.8 Preparing Solutions.
1.9 Basic Tools and operations of Analytical Chemistry.

1.1 Types of analytical chemistry & their uses .

Everything is made of chemicals. Analytical chemistry determine what and how much. In other words analytical chemistry is concerned with the separation, identification, and determination of the relative amounts of the components making up a sample.

Analytical chemistry is concerned with the chemical characterization of matter and the answer to two important questions what is it (qualitative) and how much is it (quantitative).

Analytical chemistry answering for basic questions about a material sample:

- What?
- Where?
- How much?
- What arrangement, structure or form?

Qualitative analysis: An analysis in which we determine the identity of the constituent species (the elements and compounds) in a sample.

Quantitative analysis: An analysis in which we determine how much of a constituent species is present in a sample.

Analytes: Are the components of a sample that are to be determined.

1.2 Classifying Analytical Techniques

A- *Classical techniques*

Mass, volume, and charge are the most common signals for classical techniques, and the corresponding techniques are:

1- Gravimetric techniques.
2- Volumetric techniques.
3- Coulometeric techniques.

B- *Instrumental techniques*

1- Spectroscopic methods - measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).
2- Electroanalytic methods - measure an electrical property (i.e., potential, current, resistance, amperes,etc.) chemically related to the amount of analyte.

1.3 Quantitative Analytical Methods

We compute the results of a typical quantitative analysis from two measurements.One is the mass or the volume of samole being analyzed. The second is the measurement of some quantity that is proportional to the amount of analyte in the sample such as mass, volume, intensity of light, or electrical charge. This second measurement usually completes the analysis, and we classify analytical methods according to the nature of this final measurement. Gravimetric methods determine the mass of analyte or some compound chemically related to it. In a volumetric method, the volume of a solution containing sufficient reagent to react completely with the analyte is measured. Electrochemical methods involve the measurement of such electrical properties as potential,current,resistance, and quantity of electrical charge. Spectroscopic methods are based on measurement of the interaction between electromagnetic radiation and analyte atoms or molecules or on the production of such radiation by analytes. Finally, a group of miscellaneous methods includes the measurement of such quantities as mass – to -charge ratio of molecules by mass spectrometry , rate of radioactive decay, heat of reaction,rate of reaction,simple thermal conductivity,optical activity,and refractive index.

1.4 Applications of Analytical Chemistry

Analytical chemistry used in many fields:

1, In *medicine*, analytical chemistry is the basis for clinical laboratory tests which help physicians diagnosis disease and chart progress in recovery.

2. In *industry*, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished products whose chemical composition is critical.Many household products, fuels, paints,Pharmaceutical, etc. are analysed by the procedures developed by analytical chemists before being sold to the consumer.

3. *Environmental quality* is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.

4. The nutritional value of *food* is determined by chemical analysis for major components such as protein and carbohydrates and trace components such as vitamins and minerals. Indeed, even the calories in a food are often calculated from the chemical analysis.

5. *Forensic analysis* - analysis related to criminology; DNA finger printing, finger print detection; blood analysis.

6. *Bioanalytical chemistry and analysis* - detection and/or analysis of biological components (i.e., proteins, DNA, RNA, carbohydrates, metabolites, etc.).

7. in pharmacy sciences:

· Pharmaceutical chemistry.

· Pharmaceutical industry (quality control).

· Analytical toxicology is concerned with the detection, identification and measurement of drugs and other foreign compounds (and their metabolites in biological and related specimens.

· Natural products detection, isolation, and structural determination.

Many chemists,biochemists, and medicinal chemists devote much time in the

laboratory gathering quantitative information about systems that are important and interesting to them. The central role of analytical chemistry in this enterprise and many others is illustrated in Figure 1-1. All branches of chemistry draw on the ideas and techniques of analytical chemistry. Analytical chemistry has a similar sunction with respect to the many other scientific fields listed in the diagram. Chemistry is often called the central science ; its top center position and the central position of analytical chemistry in the figure emphasize this importance.The interdisciplinary nature of chemical analysis makes it a vital tool in medical, industrial, government, and academic laboratories throughout the world.

Figure 1-1 The relationship between analytical chemistry, other branches of chemistry, and the other sciences. The central location of analytical chemistry in the diagram signifies its importance and the breadth of its interactions with many other disciplines.

1.5 Units For Expressing Concentration Of Solutions

Concentration is a general measurement unit stating the amount of solute present in a known amount of solution

$$\text{Concentration} = \frac{\text{amount of solute}}{\text{amount of solution}} \qquad \textbf{2.1}$$

Although the terms "solute" and "solution" are often associated with liquid samples, they can be extended to gas-phase and solid-phase samples as well. The actual units for reporting concentration depend on how the amounts of solute and solution are measured. Table 2.4 lists the most common units of concentration.

1.5.1 Molarity and Formality

Both molarity and formality express concentration as moles of solute per liter of solution. There is, however, a subtle difference between molarity and formality. **Molarity** is the concentration of a particular chemical species in solution. **Formality,** on the other hand, is a substance's total concentration in solution without regard to its specific chemical form. There is no difference between a substance's molarity and formality if it dissolves without dissociating into ions. The molar concentration of a solution of glucose, for example, is the same as its formality.

For substances that ionize in solution, such as NaCl, molarity and formality are different. For example, dissolving 0.1 mol of NaCl in 1 L of water gives a solution containing 0.1 mol of Na^+ and 0.1 mol of Cl^-. The molarity of NaCl, therefore, is zero since there is essentially no undissociated NaCl in solution. The solution,

Table 1.1 Common Units For Reporting Concentration

Name	Units[a]	Symbol
molarity	$\frac{\text{moles solute}}{\text{liters solution}}$	M
formality	$\frac{\text{number FWs solute}}{\text{liters solution}}$	F
normality	$\frac{\text{number EWs solute}}{\text{liters solution}}$	N
molality	$\frac{\text{moles solute}}{\text{kg solvent}}$	*m*
weight %	$\frac{\text{g solute}}{\text{100 g solution}}$	% w/w
volume %	$\frac{\text{mL solute}}{\text{100 mL solution}}$	% v/v
weight-to-volume %	$\frac{\text{g solute}}{\text{100 mL solution}}$	% w/v
parts per million	$\frac{\text{g solute}}{10^6\ \text{g solution}}$	ppm
parts per billion	$\frac{\text{g solute}}{10^9\ \text{g solution}}$	ppb

[a] FW = formula weight; EW = equivalent weight.

instead, is 0.1 M in Na^+ and 0.1 M in Cl^-. The formality of NaCl, however, is 0.1 F because it represents the total amount of NaCl in solution. The rigorous definition of molarity, for better or worse, is largely ignored in the current literature, as it is in this text. When we state that a solution is 0.1 M NaCl we understand it to consist of Na^+ and Cl^- ions. The unit of formality is used only when it provides a clearer description of solution chemistry.

Molar concentrations are used so frequently that a symbolic notation is often used to simplify its expression in equations and writing. The use of square brackets around a species indicates that we are referring to that species' molar concentration. Thus, $[Na^+]$ is read as the "molar concentration of sodium ions."

1.5.2 Normality

Normality is an older unit of concentration that, although once commonly used, is frequently ignored in today's laboratories. Normality is still used in some handbooks of analytical methods, and, for this reason, it is helpful to understand its meaning. For example, normality is the concentration unit used in *Standard Methods for the Examination of Water and Wastewater,*[1] a commonly used source of analytical methods for environmental laboratories.

Normality makes use of the chemical equivalent, which is the amount of one chemical species reacting stoichiometrically with another chemical species. Note that this definition makes an equivalent, and thus normality, a function of the chemical reaction in which the species participates. Although a solution of H_2SO_4 has a fixed molarity, its normality depends on how it reacts.

The number of **equivalents,** n, is based on a reaction unit, which is that part of a chemical species involved in a reaction. In a precipitation reaction, for example, the reaction unit is the charge of the cation or anion involved in the reaction; thus for the reaction

$$Pb^{2+}(aq) + 2I^-(aq) \rightleftharpoons PbI_2(s)$$

$n = 2$ for Pb^{2+} and $n = 1$ for I^-. In an acid–base reaction, the reaction unit is the number of H^+ ions donated by an acid or accepted by a base. For the reaction between sulfuric acid and ammonia

$$H_2SO_4(aq) + 2NH_3(aq) \rightleftharpoons 2NH_4^+(aq) + SO_4^{2-}(aq)$$

we find that $n = 2$ for H_2SO_4 and $n = 1$ for NH_3. For a complexation reaction, the reaction unit is the number of electron pairs that can be accepted by the metal or donated by the ligand. In the reaction between Ag^+ and NH_3

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

the value of n for Ag^+ is 2 and that for NH_3 is 1. Finally, in an oxidation–reduction reaction the reaction unit is the number of electrons released by the reducing agent or accepted by the oxidizing agent; thus, for the reaction

$$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons Sn^{4+}(aq) + 2Fe^{2+}(aq)$$

$n = 1$ for Fe^{3+} and $n = 2$ for Sn^{2+}. Clearly, determining the number of equivalents for a chemical species requires an understanding of how it reacts.

Normality is the number of **equivalent weights** (EW) per unit volume and, like formality, is independent of speciation. An equivalent weight is defined as the ratio of a chemical species' **formula weight** (FW) to the number of its equivalents

$$EW = \frac{FW}{n}$$

Consequently, the following simple relationship exists between normality and molarity.

$$N = n \times M$$

Example 2.1 illustrates the relationship among chemical reactivity, equivalent weight, and normality.

Example 1.1

- Calculate the equivalent weight and normality for a solution of 6.0 M H_3PO_4 given the following reactions:

(a) $H_3PO_4(aq) + 3OH^-(aq) \rightleftharpoons PO_4^{3-}(aq) + 3H_2O(\ell)$

(b) $H_3PO_4(aq) + 2NH_3(aq) \rightleftharpoons HPO_4^{2-}(aq) + 2NH_4^+(aq)$

(c) $H_3PO_4(aq) + F^-(aq) \rightleftharpoons H_2PO_4^-(aq) + HF(aq)$

SOLUTION

For phosphoric acid, the number of equivalents is the number of H^+ ions donated to the base. For the reactions in (a), (b), and (c) the number of equivalents are 3, 2, and 1, respectively. Thus, the calculated equivalent weights and normalities are

(a) $EW = \frac{FW}{n} = \frac{97.994}{3} = 32.665 \qquad N = n \times M = 3 \times 6.0 = 18\ N$

(b) $EW = \frac{FW}{n} = \frac{97.994}{2} = 48.997 \qquad N = n \times M = 2 \times 6.0 = 12\ N$

(c) $EW = \frac{FW}{n} = \frac{97.994}{1} = 97.994 \qquad N = n \times M = 1 \times 6.0 = 6.0\ N$

1.5.3 Molality

Molality is used in thermodynamic calculations where a temperature independent unit of concentration is needed. Molarity, formality and normality are based on the volume of solution in which the solute is dissolved. Since density is a temperature dependent property a solution's volume, and thus its molar, formal and normal concentrations, will change as a function of its temperature. By using the solvent's mass in place of its volume, the resulting concentration becomes independent of temperature.

LECTURE – 2

1.5.4 Converting Weight, Volume, and Weight – to – Volume Ratios

Weight percent (% w/w), **volume percent** (% v/v) and **weight-to-volume percent** (% w/v) express concentration as units of solute per 100 units of sample. A solution in which a solute has a concentration of 23% w/v contains 23 g of solute per 100 mL of solution.

Parts per million (ppm) and **parts per billion** (ppb) are mass ratios of grams of solute to one million or one billion grams of sample, respectively. For example, a steel that is 450 ppm in Mn contains 450 μg of Mn for every gram of steel. If we approximate the density of an aqueous solution as 1.00 g/mL, then solution concentrations can be expressed in parts per million or parts per billion using the following relationships.

$$\text{ppm} = \frac{\text{mg}}{\text{liter}} = \frac{\mu\text{g}}{\text{mL}}$$

$$\text{ppb} = \frac{\mu\text{g}}{\text{liter}} = \frac{\text{ng}}{\text{mL}}$$

For gases a part per million usually is a volume ratio. Thus, a helium concentration of 6.3 ppm means that one liter of air contains 6.3 μL of He.

1.5.5 Converting Between Concentration Units

The units of concentration most frequently encountered in analytical chemistry are molarity, weight percent, volume percent, weight-to-volume percent, parts per million, and parts per billion. By recognizing the general definition of concentration given in equation 2.1, it is easy to convert between concentration units.

Example 1.2

A concentrated solution of aqueous ammonia is 28.0% w/w NH_3 and has a density of 0.899 g/mL. What is the molar concentration of NH_3 in this solution?

SOLUTION

$$\frac{28.0\ \text{g NH}_3}{100\ \text{g solution}} \times \frac{0.899\ \text{g solution}}{\text{mL solution}} \times \frac{1\ \text{mole NH}_3}{17.04\ \text{g NH}_3} \times \frac{1000\ \text{mL}}{\text{liter}} = 14.8\ \text{M}$$

Example 1.3

- The maximum allowed concentration of chloride in a municipal drinking water supply is 2.50×10^2 ppm Cl^-. When the supply of water exceeds this limit, it often has a distinctive salty taste. What is this concentration in moles Cl^-/liter?

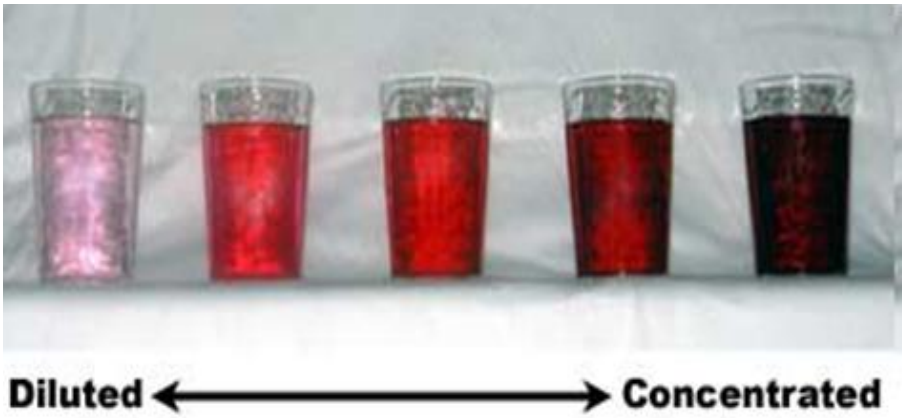
SOLUTION

$$\frac{2.50 \times 10^2\ \text{mg Cl}^-}{\text{L}} \times \frac{1\ \text{g}}{1000\ \text{mg}} \times \frac{1\ \text{mole Cl}^-}{35.453\ \text{g Cl}^-} = 7.05 \times 10^{-3}\ \text{M}$$

Concentration of Solutions

Remember:

- Solution – A mixture of a solute and a solvent
- Solvent – The liquid in which the solute is dissolved
- Solute – The substance that is dissolved in the solvent
- Dilute Solution – contains a small amount of solute per solvent
- Concentrated Solution – contains a large amount of solute per solvent
- Concentration – the amount of solute that is dissolved in a specific volume of solution
- In some solutions concentration can be indicated by colour intensity.
- The less intense the colour – dilute solution
- The more intense the colour – concentrated solution



1. % Weight per weight (% w/w)

- Mass per 100g
- Example:
  - 12% w/w means that there is 12g per 100g
  - Concentrated acid/base
  - % iron in iron tablets

- **Q: In a 125g solution, there is 22.5g of HCl. Express this concentration as %w/w.**

A: 22.5 ÷ 125 x 100 = 18% w/w

2. % Weight per volume (%w/v)

- Mass per 100cm^3
- Example:
  - 30% w/v means that there is 30g per 100cm^3
  - Saline solution – 0.91% w/v NaCl

- **Q: A 1.4% solution of $CaCl_2$ is required for an experiment. If you need 250cm^3 of this solution, how much $CaCl_2$ should be weighed out?**

A: 1.4 x 2.5 = 3.5g

3. % Volume per volume (%v/v)

- Volume per $100cm^3$
- Example:
    - 9% v/v contains $9cm^3$ per $100cm^3$
    - Concentration of alcohol in beverages

- **Q: Wine contains 14% v/v. If a person consumes a $40cm^3$ glass of wine, how much alcohol do they consume?**

  A: $14 \div 100 \times 40 = 5.6cm^3$

4. Parts per million (ppm)

- Number of milligrams per litre

- 1 ppm = 1mg per L (*remember 1000mg = 1g*)
- Used for very dilute solutions
- Example:
    - Concentrations of pollutants in water

- **Q: A sample of water is found to contain 0.003g of lead in a $250cm^3$ sample. What is the concentration of lead in ppm?**

  A: $0.003 \times 4 \times 1000 = 12$ppm

5. Molarity

- Number of moles per litre
- Most common method of expressing concentration
- 1M = 1 mol/litre = 1 mol l^{-1}
- A 1 Molar solution contains one mole of solute dissolved in 1 litre of solution

Q: A solution is labelled 0.15M HCl. How many grams of HCl are present in 1 litre?

A: M_r of HCl = 36.5g

1M solution contains 36.5g / l

0.15M solution = $36.5 \times 0.15 = 5.475$g

Q: A solution contains 4.9g H_2SO_4 in $100cm^3$.

Calculate the concentration in mol/l.

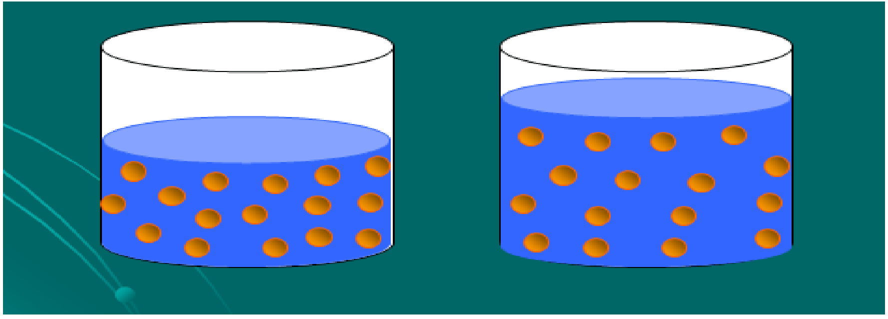
A: M_r of H_2SO_4 = 98g

$4.9 \div 98 = 0.05$mol in $100cm^3$

$0.05 \times 10 = 0.5$mol/l

Effect of Dilution on Concentration

- When a solution is diluted, more solvent is added.
- The quantity of solute remains unchanged.



- To calculate the effect of dilution on concentration:

$$\frac{V_{dil} \times M_{dil}}{1000} = \frac{V_{conc} \times M_{conc}}{1000}$$

- **Q: What volume of 18M HCl would be required to prepare 250cm^3 of 0.5M HCl?**

A: $$\frac{V_{dil} \times M_{dil}}{1000} = \frac{V_{conc} \times M_{conc}}{1000}$$

$$\frac{V_{conc} \times 18}{1000} = \frac{250 \times 0.5}{1000}$$

$$V_{conc} = \frac{250 \times 0.5}{}$$

$$V_{conc} = 6.94cm^3$$

1.6 P – Function

Sometimes it is inconvenient to use the concentration units in Table 2.4. For example, during a reaction a reactant's concentration may change by many orders of magnitude. If we are interested in viewing the progress of the reaction graphically, we might wish to plot the reactant's concentration as a function of time or as a function of the volume of a reagent being added to the reaction. Such is the case in Figure 2.1, where the molar concentration of H^+ is plotted (*y*-axis on left side of figure) as a function of the volume of NaOH added to a solution of HCl. The initial $[H^+]$ is 0.10 M, and its concentration after adding 75 mL of NaOH is 5.0×10^{-13} M. We can easily follow changes in the $[H^+]$ over the first 14 additions of NaOH. For the last ten additions of NaOH, however, changes in the $[H^+]$ are too small to be seen.

When working with concentrations that span many orders of magnitude, it is often more convenient to express the concentration as a **p-function.** The p-function of a number *X* is written as p*X* and is defined as

$$pX = -\log(X)$$

Thus, the pH of a solution that is 0.10 M H^+ is

$$pH = -\log[H^+] = -\log(0.10) = 1.00$$

and the pH of 5.0×10^{-13} M H^+ is

$$PH = -\log [H^+] = -\log(5.0\times10^{-13}) = 12.30$$

Figure 1.2 shows how plotting PH in place of $[H^+]$ provides more detail about how the concentration of H^+ changes following the addition of NaOH.

Example 1.4

What is pNa for a solution of 1.76×10^{-3} M Na_3PO_4?

SOLUTION

Since each mole of Na_3PO_4 contains three moles of Na^+, the concentration of Na^+ is

$$[Na^+] = \frac{3 \text{ mol } Na^+}{\text{mol } Na_3PO_4} \times 1.76 \times 10^{-3} \text{ M} = 5.28 \times 10^{-3} \text{ M}$$

and pNa is

$$pNa = -\log[Na^+] = -\log(5.28 \times 10^{-3}) = 2.277$$

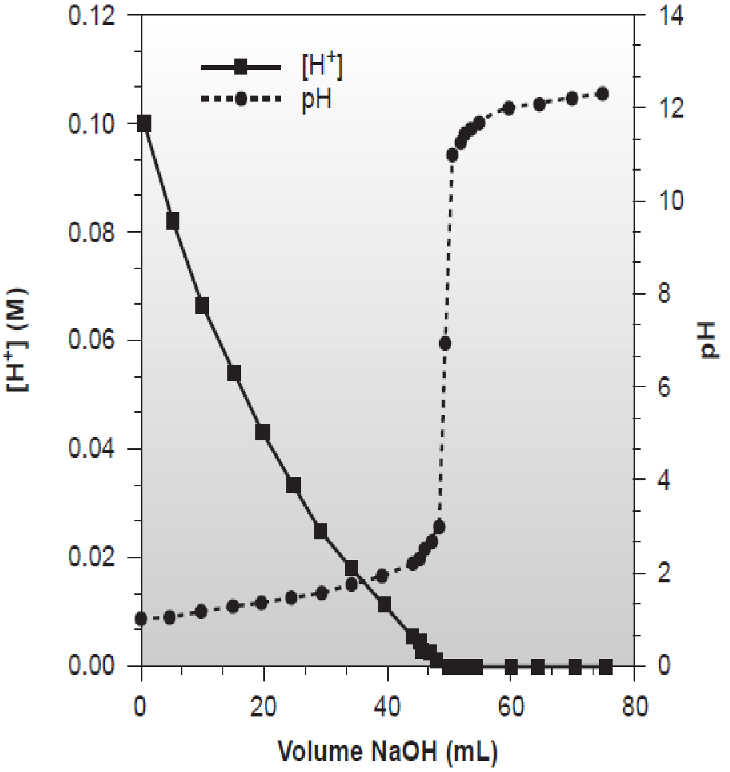


Figure 1.2 Graph of [H +] versus volume of NaOH and PH versus volume of NaOH for reaction of 0.10M HCl with 0.10M NaOH.

Example 1.5

What is the $[H^+]$ in a solution that has a pH of 5.16?

SOLUTION

The concentration of H^+ is

$$pH = -\log[H^+] = 5.16$$
$$\log[H^+] = -5.16$$
$$[H^+] = \text{antilog}(-5.16) = 10^{-5.16} = 6.9 \times 10^{-6} \text{ M}$$

1.7 Stoichiometric Calculation

A balanced chemical reaction indicates the quantitative relationships between the moles of reactants and products. These stoichiometric relationships provide the basis for many analytical calculations. Consider, for example, the problem of determining the amount of oxalic acid, $H_2C_2O_4$, in rhubarb. One method for this analysis uses the following reaction in which we oxidize oxalic acid to CO_2.

$$2Fe^{3+}(aq) + H_2C_2O_4(aq) + 2H_2O(\ell) \longrightarrow 2Fe^{2+}(aq) + 2CO_2(g) + 2H_3O^{+}(aq) \qquad \textbf{2.2}$$

The balanced chemical reaction provides the stoichiometric relationship between the moles of Fe^{3+} used and the moles of oxalic acid in the sample being analyzed—specifically, one mole of oxalic acid reacts with two moles of Fe^{3+}. As shown in Example 2.6, the balanced chemical reaction can be used to determine the amount of oxalic acid in a sample, provided that information about the number of moles of Fe^{3+} is known.

Example 1.6

- The amount of oxalic acid in a sample of rhubarb was determined by reacting with Fe^{3+} as outlined in reaction 2.2. In a typical analysis, the oxalic acid in 10.62 g of rhubarb was extracted with a suitable solvent. The complete oxidation of the oxalic acid to CO_2 required 36.44 mL of 0.0130 M Fe^{3+}. What is the weight percent of oxalic acid in the sample of rhubarb?

SOLUTION

We begin by calculating the moles of Fe^{3+} used in the reaction

$$\frac{0.0130 \text{ mol Fe}^{3+}}{\text{L}} \times 0.03644 \text{ L} = 4.737 \times 10^{-4} \text{ mol Fe}^{3+}$$

The moles of oxalic acid reacting with the Fe^{3+}, therefore, is

$$4.737 \times 10^{-4} \text{ mol Fe}^{3+} \times \frac{1 \text{ mol C}_2\text{H}_2\text{O}_4}{2 \text{ mol Fe}^{3+}} = 2.369 \times 10^{-4} \text{ mol C}_2\text{H}_2\text{O}_4$$

Converting moles of oxalic acid to grams of oxalic acid

$$2.369 \times 10^{-4} \text{ mol C}_2\text{H}_2\text{O}_4 \times \frac{90.03 \text{ g C}_2\text{H}_2\text{O}_4}{\text{mol C}_2\text{H}_2\text{O}_4} = 2.132 \times 10^{-2} \text{ g oxalic acid}$$

and converting to weight percent gives the concentration of oxalic acid in the sample of rhubarb as

$$\frac{2.132 \times 10^{-2} \text{ g C}_2\text{H}_2\text{O}_4}{10.62 \text{ g rhubarb}} \times 100 = 0.201\% \text{ w/w C}_2\text{H}_2\text{O}_4$$

1.8 Preparing Solutions

Preparing a solution of known concentration is perhaps the most common activity in any analytical lab. The method for measuring out the solute and solvent depend on the desired concentration units, and how exact the solution's concentration needs to be known. Pipets and volumetric flasks are used when a solution's concentration must be exact; graduated cylinders, beakers, and reagent bottles suffice when concentrations need only be approximate. Two methods for preparing solutions are described in this section.

1.8.1 Preparing Stock Solutions

A **stock solution** is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid and diluting to a known volume. Exactly how this is done depends on the required concentration units. For example, to prepare a solution with a desired molarity you would weigh out an appropriate mass of the reagent, dissolve it in a portion of solvent, and bring to the desired volume.

To prepare a solution where the solute's concentration is given as a volume percent, you would measure out an appropriate volume of solute and add sufficient solvent to obtain the desired total volume .

Example 1.7

Describe how you would prepare the following three solutions: (a) 500 mL of approximately 0.20 M NaOH using solid NaOH; (b) 1 L of 150.0 ppm Cu^{2+} using Cu metal; and (c) 2 L of 4% v/v acetic acid using concentrated glacial acetic acid.

SOLUTION

(a) Since the concentration only needs to be known to two significant figures, the mass of NaOH and volume of solution do not need to be measured exactly. The desired mass of NaOH is

$$\frac{0.20 \text{ mol}}{\text{L}} \times \frac{40.0 \text{ g}}{\text{mol}} \times 0.50 \text{ L} = 4.0 \text{ g}$$

To prepare the solution we place 4.0 g of NaOH, weighed to the nearest tenth of a gram, in a bottle or beaker and add approximately 500 mL of water.

(b) Since the concentration of Cu^{2+} needs to be exact, the mass of Cu metal and the final solution volume must be measured exactly. The desired mass of Cu metal is

$$\frac{150.0 \text{ mg}}{\text{L}} \times 1.000 \text{ L} = 150.0 \text{ mg} = 0.1500 \text{ g}$$

To prepare the solution we measure out exactly 0.1500 g of Cu into a small beaker. To dissolve the Cu we add a small portion of concentrated HNO_3 and gently heat until it completely dissolves. The resulting solution is poured into a 1-L volumetric flask. The beaker is rinsed repeatedly with small portions of water, which are added to the volumetric flask. This process, which is called a **quantitative transfer,** ensures that the Cu^{2+} is completely transferred to the volumetric flask. Finally, additional water is added to the volumetric flask's calibration mark.

(c) The concentration of this solution is only approximate, so volumes do not need to be measured exactly. The necessary volume of glacial acetic acid is

$$\frac{4 \text{ mL } CH_3COOH}{100 \text{ mL}} \times 2000 \text{ mL} = 80 \text{ mL } CH_3COOH$$

To prepare the solution we use a graduated cylinder to transfer 80 mL of glacial acetic acid to a container that holds approximately 2 L, and we then add sufficient water to bring the solution to the desired volume.

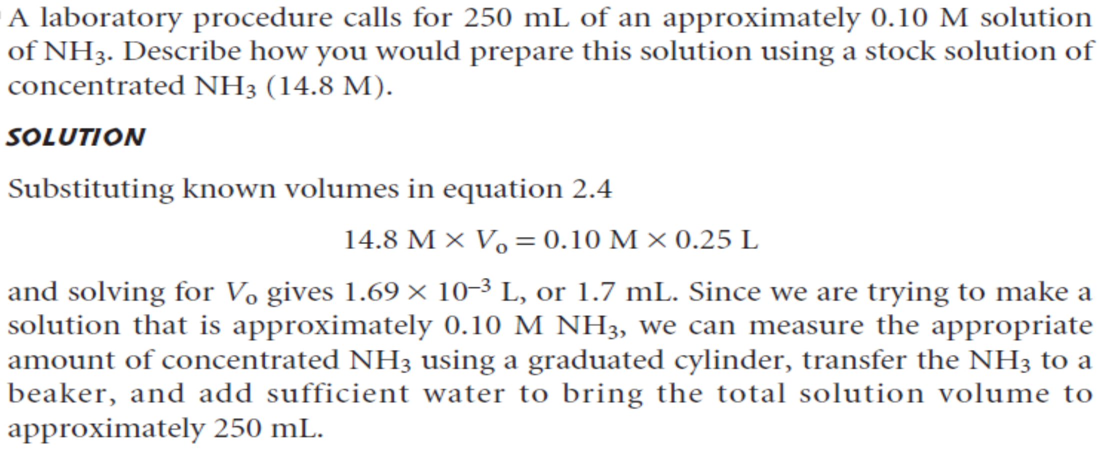
1.8.2 Preparing Solutions by Dilution

Solutions with small concentrations are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume. Since the total amount of solute is the same before and after **dilution,** we know that

$$C_o \times V_o = C_d \times V_d$$

where C_o is the concentration of the stock solution, V_o is the volume of the stock solution being diluted, C_d is the concentration of the dilute solution, and V_d is the volume of the dilute solution. Again, the type of glassware used to measure V_o and V_d depends on how exact the solution's concentration must be known

Example 1.8



A laboratory procedure calls for 250 mL of an approximately 0.10 M solution of NH_3. Describe how you would prepare this solution using a stock solution of concentrated NH_3 (14.8 M).

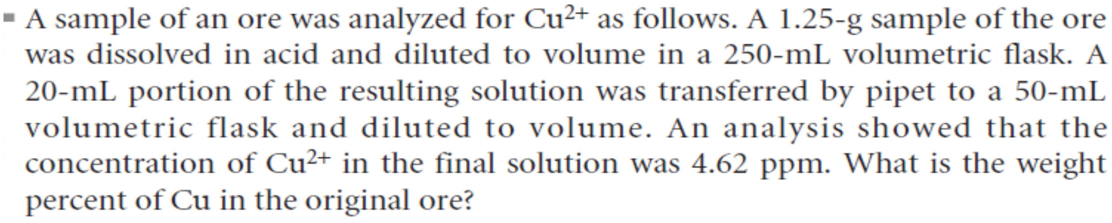
SOLUTION

Substituting known volumes in equation 2.4

$$14.8\ \text{M} \times V_o = 0.10\ \text{M} \times 0.25\ \text{L}$$

and solving for V_o gives 1.69×10^{-3} L, or 1.7 mL. Since we are trying to make a solution that is approximately 0.10 M NH_3, we can measure the appropriate amount of concentrated NH_3 using a graduated cylinder, transfer the NH_3 to a beaker, and add sufficient water to bring the total solution volume to approximately 250 mL.

Example 1.9



▪ A sample of an ore was analyzed for Cu^{2+} as follows. A 1.25-g sample of the ore was dissolved in acid and diluted to volume in a 250-mL volumetric flask. A 20-mL portion of the resulting solution was transferred by pipet to a 50-mL volumetric flask and diluted to volume. An analysis showed that the concentration of Cu^{2+} in the final solution was 4.62 ppm. What is the weight percent of Cu in the original ore?

SOLUTION

Substituting known volumes (with significant figures appropriate for pipets and volumetric flasks) into equation 2.4

$$(\text{ppm Cu}^{2+})_o \times 20.00 \text{ mL} = 4.62 \text{ ppm} \times 50.00 \text{ mL}$$

and solving for $(\text{ppm Cu}^{2+})_o$ gives the original solution concentration as 11.55 ppm. To calculate the grams of Cu^{2+} we multiply this concentration by the total volume

$$\frac{11.55\ \mu\text{g Cu}^{2+}}{\text{mL}} \times 250.0 \text{ mL} \times \frac{1 \text{ g}}{10^6\ \mu\text{g}} = 2.888 \times 10^{-3} \text{ g Cu}^{2+}$$

The weight percent Cu is then given by

$$\frac{2.888 \times 10^{-3} \text{ g Cu}^{2+}}{1.25 \text{ g sample}} \times 100 = 0.231\% \text{ w/w Cu}$$

1.9 Basic Tools and Operations of Analytical Chemistry

1.9.1 Basic Equipment

Measurements are made using appropriate equipment or instruments. The array of equipment and instrumentation used in analytical chemistry is impressive, ranging from the simple and inexpensive, to the complex and costly.

1.9.2 Equipments for Measuring Mass (Analytical Balance)

An object’s mass is measured using a **balance.** The most common type of balance is an in which the balance pan is placed over an electromagnet.
Another type of analytical balance is the ***mechanical balances*** which are replaced by the electronic balances. **electronic balance electronic balance.**

electronic balance

electronic balance

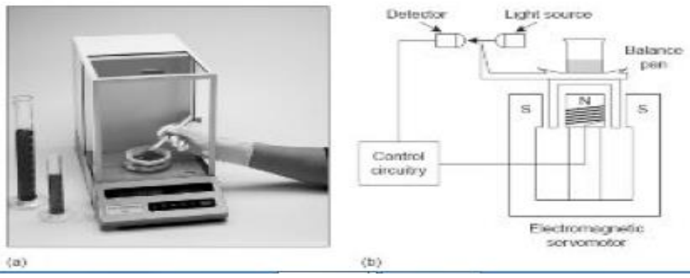
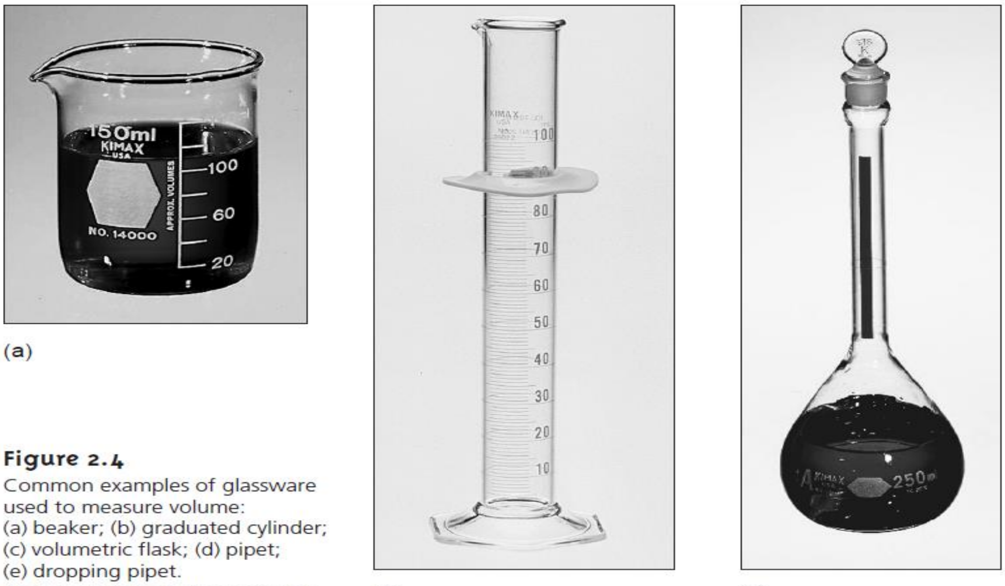


Figure 2.2
(a) Photo of a typical electronic balance.
(b) Schematic diagram of electronic balance; adding a sample moves the balance pan down, allowing more light to reach the detector. The control circuitry directs the electromagnetic servomotor to generate an opposing force, raising the sample up until the original intensity of light at the detector is restored.
Photo courtesy of Fisher Scientific.

1.9.2 Equipment for Measuring Volume

Analytical chemists use a variety of glassware to measure volume. The type of glassware used depends on how exact the volume needs to be.

Volumetric flask is designed to contain a specified volume of solution at a stated temperature, usually 20 °C.



(a)

(b)

(c)

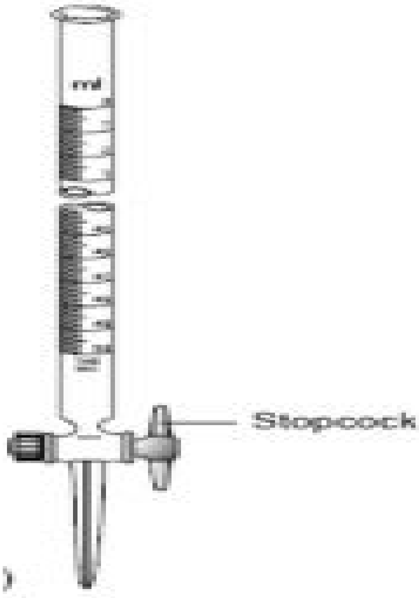
Figure 2.4
Common examples of glassware used to measure volume:
(a) beaker; (b) graduated cylinder;
(c) volumetric flask; (d) pipet;
(e) dropping pipet.
Photos courtesy of Fisher Scientific.

Pipette is used to deliver a specified volume of solution. Several different styles of

(a) (b) (c) (d)

Figure 2.5
Common types of pipets and syringes: (a) transfer pipet; (b) measuring pipet; (c) digital pipet; (d) syringe.
Photos courtesy of Fisher Scientific.

Burette is volumetric glassware used to deliver variable, but known volumes of solution. A burette is a long, narrow tube with graduated markings, and a stopcock for dispensing the solution.



1.9.3 Equipment for Drying

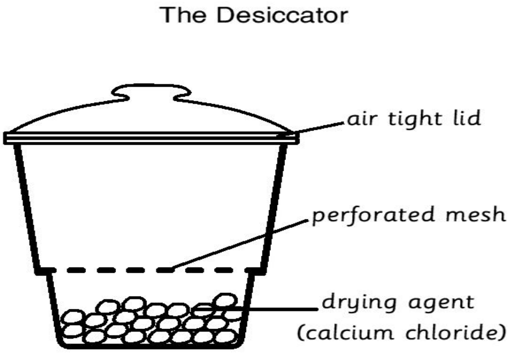
Reagents, precipitates, and glassware are conveniently dried in an oven at 110°C.Many materials need to be dried prior to their analysis to remove residual moisture.

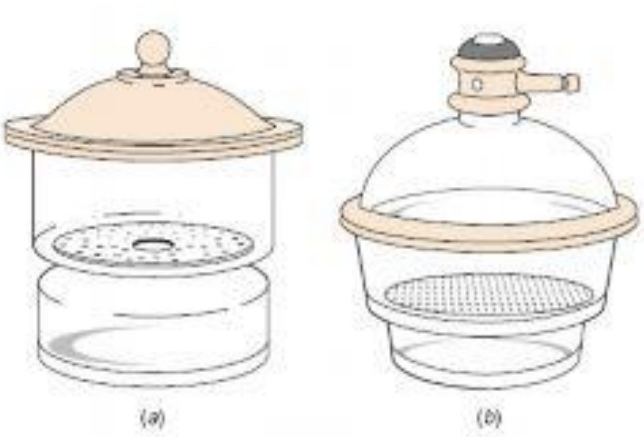
Depending on the material, heating to a temperature of 110–140 °C is usually sufficient. Other materials need to be heated to much higher temperatures to initiate thermal decomposition. Both processes can be accomplished using a ***laboratory oven*** capable of providing the required temperature. Commercial laboratory ovens are used when the maximum desired temperature is 160–325 °C (depending on the model). Higher temperatures, up to 1700° C, can be achieved using a muffle ***furnace***.

Conventional laboratory oven used for drying materials.

Example of a muffle furnace used for heating samples to maximum temperatures of 1100–1700 °C.

After drying or decomposing a sample, it should be cooled to room temperature in a desiccator to avoid the readsorption of moisture. A ***desiccator*** is a closed container that isolates the sample from the atmosphere. A drying agent, called a **desiccant,** is placed in the bottom of the container. Typical desiccants include calcium chloride and silica gel.

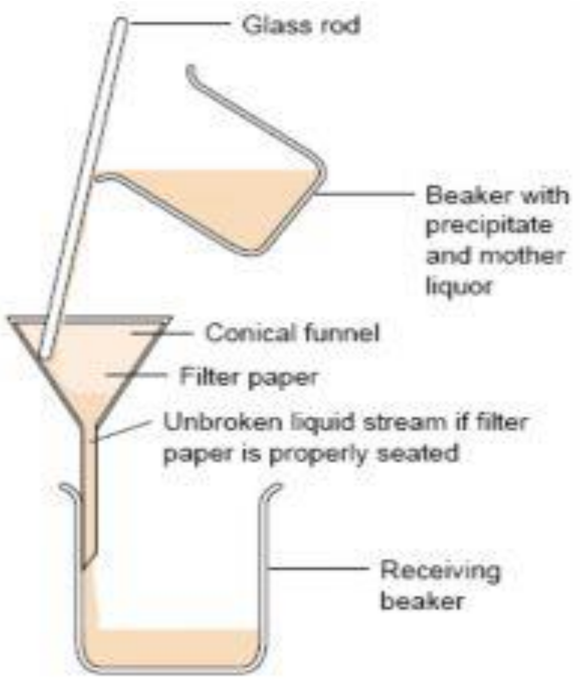




(a) Ordinary desiccator. (*b*) Vacuum desiccator

1.9.4 Filtration

In *gravimetric analysis*, the mass of product from a reaction is measured to determine how much unknown was present. Precipitates from gravimetric analyses are collected by filtration. Liquid from which a substance precipitates or crystallizes is called the **mother liquor**. Liquid that passes through the filter is called **filtrate**.

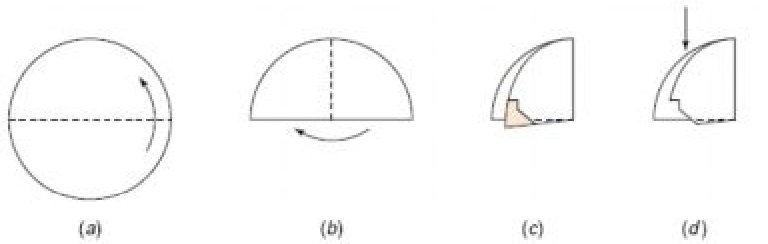


Filtering a precipitate.

The conical funnel is supported by a metal ring attached to a ring stand, neither of which is shown.

Folding filter paper for a conical funnel.

(*a*) Fold the paper in half.
(*b*) Then fold it in half again.
(*c*) Tear off a corner to allow better seating of the paper in the funnel.
(*d*) Open the side that was not torn when fitting the paper in the funnel.



LECTURE – 3

Chemical Equilibrium

2.1 Reversible Reactions and Chemical Equilibrium

2.2 Thermodynamics and Equilibrium Chemistry
2.3 Manipulating Equilibrium Constants
2.4 Equilibrium Constants for Chemical Reactions
2.4.1 Precipitation Reactions

1.1: Reversible Reactions and Chemical Equilibrium

For example, the following reaction :

$$Na_2CO_3(s) + CaCl_2(aq) \rightleftharpoons 2NaCl(aq) + CaCO_3(s)$$

Berthollet's reasoning that reactions are reversible was an important step in understanding chemical reactivity. When we mix together solutions of Na_2CO_3 and $CaCl_2$ they react to produce NaCl and $CaCO_3$. If during the reaction we monitor the mass of Ca^{2+} remaining in solution and the mass of $CaCO_3$ that precipitates, the result looks something like Figure 6.1.

At the start of the reaction the mass of Ca^{2+}decreases and the mass of $CaCO_3$ increases. Eventually the reaction reaches a point after which there is no further change in the amounts of these species. Such a condition is called a state of **equilibrium**.

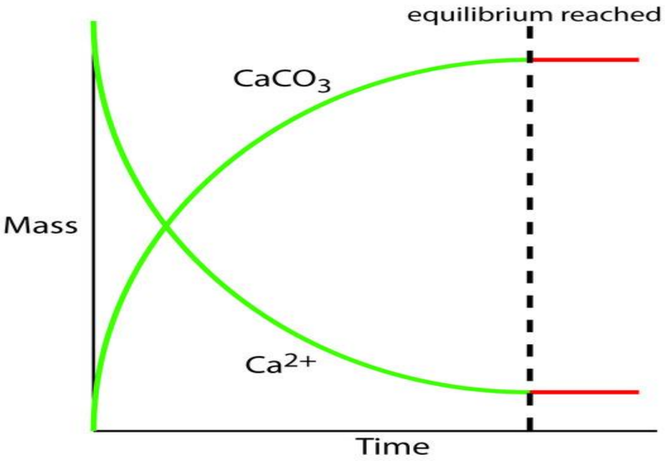


Figure 2.1 Graph showing how the masses of Ca^{2+} and $CaCO_3$ change as a function of time during the precipitation of $CaCO_3$. The dashed line indicates when the reaction reaches equilibrium. Prior to equilibrium the masses of Ca^{2+} and $CaCO_3$ are changing; after reaching equilibrium, their masses remain constant.

Although a system at equilibrium appears static on a macroscopic level, it is important to remember that the forward and reverse reactions continue to occur. A reaction at equilibrium exists in a **steady-state**, in which the rate at which a species forms equals the rate at which it is consumed.

2.2: Thermodynamics and Equilibrium Chemistry

Thermodynamics is the study of thermal, electrical, chemical, and mechanical forms of energy. The study of thermodynamics crosses many disciplines, including physics, engineering, and chemistry. Of the various branches of thermodynamics, the most important to chemistry is the study of the change in energy during a chemical reaction.

Consider, for example, the general equilibrium reaction shown in Equation 2.2.1, involving the species A, B, C, and D, with stoichiometric coefficients *a*, *b*, *c*, and *d*.

$$aA + bB \rightleftharpoons cC + dD \qquad (2.2.1)$$

NOTE : For obvious reasons, we call the double arrow, ⇋, an equilibrium arrow. By convention, we identify species on the left side of the equilibrium arrow as reactants, and those on the right side of the equilibrium arrow as products. As Berthollet discovered, writing a reaction in this fashion does not guarantee that the reaction of A and B to produce C and D is favorable. Depending on initial conditions, the reaction may move to the left, move to the right, or be in a state of equilibrium. Understanding the factors that determine the reaction’s final, equilibrium position is one of the goals of chemical thermodynamics.

The direction of a reaction is that which lowers the overall free energy. At a constant temperature and pressure, typical of many bench-top chemical reactions, a reaction’s free energy is given by the **Gibb’s free energy** function

$$\Delta G = \Delta H - T\Delta S \qquad (2.2.2)$$

where

- T is the temperature in Kelvin and
- ΔG, ΔH, and ΔS are the differences in the Gibb's free energy, the enthalpy, and the entropy between the products and the reactants.

Enthalpy is a measure of the flow of energy, as heat, during a chemical reaction. Reactions releasing heat have a negative ΔH and are called exothermic. Endothermic reactions absorb heat from their surroundings and have a positive ΔH.

Entropy is a measure of energy that is unavailable for useful, chemical work. The entropy of an individual species is always positive and tends to be larger for gases than for solids, and for more complex molecules than for simpler molecules. Reactions producing a large number of simple, gaseous products usually have a positive ΔS.

The sign of ΔG indicates the direction in which a reaction moves to reach its equilibrium position. A reaction is thermodynamically favorable when its enthalpy, ΔH, decreases and its entropy, ΔS, increases. Substituting the inequalities $\Delta H < 0$ and $\Delta S > 0$ into Equation 6.2.2 shows that a reaction is thermodynamically favorable when ΔG is negative. When ΔG is positive the reaction is unfavorable as written (although the reverse reaction is favorable). A reaction at equilibrium has a ΔG of zero.

NOTE : Equation 6.2.2 shows that the sign of ΔG depends on the signs of ΔH and ΔS, and the temperature, T. The following table summarizes the possibilities.

ΔH	ΔS	ΔG
-	+	$\Delta G < 0$ at all temperatures
-	-	$\Delta G < 0$ at low temperatures
+	+	$\Delta G < 0$ at low temperatures
+	-	$\Delta G > 0$ at all temperatures

As a reaction moves from its initial, non-equilibrium condition to its equilibrium position, the value of ΔG approaches zero. At the same time, the chemical species in the reaction experience a change in their concentrations. The Gibb's free energy, therefore, must be a function of the concentrations of reactants and products.

As shown in Equation 6.2.3, we can split the Gibb's free energy into two terms.

$$\Delta G = \Delta G^\circ + RT\ln Q \qquad (2.2.3)$$

The first term, ΔG^o, is the change in Gibb's free energy when each species in the reaction is in its **standard state**, which we define as follows: gases with partial pressures of 1 atm, solutes with concentrations of 1 mol/L, and pure solids and pure liquids. The second term, which includes the reaction quotient, Q, accounts for non-standard state pressures or concentrations. For reaction 6.2.1, the reaction quotient is

$$Q = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

2.2.4

At equilibrium the Gibb's free energy is zero, and Equation 6.2.3 simplifies to

$$\Delta G^\circ = -RT\ln K \qquad (2.2.5)$$

where K is an **equilibrium constant** that defines the reaction's equilibrium position. The equilibrium constant is just the numerical value of the reaction quotient, Q, when substituting equilibrium concentrations into Equation 2.2.4 .

Here we include the subscript "eq" to indicate a concentration at equilibrium. Although we usually will omit the "eq" when writing equilibrium constant expressions, it is important to remember that the value of K is determined by equilibrium concentrations.

$$K = \frac{[\mathrm{C}]_{\mathrm{eq}}^c[\mathrm{D}]_{\mathrm{eq}}^d}{[\mathrm{A}]_{\mathrm{eq}}^a[\mathrm{B}]_{\mathrm{eq}}^b}$$

2.2.6

NOTE : As written, Equation 6 is a limiting law that applies only to infinitely dilute solutions where the chemical behavior of one species is unaffected by the presence of other species. Strictly speaking, Equation 6 should be written in terms of activities instead of concentrations. We will return to this point in Section 6I. For now, we will stick with concentrations as this convention is already familiar to you.

2.3: Manipulating Equilibrium Constants

We will take advantage of two useful relationships when working with equilibrium constants. First, if we reverse a reaction's direction, the equilibrium constant for the new reaction is simply the inverse of that for the original reaction. For example, the equilibrium constant for the reaction

$$\mathrm{A} + 2\mathrm{B} \rightleftharpoons AB_2 \qquad K_1 = \frac{[\mathrm{AB_2}]}{[\mathrm{A}][\mathrm{B}]^2}$$

is the inverse of that for the reaction

$$AB_2 \rightleftharpoons \mathrm{A} + 2\mathrm{B} \qquad K_2 = (K_1)^{-1} = \frac{[A][\mathrm{B}]^2}{[\mathrm{AB_2}]}$$

Second, if we add together two reactions to obtain a new reaction, the equilibrium constant for the new reaction is the product of the equilibrium constants for the original reactions.

$$\mathrm{A} + \mathrm{C} \rightleftharpoons \mathrm{AC} \quad K_3 = \frac{[\mathrm{AC}]}{[\mathrm{A}][\mathrm{C}]}$$

$$\mathrm{AC} + \mathrm{C} \rightleftharpoons \mathrm{AC_2} \quad K_4 = \frac{[\mathrm{AC_2}]}{[\mathrm{AC}][\mathrm{C}]}$$

$$\mathrm{A} + 2\mathrm{C} \rightleftharpoons \mathrm{AC_2} \quad K_5 = K_3 \times K_4 = \frac{[\mathrm{AC}]}{[\mathrm{A}][\mathrm{C}]} \times \frac{[\mathrm{AC_2}]}{[\mathrm{AC}][\mathrm{C}]} = \frac{[\mathrm{AC_2}]}{[\mathrm{A}][\mathrm{C}]^2}$$

Example 2.1

Calculate the equilibrium constant for the reaction

$$2\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + 3\mathrm{D}$$

given the following information

Rxn 1 : $A + B \rightleftharpoons D$	$K_1 = 0.40$
Rxn 2 : $A + E \rightleftharpoons C + D + F$	$K_2 = 0.10$
Rxn 3 : $C + E \rightleftharpoons B$	$K_3 = 2.0$
Rxn 4 : $F + C \rightleftharpoons D + B$	$K_4 = 5.0$

Solution

The overall reaction is equivalent to

$$\text{Rxn 1} + \text{Rxn 2} - \text{Rxn 3} + \text{Rxn 4}$$

Subtracting a reaction is equivalent to adding the reverse reaction; thus, the overall equilibrium constant is

$$K = \frac{K_1 \times K_2 \times K_4}{K_3} = \frac{0.40 \times 0.10 \times 5.0}{2.0} = 0.10$$

Practice Exercise 2.1

Calculate the equilibrium constant for the reaction

$$C + D + F \rightleftharpoons 2A + 3B$$

using the equilibrium constants from Example 2.1.

The overall reaction is equivalent to

$$\text{Rxn 4} - 2 \times \text{Rxn 1}$$

Subtracting a reaction is equivalent to adding the reverse reaction; thus, the overall equilibrium constant is

$$K = \frac{K_4}{(K_1)^2} = \frac{5.0}{(0.40)^2} = 31.25 \approx 31$$

2.4: Equilibrium Constants for Chemical Reactions

Several types of chemical reactions are important in analytical chemistry, either in preparing a sample for analysis or during the analysis. The most significant of these are: precipitation reactions, acid–base reactions, complexation reactions, and oxidation–reduction (redox) reactions. In this section we review these reactions and their equilibrium constant expressions.

2.4.1 Precipitation Reactions

In a precipitation reaction, two or more soluble species combine to form an insoluble **precipitate**. The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. For example, if we add a solution of lead nitrate, $Pb(NO_3)_2$, to a solution of potassium chloride, KCl, the result is a precipitate of lead chloride, $PbCl_2$. We usually write a precipitation reaction as a net ionic equation, showing only the precipitate and those ions forming the precipitate. Thus, the precipitation reaction for $PbCl_2$ is

$$Pb^{2+}(aq) + 2Cl^{-}(aq) \rightleftharpoons PbCl_2(s) \qquad (2.4.1)$$

When writing an equilibrium constant for a precipitation reaction, we focus on the precipitate's solubility. Thus, for $PbCl_2$, the solubility reaction is

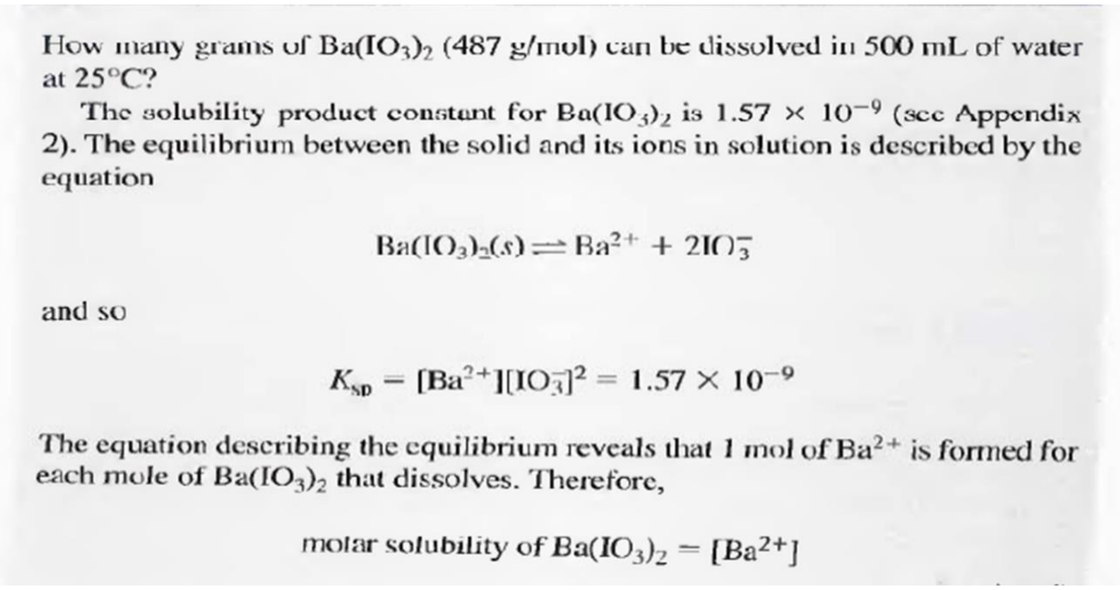
$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq) \qquad (2.4.2)$$

and its equilibrium constant, which we call the **solubility product**, K_{sp}, is

$$Ksp = [Pb^{2+}]\,[Cl^{-}]^2 = 1.7 \times 10^{-5} \qquad (2.4.3)$$

Even though it does not appear in the K_{sp} expression, it is important to remember that equation 2.4.3 is valid only if $PbCl_2(s)$ is present and in equilibrium with Pb^{2+} and Cl^{-}. You will find values for selected solubility products in Appendix 10.

Example 2.2



How many grams of $Ba(IO_3)_2$ (487 g/mol) can be dissolved in 500 mL of water at 25°C?

The solubility product constant for $Ba(IO_3)_2$ is 1.57×10^{-9} (see Appendix 2). The equilibrium between the solid and its ions in solution is described by the equation

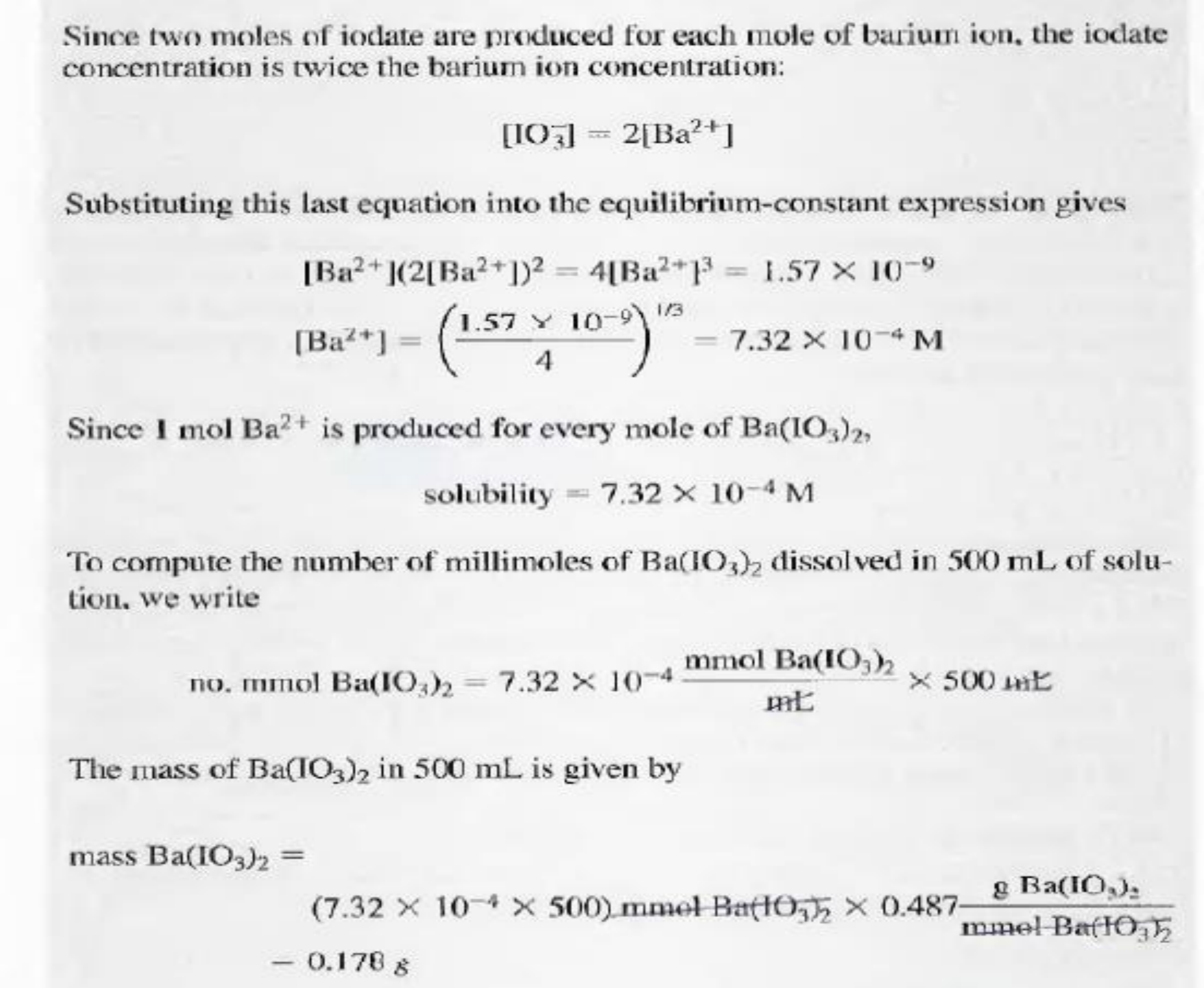
$$Ba(IO_3)_2(s) \rightleftharpoons Ba^{2+} + 2IO_3^-$$

and so

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = 1.57 \times 10^{-9}$$

The equation describing the equilibrium reveals that 1 mol of Ba^{2+} is formed for each mole of $Ba(IO_3)_2$ that dissolves. Therefore,

$$\text{molar solubility of } Ba(IO_3)_2 = [Ba^{2+}]$$



Since two moles of iodate are produced for each mole of barium ion, the iodate concentration is twice the barium ion concentration:

$$[IO_3^-] = 2[Ba^{2+}]$$

Substituting this last equation into the equilibrium-constant expression gives

$$[Ba^{2+}](2[Ba^{2+}])^2 = 4[Ba^{2+}]^3 = 1.57 \times 10^{-9}$$

$$[Ba^{2+}] = \left(\frac{1.57 \times 10^{-9}}{4}\right)^{1/3} = 7.32 \times 10^{-4}\ M$$

Since 1 mol Ba^{2+} is produced for every mole of $Ba(IO_3)_2$,

$$\text{solubility} = 7.32 \times 10^{-4}\ M$$

To compute the number of millimoles of $Ba(IO_3)_2$ dissolved in 500 mL of solution, we write

$$\text{no. mmol } Ba(IO_3)_2 = 7.32 \times 10^{-4} \frac{\text{mmol } Ba(IO_3)_2}{\cancel{\text{mL}}} \times 500\ \cancel{\text{mL}}$$

The mass of $Ba(IO_3)_2$ in 500 mL is given by

$$\text{mass } Ba(IO_3)_2 =$$

$$(7.32 \times 10^{-4} \times 500)\ \cancel{\text{mmol } Ba(IO_3)_2} \times 0.487 \frac{\text{g } Ba(IO_3)_2}{\cancel{\text{mmol } Ba(IO_3)_2}}$$

$$= 0.178\ g$$

LECTURE – 4

2.4.2 Acid–Base Reactions

2.4.3 Complexation Reactions

2.4.4 Oxidation–Reduction (Redox) Reactions

2.4.2 Acid–Base Reactions

A useful definition of acids and bases is that independently introduced in 1923 by Johannes Brønsted and Thomas Lowry. In the Brønsted-Lowry definition, an **acid** is a proton donor and a **base** is a proton acceptor.

Note : the connection in these definitions—defining a base as a proton acceptor implies that there is an acid available to donate the proton. For example, in reaction 2.4.4 acetic acid, CH_3COOH, donates a proton to ammonia, NH_3, which serves as the base.

$$CH3COOH\ (aq) + NH_3(aq) \rightleftharpoons NH_4^+\ (aq) + CH3COO^-(aq) \qquad (2.4.4)$$

When an acid and a base react, the products are a new acid and a new base. For example, the acetate ion, CH_3COO^-, in reaction 2.4.4 is a base that can accept a proton from the acidic ammonium ion, NH_4^+, forming acetic acid and ammonia. We call the acetate ion the conjugate base of acetic acid, and the ammonium ion is the conjugate acid of ammonia.

Strong and Weak Acids

The reaction of an acid with its solvent (typically water) is an acid dissociation reaction. We divide acids into two categories—strong and weak—based on their ability to donate a proton to the solvent. A strong acid, such as HCl, almost completely transfers its proton to the solvent, which acts as the base.

$$HCl\ (aq) + H_2O\ (l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad (2.4.5)$$

We use a single arrow (→) in place of the equilibrium arrow (⇋) because we treat HCl as if it completely dissociates in aqueous solutions. In water, the common strong acids are hydrochloric acid (HCl), hydroiodic acid (HI), hydrobromic acid (HBr), nitric acid (HNO_3), perchloric acid ($HClO_4$), and the first proton of sulfuric acid (H_2SO_4).

Note : In a different solvent, HCl may not be a strong acid. For example, HCl does not act as a strong acid in methanol. In this case we use the equilibrium arrow when writing the acid–base reaction.

$$HCl\ (aq) + CH_3OH\ (l) \rightleftharpoons CH3OH_2^+\ (aq) + Cl^-(aq) \qquad (2.4.6)$$

A weak acid, of which aqueous acetic acid is one example, does not completely donate its acidic proton to the solvent. Instead, most of the acid remains undissociated, with only a small fraction present as the conjugate base.

$$CH_3COOH(aq) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-\ (aq) \qquad (2.4.7)$$

The equilibrium constant for this reaction is an **acid dissociation constant**, K_a, which we write as

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5}$$

2.4.8

Note

Earlier we noted that we omit pure solids and pure liquids from equilibrium constant expressions. Because the solvent, H_2O, is not pure, you might wonder why we have not included it in acetic acid's Ka expression. Recall that we divide each term in the equilibrium constant expression by its standard state value. Because the concentration of H_2O is so large—it is approximately 55.5 mol/L—its concentration as a pure liquid and as a solvent are virtually identical. The ratio

$$\frac{[H_2O]}{[H_2O]^\circ}$$

6.4.9

is essentially 1.00.

The magnitude of K_a provides information about a weak acid's relative strength, with a smaller $K_a$corresponding to a weaker acid. The ammonium ion, NH_4^+, for example, with a K_a of 5.702×10^{-10}, is a weaker acid than acetic acid.

Monoprotic weak acids, such as acetic acid, have only a single acidic proton and a single acid dissociation constant. Other acids, such as phosphoric acid, have more than one acidic proton, each characterized by an acid dissociation constant. We call such acids **polyprotic**weak acids. Phosphoric acid, for example, has three acid dissociation reactions and three acid dissociation constants.

$$H_3PO_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + H_2PO^-_4(aq) \qquad (2.4.10)$$

$$K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = 7.11 \times 10^{-3}$$

(2.4.11)

$$H_2PO_4^-\,(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{\,2-}\,(aq) \qquad (2.4.12)$$

$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} = 6.32 \times 10^{-8}$$

(2.4.13)

$$HPO_4^{2-}\,(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}\,(aq) \qquad (2.4.14)$$

$$K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} = 4.5 \times 10^{-13}$$

(2.4.15)

The decrease in the acid dissociation constants from K_{a1} to K_{a3} tells us that each successive proton is harder to remove. Consequently, H_3PO_4 is a stronger acid than $H_2PO_4^-$, and $H_2PO_4^-$ is a stronger acid than HPO_4^{2-}.

Strong and Weak Bases

The most common example of a strong base is an alkali metal hydroxide, such as sodium hydroxide, NaOH, which completely dissociates to produce hydroxide ion.

$$NaOH\ (s) \rightarrow Na^+\ (aq) + OH^-\ (aq) \qquad (2.4.16)$$

A weak base, such as the acetate ion, CH_3COO^-, only partially accepts a proton from the solvent, and is characterized by a **base dissociation constant**, K_b. For example, the base dissociation reaction and the base dissociation constant for the acetate ion are

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-(aq) + CH3COOH\ (aq) \qquad (2.4.17)$$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.7 \times 10^{-10} \qquad (2.4.18)$$

A polyprotic weak base, like a polyprotic acid, has more than one base dissociation reaction and more than one base dissociation constant.

Amphiprotic Species

Some species can behave as either a weak acid or as a weak base. For example, the following two reactions show the chemical reactivity of the bicarbonate ion, HCO_3^-, in water.

$$HCO_3^-\ (aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{\ 2-}\ (aq) \qquad (2.4.19)$$

$$HCO_3^-\ (aq) + H_2O\ (l) \rightleftharpoons OH-(aq) + H_2CO_3\ (aq) \qquad (2.4.20)$$

A species that is both a proton donor and a proton acceptor is called **amphiprotic**. Whether an amphiprotic species behaves as an acid or as a base depends on the equilibrium constants for the competing reactions. For bicarbonate, the acid dissociation constant for reaction 2.4.19

$$K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} = 4.69 \times 10^{-11} \qquad (2.4.21)$$

is smaller than the base dissociation constant for reaction 2.4.20.

$$K_{b2} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.25 \times 10^{-8} \qquad (2.4.22)$$

Because bicarbonate is a stronger base than it is an acid, we expect an aqueous solution of $HCO_3^–$ to be basic.

Dissociation of Water

Water is an amphiprotic solvent because it can serve as an acid or as a base. An interesting feature of an amphiprotic solvent is that it is capable of reacting with itself in an acid–base reaction.

$$2H_2O\ (l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad (2.4.23)$$

We identify the equilibrium constant for this reaction as water’s dissociation constant, K_w,

$$K_w = [H_3O^+]\ [OH^-] = 1.00\times10^{-14} \qquad (2.4.24)$$

which has a value of 1.0000×10^{-14} at a temperature of 24°C. The value of K_w varies substantially with temperature. For example, at 20°CK_w is 6.809×10^{-15}, while at 30°C K_w is 1.469×10^{-14}. At 25°C, K_w is 1.008×10^{-14}, which is sufficiently close to 1.00×10^{-14} that we can use the latter value with negligible error.

An important consequence of equation 6.4.24 is that the concentration of H_3O^+ and the concentration of $OH^–$ are related. If we know $[H_3O^+]$ for a solution, then we can calculate $[OH^–]$ using Equation 6.4.24 .

Example 2.3

What is the $[OH^–]$ if the $[H_3O^+]$ is 6.12×10^{-5} M?

Solution

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{6.12 \times 10^{-5}} = 1.63 \times 10^{-10} \qquad (2.4.25)$$

The pH Scale

Equation 6.4.24 allows us to develop a **pH scale** that indicates a solution’s acidity ($pH = –\log[H_3O^+]$). When the concentrations of $H_3O^+$and $OH^–$ are equal a solution is neither acidic nor basic; that is, the solution is neutral. Letting

$$[H3O^+] = [OH^-] \qquad (2.4.26)$$

substituting into equation 2.4.24

$$K_w = [H_3O^+]^2 = 1.00\times10^{-14} \qquad (2.4.27)$$

and solving for $[H_3O^+]$ gives

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \qquad (2.4.28)$$

A neutral solution **at room temperature** has a hydronium ion concentration of 1.00 × 10^{-7} M and a pH of 7.00. For a solution to be acidic the concentration of H_3O^+ must be greater than that for OH^-, which means that

$$[H_3O^+] > 1.00\times10^{-7} \text{ M} \qquad (2.4.29)$$

The pH of an acidic solution, therefore, must be less than 7.00. A basic solution, on the other hand, has a pH greater than 7.00. Figure 6.2 shows the pH scale and pH values for some representative solutions.

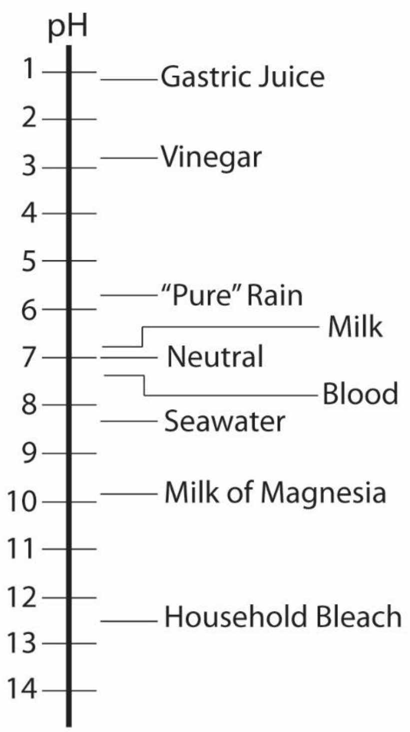


***Figure 2.2**: Scale showing the pH value for representative solutions. Milk of Magnesia is a saturated solution of $Mg(OH)_2$.*

Tabulating Values for K_a and K_b

A useful observation about acids and bases is that the strength of a base is inversely proportional to the strength of its conjugate acid. Consider, for example, the dissociation reactions of acetic acid and acetate.

$$CH_3COOH\,(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \qquad (2.4.30)$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-\,(aq) + CH_3COOH\,(aq) \qquad (2.4.31)$$

Adding together these two reactions gives the reaction

$$2H_2O\ (l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad (2.4.32)$$

for which the equilibrium constant is K_w. Because adding together two reactions is equivalent to multiplying their respective equilibrium constants, we may express K_w as the product of K_a for CH_3COOH and K_b for CH_3COO^-.

$$K_w = K_{a},CH_3COOH \times K_{b},CH_3COO^- \qquad (2.4.33)$$

For any weak acid, HA, and its conjugate weak base, A^-, we can generalize this to the following equation.

$$K_w = K_a,\ HA \times K_b,\ A^- \qquad (2.4.34)$$

The relationship between K_a and K_b for a conjugate acid–base pair simplifies our tabulation of acid and base dissociation constants. Appendix 11 includes acid dissociation constants for a variety of weak acids. To find the value of K_b for a weak base, use equation 6.4.34and the K_a value for its corresponding weak acid.

Note : A common mistake when using equation 2.4.34 is to forget that it applies only to a conjugate acid–base pair.

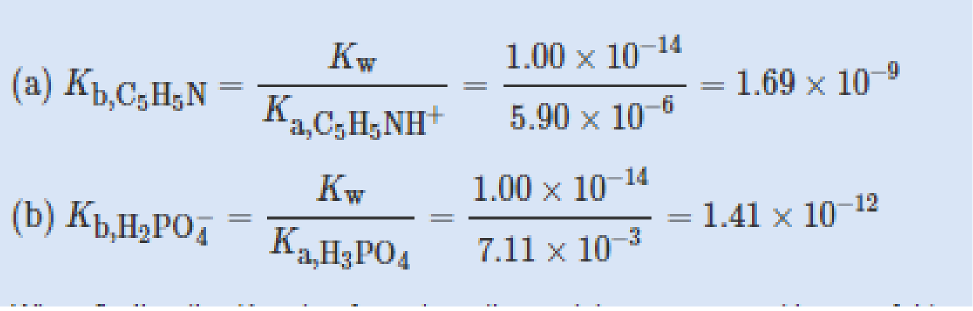
Example 2.4

Using Appendix 11, calculate values for the following equilibrium constants.

(a) K_b for pyridine, C_5H_5N

(b) K_b for dihydrogen phosphate, H_2PO^{-4}

Solution



$$\text{(a) } K_{b,C_5H_5N} = \frac{K_w}{K_{a,C_5H_5NH^+}} = \frac{1.00 \times 10^{-14}}{5.90 \times 10^{-6}} = 1.69 \times 10^{-9}$$

$$\text{(b) } K_{b,H_2PO_4^-} = \frac{K_w}{K_{a,H_3PO_4}} = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$$

When finding the K_b value for polyprotic weak base, you must be careful to choose the correct K_a value. Remember that equation 2.4.34 applies only to a conjugate acid–base pair. The conjugate acid of $H_2PO_4^-$ is H_3PO_4, not HPO_4^{2-}.

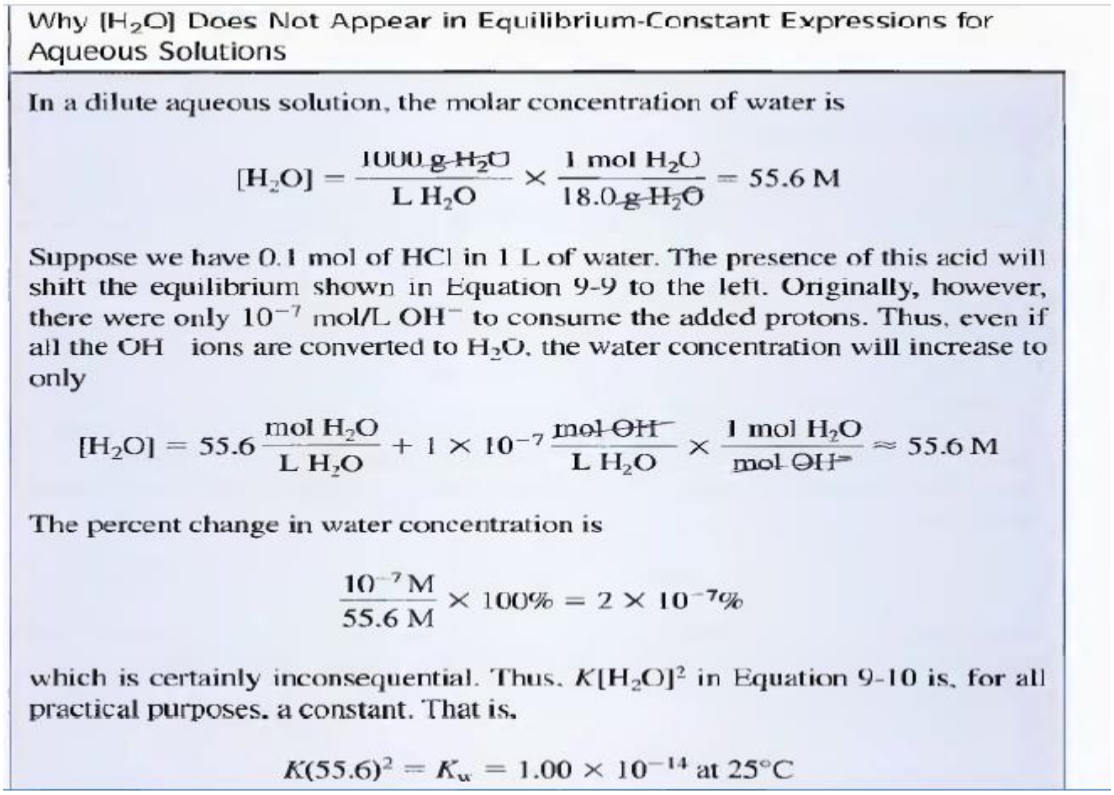
Practice Exercise 2.2 Using Appendix 11, calculate the K_b values for hydrogen oxalate, $HC_2O_4^-$, and oxalate $C_2O_4^{2-}$.The K_b for hydrogen oxalate is

$$K_{b,HC_2O_4^-} = \frac{K_w}{K_{a,H_2C_2O_4}} = \frac{1.00 \times 10^{-14}}{5.60 \times 10^{-2}} = 1.79 \times 10^{-13}$$

and the K_b for oxalate is

$$K_{b,C_2O_4^{2-}} = \frac{K_w}{K_{a,HC_2O_4^-}} = \frac{1.00 \times 10^{-14}}{5.42 \times 10^{-5}} = 1.85 \times 10^{-10}$$

As we expect, the K_b value for $C_2O_4^{2-}$ is larger than that for $HC_2O_4^-$.



Why $[H_2O]$ Does Not Appear in Equilibrium-Constant Expressions for Aqueous Solutions

In a dilute aqueous solution, the molar concentration of water is

$$[H_2O] = \frac{1000\,\cancel{g\,H_2O}}{L\,H_2O} \times \frac{1\text{ mol }H_2O}{18.0\,\cancel{g\,H_2O}} = 55.6\text{ M}$$

Suppose we have 0.1 mol of HCl in 1 L of water. The presence of this acid will shift the equilibrium shown in Equation 9-9 to the left. Originally, however, there were only 10^{-7} mol/L OH^- to consume the added protons. Thus, even if all the OH ions are converted to H_2O, the water concentration will increase to only

$$[H_2O] = 55.6\frac{\text{mol }H_2O}{L\,H_2O} + 1 \times 10^{-7}\frac{\cancel{\text{mol }OH^-}}{L\,H_2O} \times \frac{1\text{ mol }H_2O}{\cancel{\text{mol }OH^-}} \approx 55.6\text{ M}$$

The percent change in water concentration is

$$\frac{10^{-7}\text{ M}}{55.6\text{ M}} \times 100\% = 2 \times 10^{-7}\%$$

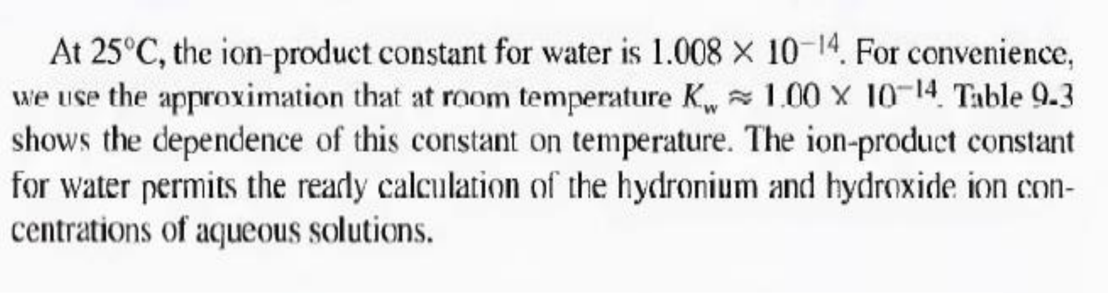
which is certainly inconsequential. Thus, $K[H_2O]^2$ in Equation 9-10 is, for all practical purposes, a constant. That is,

$$K(55.6)^2 = K_w = 1.00 \times 10^{-14} \text{ at } 25°C$$

$$2H_2O\,(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad (9\text{-}9)$$

$$K_c = \frac{[H_3O][OH^-]}{[H_2O]^2} \qquad (9\text{-}10)$$

$$K\,(55.6)^2 = K_w = [H_3O^+]\,[OH^-] = 1.00\times10^{-14} \quad \text{at 25 C} \qquad (9\text{-}11)$$



At 25°C, the ion-product constant for water is 1.008×10^{-14}. For convenience, we use the approximation that at room temperature $K_w \approx 1.00 \times 10^{-14}$. Table 9-3 shows the dependence of this constant on temperature. The ion-product constant for water permits the ready calculation of the hydronium and hydroxide ion concentrations of aqueous solutions.

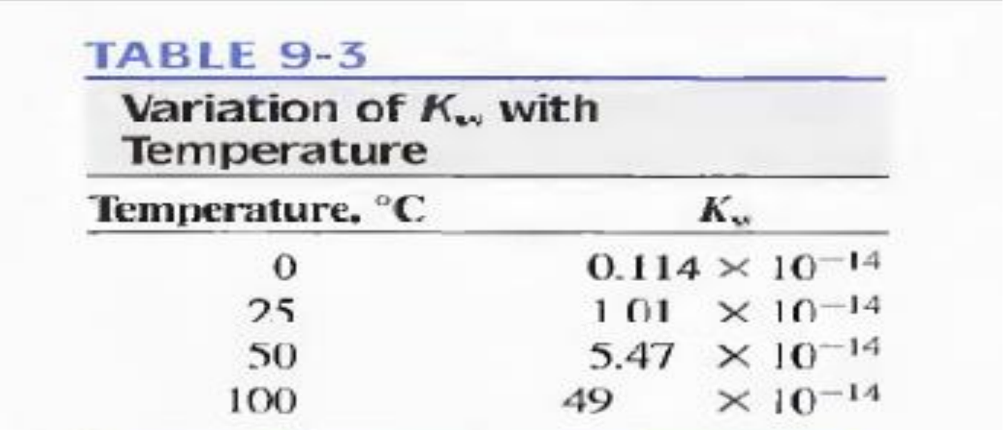
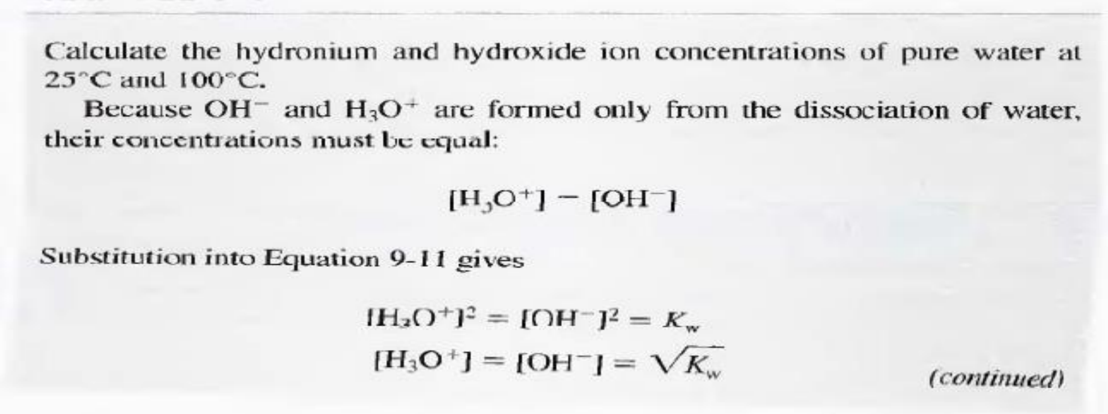


TABLE 9-3

Variation of K_w with Temperature

Temperature. °C	K_w
0	0.114×10^{-14}
25	1.01×10^{-14}
50	5.47×10^{-14}
100	49×10^{-14}

Example 2.5



Calculate the hydronium and hydroxide ion concentrations of pure water at 25°C and 100°C.

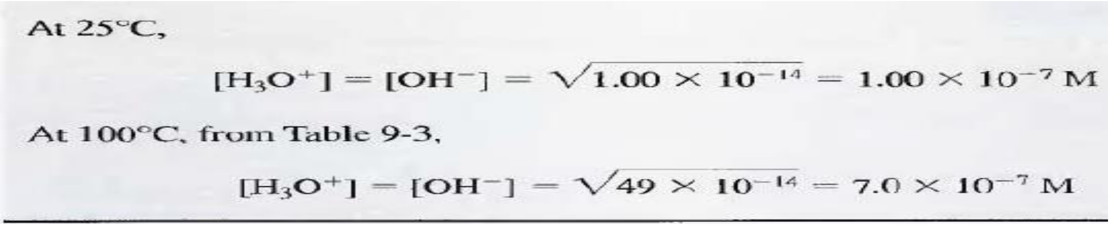
Because OH^- and H_3O^+ are formed only from the dissociation of water, their concentrations must be equal:

$$[H_3O^+] = [OH^-]$$

Substitution into Equation 9-11 gives

$$[H_3O^+]^2 = [OH^-]^2 = K_w$$
$$[H_3O^+] = [OH^-] = \sqrt{K_w}$$

(continued)



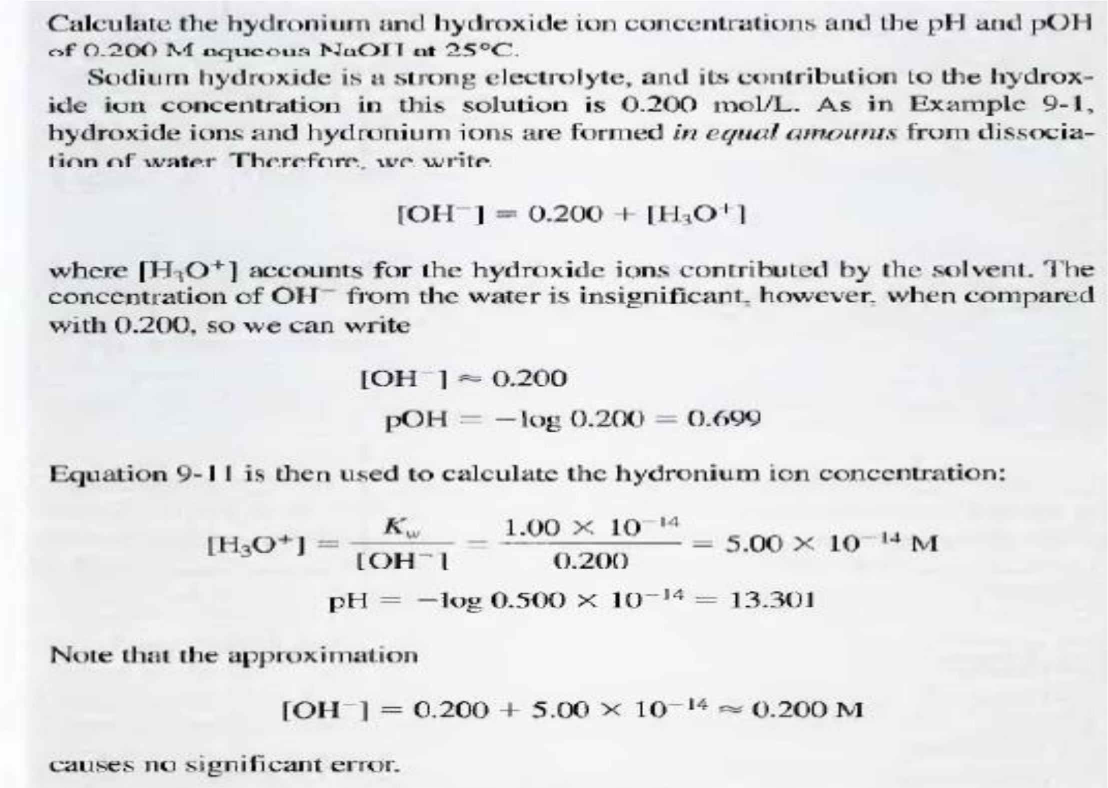
At 25°C,

$$[H_3O^+] = [OH^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\ M$$

At 100°C, from Table 9-3,

$$[H_3O^+] = [OH^-] = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}\ M$$

Example 2.6



Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of 0.200 M aqueous NaOH at 25°C.

Sodium hydroxide is a strong electrolyte, and its contribution to the hydroxide ion concentration in this solution is 0.200 mol/L. As in Example 9-1, hydroxide ions and hydronium ions are formed *in equal amounts* from dissociation of water. Therefore, we write

$$[OH^-] = 0.200 + [H_3O^+]$$

where $[H_3O^+]$ accounts for the hydroxide ions contributed by the solvent. The concentration of OH^- from the water is insignificant, however, when compared with 0.200, so we can write

$$[OH^-] \approx 0.200$$
$$pOH = -\log 0.200 = 0.699$$

Equation 9-11 is then used to calculate the hydronium ion concentration:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14}\ M$$
$$pH = -\log 0.500 \times 10^{-14} = 13.301$$

Note that the approximation

$$[OH^-] = 0.200 + 5.00 \times 10^{-14} \approx 0.200\ M$$

causes no significant error.

2.4.3 Complexation Reactions

A more general definition of acids and bases was proposed in1923 by G. N. Lewis. The Brønsted-Lowry definition of acids and bases focuses on an acid’s proton-donating ability and a base’s proton-accepting ability. Lewis theory, on the other hand, uses the breaking and forming of covalent bonds to describe acid–base characteristics. In this treatment, an acid is an electron pair acceptor and a base in an electron pair donor. Although we can apply Lewis theory to the treatment of acid–base reactions, it is more useful for treating complexation reactions between metal ions and ligands.

The following reaction between the metal ion Cd^{2+} and the **ligand** NH_3 is typical of a complexation reaction.

$$Cd^{2+}\ (aq) + 4{:}NH_3\ (aq) \rightleftharpoons Cd({:}NH_3)_4^{2+}\ (aq) \qquad (2.4.35)$$

The product of this reaction is a **metal–ligand complex**. In writing this reaction we show ammonia as $:NH_3$, using a pair of dots to emphasize the pair of electrons it donates to Cd^{2+}. In subsequent reactions we will omit this notation.

Metal-Ligand Formation Constants

We characterize the formation of a metal–ligand complex by a **formation constant**, K_f. The complexation reaction between Cd^{2+} and NH_3, for example, has the following equilibrium constant.

$$K_f = \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = 5.5 \times 10^7 \quad (2.4.36)$$

The reverse of reaction 2.4.35 is a dissociation reaction, which we characterize by a **dissociation constant**, K_d, that is the reciprocal of K_f.

Many complexation reactions occur in a stepwise fashion. For example, the reaction between Cd^{2+} and NH_3 involves four successive reactions.

$$Cd^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)^{2+}(aq) \quad (2.4.37)$$

$$Cd(NH_3)^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH3)_2{}^{2+}(aq) \quad (2.4.38)$$

$$Cd(NH_3)_2^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_3^{2+}(aq) \quad (2.4.39)$$

$$Cd(NH3)_3^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH3)_4^{2+}(aq) \quad (2.4.40)$$

To avoid ambiguity, we divide formation constants into two categories. **Stepwise formation constants**, which we designate as K_i for the *i*th step, describe the successive addition of one ligand to the metal–ligand complex from the previous step. Thus, the equilibrium constants for reactions 2.4.37–2.4.40 are, respectively, K_1, K_2, K_3, and K_4. Overall, or **cumulative formation constants**, which we designate as β_i, describe the addition of *i* ligands to the free metal ion. The equilibrium constant in equation 2.4.36 is correctly identified as β_4, where

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \quad (2.4.41)$$

In general

$$B_i = K_1 \times K_2 \times ... \times K_i \quad (2.4.42)$$

Stepwise and overall formation constants for selected metal–ligand complexes are in Appendix 12.

Metal-Ligand Complexation and Solubility

A formation constant characterizes the addition of one or more ligands to a free metal ion. To find the equilibrium constant for a complexation reaction involving a solid, we combine appropriate K_{sp} and K_f expressions. For example, the solubility of AgCl increases in the presence of excess chloride as the result of the following complexation reaction.

$$AgCl\,(s) + Cl^-\,(aq) \rightleftharpoons AgCl_2^-\,(aq) \qquad (2.4.43)$$

We can write this reaction as the sum of three other reactions with known equilibrium constants—the solubility of AgCl, described by its K_{sp}

$$AgCl(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq) \qquad (2.4.44)$$

and the stepwise formation of $AgCl_2^-$, described by K_1 and K_2.

$$Ag^+\,(aq) + Cl^-\,(aq) \rightleftharpoons AgCl\,(aq) \qquad (2.4.45)$$

$$AgCl\,(aq) + Cl^-\,(aq) \rightleftharpoons AgCl_2^-\,(aq) \qquad (2.4.46)$$

The equilibrium constant for reaction 6.4.43, therefore, is $K_{sp} \times K_1 \times K_2$.

Example 2.7

Determine the value of the equilibrium constant for the reaction

$$PbCl_2\,(s) \rightleftharpoons PbCl_2\,(aq) \qquad (2.4.47)$$

Solution

We can write this reaction as the sum of three other reactions. The first of these reactions is the solubility of $PbCl_2(s)$, described by itsK_{sp} reaction.

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-(aq) \qquad (2.4.48)$$

The remaining two reactions are the stepwise formation of $PbCl_2(aq)$, described by K_1 and K_2.

$$Pb^{2+}\,(aq) + Cl^-\,(aq) \rightleftharpoons PbCl^+\,(aq) \qquad (2.4.49)$$

$$PbCl^+\,(aq) + Cl^-\,(aq) \rightleftharpoons PbCl_2\,(aq) \qquad (2.4.50)$$

Using values for K_{sp}, K_1, and K_2 from Appendix 10 and Appendix 12, we find that the equilibrium constant is

$$K = K_{sp} \times K_1 \times K_2 = (1.7\times10^{-5}) \times 38.9 \times 1.62 = 1.1\times10^{-3} \qquad (2.4.51)$$

Practice Exercise 2.3

What is the equilibrium constant for the following reaction? You will find appropriate equilibrium constants in Appendix 10 andAppendix 11.

$$AgBr\ (s) + 2S_2O_3{}^{2-}\ (aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq) + Br^-(aq) \qquad (2.4.52)$$

We can write the reaction as a sum of three other reactions. The first reaction is the solubility of AgBr(s), which we characterize by its K_{sp}.

$$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq)$$

The remaining two reactions are the stepwise formation of $Ag(S_2O_3)_2{}^{3-}$, which we characterize by K_1 and K_2.

$$Ag^+\ (aq) + S_2O_3{}^{2-}\ (aq) \rightleftharpoons Ag(S_2O_3)^-\ (aq)$$

$$Ag(S_2O_3)^-\ (aq) + S_2O_3{}^{2-}\ (aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}\ (aq)$$

Using values for K_{sp}, K_1, and K_2 from Appendix 10 and Appendix 11, we find that the equilibrium constant for our reaction is

$$K = K_{sp} \times K_1 \times K_2 = (5.0\times10^{-13})(6.6\times10^{8})(7.1\times10^{4}) = 23$$

2.4.4 Oxidation–Reduction (Redox) Reactions

An oxidation–reduction reaction occurs when electrons move from one reactant to another reactant. As a result of this electron transfer, these reactants undergo a change in oxidation state. Those reactants that experience an increase in oxidation state undergo **oxidation**, and those experiencing a decrease in oxidation state undergo **reduction**. For example, in the following redox reaction between Fe^{3+} and oxalic acid, $H_2C_2O_4$, iron is reduced because its oxidation state changes from +3 to +2.

$$2Fe^{3+}\ (aq) + H_2C_2O_4\ (aq) + 2H_2O(l) \rightleftharpoons 2Fe^{2+}\ (aq) + 2CO_2(g) + 2H_3O^+\ (aq) \qquad (2.4.53)$$

Oxalic acid, on the other hand, undergoes oxidation because the oxidation state for carbon increases from +3 in $H_2C_2O_4$ to +4 in CO_2.

We can divide a redox reaction, such as reaction 2.4.53, into separate **half-reactions** that show the oxidation and the reduction processes.

$$H_2C_2O_4\ (aq) + 2H_2O\ (l) \rightleftharpoons 2CO_2(g) + 2H_3O^+(aq) + 2e- \qquad (2.4.54)$$

$$Fe^{3+}\ (aq) + e- \rightleftharpoons Fe^{2+}\ (aq) \qquad (2.4.55)$$

It is important to remember, however, that an oxidation reaction and a reduction reaction occur as a pair. We formalize this relationship by identifying as a **reducing agent** the reactant undergoing oxidation, because it provides the electrons for the reduction half-reaction. Conversely, the reactant undergoing reduction is an **oxidizing agent**. In reaction 2.4.53, Fe^{3+} is the oxidizing agent and $H_2C_2O_4$ is the reducing agent.

The products of a redox reaction also have redox properties. For example, the Fe^{2+} in reaction 2.4.53 can be oxidized to Fe^{3+}, while CO_2 can be reduced to $H_2C_2O_4$. Borrowing some terminology from acid–base chemistry, Fe^{2+} is the conjugate reducing agent of the oxidizing agent Fe^{3+}, and CO_2 is the conjugate oxidizing agent of the reducing agent $H_2C_2O_4$.

Thermodynamics of Redox Reactions

Unlike precipitation reactions, acid–base reactions, and complexation reactions, we rarely express the equilibrium position of a redox reaction using an equilibrium constant. Because a redox reaction involves a transfer of electrons from a reducing agent to an oxidizing agent, it is convenient to consider the reaction's thermodynamics in terms of the electron.

For a reaction in which one mole of a reactant undergoes oxidation or reduction, the net transfer of charge, *Q*, in coulombs is

$$Q = nF \qquad (2.4.56)$$

where *n* is the moles of electrons per mole of reactant, and *F* is Faraday's constant (96,485 C/mol). The free energy, Δ*G*, to move this charge, *Q*, over a change in **potential**, *E*, is

$$\Delta G = EQ \qquad (2.4.57)$$

The change in free energy (in kJ/mole) for a redox reaction, therefore, is

$$\Delta G = -nFE \qquad (2.4.58)$$

where Δ*G* has units of kJ/mol. The minus sign in equation 6.4.58 is the result of a difference in the conventions for assigning a reaction's favorable direction. In thermodynamics, a reaction is favored when Δ*G* is negative, but a redox reaction is favored when *E* is positive. Substituting equation 2.4.58 into equation 2.2.3

$$-\ nFE = -nFE^{\circ} + RT\ln Q \qquad (2.4.59)$$

and dividing by -*nF*, leads to the well-known **Nernst equation**

$$E = E^{\circ} - \frac{RT}{nF}\ln Q \qquad (2.4.60)$$

where E^{o} is the potential under standard-state conditions. Substituting appropriate values for *R* and *F*, assuming a temperature of 25°C (298 K), and switching from *ln* to *log* (ln(*x*) = 2.303log(*x*)) gives the potential in volts as

$$E = E^{\circ} - \frac{0.05916}{n}\ln Q \qquad (2.4.61)$$

Standard Potentials

A redox reaction's **standard potential**, E^o, provides an alternative way of expressing its equilibrium constant and, therefore, its equilibrium position. Because a reaction at equilibrium has a ΔG of zero, the potential, E, also must be zero at equilibrium. Substituting these values into equation 6.4.61 and rearranging provides a relationship between E^o and K.

$$E^\circ = \frac{0.05916}{n}\log K \qquad (2.4.62)$$

Note : A standard potential is the potential when all species are in their standard states. You may recall that we define standard state conditions as: all gases have partial pressures of 1 atm, all solutes have concentrations of 1 mol/L, and all solids and liquids are pure.

We generally do not tabulate standard potentials for redox reactions. Instead, we calculate E^o using the standard potentials for the corresponding oxidation half-reaction and reduction half-reaction. By convention, standard potentials are provided for reduction half-reactions. The standard potential for a redox reaction, E^o, is

$$E^\circ = E^\circ_{red} - E^\circ_{ox} \qquad (2.4.63)$$

where E^o_{red} and E^o_{ox} are the standard reduction potentials for the reduction half-reaction and the oxidation half-reaction.

Because we cannot measure the potential for a single half-reaction, we arbitrarily assign a standard reduction potential of zero to a reference half-reaction and report all other reduction potentials relative to this reference. The reference half-reaction is

$$2H_3O^+(aq) + 2e^- \rightleftharpoons 2H_2O\,(l) + H_2(g) \qquad (2.4.64)$$

Appendix 13 contains a list of selected standard reduction potentials. The more positive the standard reduction potential, the more favorable the reduction reaction under standard state conditions. Thus, under standard state conditions the reduction of Cu^{2+} to Cu (E^o = +0.3419 V) is more favorable than the reduction of Zn^{2+} to Zn (E^o = –0.7618 V).

Example 2.8

Calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential when $[Ag^+]$ = 0.020 M and $[Cd^{2+}]$ = 0.050 M, for the following reaction at 25°C.

$$Cd\,(s) + 2Ag^+(aq) \rightleftharpoons 2Ag\,(s) + Cd^{2+}(aq) \qquad (2.4.65)$$

Solution

(a) In this reaction Cd is undergoing oxidation and Ag^+ is undergoing reduction. The standard cell potential, therefore, is

$$E° = E°_{Ag+/Ag} - E°_{Cd^{2+}/Cd} = 0.7996-(-0.4030) = 1.2026\ V \qquad (2.4.66)$$

(b) To calculate the equilibrium constant we substitute appropriate values into equation 2.4.62.

$$E^\circ = 1.2026\ \mathrm{V} = \frac{0.05916\ \mathrm{V}}{2} \log K \qquad (2.4.67)$$

Solving for *K* gives the equilibrium constant as

$$\text{Log } K = 40.6558 \qquad (2.4.68)$$

$$K = 4.527 \times 10^{40} \qquad (2.4.69)$$

(c) To calculate the potential when $[Ag^+]$ is 0.020 M and $[Cd^{2+}]$ is 0.050 M, we use the appropriate relationship for the reaction quotient,*Q*, in equation 2.4.61.

$$E = E^\circ - \frac{0.05916\ \mathrm{V}}{n} \log \frac{[\mathrm{Cd^{2+}}]}{[\mathrm{Ag^+}]^2} \qquad (2.4.70)$$

$$E = 1.2606\ \mathrm{V} - \frac{0.05916\ \mathrm{V}}{2} \log \frac{(0.050)}{(0.020)^2} \qquad (2.4.71)$$

$$E = 1.14V \qquad (2.4.72)$$

Practice Exercise 2.4

For the following reaction at 25°C

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightleftharpoons 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l) \qquad (6.4.73)$$

calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential under these conditions: $[Fe^{2+}] = 0.50$ M, $[Fe^{3+}] = 0.10$ M, $[MnO_4^-] = 0.025$ M, $[Mn^{2+}] = 0.015$ M, and a pH of 7.00. See Appendix 13 for standard state reduction potentials.

The two half-reactions are the oxidation of Fe^{2+} and the reduction of MnO_4^-.

$$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e-$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

From Appendix 13, the standard state reduction potentials for these half-reactions are

$$E°_{Fe3+/Fe2+} = 0.771\ V \quad E°_{MnO4-/Mn2+} = 1.51\ V$$

(a) The standard state potential for the reaction is

$$E° = E°_{MnO4^-/Mn^{2+}} - E°_{Fe^{3+}/Fe^{2+}} = 1.51V - 0.771V = 0.74V$$

(b) To calculate the equilibrium constant we substitute appropriate values into equation 6.4.62.

$$E^\circ = 0.74\ \text{V} = \frac{0.05916}{5}\log K$$

Solving for *K* gives its value as

$\text{Log } K = 62.5$ $\quad K = 3.2 \times 10^{62}$

(c) To calculate the potential under these non-standard state conditions, we make appropriate substitutions into the Nernst equation.

$$E = E^\circ - \frac{RT}{nF}\ln\frac{[\mathrm{Mn^{2+}}][\mathrm{Fe^{3+}}]^5}{[\mathrm{MnO_4^-}][\mathrm{Fe^{2+}}]^5[\mathrm{H^+}]^8}$$

$$E = 0.74 - \frac{0.05916}{5}\log\frac{(0.015)(0.10)^5}{(0.025)(0.50)^5(1\times10^{-7})^8}$$

$$E = 0.74 - \frac{0.05916}{5}\log\frac{(0.015)(0.10)^5}{(0.025)(0.50)^5(1\times10^{-7})^8} = 0.12\ \text{V}$$

Note: When writing precipitation, acid–base, and metal–ligand complexation reaction, we represent acidity as H_3O^+. Redox reactions are more commonly written using H^+ instead of H_3O^+. For the reaction in Practice Exercise 6.4, we could replace H^+ with H_3O^+ and increase the stoichiometric coefficient for H_2O from 4 to 12, e.g.,

$$5\mathrm{Fe^{2+}}(aq) + \mathrm{MnO_4^-}(aq) + 8\mathrm{H_3O^+}(aq) \rightleftharpoons 5\mathrm{Fe^{3+}}(aq) + \mathrm{Mn^{2+}}(aq) + 12\mathrm{H_2O}(l) \quad (2.4.74)$$

2.5 Le Chatelier's Principle

The equilibrium position for any reaction is defined by a fixed equilibrium constant, not by a fixed combination of concentrations for the reactants and products. This is easily appreciated by examining the equilibrium constant expression for the dissociation of acetic acid.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.75 \times 10^{-5} \qquad \textbf{6.26}$$

As a single equation with three variables, equation 6.26 does not have a unique solution for the concentrations of CH_3COOH, CH_3COO^-, and H_3O^+. At constant temperature, different solutions of acetic acid may have different values for $[H_3O^+]$, $[CH_3COO^-]$ and $[CH_3COOH]$, but will always have the same value of K_a.

If a solution of acetic acid at equilibrium is disturbed by adding sodium acetate, the $[CH_3COO^-]$ increases, suggesting an apparent increase in the value of K_a. Since K_a must remain constant, however, the concentration of all three species in equation 6.26 must change in a fashion that restores K_a to its original value. In this case, equilibrium is reestablished by the partial reaction of CH_3COO^- and H_3O^+ to produce additional CH_3COOH.

The observation that a system at equilibrium responds to a stress by reequilibrating in a manner that diminishes the stress, is formalized as **Le Châtelier's principle.** One of the most common stresses that we can apply to a reaction at equilibrium is to change the concentration of a reactant or product. We already have seen, in the case of sodium acetate and acetic acid, that adding a product to a reaction mixture at equilibrium converts a portion of the products to reactants. In this instance, we disturb the equilibrium by adding a product, and the stress is diminished by partially reacting the excess product. Adding acetic acid has the opposite effect, partially converting the excess acetic acid to acetate.

In our first example, the stress to the equilibrium was applied directly. It is also possible to apply a concentration stress indirectly. Consider, for example, the following solubility equilibrium involving AgCl

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad \textbf{6.27}$$

The effect on the solubility of AgCl of adding $AgNO_3$ is obvious,* but what is the effect of adding a ligand that forms a stable, soluble complex with Ag^+? Ammonia, for example, reacts with Ag^+ as follows

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad \textbf{6.28}$$

Adding ammonia decreases the concentration of Ag^+ as the $Ag(NH_3)_2^+$ complex forms. In turn, decreasing the concentration of Ag^+ increases the solubility of AgCl as reaction 6.27 reestablishes its equilibrium position. Adding together reactions 6.27 and 6.28 clarifies the effect of ammonia on the solubility of AgCl, by showing that ammonia is a reactant.

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad \textbf{6.29}$$

Example 2.9

What is the effect on the solubility of AgCl if HNO_3 is added to the equilibrium solution defined by reaction 6.29?

SOLUTION

Nitric acid is a strong acid that reacts with ammonia as shown here

$$HNO_3(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + NO_3^-(aq)$$

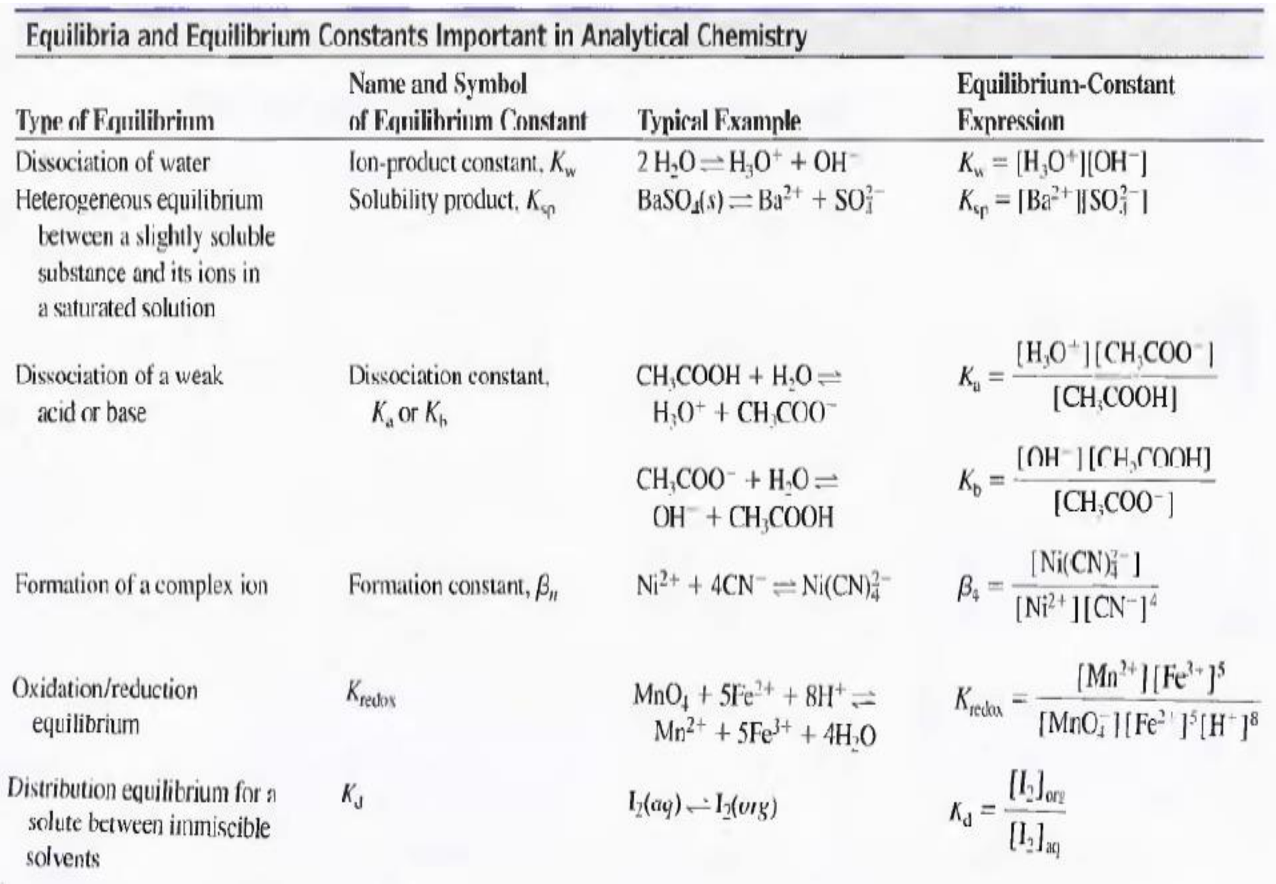
Adding nitric acid lowers the concentration of ammonia. Decreasing ammonia's concentration causes reaction 6.29 to move from products to reactants, decreasing the solubility of AgCl.

Increasing or decreasing the partial pressure of a gas is the same as increasing ecreasing its concentration.† The effect on a reaction's equilibrium position can nalyzed as described in the preceding example for aqueous solutes. Since the centration of a gas depends on its partial pressure, and not on the total pressure e system, adding or removing an inert gas has no effect on the equilibrium po- n of a gas-phase reaction.

Equilibrium Constants For Chemical Reactions

Several types of reactions are commonly used in analytical procedures, either in preparing samples for analysis or during the analysis itself. The most important of these are precipitation reactions, acid–base reactions, complexation reactions, and oxidation–reduction reactions. In this section we review these reactions and their equilibrium constant expressions.

Table 2.1 Summarizes the types of chemical constants and equilibrium constants that are importance in analytical chemistry. Simple applications of some of these constants are illustrated in the sections that follow



Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
		$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4 + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

REFERENCES

- Fundamental of Analytical Chemistry,8th Edition,Skoog.
- Modern of analytical chemistry by David Harvey (DePauw University)

Lecture – 5 Electrochemistry

Electrochemistry Basics

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction.

Introduction

A redox reaction is a reaction that involves a change in oxidation state of one or more elements. When a substance loses an electron, its oxidation state increases; thus, it is oxidized. When a substance gains an electron, its oxidation state decreases, thus being reduced. For example, for the redox reaction

$$H_2 + F_2 \rightarrow 2HF \qquad (1)$$

can be rewritten as follows:

- Oxidation: $H_2 \rightarrow 2H^+ + 2e^-$ (2a)
- Reduction: $F_2 + 2e^- \rightarrow 2F^-$ (2b)

- Overall Reaction : $H_2 + F_2 \rightarrow 2H^+ + 2F^-$ (2c)

Oxidation is the loss of electrons, whereas reduction refers to the acquisition of electrons, as illustrated in the respective reactions above. The species being oxidized is also known as the reducing agent or reductant, and the species being reduced is called the oxidizing agent or oxidant. In this case, H_2 is being oxidized (and is the reducing agent), while F_2 is being reduced (and is the oxidizing agent). The following acronym is useful in remembering this concept:

OIL RIG:

Oxidation Is Losing electrons; Reduction Is Gaining electrons

Example 1: Fe-V Couple

Given the redox reaction $Fe^{3+} + V^{2+} \rightarrow Fe^{2+} + V^{3+}$, which species is oxidized? Which is reduced? Identify the reducing agent and the oxidizing agent.

SOLUTION

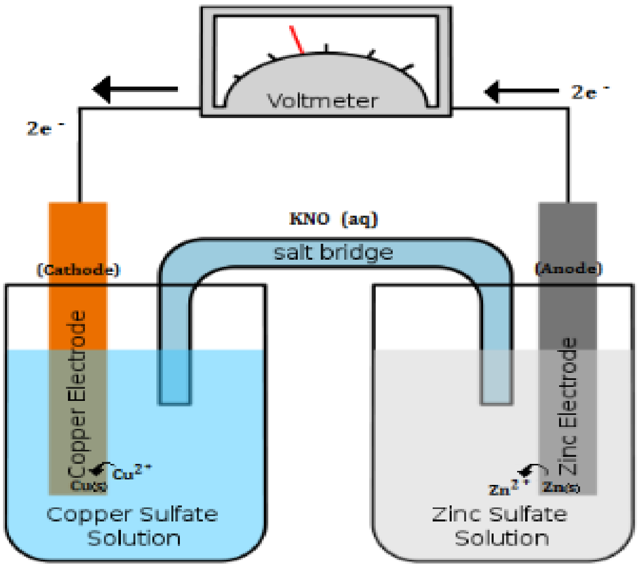
Fe^{3+} is reduced into Fe^{2+}, and V^{2+} is oxidized into V^{3+}. This is because the oxidized species loses electrons, and the reduced species gains electrons. Iron gains an electron ($Fe^{3+} \rightarrow Fe^{2+}$), and vanadium loses an electron ($V^{2+} \rightarrow V^{3+}$). Thus, Fe^{3+} is the oxidizing agent and V^{2+} is the reducing agent.

Voltaic Cells-Galvanic Cells

Voltaic (galvanic) cells are electrochemical cells that contain a spontaneous reaction, and always have a positive voltage. The electrical energy released during the reaction can be used to do work. A voltaic cell consists of two compartments called half-cells. The half-cell where oxidation occurs is called the anode. The other half-cell, where reduction occurs, is called the cathode. The electrons in voltaic cells flow from the negative electrode to the positive electrode—from anode to cathode (see figure below). (Note: the electrodes are the sites of the oxidation and reduction reactions). The following acronym is useful in keeping this information straight: **Red Cat and An Ox**

Reduction Cathode and Anode Oxidation

For an oxidation-reduction reaction to occur, the two substances in each respective half-cell are connected by a closed circuit such that electrons can flow from the reducing agent to the oxidizing agent. A salt bridge is also required to maintain electrical neutrality and allow the reaction to continue.



: The figure above shows that Zn(s) is continuously oxidized, producing aqueous Zn^{2+}:

$$Zn_{(s)} \rightarrow Zn^{2+}\,(aq) + 2e- \qquad (1.1)$$

Conversely, in the cathode, Cu^{2+} is reduced and continuously deposits onto the copper bar:

$$Cu^{2+}\,(aq) + 2e- \rightarrow Cu_{(s)} \qquad (1.2)$$

As a result, the solution containing Zn(s) becomes more positively charged as the solution containing Cu(s) becomes more negatively charged. For the voltaic cell to work, the solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO_3 is added to keep the solutions neutral by adding NO_3^-, an anion, into the anode solution and K^+, a cation, into the cathode solution. As oxidation and reduction proceed, ions from the salt bridge migrate to prevent charge buildup in the cell compartments.

The cell diagram is a shorthand notation to represent the redox reactions of an electrical cell. For the cell described, the cell diagram is as follows

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \mid\mid Cu^{2+}_{(aq)} \mid Cu_{(s)} \qquad (1.3)$$

- A double vertical line (||) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.
  - The anode (where oxidation occurs) is placed on the left side of the ||.
  - The cathode (where reduction occurs) is placed on the right side of the ||.
- A single vertical line (|) is used to separate <u>different</u> states of matter on the same side, and a comma is used to separate <u>like</u> states of matter on the same side. For example:

$$Fe^{2+}_{(aq)} , Fe^{3+}_{(aq)} \mid\mid Ag^{+}_{(aq)} \mid Ag_{(s)} \qquad (1.4)$$

Example 2

Write the cell diagram for this reaction:

$$Cu_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

SOLUTION

$$Cu_{(s)} \mid Cu^{2+}_{(aq)} \mid\mid Ag^{+}_{(aq)} \mid Ag_{(s)}$$

Example 3 Al-Sn Couple

Write cell reactions for this cell diagram:

$$Al_{(s)} \mid Al^{3+}_{(aq)} \mid\mid Sn^{2+}_{(aq)} \mid Sn_{(s)} \qquad (1.5)$$

SOLUTION

Oxidation: $\{Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\} \times 2$

Reduction: $\{Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}\} \times 3$

Net: $2Al_{(s)} + 3Sn^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Sn_{(s)}$

Cell Potential

The oxidation of Zn(s) into Zn^{2+} and the reduction of Cu^{2+} to Cu(s) occur spontaneously. In other words, the redox reaction between Zn and Cu^{2+} is spontaneous. This is due to the difference in potential energy between the two substances. The difference in potential energy between the anode and cathode dictates the direction of electronic movement. Electrons move from areas of higher potential energy to areas of lower potential energy. In this case, the anode has a higher potential energy; electrons therefore move from anode to cathode. The potential difference between the two electrodes is measured in units of volts. One volt (V) is the potential difference necessary to generate a charge of 1 coulomb (C) from 1 joule (J) of energy.

For a voltaic cell, this potential difference is called the **cell potential (or EMF for electromotive force, although it is not really a force)**, which is denoted $\mathbf{E_{cell}}$. For a spontaneous reaction, E_{cell} is positive and ΔG (Gibbs free energy, used to determine if a reaction occurs spontaneously) is negative. Thus, when ΔG is negative the reaction is spontaneous. Merging electrochemistry with thermodynamics gives this formula:

$$\Delta G = -\, n\, F\, E_{cell} \qquad (1.6)$$

Cell potential is different for each voltaic cell; its value depends upon the concentrations of specific reactants and products as well as temperature of the reaction. For standard cell potential, temperature of the reaction is assumed to be 25° Celsius, the concentration of the reactants and products is 1 M, and reaction occurs at 1 atm pressure.
The standard cell potential is denoted E^o_{cell}, and can be written as oxidation potential + reduction potential. For voltaic cells:

$$E^o_{cell} = E^o_{cathode} - E^o_{Anode} \qquad (1.7)$$

Example 4

Calculate E^o_{cell} for the following redox reaction under standard conditions:

$$2Al_{(s)} + 3Sn^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Sn_{(s)} \qquad (1.8)$$

Solution

Oxidation: $\{Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-\} \times 2$ $\quad -E^o = +1.676V$

Reduction: $\{Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}\} \times 3$ $\quad E^o = -0.137V$

Net: $2Al_{(s)} + 3Sn^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Sn_{(s)}$ $\quad E^o_{cell} = -0.137V - (-1.676V)$

$E^o_{cell} = +1.539$ V.

Because the values of the standard potential are given in the form of standard reduction potential for each half-reaction, to calculate the standard cell potential E_{cell}, the substance is being oxidized must be identified; then the standard reduction potential of the oxidation reaction is subtracted from the standard reduction potential of the reducing reaction. For example:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (1.9)$$

Zn is being oxidized, and Cu is being reduced. The potentials for the two half reaction are given in the reduction form:

$$Zn(s) \rightarrow Zn^{2+}(aq) + e- \qquad (1.10)$$

$$Cu^{2+}(aq) + e- \rightarrow Cu(s) \qquad (1.11)$$

The cell potentials indicate which reaction takes place at the anode and which at the cathode. The cathode has a more positive potential energy, and thus:

- Cu is the cathode
- Zn is the anode.

To calculate E^o cell, subtract the E^o of the oxidized half reaction from the E^o cell of the reduction half reaction, which is:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} \qquad (1.12)$$

- Oxidation half reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + e-$ $E^o = -0.763V$
- Reduction half reaction: $Cu^{2+}(aq) + e- \rightarrow Cu(s)$ $E^o = +0.342V$

Net reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (1.13)$$

Therefore:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{cell} = 0.340V - (-0.763V) = +1.103V \qquad (1.14)$$

Example 5: Iron/Vanadium Chemistry

Calculate the cell potential in the following redox reaction under standard conditions:

$$Fe^{3+}(aq) + V^{2+}(aq) \rightarrow Fe^{2+}(aq) + V^{3+}(aq) \qquad (1.15)$$

SOLUTION

Consult the table of standard reduction potentials (Table P1) for each half reaction:

$$Fe^{3+}(aq) + e- \rightarrow Fe^{2+}(aq) \quad \text{with } E^o = 0.771V \qquad (1.16)$$

$$V^{2+}(aq) \rightarrow V^{3+}(aq) + e- \quad \text{with } E^o = -0.255V \qquad (1.17)$$

The cell potential is

$$E^o\ \text{cell} = E^o\ \text{cathode} - E^o\ \text{anode} = 0.771\text{V} - (-0.255\text{V}) = 1.026\text{V} \qquad (1.18)$$

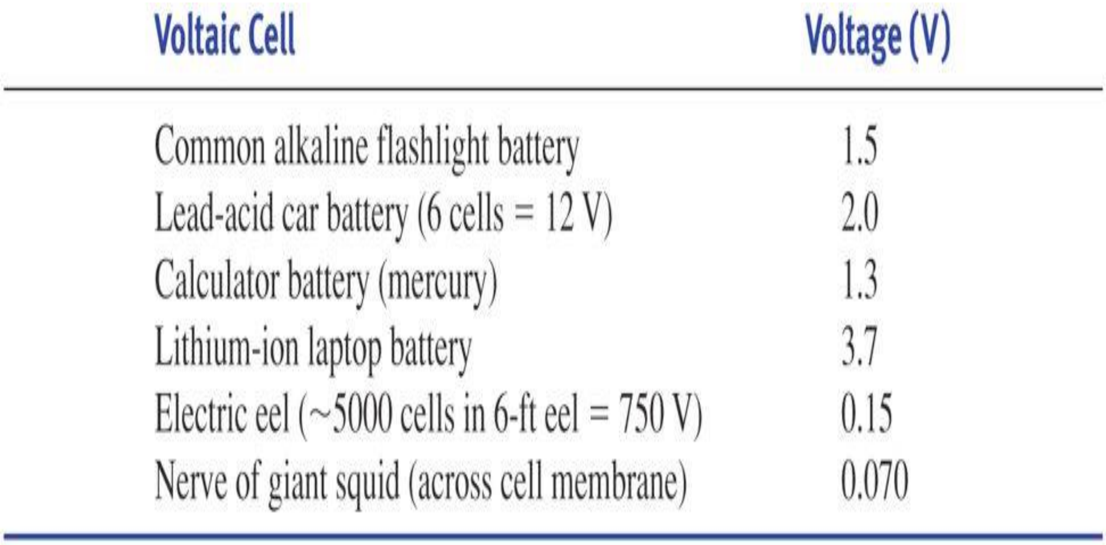
Balancing Redox Reactions

Method 1: Oxidation Number Method

- Step 1: Assign oxidation numbers to each atom.
- Step 2: Determine the net change in charge to determine the ratio of atoms
- Step 3: Use the ratio to eliminate the net charge change
- Step 4: Use the ratio as coefficients for the elements
- Step 5: Add H^+ (under acidic conditions), OH^- (under basic conditions), and H_2O to balance charges.

Method 2: Half-Reaction Method

- Step 1: Determine oxidation numbers for each atom
- Step 2: Use oxidation numbers to determine what is oxidized and what is reduced.
- Step 3: Write a half-reaction for reduction
- Step 4: Write a half-reaction for oxidation
- Step 5: Balance all elements except H and O
  - ○ if have acid redox reaction: Balance the O using H_2O, balance the H using protons
  - ○ if have base redox reaction: Balance O using OH^-
- Step 6: Add up the charge on each side
- Step 7: Balance the charges by adding electrons
- Step 8: Multiply the half-reactions by factors that cancel out electrons
- Step 9: Add the two half-reactions back together to eliminate out intermediates



Voltaic Cell	Voltage (V)
Common alkaline flashlight battery	1.5
Lead-acid car battery (6 cells = 12 V)	2.0
Calculator battery (mercury)	1.3
Lithium-ion laptop battery	3.7
Electric eel (~5000 cells in 6-ft eel = 750 V)	0.15
Nerve of giant squid (across cell membrane)	0.070

18A Characterizing oxidation/reduction reactions

In an oxidation/reduction reaction or redox reaction, electrons are transferred from one reactant to another.

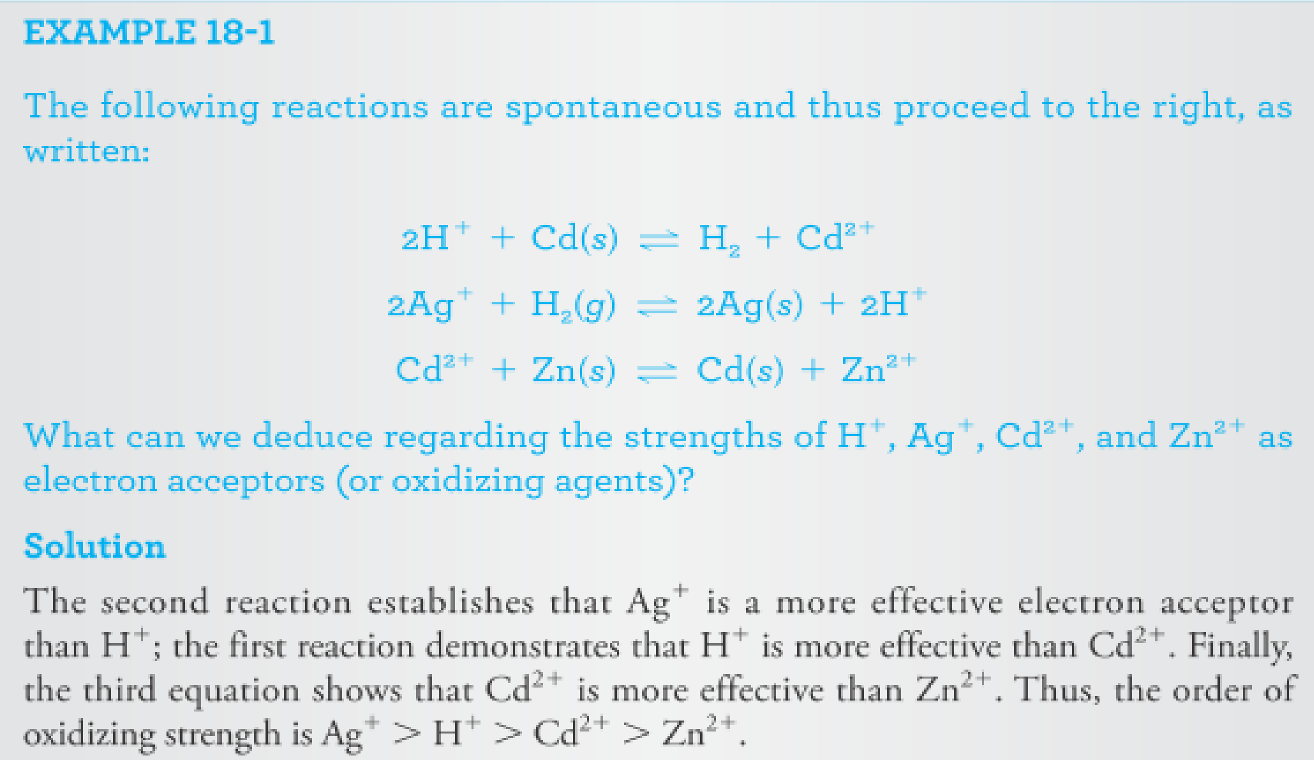
Example, $Ce^{+4} + Fe^{+2} \rightarrow Ce^{+3} + Fe^{+3}$

Iron(II) is oxidized by cerium(IV) ions. A reducing agent is an electron donor. An oxidizing agent is an electron acceptor.

Comparing Redox Reactions to Acid/Base Reactions

Oxidation/reduction reactions can be considered analogous to the Bronsted-Lowry concept of acid/base reactions.

When an acid donates a proton, it becomes a conjugate base that is capable



EXAMPLE 18-1

The following reactions are spontaneous and thus proceed to the right, as written:

$$2H^+ + Cd(s) \rightleftharpoons H_2 + Cd^{2+}$$
$$2Ag^+ + H_2(g) \rightleftharpoons 2Ag(s) + 2H^+$$
$$Cd^{2+} + Zn(s) \rightleftharpoons Cd(s) + Zn^{2+}$$

What can we deduce regarding the strengths of H^+, Ag^+, Cd^{2+}, and Zn^{2+} as electron acceptors (or oxidizing agents)?

Solution

The second reaction establishes that Ag^+ is a more effective electron acceptor than H^+; the first reaction demonstrates that H^+ is more effective than Cd^{2+}. Finally, the third equation shows that Cd^{2+} is more effective than Zn^{2+}. Thus, the order of oxidizing strength is $Ag^+ > H^+ > Cd^{2+} > Zn^{2+}$.

18B Electrochemical cells

An electrochemical cell consists of two conductors called electrodes, each of which is immersed in an electrolyte solution.

Conduction of electricity from one electrolyte solution to the other occurs by migration of potassium ions in the salt bridge in one direction and chloride ions in the other.

Cathodes and Anodes

A cathode is an electrode where reduction occurs.

Examples of typical cathodic reactions:

$$Ag^+ + e^- \Leftrightarrow Ag(s)$$

$$Fe^{+3} + e^- \Leftrightarrow Fe^{+2}$$

An anode is an electrode where oxidation occurs. Typical anodic reactions are:

$$Cu(s) \Leftrightarrow Cu^{+2} + 2e^-$$

$$2Cl^- \Leftrightarrow Cl_2(g) + 2e^-$$

$$Fe^{+2} \Leftrightarrow Fe^{+3} + e^-$$

In a reversible cell, reversing the current reverses the cell reaction.

In an irreversible cell, reversing the current causes a different half-reaction to occur at one or both of the electrodes.

Since the negative terminal of the external voltage source is electron rich, electrons flow from this terminal to the copper electrode, Where reduction of Cu^{2+} to Cu(s) occurs. The current is sustained by the oxidation of Ag (s) to Ag+ at the right hand electrode, producing electrons that flow to the positive terminal of the voltage sourse.

Note : **That in the electrolytic cell, direction of the current is the reverse of that in the galvanic cell in Figure 18.2b. and the reactions at the electrodes are reversed as well.**

The silver electrode is forced to become the anode, while the copper electrode is forced to become the cathode.

The net reaction that occurs:

$$2Ag(s) + Cu^{2+} \Leftrightarrow 2Ag^{+} + Cu(s)$$

Electrolytic Cells

Voltaic cells are driven by a *spontaneous* chemical reaction that produces an electric current through an outside circuit. These cells are important because they are the basis for the batteries that fuel modern society. But they are not the only kind of electrochemical cell. **The reverse reaction in each case is non-spontaneous** and requires electrical energy to occur.

Introduction

The general form of the reaction can be written as:

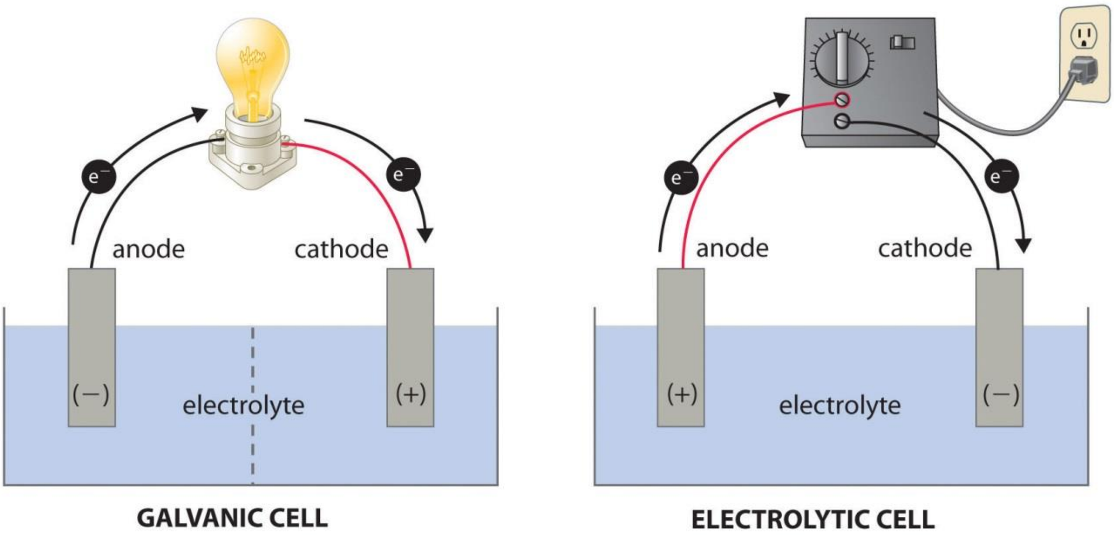
$$\textbf{Reactants} \underset{\longleftarrow \textit{Non spontaneous}}{\overset{\textit{Spontaneous} \longrightarrow}{\rightleftharpoons}} \textbf{Products} + \textbf{Electrical Energy}$$

It is possible to construct a cell that does work on a chemical system by driving an electric current through the system. These cells are called **electrolytic cells**, and operate through **electrolysis.** Electrolysis is used to drive an oxidation-reduction reaction in a direction in which it does not occur spontaneously by *driving an electric current through the system* while doing work on the chemical system itself, and therefore is *non-spontaneous*.

Electrolytic cells, like galvanic cells, are composed of two half-cells--one is a reduction half-cell, the other is an oxidation half-cell. The direction of electron flow in electrolytic cells, however, may be reversed from the direction of spontaneous electron flow in galvanic cells, but the definition of both cathode and anode remain the same, where reduction takes place at the cathode and oxidation occurs at the anode. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

Differences between Galvanic and an Electrolytic cells

Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both require a salt bridge, both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined below:



GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
$Y \rightarrow Y^+ + e^-$

Reduction half-reaction:
$Z + e^- \rightarrow Z^-$

Overall cell reaction:
$Y + Z \rightarrow Y^+ + Z^-$ $(G < 0)$

ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:
$Z^- \rightarrow Z + e^-$

Reduction half-reaction:
$Y^+ + e^- \rightarrow Y$

Overall cell reaction:
$Y^+ + Z^- \rightarrow Y + Z$ $(G > 0)$

Figure 1: Electrochemical Cells. *A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.*

***Table 1**: Properties of Galvanic and Electrochemical Cells*

Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.	Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

Representing Cells Schematically (Cell Notation)

Shorthand notation to describe electrochemical cells:

$$Cu|Cu^{+2}\ (0.0200\ M)||Ag^{+}\ (0.0200\ M)|Ag$$

Recall that standard cell potentials can be calculated from potentials E^0_{cell} for both oxidation and reduction reactions. A positive cell potential indicates that the reaction proceeds spontaneously in the direction in which the reaction is written. Conversely, a reaction with a negative cell potential proceeds spontaneously in the reverse direction.

Cell notations are a shorthand description of voltaic or galvanic (spontaneous) cells. The reaction conditions (pressure, temperature, concentration, etc.), the anode, the cathode, and the electrode components are all described in this unique shorthand.

Recall that oxidation takes place at the anode and reduction takes place at the cathode. When the anode and cathode are connected by a wire, electrons flow from anode to cathode.

Lecture – 6 Electrochemistry

Cell Notation Rules:

1. The anode half-cell is described first; the cathode half-cell follows. Within a given half-cell, the **reactants** are specified first and the **products** last. The description of the oxidation reaction is first, and the reduction reaction is last; when you read it, your eyes move in the direction of electron flow. **Spectator ions** are not included.
2. A single vertical line (|) is drawn between two chemical species that are in different phases but in physical contact with each other (e.g., solid electrode | liquid with **electrolyte**). A double vertical line (||) represents a salt bridge or porous membrane separating the individual half-cells.
3. The phase of each chemical (s, l, g, aq) is shown in parentheses. If the electrolytes in the cells are not at standard conditions, concentrations and/or pressure, they are included in parentheses with the phase notation. If no concentration or pressure is noted, the electrolytes in the cells are assumed to be at standard conditions (1.00 M or 1.00 atm and 298 K).

Using these rules, the notation for the cell we put together is:

$$Cd\ (s)\ |\ Cd^{2+}\ (aq,\ 0.15\ M)\ ||\ Ag^{+}\ (aq,\ 0.20\ M)\ |\ Ag\ (s)$$

The cell potential E_{cell} is related to the free energy of the reaction ΔG by

$$\Delta G = -\ nFE_{cell}$$

If the reactants and products are in their standard states, the resulting cell potential is called the standard cell potential.

$$\Delta G^{\circ} = -nFE^{\circ}_{cell} = -RT\ \ln K_{eq}$$

The Relationship between Cell Potential and the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^{\circ} = -\ RT\ \ln K \qquad (20.3.17)$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation $\Delta G^{0} = -\ n\ FE^{0}_{cell}$), we can write

$$-\,n\,F\,E^\circ_{cell} = -\,R\,T\ln K \qquad (20.3.18)$$

Rearranging this equation,

$$E^\circ_{cell} = \left(\frac{RT}{nF}\right)\ln K \qquad (20.3.19)$$

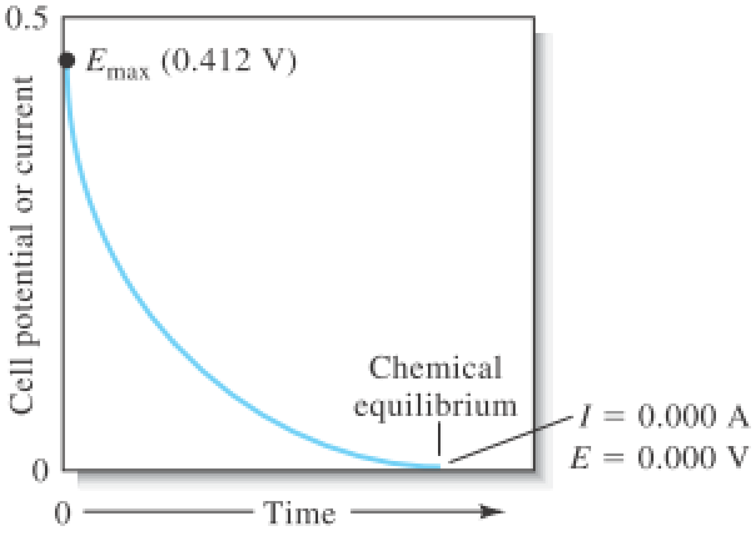
For T = 298 K, Equation 20.3.19 can be simplified as follows:

$$E^\circ_{cell} = \left(\frac{RT}{nF}\right)\ln K = \left[\frac{[8.314\ \mathrm{J/(mol\cdot K)}](298\ \mathrm{K})]}{n[96{,}486\ \mathrm{J/(V\cdot mol)}]}\right]2.303\log K = \left(\frac{0.0591\ \mathrm{V}}{n}\right)\log K \qquad (20.3.20)$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Discharging a Galvanic Cell

Cell potential in the galvanic cell as a function of time. The cell current, which is directly related to the cell potential, also decreases with the same time behavior.



The Standard Hydrogen Reference Electrode (SHE)

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 20.2.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad (20.2.4)$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

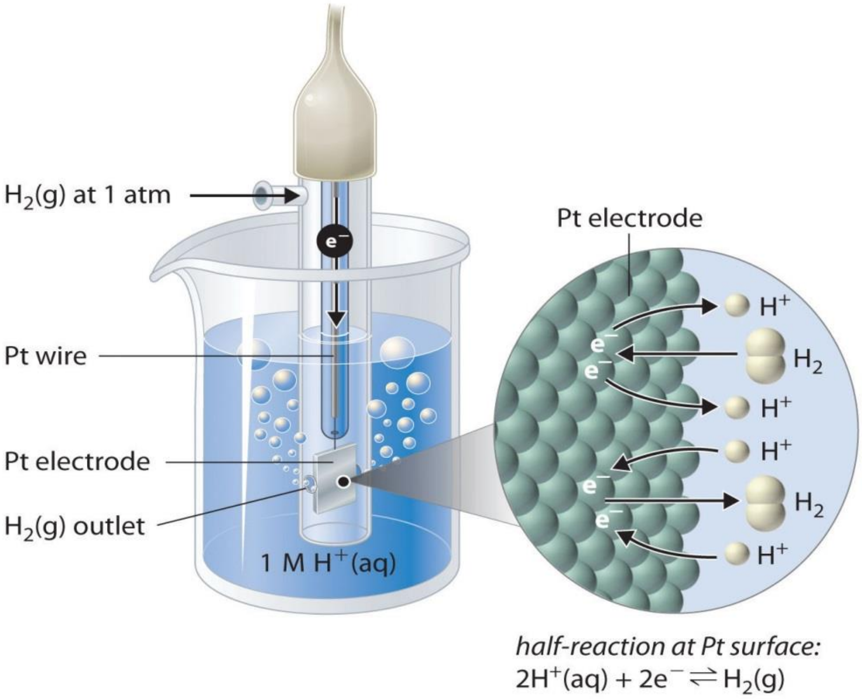


***Figure* 20.2.2:** *The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.*

Figure 20.2.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+}ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn(s) \mid Zn^{2+}(aq) \parallel H^+(aq,1M) \mid H_2(g,1atm) \mid Pt(s) \qquad (20.2.5)$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ E°cathode = 0V (20.2.6)
- anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ E°anode = −0.76V (20.2.7)
- overall: $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$ (20.2.8)

$$E°_{cell} = E°_{cathode} - E°_{anode} = 0.76V \qquad (20.2.9)$$

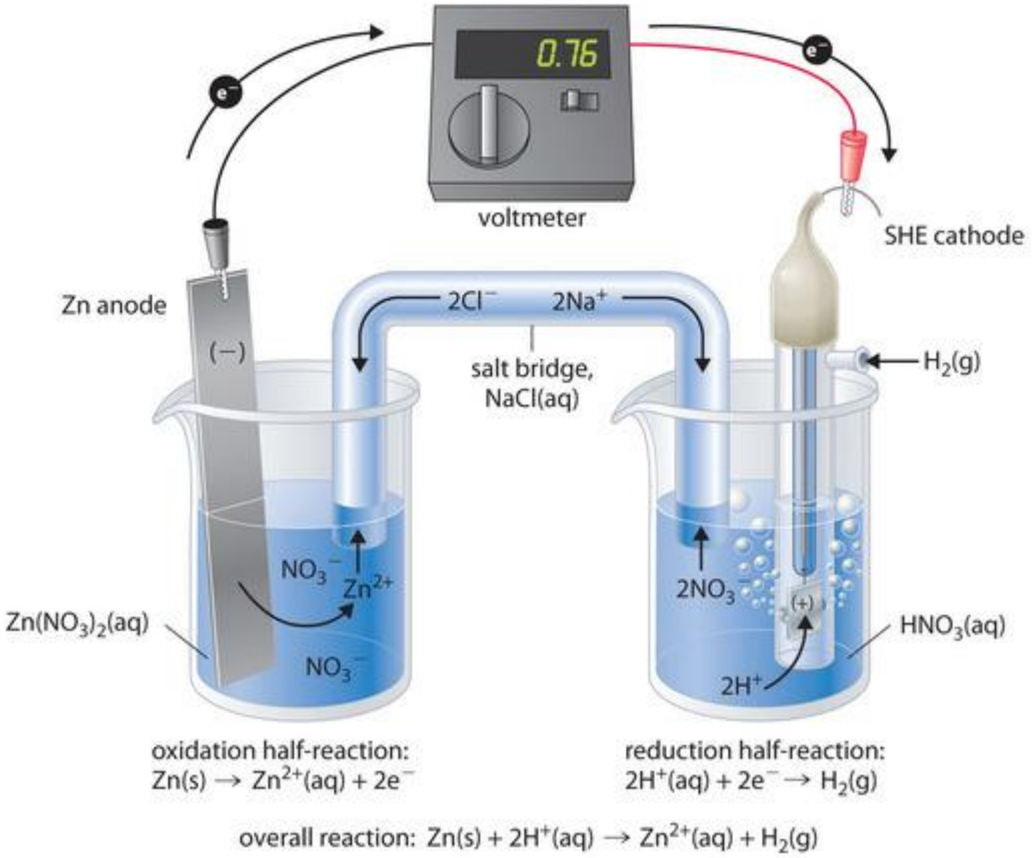


Figure* 20.2.3*: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ is reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain

$$E°_{cell}: 0 - (-0.76\ V) = 0.76\ V.$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

Note : E° values do **NOT** depend on the stoichiometric coefficients for a half-reaction, because it is an *intensive* property.

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq,1M) \parallel Cu^{2+}(aq,1M) \mid Cu(s) \qquad (20.2.15)$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

- cathode:
  $$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \qquad E°cathode = 0.34V \qquad (20.2.16)$$
- anode:
  $$Zn(s) \rightarrow Zn^{2+}(aq,1M) + 2e^{-} \qquad E°anode = -0.76V \qquad (20.2.17)$$

overall:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad (20.2.18)$$

$$E°cell = E°cathode - E°anode = 1.10V \qquad (20.2.19)$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 4 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

Note : A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.

Example 20.2.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$\text{cathode: } Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$$

$$\text{anode: } Ga(s) \rightarrow Ga^{3+}(aq) + 3e^{-}$$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

B. Use Equation 20.2.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution:

A.. We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^{-} \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B. Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of $Ni^{2+}$to Ni from Equation 20.2.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$0.27\ V = E°_{cathode} - (-\ 0.55\ V)$$

$$E°_{cathode} = -0.28\ V$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\ V) = 0.28\ V$ for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

Exercise 20.2.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$
- anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode? **(Answer:** 0.85 V)

We can use this procedure described to measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table P2. These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table 20.2.1. All reactants that lie below the SHE in the table are stronger oxidants than H^+, and all those that lie above the SHE are weaker. The strongest oxidant in the table is F_2, with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

***Table** 20.2.1: Standard Potentials for Selected Reduction Half-Reactions at 25°C*

Half-Reaction	E° (V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.040
$Be^{2+}(aq) + 2e^- \rightleftharpoons Be(s)$	–1.99

Table 20.2.1*: Standard Potentials for Selected Reduction Half-Reactions at 25°C*

Half-Reaction	E° (V)
$Al^{3+}(aq) + 3e^{-} \rightleftharpoons Al(s)$	–1.676
$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	–0.7618
$Ag_2S(s) + 2e^{-} \rightleftharpoons 2Ag(s) + S^{2-}(aq)$	–0.71
$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$	–0.44
$Cr^{3+}(aq) + e^{-} \rightleftharpoons Cr^{2+}(aq)$	–0.424
$Cd^{2+}(aq) + 2e^{-} \rightleftharpoons Cd(s)$	–0.4030
$PbSO_4(s) + 2e^{-} \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	–0.356
$Ni^{2+}(aq) + 2e^{-} \rightleftharpoons Ni(s)$	–0.257
$2SO_4^{2-}(aq) + 4H^{+}(aq) + 2e^{-} \rightleftharpoons S_2O_6^{2-}(aq) + 2H_2O(l)$	–0.25
$Sn^{2+}(aq) + 2e^{-} \rightleftharpoons Sn(s)$	−0.14
$2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^{-} \rightleftharpoons Sn^{2+}(aq)$	0.154
$Cu^{2+}(aq) + e^{-} \rightleftharpoons Cu^{+}(aq)$	0.159
$AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-}(aq)$	0.2223
$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$	0.3419
$O_2(g) + 2H_2O(l) + 4e^{-} \rightleftharpoons 4OH^{-}(aq)$	0.401
$H_2SO_3(aq) + 4H^{+}(aq) + 4e^{-} \rightleftharpoons S(s) + 3H_2O(l)$	0.45
$I_2(s) + 2e^{-} \rightleftharpoons 2I^{-}(aq)$	0.5355
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^{-} \rightleftharpoons MnO_2(s) + 4OH^{-}(aq)$	0.60
$O_2(g) + 2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2O_2(aq)$	0.695
$H_2SeO_3(aq) + 4H^{+} + 4e^{-} \rightleftharpoons Se(s) + 3H_2O(l)$	0.74
$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$	0.771
$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$	0.7996
$NO_3^{-}(aq) + 3H^{+}(aq) + 2e^{-} \rightleftharpoons HNO_2(aq) + H_2O(l)$	0.94
$Br_2(aq) + 2e^{-} \rightleftharpoons 2Br^{-}(aq)$	1.087
$MnO_2(s) + 4H^{+}(aq) + 2e^{-} \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	1.23
$O_2(g) + 4H^{+}(aq) + 4e^{-} \rightleftharpoons 2H_2O(l)$	1.229
$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.36
$Cl_2(g) + 2e^{-} \rightleftharpoons 2Cl^{-}(aq)$	1.396
$Ce^{4+}(aq)+e^{-} \rightleftharpoons Ce^{3+}(aq)$ (20.2.53)	1.44
$PbO_2(s) + HSO_4^{-}(aq) + 3H^{+}(aq) + 2e^{-} \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	1.690
$H_2O_2(aq) + 2H^{+}(aq) + 2e^{-} \rightleftharpoons 2H_2O(l)$	1.763
$F_2(g) + 2e^{-} \rightleftharpoons 2F^{-}(aq)$	2.87

Similarly, all species in Table 20.2.1 that lie above H_2 are stronger reductants than H_2, and those that lie below H_2 are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of −3.04 V. This fact might be surprising because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the Li^+ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a significantly greater $\Delta H_{hydration}$ for Li^+ compared with Cs^+. Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

Note : Species in Table 20.2.1 (or Table P2) that lie above H_2 are stronger reducing agents (more easily oxidized) than H_2. Species that lie below H_2 are stronger oxidizing agents.

Because the half-reactions shown in Table 20.2.1 are arranged in order of their E° values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies below it in the table. Conversely, any species on the right side of a half-reaction will spontaneously reduce any species on the left side of another half-reaction that lies above it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E°_{cell} > 0$), as illustrated below.

The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce MnO_2, and oxygen gas will evolve from the solution.

Exercise 20.2.4 / Use the data in Table 20.2.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $2Ce^{4+}(aq) + 2Cl^{-}(aq) \rightarrow 2Ce^{3+}(aq) + Cl_2(g)$
2. $4MnO_2(s) + 3O_2(g) + 4OH^{-}(aq) \rightarrow 4MnO_4^{-}(aq) + 2H_2O$

Answer

1. spontaneous ($E°_{cell} = 0.36$ V)
2. nonspontaneous ($E°_{cell} = -0.20$ V)

Although the sign of $E°_{cell}$ tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what extent the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics.

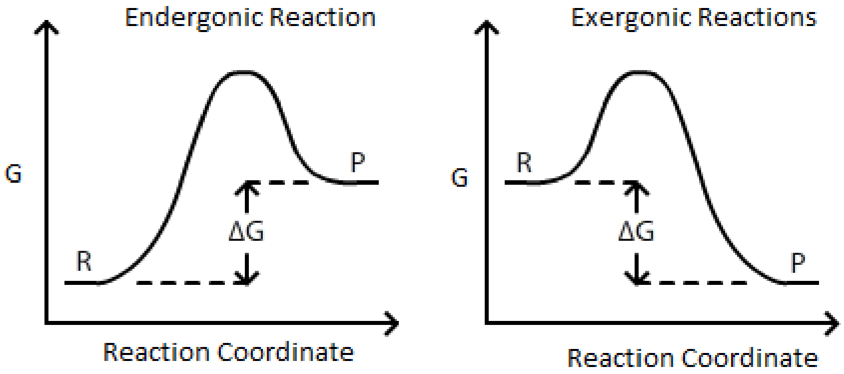
Connection between Ecell, ∆G, and K

The connection between cell potential, Gibbs energy and constant equilibrium are directly related in the following multi-part equation:

$$\Delta G^{o} = -RT\ln K_{eq} = -nFE^{o}cell$$

ΔG: Gibbs Energy

ΔG is the change of Gibbs (free) energy for a system and ΔG° is the Gibbs energy change for a system under standard conditions (1 atm, 298K). On an energy diagram, ΔG can be represented as:



Where ΔG is the difference in the energy between reactants and products. In addition ΔG is unaffected by external factors that change the kinetics of the reaction. For example if E_a(activation energy) were to decrease in the presence of a catalyst or the kinetic energy of molecules increases due to a rise in temperature, the ΔG value would remain the same

$E°_{cell}$: Standard Cell Potential

$E°_{cell}$ is the electromotive force (also called cell voltage or cell potential) between two half-cells. The greater the $E°_{cell}$ of a reaction the greater the driving force of electrons through the system, the more likely the reaction will proceed (more spontaneous). $E°_{cell}$ is measured in volts (V). The overall voltage of the cell = the half-cell potential of the reduction reaction + the half-cell potential of the oxidation reaction. To simplify,

$$E_{cell} = E_{reduction} + E_{oxidation} \qquad (1)$$

or

$$E_{cell} = E_{cathode} + E_{anode} \qquad (2)$$

The potential of an oxidation reduction (loss of electron) is the negative of the potential for a reduction potential (gain of electron). Most tables only record the standard reduction half-reactions. In other words, most tables only record the standard reduction potential; so in order to find the standard oxidation potential, simply reverse the sing of the standard reduction potential.

Lecture – 7 Electrochemistry

Difference between E_{cell} and E^o_{cell}

E^o cell is the standard state cell potential, which means that the value was determined under standard states. The standard states include a concentration of 1 Molar (mole per liter) and an atmospheric pressure of 1. Similar to the standard state cell potential, E^o_{cell}, the E_{cell} is the non-standard state cell potential, which means that it is not determined under a concentration of 1 M and pressure of 1 atm. The two are closely related in the sense that the standard cell potential is used to calculate for the cell potential in many cases.

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q \qquad (3)$$

Other simplified forms of the equation that we typically see:

$$E_{cell} = E^o_{cell} - \frac{0.0257}{n} \ln Q \qquad (4)$$

or in terms of log10log10 (base 10) instead of the natural logarithm (base e)

$$E_{cell} = E^o_{cell} - \frac{0.0592}{n} \log_{10} Q \qquad (5)$$

Both equations applies when the temperature is 25ºC. Deviations from 25ºC requires the use of the original equation. Essentially, E^o is E at standard conditions

Example 1

What is the value of E_{cell} for the voltaic cell below:

$$Pt(s) \mid Fe^{2+}(0.1M), Fe^{3+}(0.2M) \mid\mid Ag^{+}(0.1M) \mid Ag(s)$$

SOLUTION

To use the **Nernst equation**, we need to establish E^o_{cell} and the reaction to which the cell diagram corresponds so that the form of the reaction quotient (Q) can be revealed. Once we have determined the form of the **Nernst equation**, we can insert the concentration of the species.

Solve: $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$= E^o_{Ag+/Ag} - E^o_{Fe3+/Fe2+}$

$= 0.800V - 0.771V = 0.029V$

Now to determine Ecell for the reaction

$$Fe^{2+}(0.1M) + Ag^{+}(1.0M) \rightarrow Fe^{3+}(0.20M) + Ag(s)$$

Use the Nernst equation

$$E_{cell} = 0.029V - (0.0592V / 1) \log [Fe^{3+}] / [Fe^{2+}][Ag+]$$

$$=0.029V - 0.0592V*\log [0.2] / [0.1]*[1.0]$$

$$= 0.011V$$

K: The Equilibrium Constant

K is the equilibrium constant of a general reaction

$$aA + bB \leftrightharpoons cC + dD \qquad (6)$$

and is expressed by the reaction quotient:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (7)$$

Example 2

Given $K = 2.81\times10^{-16}$ for a following reaction

$$Cu^{2+}(aq) + Ag(s) \rightleftharpoons Cu(s) + 2Ag^{+}$$

Find ∆G.

Solution:

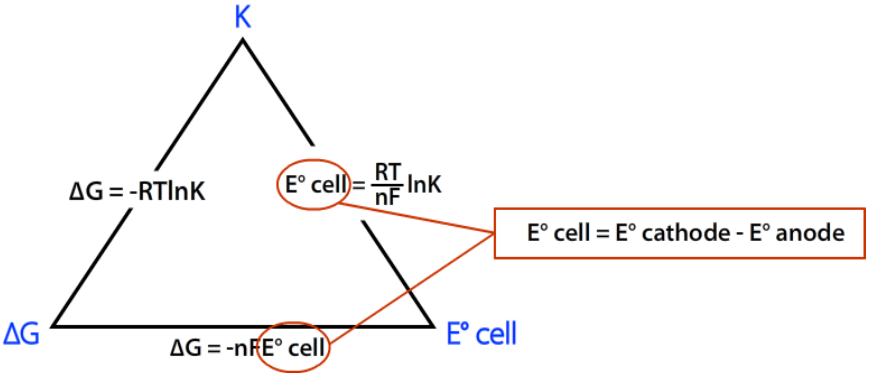
Use the following formula: **$\Delta G = - RT \ln K$**

$$= 8.314 \times 298 \times \ln(2.81\times10^{-16}) = - 8.87\times10^{5}$$

$$= \mathbf{8.871\ kJ}$$

The Relationship Between the Three

The relationship between ∆G, K, and E° cell can be represented by the following diagram.



where

- R = 8.314 J mol C^{-1}
- T = Temp in K
- n = moles of e^- from balanced redox reaction
- F = Faraday's constant = 96,485 C/mol

$E°_{cell}$ can be calculated using the following formula:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{Reduction} - E^o_{Oxidation} \qquad (8)$$

Summary Table

E° cell	∆G	Q & K Relationship	Reaction Direction	Spontaneity (as written)
> 0	-	Q < K	Forward	Spontaneous
< 0	+	Q > K	Backward	Non-spontaneous
= 0	= 0	Q = K	No Reaction	N/A

Example 3: Using ∆G = - RT lnK

Question Find the E° cell for the following coupled half-reactions

SOLUTION

1. Determine the cathode and anode in the reaction

$Zn_{(s)} \leftrightarrow Zn^{2+}_{(aq)} + 2e^-$ Anode, Oxidation (since $Zn_{(s)}$ increase oxidation state from 0 to +2)

$Cu^{2+}_{(aq)} + 2e^- \leftrightarrow Cu_{(s)}$ Cathode, Reduction (since $Cu^{2+}_{(aq)}$ decreases oxidation state from +2 to 0)

2. Determine the E° cell values using the standard reduction potential table (Table P1)

$Zn_{(s)} \leftrightarrow Zn^{2+}_{(aq)} + 2e^-$ -0.763

$Cu^{2+}_{(aq)} + 2e^- \leftrightarrow Cu_{(s)}$ +0.340

3. Use **E° cell = E°cathode - E°anode**

= 0.340 - (-0.763)

= 1.103 V

Example 5: Using E° cell = (RT/nF) lnK

Given the E° cell for the reaction

Cu(s) + 2H+(aq) ⇌ Cu2+(aq) + H2(g)

is -0.34V, find the equilibrium constant (K) for the reaction.

SOLUTION

Step 1: Split into two half reaction

$Cu_{(s)} \leftrightarrow Cu^{2+(aq)}$

$2H^+_{(aq)} \leftrightarrow H_{2(g)}$

Step 2: Balance the half reactions with charges to determine n

$Cu_{(s)} \leftrightarrow Cu^{2+}_{(aq)} + 2e^-$

$2H^+_{(aq)} + 2e^- \leftrightarrow H_{2(g)}$

Therefore n=2

Step 3: From the example above, E° cell = - 0.34V

- 0.34 = (0.025693/2) lnK

$K = e^{(-0.34 \times 2 / 0.025693)}$

K = 3.19 x 10^{-12}

Effect of Concentration on Electrode Potentials: The Nernst Equation

Consider the reversible half-reaction

$$aA + bB + \dots + ne^- \Leftrightarrow cC + dD + \dots$$

where the capital letters represent formulas for the participating species, e^- represents the electrons, and the lower case italic letters indicate the number of moles of each species appearing in the half-reaction as it has been written.

The electrode potential for this process is given by the equation

$$E = E^0 - \frac{RT}{nF}\ln\frac{[C]^c[D]^d\dots}{[A]^a[B]^b\dots}$$

$$E = E^0 - \frac{0.0592}{n}\log\frac{[C]^c[D]^d\dots}{[A]^a[B]^b\dots}$$

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

Introduction

The *Nernst Equation* is derived from the Gibbs free energy **under standard conditions**.

$$E^o = E^o_{reduction} - E^o_{oxidation} \qquad (1)$$

ΔG is also related to E under general conditions (standard or not) via

$$\Delta G = -nFE \qquad (2)$$

with

- n is the number of electrons transferred in the reaction (from balanced reaction),
- F is the Faraday constant (96,500 C/mol), and
- E is potential difference.

Under standard conditions, equation 2 is then

$$\Delta G^o = -nFE^o. \qquad (3).$$

Hence, when E^o is positive, the reaction is spontaneous and when E^o is negative, the reaction is non-spontaneous. From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard equations via

$$\Delta G = \Delta G^o + RT \ln Q \qquad (4)$$

Substituting $\Delta G = -nFE$ and $\Delta G^o = -nFE^o$ into equation 4we have:

$$-\ nFE = -nFE^o + RT \ln Q \qquad (5)$$

Divide both sides of the equation above by $-nF$, we have

$$E = E^o - \frac{RT}{nF}\ln Q$$

Equation 6 can be rewritten in the form of log10log10:

$$E = E^o - \frac{2.303RT}{nF}\log Q \qquad \text{(Generalized Nernst Equation)}$$

At standard temperature T = 298 K, the $\frac{2.303RT}{F}$ term equals 0.0592 V and this equation turns into:

$$E = E^o - \frac{0.0592\,V}{n}\log Q \qquad \text{(Nernst Equation @ 298 K)}$$

The equation above indicates that the electrical potential of a cell depends upon the reaction quotient Q of the reaction. As the redox reaction proceeds, reactants are consumed, and thus concentration of reactants decreases. Conversely, the products concentration increases due to the increased in products formation. As this happens, cell potential gradually *decreases* until the reaction is at equilibrium, at which $\Delta G = 0$. At equilibrium, the reaction quotient $Q = Keq$. Also, at equilibrium, $\Delta G = 0$ and $\Delta G = -nFE$, so $E = 0$.

Therefore, substituting $Q=Keq$ and $E=0$ into the Nernst equation, we have:

$$0 = E^o - \frac{RT}{nF}\ln K_{eq} \qquad (7)$$

At room temperature, the equation above simplifies into (notice natural log was converted to log base 10):

$$0 = E^o - \frac{0.0592\,V}{n}\log K_{eq} \qquad (8)$$

This equation can be rearranged into:

$$\log K_{eq} = \frac{nE^o}{0.0592V} \tag{9}$$

The equation above indicates that the equilibrium constant Keq **is proportional to the standard potential** of the reaction. Specifically, when:

- $K > 1$, $E^o > 0$, reaction favors products formation.
- $K < 1$, $E^o < 0$, reaction favors reactants formation.

This result fits Le Châtlier's Principle, which states that when a system at equilibrium experiences a change, the system will minimize that change by shifting the equilibrium in the opposite direction.

Example 1

The $E^o\text{cell} = +1.10V$ for the Zn-Cu redox reaction:

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s).$$

What is the equilibrium constant for this reversible reaction?

SOLUTION

Under standard conditions, $[Cu^{2+}] = [Zn^{2+}] = 1.0$ M, and T = 298 K. As the reaction proceeds, $[Cu^{2+}]$ decreases as $[Zn^{2+}]$increases. Lets say after one minute, $[Cu^{2+}] = 0.05M$ while $[Zn^{2+}] = 1.95M$. According to the Nernst equation, the cell potential after 1 minute is:

$$E = E^o - \frac{0.0592V}{n}\log Q$$

$$E = 1.10V - \frac{0.0592V}{2}\log\frac{1.95\ M}{0.05\ M}$$

$$E = 1.05\ V$$

$$E = 1.05V$$

As you can see, the initial cell potential is $E = 1.10V$, after 1 minute, the potential drops to 1.05 V. This is after 95% of the reactants have been consumed. As the reaction continues to progress, more Cu^{2+} will be consumed and more Zn^{2+} will be generated (at a 1:1 ratio). As a result, the cell potential continues to decrease and when the cell potential drops down to 0, the concentration of reactants and products stops changing.

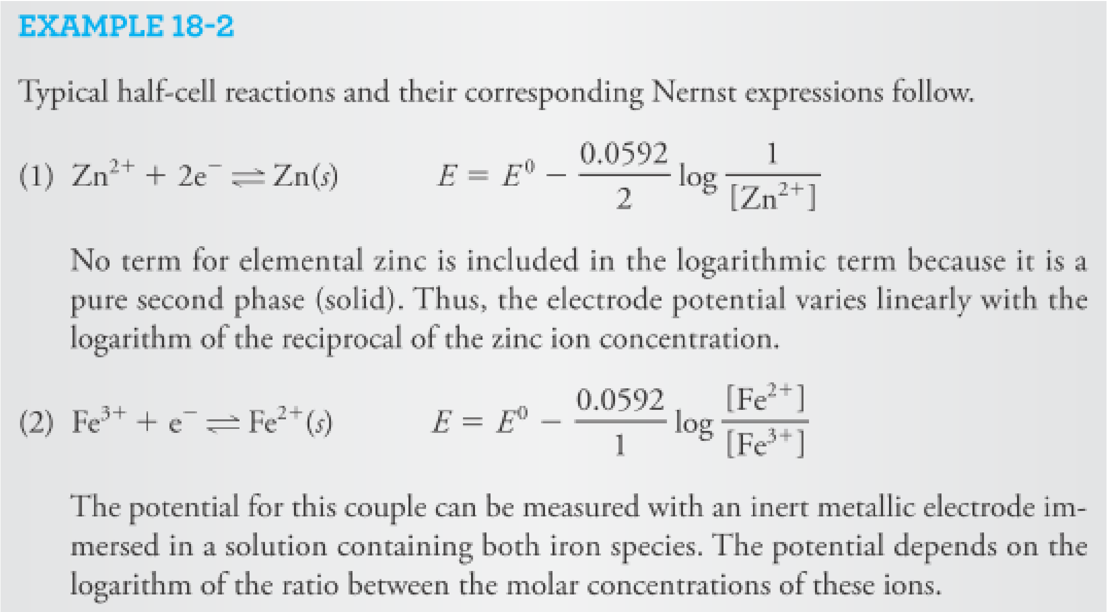
This is when the reaction is at equilibrium. From from equation 9, the Keq can be calculated from

$$\log K_{eq} = \frac{2 \times 1.10\,V}{0.0592\,V}$$

Log Keq = 37.2

$$K_{eq} = 10^{37.2} = 1.58 \times 10^{37}$$

This make sense from a Le Châtlier's Principle, since the reaction strongly favors the products over the reactants to result in a large E^o cell of 1.103 V. Hence, the cell is greatly out of equilibrium under standard conditions. Reactions that are just weakly out of equilibrium will have smaller E^0 cell values (neglecting a change in n of course).



EXAMPLE 18-2

Typical half-cell reactions and their corresponding Nernst expressions follow.

(1) $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ $\qquad E = E^0 - \frac{0.0592}{2}\log\frac{1}{[Zn^{2+}]}$

No term for elemental zinc is included in the logarithmic term because it is a pure second phase (solid). Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration.

(2) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}(s)$ $\qquad E = E^0 - \frac{0.0592}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$

The potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species. The potential depends on the logarithm of the ratio between the molar concentrations of these ions.

(3) $2H^+ + 2e^- \rightleftharpoons H_2(g)$ $$E = E^0 - \frac{0.0592}{2} \log \frac{p_{H_2}}{[H^+]^2}$$

In this example, p_{H_2} is the partial pressure of hydrogen (in atmospheres) at the surface of the electrode. Usually, its value will be the same as atmospheric pressure.

(4) $MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$

$$E = E^0 - \frac{0.0592}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

In this situation, the potential depends not only on the concentrations of the manganese species but also on the pH of the solution.

(5) $AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$ $$E = E^0 - \frac{0.0592}{1} \log [Cl^-]$$

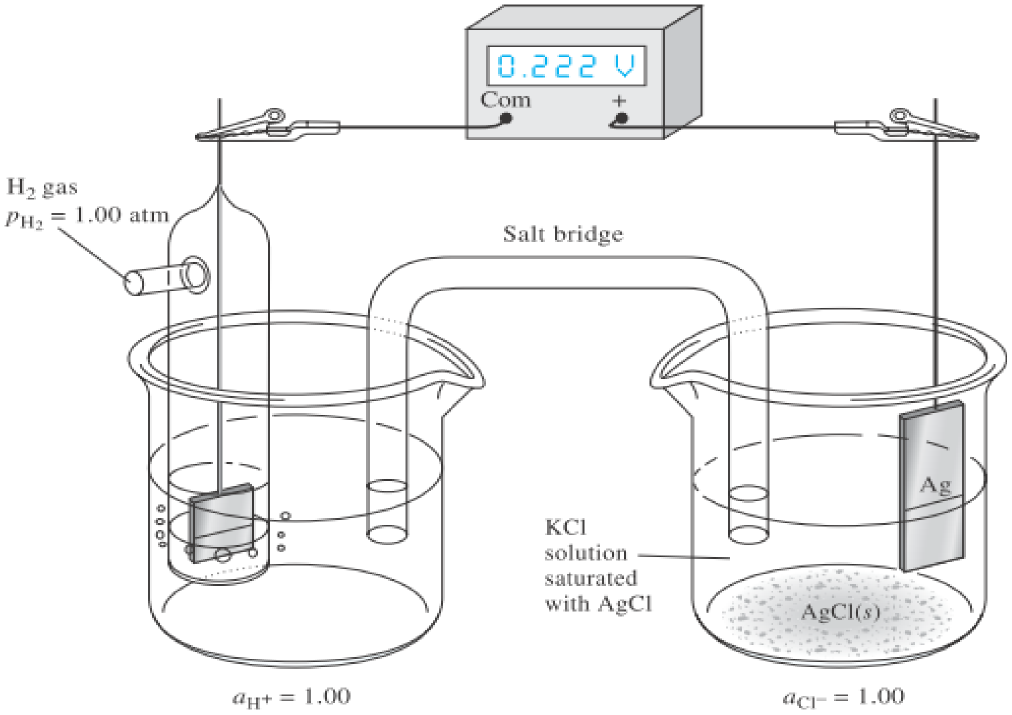
This half-reaction describes the behavior of a silver electrode immersed in a chloride solution that is *saturated* with AgCl. To ensure this condition, an excess of the solid AgCl must always be present. Note that this electrode reaction is the sum of the following two reactions:

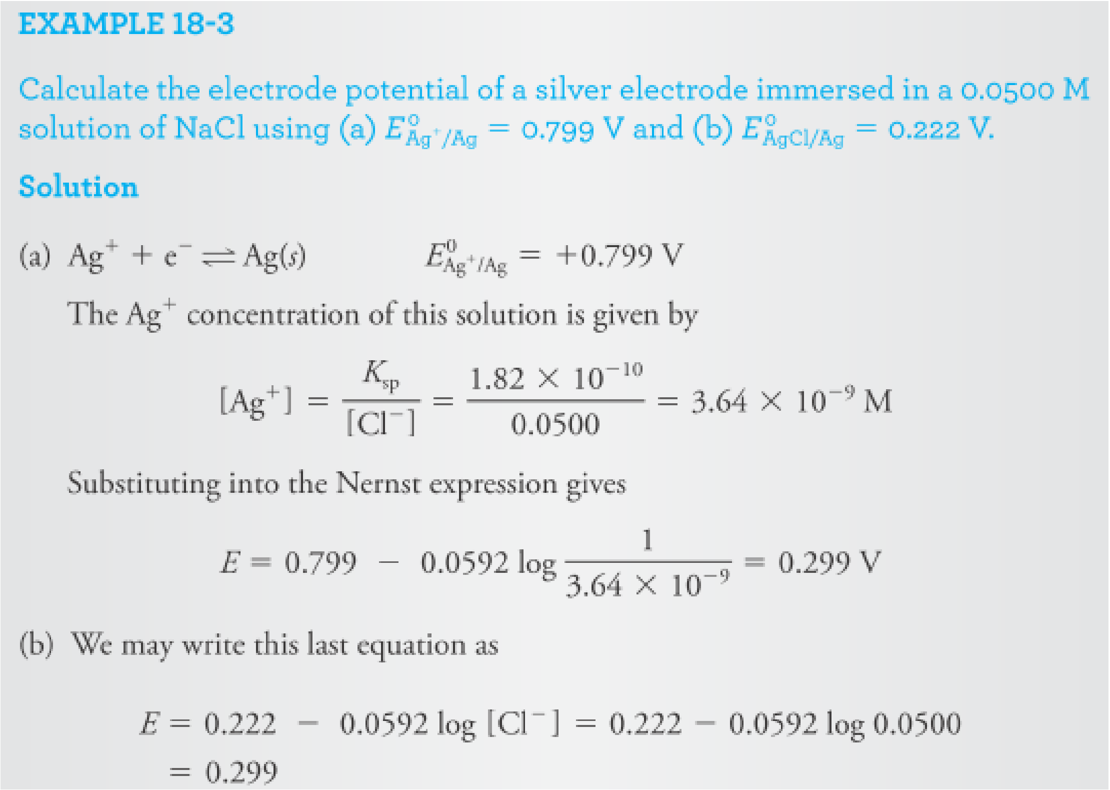
$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$
$$Ag^+ + e^- \rightleftharpoons Ag(s)$$

Note also that the electrode potential is independent of the amount of AgCl present as long as there is at least some present to keep the solution saturated.

Systems Involving Precipitates or Complex Ions

Figure 18-9 The measurement of the standard electrode potential for the Ag/AgCl electrode.





EXAMPLE 18-3

Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^0_{Ag^+/Ag} = 0.799$ V and (b) $E^0_{AgCl/Ag} = 0.222$ V.

Solution

(a) $Ag^+ + e^- \rightleftharpoons Ag(s)$ $\qquad E^0_{Ag^+/Ag} = +0.799$ V

The Ag^+ concentration of this solution is given by

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9}\ M$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299\ V$$

(b) We may write this last equation as

$$E = 0.222 - 0.0592 \log [Cl^-] = 0.222 - 0.0592 \log 0.0500$$
$$= 0.299$$

References

- Fundamental of Analytical Chemistry,8th Edition,Skoog.
- Petrucci, et al. General Chemistry: Principles & Modern Applications. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.

Contributors

- Justin Shorb (Hope College), Yong Chul Yoon (Hope College)

LECTURE- 8

Volumetric Methods of Analysis
Titrimetric Analysis

By
Assist. Prof. Dr. Hamad K. AbdulKadir

Introduction

The term titrimetric analysis refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of a substance to be determined. The solution of accurately known concentration is called ***standard solution***.

The term volumetric analysis was used for this form of quantitative determination but it has now been replaced by titrimetric analysis. In titrimetric analysis the reagent of known concentration is called ***titrant*** and the substance being titrated is termed the ***titrand***.

The standard solution is usually add from a long graduated tube called burette. The process of adding the standard solution until the reaction is just complete is termed titration. The point at which this occurs is called ***equivalence point*** or the theoretical (or stoichiometric) end point. The completion of the titration is detected by some physical change, produced by the standard solution itself or, more usually, by the addition of an auxiliary reagent, known as an ***indicator*** ; alternatively some other physical measurement may be used. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change (either a color change or the formation of turbidity) in the liquid being titrated. The point at which this occurs is called the end point of the titration. In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs this represents the ***titration error***. The indicator and experimental conditions should be so selected that the difference between the visible end point and equivalence point is as small as possible.

For use in titrimetric analysis a reaction must have the following conditions:

1- There must be a simple reaction which can be expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric or equivalent properties.

2- The reaction should be relatively fast. (Most ionic reaction satisfy this condition.) In some cases the addition of a catalyst may be necessary to increase the speed of a reaction.

3- There must be an alteration in some physical or chemical property of the solution at the equivalence point.

4- An indicator should be available which, by a change in physical properties (color or formation of a precipitate), should sharply define the end point of the reaction.

Definition of some terms

Titration

Titration is the process in which the standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is complete.

Equivalence point and End point

The equivalence point of a titration is a theoretical point that can not be determined experimentally. Instead, we can only estimate its position by observing some physical change associated with the condition of equivalence. This change is called the end point for titration.

Titration error

The difference between the observed end point and the true equivalence point in a titration.

$$TE = V_{ep} - V_{eq}$$

Indicators

Indicators are often added to analyte solution in order to give an observable physical change (end point) at or near the equivalence point. In other wards indicator is a compound having a physical property (usually color) that changes abruptly near the equivalence point of a chemical reaction.

End Points in Volumetric Analysis

Detection of an end point involves the observation of some property of the solution that change in a characteristic way <u>at or near the equivalent point.</u> The properties that have been used for this purpose are numerous and varied; they include:

1. Color due to the reagent, the substance being determined, or an indicator substance.
2. Turbidity changes resulting from the formation or disappearance of solid phase.
3. Electric conductivity of the solution.
4. Electric potential between a pair of electrodes immersed in the solution.
5. Refractive index of the solution.
6. Temperature of the solution.
7. Electric current passing through the solution.

Primary standard

A primary standard is a highly purified compound that serve as a reference material in all volumetric method. The accuracy of method is critically dependent on the properties of this compound. Important requirements for primary standard are:

1- High purity.
2- Stability toward air.
3- Absence of hydrated water.
4- Ready availability at modest cost.
5- Reasonable solubility in titration medium.
6- Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

Compound that meet or even approach these criteria are very few , and only a limited number of primary standard substances are available to the chemist.

Secondary standard

A secondary standard is a compound whose purity has been established by chemical analysis and serves as the reference material for titrmetric method of analysis.

Compound such as sodium hydroxide or hydrochloric acid cannot be considered as primary standard since their purity is quite variable. So for instance sodium hydroxide solution must be standardized against potassium hydrogen phethalate (primary standard), which is available in high purity. The standardized sodium hydroxide solution (secondary standard) may be used to standardize solutions.

Standard solution

Standard solution is the reagent of exactly known concentration that is used in titrimetric analysis. Standard solutions play a central role in all titrimetric method of analysis. Therefore we need to consider the desirable properties for such solutions, how they are prepared and how their concentration are expressed.

Desirable properties of standard solutions

The ideal standard solution for titrmetric method will:

1- be sufficiently stable so that it is only necessary to determine the concentration once,

2- react rapidly with the analyte so that the time required between additions of reagent is minimized .

3- react more or less completely with the analyte so that satisfactory end points are realized.

4- Undergo a selective reaction with the analyte that can be described by simple balanced equation.

Few reagents meet all these ideal perfectly.

Methods for establishing the concentration of standard solutions

Two basic methods are used to establish the concentration of such solutions. **The first** is the direct method in which a carefully weighed quantity of primary standard is dissolved in a suitable solvent and diluted to an exactly known volume in a volumetric flask.

The second is by standardization the process whereby the concentration of a reagent is determined by reaction with a known quantity of a second reagent. A titrant that is standardized against another standard solution is some times referred as a secondary standard solution. If there is a choice, then solution are prepared by the direct method. On the other hand , many reagents lack the properties required for a primary standard and therefore required standardization.

Method for expressing the concentration of standard solution

The concentrations of standard solution are generally expressed in units of either molarity or normality. The first gives the number of moles of reagents contained in 1L of solution, and the second gives the number of equivalents of reagent in the same volume.

Direct titration and back titration

When a titrant reacts directly with an analyte, the procedure is termed a direct titration. It is some times necessary to add an excess of standard titrant and then determine the excess amount by back titration with a second standard titrant. In other wards back titration is a process in which the excess of standard solution used to react with an analyte is determined by titration with a second standard solution. Back – titration are often required when the rate of reaction between the analyte and reagent is slow or when the standard solution lacks stability. In back – titration, the equivalence point corresponds to the point when the amount of initial titrant is chemically equivalent to the amount af analyte plus the amount of back titrant.

Classification of reaction in titrimetric analysis

The reaction employed in titrmetric analysis fall into four main classes. The first three of these involve no change in oxidation state as they are dependent upon the combination of ions. But the fourth class, oxidation-reduction reactions, involves a change of oxidation state or, expressed another, a transfer of electron.

1- **Neutralization reaction, or acidimetry and alkalimetry**. These include the titration of free bases, or those formed from salts of weak acids by hydrolysis with a standard acid (acidimetry), and the titration of free acids, or those formed by the hydrolysis of salts or weak bases, with a standard base (alkalimertry). The reaction involve the combination of hydrogen and hydroxide ions to form water. *Also under this heading must be included titrations in non-aqueous solvents, most of which involve organic compounds.*

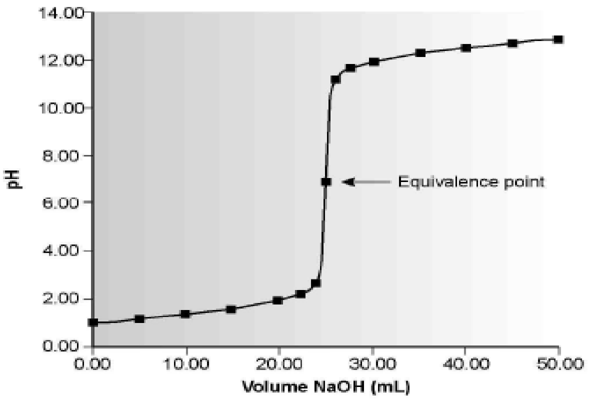
2- Precipitation reaction. These depend upon the combination of ions to form a simple precipitate as in the titration of silver ion with solution of chloride. No change in oxidation state occurs.

3- Complex formation reaction. These depend upon the combination of ions, other than hydrogen or hydroxide ion, to form a soluble slightly dissociated ion or compound, as in the titration of a solution af a cyanide with silver nitrate.
Ethylendiaminetera-acetic acid, largely as the disodium salt of EDTA, is a very important reagent for complex formation titration and has become on of the most important reagents used in titrimetric analysis.

4- Oxidation-reduction reaction. Under this heading are included all reactions involving change in oxidation number or transfer of electrons among the reactive substance. The standard solutions are either oxidizing or reducing agents.

Titration Curves

To find the end point we monitor some property of the titration reaction that has a well defined value at the equivalence point. For example, the equivalence point for a titration of HCl with NaOH occurs at a pH of 7.0. We can find the end point, therefore, by monitoring the pH with a pH electrode or by adding an indicator that changes color at a pH of 7.0.



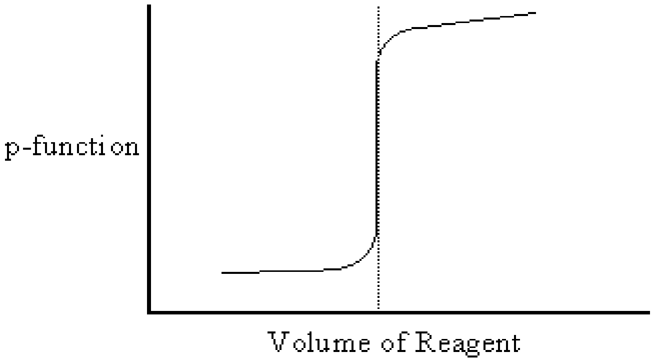
Acid-base titration curve for 25.0 mL of 0.100 M HCl with 0.100 M NaOH.

Suppose that the only available indicator changes color at a pH of 6.8. Is this end point close enough to the equivalence point that the titration error may be safely ignored? To answer this question we need to know how the pH changes during the titration.

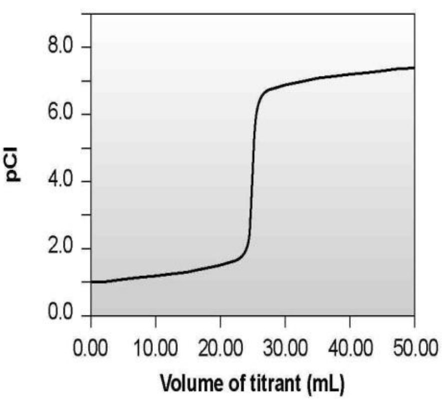
A ***titration curve*** provides us with a visual picture of how a property, such as pH, changes as we add titrant. We can measure this titration curve experimentally by suspending a pH electrode in the solution containing the analyte, monitoring the pH as titrant is added. We can also calculate the expected titration curve by considering the reactions responsible for the change in pH. However we arrive at the titration curve, we may use it to evaluate an indicator's likely titration error. For example, the titration curve in the above figure shows us that an end point pH of 6.8 produces a small titration error.
Stopping the titration at an end point pH of 11.6, on the other hand, gives an unacceptably large titration error.

A titration curve is a plot of reagent volume added versus some function of the analyte concentration. Volume of added reagent is generally plotted on the x axis. The measured parameter that is a function of analyte concentration is plotted on the y axis.

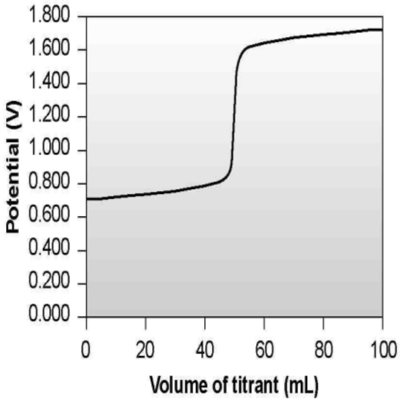
Two general titration curve types are seen:
1. Sigmoidal curve - a "z" or "s"-shaped curve where the y axis is a p-function of the analyte (or the reagent reacted with the analyte during titration) or the potential of an ion-specific electrode.



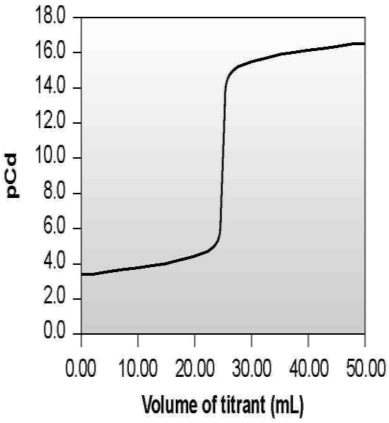
The equivalent point is observed in the middle of the "middle" segment of the "z" or "s."
Examples of Sigmoidal titration curves



Precipitation titration.

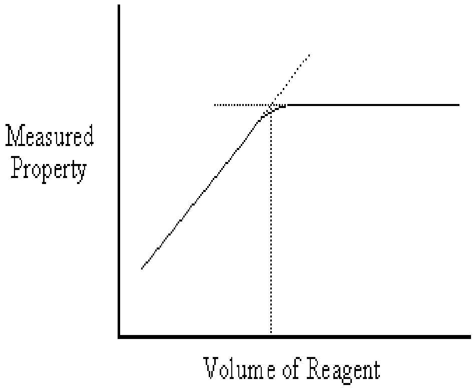


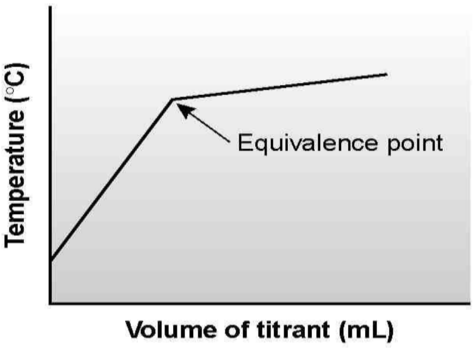
Redox titration



Complexation titration

2. Linear-segment curve - a curve generally consisting of two line segments that intersec at an angle.





Applications of Titrimetry in Pharmaceutical Analysis

Titrimetric methods are still widely used in pharmaceutical analysis because of their robustness, cheapness and capability for high precision. The only requirement of an analytical method that they lack is specificity.

Applications

- Provide standard pharmacopoeial methods for the assay of unformulated drugs and excipients and some formulated drugs, e.g. those that lack a strong chromophore.
- Used for standardisations of raw materials and intermediates used in drug synthesis in industry. Suppliers of raw materials may provide these materials at a specified purity which has been assayed titrimetrically to a pharmacopoeial standard.
- Certain specialist titrations, such as the Karl Fischer titration used to estimate water content, are widely used in the pharmaceutical industry.

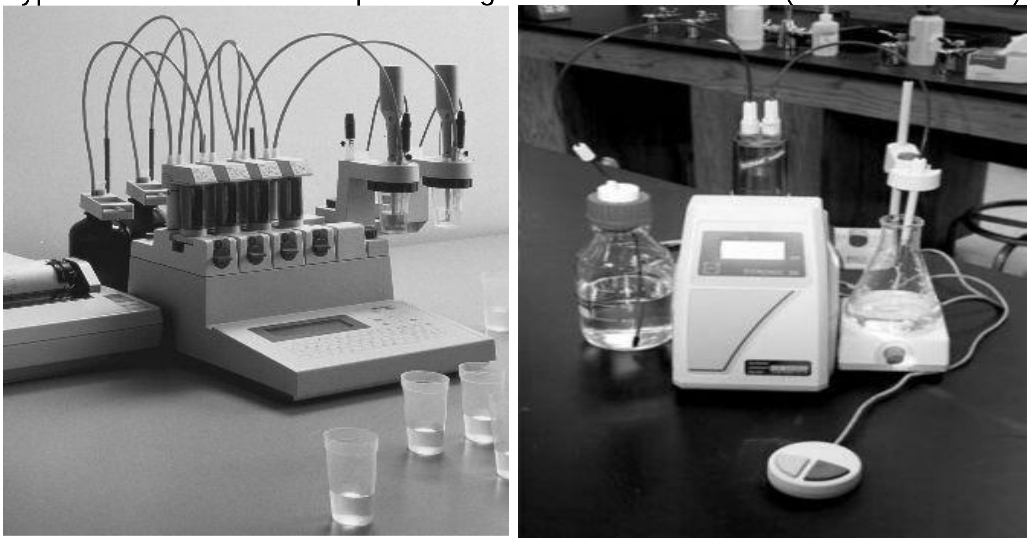
Advantages

- Capable of a higher degree of precision and accuracy than instrumental methods of analysis.
- The methods are generally robust.
- Analyses can be automated.
- Cheap to perform and do not require specialised apparatus.
- They are absolute methods and are not dependent on the calibration of an instrument.

Limitations

- Non-selective.
- Time-consuming if not automated and require a greater level of operator skill than routine instrumental methods.
- Require large amounts of sample and reagents.
- Reactions of standard solutions with the analyte should be rapid and complete.

Typical instrumentation for performing an automatic titration (automatic titrator).



Lacture-9

Titrations Based on Acid-Base Reactions

The earliest acid-base titrations involved the determination of the acidity or alkalinity of solutions, and the purity of carbonates and alkaline earth oxides. Various acid-base titration reactions, including a number of scenarios of base in the burette, acid in the reaction flask, and vice versa, as well as various monoprotic and polyprotic acids titrated with strong bases and various weak monobasic and polybasic bases titrated with strong acids. A **monoprotic acid** is an acid that has only one hydrogen ion (or proton) to donate per formula. Examples are hydrochloric acid, HCl, a strong acid, and acetic acid, $HC_2H_3O_2$, a weak acid. A **polyprotic acid** is an acid that has two or more hydrogen ions to donate per formula. Examples include sulfuric acid, H_2SO_4, a **diprotic acid,** and phosphoric acid, H_3PO_4, a **triprotic** acid.

A **monobasic base** is one that will accept just one hydrogen ion per formula.Examples include sodium hydroxide, NaOH, a strong base; ammonium hydroxide, NH_4OH, a weak base; and sodium bicarbonate, $NaHCO_3$, a weak base. A **polybasic base** is one that will accept two or more hydrogen ions per formula. Examples include sodium carbonate, Na_2CO_3, a **dibasic base,** and sodium phosphate, Na_3PO_4, a **tribasic base.**

Acid-Base Titration Curves

In the overview to the titration we noted that the experimentally determined end point should coincide with the titration's equivalence point. For an acid-base titration, the equivalence point is characterized by a pH level that is a function of the acid-base strengths and concentrations of the analyte and titrant. The pH at the end point, however, may or may not correspond to the pH at the equivalence point. To understand the relationship between end points and equivalence points we must know how the pH changes during a titration. In this section we will learn how to construct titration curves for
several important types of acid-base titrations.

Titrating Strong Acids and Strong Bases

For our first titration curve let's consider the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH. For the reaction of a strong base with a strong acid the only equilibrium reaction of importance is

$$H_3O^+(aq) + OH^-(aq) = 2H_2O(l)$$

The first task in constructing the titration curve is to calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point we know from reaction above that

Moles HCl = moles NaOH

$$M_aV_a = M_bV_b$$

where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH. The volume of NaOH needed to reach the equivalence point, therefore, is

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100\text{ M})(50.0\text{ mL})}{(0.200\text{ M})} = 25.0\text{ mL}$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl. Initially the solution is 0.100 M in HCl, which, since HCl is a strong acid, means that the pH is

$$\text{pH} = -\log[H_3O^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

The equilibrium constant for reaction is $(K_w)^{-1}$, or 1.00×10^{14}. Since this is such a large value we can treat reaction as though it goes to completion. After adding 10.0 mL of NaOH, therefore, the concentration of excess HCl is

$$[\text{HCl}] = \frac{\text{moles excess HCl}}{\text{total volume}} = \frac{M_a V_a - M_b V_b}{V_a + V_b}$$

$$= \frac{(0.100\text{ M})(50.0\text{ mL}) - (0.200\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 0.050\text{ M}$$

giving a pH of 1.30.

At the equivalence point the moles of HCl and the moles of NaOH are equal. Since neither the acid nor the base is in excess, the pH is determined by the dissociation of water.

$$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-] = [H_3O^+]^2$$

$$[H_3O^+] = 1.00 \times 10^{-7}\text{ M}$$

Thus, the pH at the equivalence point is 7.00.

Finally, for volumes of NaOH greater than the equivalence point volume, the pH is determined by the concentration of excess OH^-. For example, after adding 30.0 mL of titrant the concentration of OH^- is

$$[OH^-] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_b V_b - M_a V_a}{V_a + V_b}$$

$$= \frac{(0.200\text{ M})(30.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 30.0\text{ mL}} = 0.0125\text{ M}$$

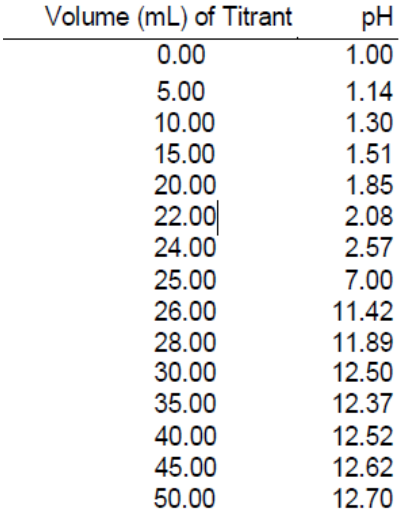
To find the concentration of H_3O^+, we use the K_w expression

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.0125} = 8.00 \times 10^{-13}$$

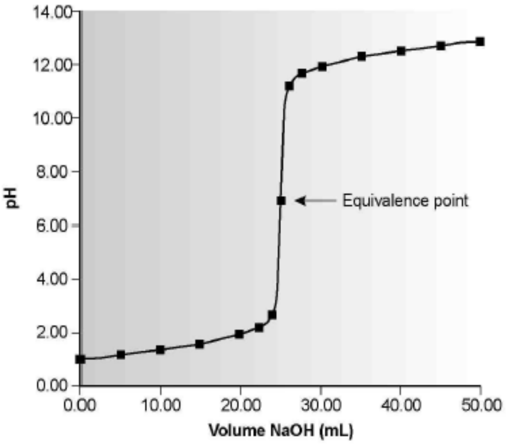
giving a pH of 12.10.

The table and the figure below show additional results for this titration curve.

Data for Titration of 50.00 mL of 0.100 M HCI with 0.0500 M NaOH



Volume (mL) of Titrant	pH
0.00	1.00
5.00	1.14
10.00	1.30
15.00	1.51
20.00	1.85
22.00	2.08
24.00	2.57
25.00	7.00
26.00	11.42
28.00	11.89
30.00	12.50
35.00	12.37
40.00	12.52
45.00	12.62
50.00	12.70



Calculating the titration curve for the titration of a strong base with a strong acid is handled in the same manner, except that the strong base is in excess before the equivalence point and the strong acid is in excess after the equivalence point.

Titrating a Weak Acid with a Strong Base

For this example let's consider the titration of 50.0 mL of 0.100 M acetic acid, CH_3COOH, with 0.100 M NaOH. Again, we start by calculating the volume of NaOH needed to reach the equivalence point; thus

$$\text{Moles } CH_3COOH = \text{Moles NaOH}$$

$$M_aV_a = M_bV_b$$

$$V_{eq} = V_b = \frac{M_aV_a}{M_b} = \frac{(0.100\text{ M})(50.0\text{ mL})}{(0.100\text{ M})} = 50.0\text{ mL}$$

Before adding any NaOH the pH is that for a solution of 0.100 M acetic acid. Since acetic acid is a weak acid, we calculate the pH using this method

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

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$x = [H_3O^+] = 1.32 \times 10^{-3}$$

We can use the following equation :

$$[H_3O^+] = \sqrt{K_a\, c(HA)}$$

At the beginning of the titration the pH is 2.88.

Adding NaOH converts a portion of the acetic acid to its conjugate base.

$$CH_3COOH(aq) + OH^-(aq) = H_2O(l) + CH_3COO^-(aq)$$

Any solution containing comparable amounts of a weak acid, HA, and its conjugate weak base, A^-, is a buffer. As we learned before, we can calculate the pH of a buffer using the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

The equilibrium constant for the above reaction is large ($K = K_a/K_w = 1.75 \times 10^9$), so we can treat the reaction as one that goes to completion. Before the equivalence point, the concentration of unreacted acetic acid is

$$[CH_3COOH] = \frac{\text{moles unreacted } CH_3COOH}{\text{total volume}} = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

and the concentration of acetate is

$$[CH_3COO^-] = \frac{\text{moles NaOH added}}{\text{total volume}} = \frac{M_bV_b}{V_a + V_b}$$

For example, after adding 10.0 mL of NaOH the concentrations of CH_3COOH and CH_3COO^- are

$$(0.100\ \text{M})(50.0\ \text{mL}) - (0.100\ \text{M})(10.0\ \text{mL})$$

$$[CH_3COOH] = \frac{}{50.0\text{ mL} + 10.0\text{ mL}} = 0.0667\text{ M}$$

$$[CH_3COO^-] = \frac{(0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 0.0167\text{ M}$$

giving a pH of

$$pH = 4.76 + \log\frac{[0.0167]}{[0.0667]} = 4.16$$

A similar calculation shows that the pH after adding 20.0 mL of NaOH is 4.58.

At the equivalence point, the moles of acetic acid initially present and the moles of NaOH added are identical. Since their reaction effectively proceeds to completion, the predominate ion in solution is CH_3COO^-, which is a weak base. To calculate the pH we first determine the concentration of CH_3COO^-.

$$[CH_3COO^-] = \frac{\text{moles } CH_3COOH}{\text{total volume}} = \frac{(0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 50.0\text{ mL}} = 0.0500\text{ M}$$

The pH is then calculated for a weak base.

$$CH_3COO^-(aq) + H_2O(l) = OH^-(aq) + CH_3COOH(aq)$$

$$[OH^-] = \sqrt{K_b\, c(B)}$$

$$[OH^-] = 5.34 \times 10^{-6}\text{ M}$$

The concentration of H_3O^+, therefore, is 1.87×10^{-9}, or a pH of 8.73.

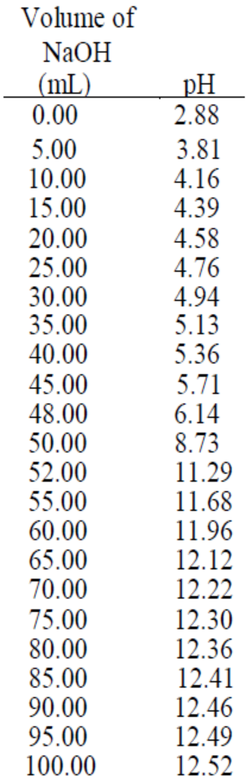
After the equivalence point NaOH is present in excess, and the pH is determined in the same manner as in the titration of a strong acid with a strong base. For example, after adding 60.0 mL of NaOH, the concentration of OH^- is

$$[OH] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_bV_b - M_aV_a}{V_a + V_b} = 0.00909M$$

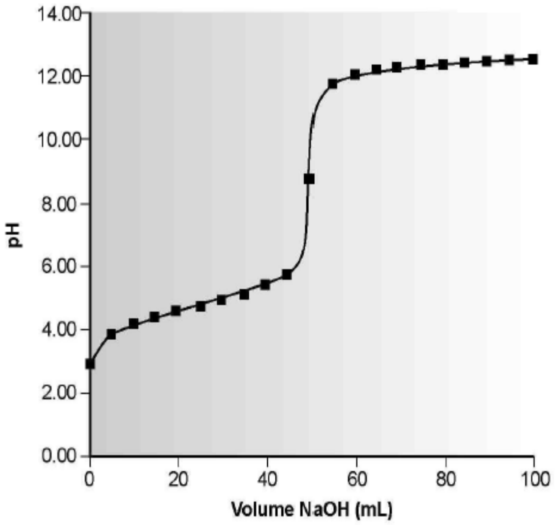
$$= \frac{(0.100\text{ M})(60.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 60.0\text{ mL}} = 0.0125\text{ M}$$

giving a pH of 11.96. The table and figure below show additional results for this titration.

The calculations for the titration of a weak base with a strong acid are handled in a similar manner except that the initial pH is determined by the weak base, the pH at the equivalence point by its conjugate weak acid, and the pH after the equivalence point by the concentration of excess strong acid.



Volume of NaOH (mL)	pH
0.00	2.88
5.00	3.81
10.00	4.16
15.00	4.39
20.00	4.58
25.00	4.76
30.00	4.94
35.00	5.13
40.00	5.36
45.00	5.71
48.00	6.14
50.00	8.73
52.00	11.29
55.00	11.68
60.00	11.96
65.00	12.12
70.00	12.22
75.00	12.30
80.00	12.36
85.00	12.41
90.00	12.46
95.00	12.49
100.00	12.52



Data and titration curve for Titration of 50.0 mL of 0.100 M Acetic Acid with 0.100 M NaOH.

Method for finding the end point in acid-base titration

1- Finding the End Point with a Visual Indicator.
2- Finding the End Point by Monitoring pH.
3- Finding the End Point by Monitoring Temperature.

Lecture- 10

Titrations Based on Precipitation Reactions

Precipitation Titrations

Thus far we have examined titrimetric methods based on acid-base reactions. A reaction in which the analyte and titrant form an insoluble precipitate also can form the basis for a titration. We call this type of titration a **precipitation titration.**

One of the earliest precipitation titrations, developed at the end of the eighteenth century, was for the analysis of K_2CO_3 and K_2SO_4 in potash. Calcium nitrate, $Ca(N0_3)_2$, was used as a titrant, forming a precipitate of $CaCO_3$ and $CaSO_4$ The end point was signaled by noting when the addition of titrant ceased to generate additional precipitate.

The importance of precipitation titrimetry as an analytical method reached its zenith in the nineteenth century when several methods were developed for determining Ag_+ and halide ions.

Precipitation Reactions

A precipitation reaction occurs when two or more soluble species combine to form an insoluble product that we call a **precipitate.** The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. When a solution of lead nitrate is added to a solution of potassium chloride, for example, a precipitate of lead chloride forms. We usually write the balanced reaction as a net ionic equation, in which only the precipitate and those ions involved in the reaction are included.

Thus, the precipitation of $PbCl_2$ is written as

$$Pb^{2+}(aq) + 2Cl^{-}(aq) = PbCl_{2}(s)$$

In the equilibrium treatment of precipitation, however, the reverse reaction describing the dissolution of the precipitate is more frequently encountered.

$$PbCl_{2}(s) = Pb^{2+}(aq) + 2Cl^{-}(aq)$$

The equilibrium constant for this reaction is called the **solubility product,** K_{sp}, and is given as

$$K_{sp} = [Pb^{2+}]\,[Cl^{-}]^{2} = 1.7 \text{ X } I0^{-5}$$

Note that the precipitate, which is a solid, does not appear in the K_{sp} expression. It is important to remember, however, that equation is valid only if $PbCl_{2}(s)$ is present and in equilibrium with the dissolved Pb_{2+} and Cl.

Titration Curves

The titration curve for a precipitation titration follows the change in either the analyte's or titrant's concentration as a function of the volume of titrant. For example, in an analysis for I using Ag^+ as a titrant

$$Ag^+(aq) + I\ (aq) = AgI(s)$$

the titration curve may be a plot of pAg or pI as a function of the titrant's volume. As we have done with previous titrations, we first show how to calculate the titration curve.

Calculating the Titration Curve

As an example, let's calculate the titration curve for the titration of 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+. The reaction in this case is

$$Ag^+(aq) + Cl^-\ (aq) = AgCl(s)$$

The equilibrium constant for the reaction is

$$K = (K_{sp})^{-1} = (1.8 \times 10^{-10})^{-1} = 5.6 \times 10^9$$

Since the equilibrium constant is large, we may assume that Ag^+ and Cl^- react completely.

By now you are familiar with our approach to calculating titration curves. The first task is to calculate the volume of Ag^+ needed to reach the equivalence point. The stoichiometry of the reaction requires that

$$\text{Moles } Ag^+ = \text{moles Clor}$$

$$M_{Ag}V_{Ag} = M_{Cl}V_{Cl}$$

Solving for the volume of Ag^+

$$V_{Ag} = \frac{M_{Cl}V_{Cl}}{M_{Ag}} = \frac{(0.050\ M)(50.0\ mL)}{(0.100\ M)} = 25.0\ mL$$

shows that we need 25.0 mL of Ag^+ to reach the equivalence point.

Before the equivalence point Cl^- is in excess. The concentration of unreacted Cl^- after adding 10

$$[Cl^-] = \frac{\text{moles excess } Cl^-}{\text{total volume}} = \frac{M_{Cl}V_{Cl} - M_{Ag}V_{Ag}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.050\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(10.0\text{ mL})}{50.0\text{ mL} + 10.0\text{ mL}} = 2.50 \times 10^{-2}\text{ M}$$

.0 mL of Ag^+,

for example, is

If the titration curve follows the change in concentration for Cl, then we calculate pCl as

$pCl = -\log[Cl^-] = -\log(2.50 \times 10^{-2}) = 1.60$

However, if we wish to follow the change in concentration for Ag_+ then we must first calculate its concentration. To do so we use the K_{sp} expression for AgCl

$$K_{sp}=[Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

Solving for the concentration of Ag^+

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{2.50 \times 10^{-2}} = 7.2 \times 10^{-9}\text{ M}$$

gives a pAg of 8.14.

At the equivalence point, we know that the concentrations of Ag^+ and Cl^- are equal. Using the solubility product expression

$$K_{sp}=[Ag^+][Cl^-] =[Ag^+]^2 = 1.8 \times 10^{-10}$$

gives

$$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}\text{M}$$

At the equivalence point, therefore, pAg and pCl are both 4.89.

After the equivalence point, the titration mixture contains excess Ag^+. The concentration of Ag^+ after adding 35.0 mL of titrant is

$$[Ag^+] = \frac{\text{moles excess } Ag^+}{\text{total volume}} = \frac{M_{Ag}V_{Ag} - M_{Cl}V_{Cl}}{V_{Cl} + V_{Ag}}$$

$$= \frac{(0.10\ M)(35.0\ mL) - (0.050\ M)(50.0\ mL)}{50.0\ mL + 35.0\ mL} = 1.18\ x10^{-2}\ M$$

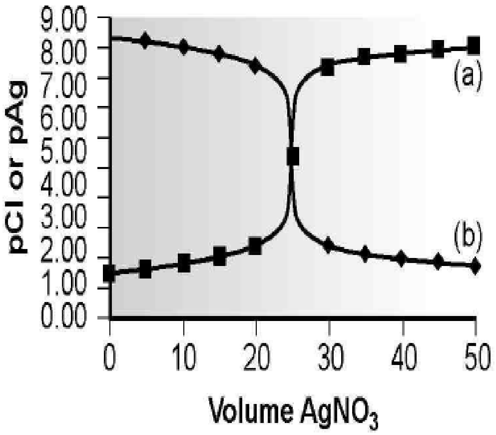
or a pAg of 1.93. The concentration of Cl^- is

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8\ x\ 10^{-10}}{1.18\ x10^{-2}} = 1.5\ x\ 10^{-8}\ M$$

or a pCl of 7.82.

Volume AgN0$_3$ (mL)	pCl	pAg
0.00	1.30	—
5.00	1.44	8.31
10.00	1.60	8.14
15.00	1.81	7.93
20.00	2.15	7.60
25.00	4.89	4.89
30.00	7.54	2.20
35.00	7.82	1.93
40.00	7.97	1.78
45.00	8.07	1.68
50.00	8.14	1.60

Data for Titration of 50.0 mL of 0.0500 M Cl" with 0.100 M Ag^+



Precipitation titration curve for 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+. (a) pCl versus volume of titrant; (b) pAg versus volume of titrant

Methods for finding the end point in Precipitation Titration:

1- Finding the End Point with a Visual Indicator

There three methods to find end point in precipitation titration with visual indicator. **First** important visual indicator to be developed was the ***Mohr method*** for Cl^- using Ag^+ as a titrant. By adding a small amount of K_2CrO_4 to the solution containing the analyte, the formation of a precipitate of reddish-brown Ag_2CrO_4 signals the end point.

$Ag^+ + Cl^- = AgCl_{(s)}$ White precipitate

$2Ag^+ + CrO_4^{2-} = Ag_2CrO_{4(s)}$ Red precipitate

A second end point is the ***Volhard method*** in which Ag^+ is titrated with SCN^- in the presence of Fe^{3+}. The end point for the titration reaction

$Ag^+_{(aq)} + SCN^-_{(aq)} = AgSCN_{(s)}$

is the formation of the reddish colored $Fe(SCN)^{2+}$ complex.

$$SCN^-_{(aq)} + Fe^{3+}_{(aq)} = Fe(SCN)^{2+}_{(aq)}$$

The titration must be carried out in a strongly acidic solution to achieve the desired end point.

A third end point is evaluated with ***Fajans' method***, which uses an adsorption indicator whose color when adsorbed to the precipitate is different from that when it is in solution.

For example, when titrating Cl^- with Ag^+ the anionic dye dichloro-fluoroscein is used as the indicator. Before the end point, the precipitate of AgCl has a negative surface charge due to

the adsorption of excess $Cl^{-\cdot}$ The anionic indicator is repelled by the precipitate and remains in solution where it has a greenish yellow color. After the end point, the precipitate has a positive surface charge due to the adsorption of excess Ag^+. The anionic indicator now adsorbs to the precipitate's surface where its color is pink. This change in color signals the end point.

2- Finding the End Point Potentiometrically.

Lecture- 11

Titrations Based on Complexation Reactions

Introduction

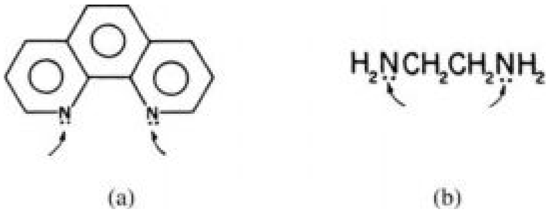
Complexation ractions are important in many areas of science. Complexes play an important role in many chemical and biochemical process. For example the heme molecule in blood holds the iron atom tightly because the nitrogen of the heme form strong complexing bonds, that is nitrogen is a good complexer. Complextion reactions are widely used in analytical chemistry. One of the first uses of these reactions was for titrating cations.

Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or ***ligand*** must have at least one pair of unshared electrons available for bond formation.

A ligand is an ion or molecule that forms a covalent bond with a cation or neutral metal atom by donating a pair of electrons, which are then shared by the two. Ligands can be classified into inorganic ligands such as water, ammonia, and halide ions, and organic ligands such as 8-hydroxyquinoline.

The widely compounds (ligands) used in complexemetric titrations called ***chelates***. A chelate is produced when a metal ion coordinates with two or more doner groups of a single ligand to form a five or six member heterocyclic ring.
A ligand that has:

single donor group is called ***unidentate***
two donor groups is called ***bidentate***
three donor groups is called ***tridentate***
four donor groups is called ***tetradentate***
five donor groups is called ***pentadentate***
six donor groups is called ***hexadentate***



Two bidentate ligands: (a) 1,10 phenanthroline, and (b) ethylenediamine. The arrows point out the bonding sites.

Tetradentate and hexadentate ligands are more satisfactory as titrants than ligands with a lesser number of donor groups because their reactions with cations are more complete and because they tend to form 1:1complexes.

Aminocarboxylic acid titration

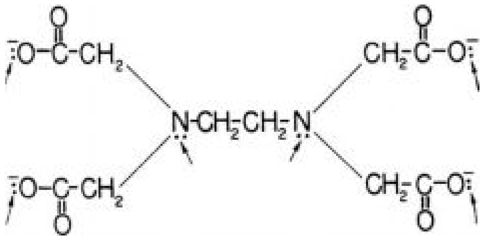
Aminocarboxylic acid compounds are multidentate ligands capable of forming stable 1:1 complexes with metal ions. The most widely used of the new ligands was ethylendiaminetetraacetic acid EDTA which is a hexadentate ligand

and the most important and widely used reagent in titrimetry. The advantages of EDTA is

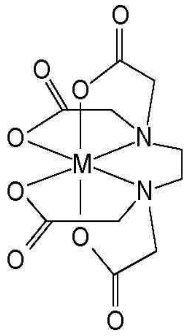
1- form strong 1:1 complexes.
2- react with many metal ions.

Chemistry and Properties of EDTA

The structure of EDTA is shown in below. EDTA, which is a Lewis acid, has six binding sites (the four carboxylate groups and the two amino groups), providing six pairs of electrons.



The resulting metal-ligand complex, in which EDTA forms a cage-like structure around the metal ion is very stable. The actual number of coordination sites depends on the size of the metal ion; however, all metal-EDTA complexes have a 1:1 stoichiometry.



six-coordinate metal-EDTA complex.

Metal—EDTA Formation Constants

To illustrate the formation of a metal-EDTA complex consider the reaction between Cd^{2+} and EDTA

$$Cd^{2+}(aq) + Y^{4-}(aq) = CdY^{2-}(aq)$$

where Y^{4-} is a shorthand notation for the chemical form of EDTA. The formation constant for this reaction

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = 2.9 \times 10^{16}$$

is quite large, suggesting that the reaction's equilibrium position lies far to the right.

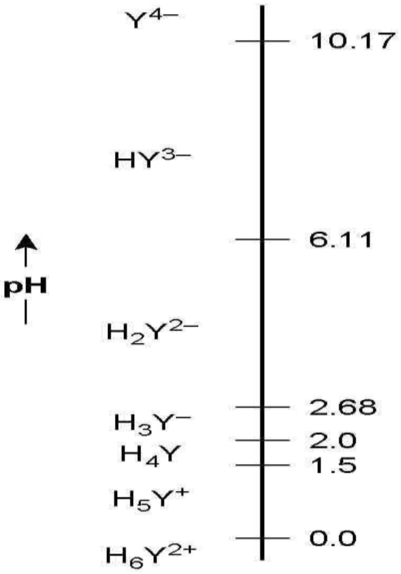
EDTA Is a Weak Acid

Besides its properties as a ligand, EDTA is also a weak acid. The fully protonated form of EDTA, H_6Y^{2+}, is a hexaprotic weak acid with successive pK_a values of

$pK_{a1} = 0.0$ $pK_{a2} = 1.5$ $pK_{a3} = 2.0$ $pK_{a4} = 2.68$ $pK_{a5} = 6.11$ $pK_{a6} = 10.17$

The first four values are for the carboxyl protons, and the remaining two values are for the ammonium protons.

A ladder diagram for EDTA is shown below.



The species Y^{4-} becomes the predominate form of EDTA at pH levels greater than 10.17. It is only for pH levels greater than 12 that Y^{4-} becomes the only significant form of EDTA.

Conditional Metal—Ligand Formation Constants

Recognizing EDTA's acid-base properties is important. The formation constant for CdY^{2-} assumes that EDTA is present as Y^{4-}. If we restrict the pH to levels greater than 12, then equation

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}][Y^{4-}]} = 2.9 \times 10^{16}$$

provides an adequate description of the formation of CdY^{2-}. For pH levels less than 12, however, K_f overestimates the stability of the CdY^{2-} complex. At any pH a mass balance requires that the total concentration of unbound EDTA equal the combined concentrations of each of its forms.

$$C_{EDTA} = [H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]$$

To correct the formation constant for EDTA's acid-base properties, we must account for the fraction, $\alpha_{Y^{4-}}$, of EDTA present as Y^{4-}.

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{C_{EDTA}}$$

Values of $\alpha_{Y^{4-}}$ for selected PHs

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
2	3.7×10^{-14}	8	5.4×10^{-3}
3	2.5×10^{-11}	9	5.2×10^{-2}
4	3.6×10^{-9}	10	0.35
5	3.5×10^{-7}	11	0.85
6	2.2×10^{-5}	12	0.98
7	4.8×10^{-4}	13	1.00

Solving equation

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,[Y^{4-}]} = 2.9 \times 10^{16}$$

for $[Y^{4-}]$ and substituting gives

$$K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,\alpha_{Y^{4-}}\,C_{EDTA}}$$

If we fix the pH using a buffer, then $\alpha_{Y^{4-}}$ is a constant. Combining $\alpha_{Y^{4-}}$ with K_f gives

$$K_f' = \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\,C_{EDTA}}$$

where K_f' is a **conditional formation constant** whose value depends on the pH. As shown in following table for CdY^{2-},

pH	K_f'	pH	K_f'
2	1.1×10^{3}	8	1.6×10^{14}
3	7.3×10^{5}	9	1.5×10^{15}
4	1.0×10^{8}	10	1.0×10^{16}
5	1.0×10^{10}	11	2.5×10^{16}
6	6.4×10^{11}	12	2.8×10^{16}
7	1.4×10^{13}	13	2.9×10^{16}

the conditional formation constant becomes smaller, and the complex becomes less stable at lower pH levels.

EDTA Must Compete with Other Ligands

To maintain a constant pH, we must add a buffering agent. If one of the buffer's components forms a metal-ligand complex with Cd^{2+}, then EDTA must compete with the ligand for Cd^{2+}. For example, an NH_4^+/NH_3 buffer includes the ligand NH_3, which forms several stable Cd^{2+}-NH_3 complexes. EDTA forms a stronger complex with Cd^{2+} and will displace NH_3. The presence of NH_3, however, decreases the stability of the Cd^{2+}-EDTA complex.

We can account for the effect of an **auxiliary complexing agent,** such as NH_3, in the same way we accounted for the effect of pH. Before adding EDTA, a mass balance on Cd^{2+} requires that the total concentration of Cd^{2+}, C_{cd}, be

$$C_{cd} = [Cd^{2+}] + [Cd(NH_3)^{2+}] + [Cd(NH_3)_2^{2+}] + [Cd(NH_3)_3^{2+}] + [Cd(NH_3)_4^{2+}]$$

The fraction, αcd^{2+} present as uncomplexed Cd^{2+} is

$$\alpha_{cd^{2+}} = \frac{[Cd^{2+}]}{C_{cd}}$$

Solving equation

$$K_f' = \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{[Cd^{2+}]\, C_{EDTA}}$$

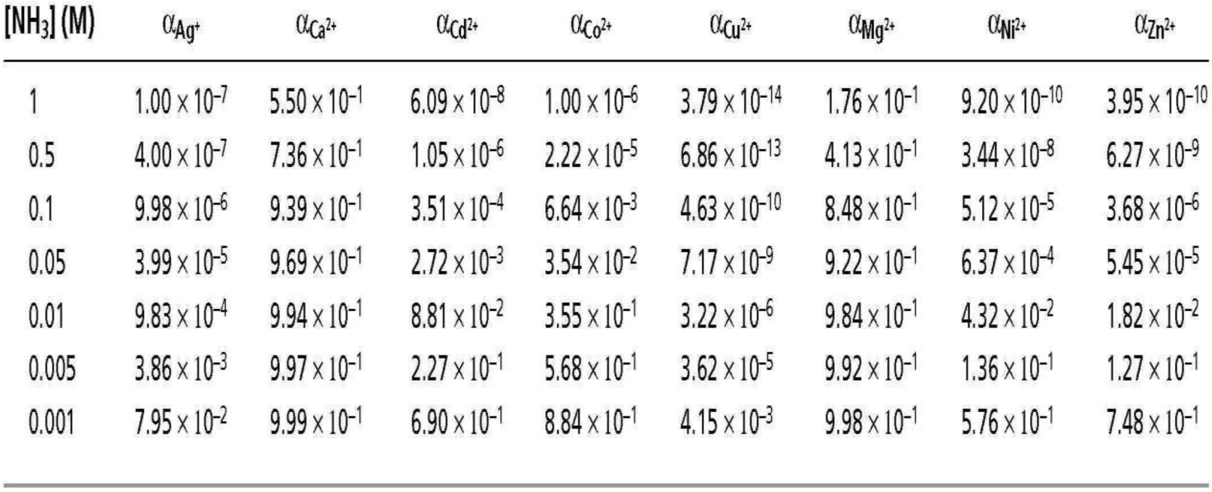
for $[Cd^{2+}]$ and substituting gives

$$K_f' = \alpha_{Y^{4-}} \times K_f = \frac{[CdY^{2-}]}{\alpha_{cd^{2+}}\, C_{cd}\, C_{EDTA}}$$

If the concentration of NH_3 is held constant, as it usually is when using a buffer, then we can rewrite this equation as

$$K_f'' = \alpha_{cd}^{2+} \times \alpha_{Y}^{4-} \times K_f = \frac{[CdY^{2-}]}{C_{cd}\, C_{EDTA}}$$

where K_f'' is a new conditional formation constant accounting for both pH and the presence of an auxiliary complexing agent. Values of α_{Mn+} for several metal ions are provided in following table



$[NH_3]$ (M)	α_{Ag^+}	$\alpha_{Ca^{2+}}$	$\alpha_{Cd^{2+}}$	$\alpha_{Co^{2+}}$	$\alpha_{Cu^{2+}}$	$\alpha_{Mg^{2+}}$	$\alpha_{Ni^{2+}}$	$\alpha_{Zn^{2+}}$
1	1.00×10^{-7}	5.50×10^{-1}	6.09×10^{-8}	1.00×10^{-6}	3.79×10^{-14}	1.76×10^{-1}	9.20×10^{-10}	3.95×10^{-10}
0.5	4.00×10^{-7}	7.36×10^{-1}	1.05×10^{-6}	2.22×10^{-5}	6.86×10^{-13}	4.13×10^{-1}	3.44×10^{-8}	6.27×10^{-9}
0.1	9.98×10^{-6}	9.39×10^{-1}	3.51×10^{-4}	6.64×10^{-3}	4.63×10^{-10}	8.48×10^{-1}	5.12×10^{-5}	3.68×10^{-6}
0.05	3.99×10^{-5}	9.69×10^{-1}	2.72×10^{-3}	3.54×10^{-2}	7.17×10^{-9}	9.22×10^{-1}	6.37×10^{-4}	5.45×10^{-5}
0.01	9.83×10^{-4}	9.94×10^{-1}	8.81×10^{-2}	3.55×10^{-1}	3.22×10^{-6}	9.84×10^{-1}	4.32×10^{-2}	1.82×10^{-2}
0.005	3.86×10^{-3}	9.97×10^{-1}	2.27×10^{-1}	5.68×10^{-1}	3.62×10^{-5}	9.92×10^{-1}	1.36×10^{-1}	1.27×10^{-1}
0.001	7.95×10^{-2}	9.99×10^{-1}	6.90×10^{-1}	8.84×10^{-1}	4.15×10^{-3}	9.98×10^{-1}	5.76×10^{-1}	7.48×10^{-1}

Complexometric EDTA Titration Curves

Now that we know something about EDTA's chemical properties, we are ready to evaluate its utility as a titrant for the analysis of metal ions. To do so we need to know the shape of a complexometric EDTA titration curve. We saw that an acid-base titration curve shows the change in pH following the addition of titrant. The analogous result for a titration with EDTA shows the change in pM, where M is the metal ion, as a function of the volume of EDTA.

Calculating the Titration Curve

As an example, let's calculate the titration curve for 50.0 mL of 5.00 X 10^{-3} M Cd^{2+} with 0.0100 M EDTA at a pH of 10 and in the presence of 0.0100 M NH_3. The formation constant for Cd^{2+}- EDTA is 2.9 X 10^{16}.

Since the titration is carried out at a pH of 10, some of the EDTA is present in forms other than Y^{4-}. In addition, the presence of NH_3 means that the EDTA must compete for the Cd^{2+}. To evaluate the titration curve, therefore, we must use the appropriate conditional formation constant. We find that $\alpha_{Y^{4-}}$ is 0.35 at a pH of 10, and that $\alpha_{cd^{2+}}$ is
0.0881 when the concentration of NH_3 is 0.0100 M. Using these values, we calculate that the conditional formation constant is

$K_f'' = \alpha_{cd^{2+}} \times \alpha_{Y^{4-}} \times K_f = (0.35)(0.0881)(2.9 \times 10^{16}) = 8.9 \times 10^{14}$

Because K_f'' is so large, we treat the titration reaction as though it proceeds to completion.

The first task in calculating the titration curve is to determine the volume of EDTA needed to reach the equivalence point. At the equivalence point we know that

$$\text{Moles EDTA} = \text{Moles Cd}^{2+}$$

or

$$M_{EDTA}V_{EDTA} = M_{Cd}V_{Cd}$$

Solving for the volume of EDTA

$$V_{EDTA} = \frac{M_{Cd}V_{Cd}}{M_{EDTA}} = \frac{(0.005\ M)(50.0\ mL)}{(0.01\ M)} = 25.0\ mL$$

shows us that 25.0 mL of EDTA is needed to reach the equivalence point.

Before the equivalence point, Cd^{2+} is in excess, and pCd is determined by the concentration of free Cd^{2+} remaining in solution. Not all the untitrated Cd^{2+} is free (some is complexed with NH_3), so we will have to account for the presence of NH_3.

For example, after adding 5.0 mL of EDTA, the total concentration of Cd^{2+} is

$$C_{Cd} = \frac{\text{moles excess Cd}^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd} - M_{EDTA}V_{EDTA}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005\ M)(50.0\ mL) - (0.010\ M)(5.0\ mL)}{50.0\ mL + 5.0\ mL} = 3.64 \times 10^{-3}\ M$$

To calculate the concentration of free Cd^{2+} we use equation

$$\alpha_{cd^{2+}} = \frac{[Cd^{2+}]}{C_{cd}}$$

$[Cd^{2+}] = \alpha_{cd^{2+}} \times C_{cd} = (0.0881)(3.64 \times 10^{-3}\ M) = 3.21 \times 10^{-4}\ M$

Thus, pCd is

pCd = -log[Cd^{2+}] = -log(3.21×10^{-4}) = 3.49

At the equivalence point, all the Cd^{2+} initially present is now present as CdY^{2-}. The concentration of Cd^{2+}, therefore, is determined by the dissociation of the CdY^{2-} complex. To find pCd we must first calculate the concentration of the complex.

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005\ M)(50.0\ mL)}{50.0\ mL + 25.0\ mL} = 3.33 \times 10^{-3}\ M$$

Letting the variable x represent the concentration of Cd^{2+} due to the dissociation of the CdY^{2-} complex, we have

$$K_f'' = \frac{[CdY^{2-}]}{C_{cd}\, C_{EDTA}} = \frac{3.33 \times 10^{-3}}{(X)\,(X)} = 8.94 \times 10^{14}$$

$X = C_{Cd} = 1.93 \times 10^{-9}$ M
Once again, to find the [Cd^{2+}] we must account for the presence of NH_3; thus
[Cd^{2+}] = $\alpha_{cd^{2+}} \times C_{Cd}$ = (0.0881)(1.93×10^{-9} M) = 1.70×10^{-10} M
giving pCd as 9.77.

After the equivalence point, EDTA is in excess, and the concentration of Cd^{2+} is determined by the dissociation of the CdY^{2-} complex. Examining the equation for the complex's conditional formation constant, we see that to calculate C_{Cd} we must first calculate [CdY^{2-}] and C_{EDTA}. After adding 30.0 mL of EDTA, these concentrations are

$$[CdY^{2-}] = \frac{\text{initial moles } Cd^{2+}}{\text{total volume}} = \frac{M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.005\ M)(50.0\ mL)}{50.0\ mL + 30.0\ mL} = 3.13 \times 10^{-3}\ M$$

$$C_{EDTA} = \frac{\text{moles excess EDTA}}{\text{total volume}} = \frac{M_{EDTA}V_{EDTA} - M_{Cd}V_{Cd}}{V_{Cd} + V_{EDTA}}$$

$$= \frac{(0.01\ M)(30.0\ mL) - (0.005\ M)(50.0\ mL)}{50.0\ mL + 30.0\ mL} = 6.25 \times 10^{-4}\ M$$

Substituting these concentrations into equation

$$K_f'' = \frac{[CdY^{2-}]}{C_{cd}\, C_{EDTA}}$$

and solving for C_{Cd} gives

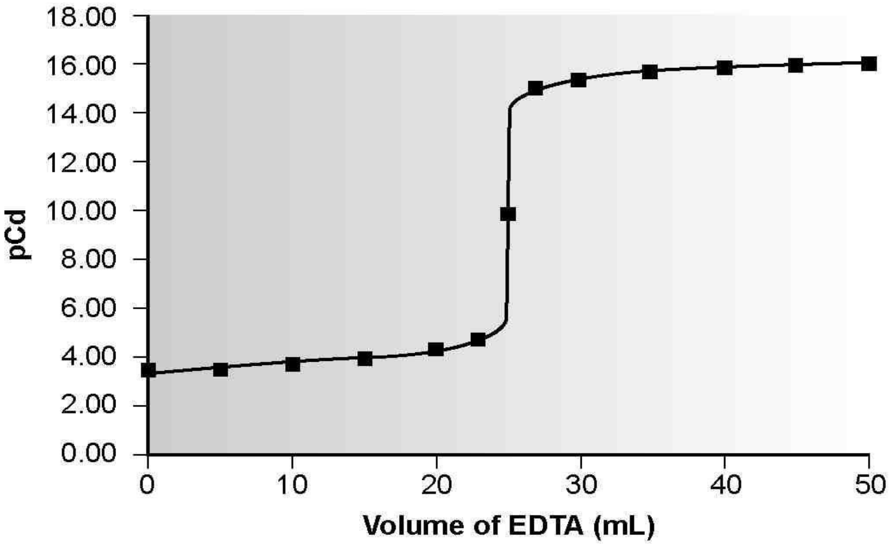
$$K_f'' = \frac{[CdY^{2-}]}{C_{cd}\, C_{EDTA}} = \frac{3.13 \times 10^{-3}\ M}{C_{cd}\,(6.25 \times 10^{-4}\ M)} = 8.94 \times 10^{14}$$

$C_{Cd} = 5.6 \times 10^{-15}$ M

Thus,

$$[Cd^{2+}] = \alpha_{cd^{2+}} \times C_{cd} = (0.0881)(5.6 \times 10^{-15}\ M) = 4.93 \times 10^{-16}\ M$$

and pCd is 15.31.



Complexometric titration curve for 50.0 mL of 5.00 x 10^{-3} M $Cd^{2+}$with 0.0100 M EDTA at a pH of 10.0 in the presence of 0.0100 M NH_3.

Volume of EDTA (mL)	pCd
0.00	3.36
5.00	3.49
10.00	3.66
15.00	3.87
20.00	4.20
23.00	4.62
25.00	9.77
27.00	14.91
30.00	15.31
35.00	15.61
40.00	15.78
45.00	15.91
50.00	16.01

Data for Titration of 5.00 x 10_3 M Cd^{2+} with 0.0100 M EDTA at a pH of 10.0 and in the Presence of 0.0100 M NH_3

Methods for finding the end point in Precipitation Titration

1- Finding the End Point with a Visual Indicator.

Most indicators for complexation titrations are organic dyes that form stable complexes with metal ions. These dyes are known as **metallochromic indicators.**

2- Finding the End Point by Monitoring Absorbance.

References

- Modern of analytical chemistry by David Harvey (DePauw University).
- Fundamental of Analytical Chemistry,8th Edition,Skoog.

Lectures- 12

Titrations Based on Redox reactions

Analytical titrations using redox reactions were introduced shortly after the development of acid–base titrimetry. The earliest **Redox titration** took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl_2, HCl, and HOCl) based on its ability to oxidize indigo, a dye that is colorless in its oxidized state. In 1814, Joseph Gay-Lussac developed a similar method for determining chlorine in bleaching powder. In both methods the end point is a change in color. Before the equivalence point the solution is colorless due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^-, $Cr_2O_7^{2-}$, and I_2 as oxidizing titrants, and of Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in color. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless. Other titrants require a separate indicator. The first such indicator, diphenylamine, was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry.

Redox Titration Curves

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species.

You may recall from Chapter 6 that the Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

$$A_{red} + B_{ox} \rightleftharpoons B_{red} + A_{ox}$$

where A_{ox} is the titrand's oxidized form, and B_{red} is the titrant's reduced form. The reaction's potential, E_{rxn}, is the difference between the reduction potentials for each half-reaction.

$$E_{rxn} = E_{Box / Bred} - E_{Aox / Ared}$$

After each addition of titrant the reaction between the titrand and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the titrand's and the titrant's reduction potentials are identical.

$$E_{Box/Bred} = E_{Aox/Ared}$$

This is an important observation because we can use either half-reaction to monitor the titration's progress.

Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction

$$E_{rxn} = E^{o}_{A_{ox}/A_{red}} - \frac{RT}{nF} \ln \frac{[A_{red}]}{[A_{ox}]}$$

Note **:** Although the Nernst equation is written in terms of the half-reaction's standard state potential, a matrix-dependent **formal potential**often is used in its place. See Appendix 13 for the standard state potentials and formal potentials for selected half-reactions.

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{rxn} = E^{o}_{B_{ox}/B_{red}} - \frac{RT}{nF} \ln \frac{[B_{red}]}{[B_{ox}]}$$

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$. The reaction in this case is

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq) \qquad 12.1$$

Note

In 1 M $HClO_4$, the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to $Ce^{3+}$is +1.70 V.

Because the equilibrium constant for reaction 12.1 is very large—it is approximately 6×10^{15}—we may assume that the analyte and titrant react completely.

Note

Step 1: Calculate the volume of titrant needed to reach the equivalence point.

The first task is to calculate the volume of Ce^{4+} needed to reach the titration's equivalence point. From the reaction's stoichiometry we know that

moles Fe^{2+} = moles Ce^{4+}

$M_{Fe} \times V_{Fe} = M_{Ce} \times V_{Ce}$

Solving for the volume of Ce^{4+} gives the equivalence point volume as

$$V_{eq} = V_{Ce} = \frac{M_{Fe}V_{Fe}}{M_{Ce}} = \frac{(0.100\ \text{M})(50.0\ \text{mL})}{(0.100\ \text{M})} = 50.0\ \text{mL}$$

Note

Step 2: Calculate the potential before the equivalence point by determining the concentrations of the titrand's oxidized and reduced forms, and using the Nernst equation for the titrand's reduction half-reaction.

Before the equivalence point, the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction.

$$E = E^{o}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.767\text{V} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad 12.2$$

For example, the concentrations of Fe^{2+} and Fe^{3+} after adding 10.0 mL of titrant are

$$[\text{Fe}^{2+}] = \frac{\text{initial moles Fe}^{2+} - \text{moles Ce}^{4+}\text{ added}}{\text{total volume}} = \frac{M_{Fe}V_{Fe} - M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100\ \text{M})(50.0\ \text{mL}) - (0.100\ \text{M})(10.0\ \text{mL})}{50.0\ \text{mL} + 10.0\ \text{mL}} = 6.67 \times 10^{-2}\ \text{M}$$

$$[\text{Fe}^{3+}] = \frac{\text{moles Ce}^{4+}\text{ added}}{\text{total volume}} = \frac{M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100\ \text{M})(10.0\ \text{mL})}{50.0\ \text{mL} + 10.0\ \text{mL}} = 1.67 \times 10^{-2}\ \text{M}$$

Substituting these concentrations into equation 9.2 gives a potential of

$$E = +0.767\ \text{V} - 0.05916\log\frac{6.67 \times 10^{-2}\ \text{M}}{1.67 \times 10^{-2}\ \text{M}} = +0.731\ \text{V}$$

Note

Step 3: Calculate the potential after the equivalence point by determining the concentrations of the titrant's oxidized and reduced forms, and using the Nernst equation for the titrant's reduction half-reaction.

After the equivalence point, the concentration of Ce^{3+} and the concentration of excess Ce^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Ce^{4+}/Ce^{3+} half-reaction.

$$E = E^{o}_{Ce^{4+}/Ce^{3+}} - \frac{RT}{nF}\log\frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.70\ \text{V} - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]} \qquad 12.3$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and

$$[Ce^{3+}] = \frac{\text{initial moles Fe}^{2+}}{\text{total volume}} = \frac{M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}}$$
$$= \frac{(0.100\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 60.0\ \text{mL}} = 4.55 \times 10^{-3}\ \text{M}$$

$$[Ce^{4+}] = \frac{\text{moles Ce}^{4+}\text{ added} - \text{initial moles Fe}^{2+}}{\text{total volume}} = \frac{M_{Ce}V_{Ce} - M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}}$$
$$= \frac{(0.100\ \text{M})(60.0\ \text{mL}) - (0.100\ \text{M})(50.0\ \text{mL})}{50.0\ \text{mL} + 60.0\ \text{mL}} = 9.09 \times 10^{-3}\ \text{M}$$

Ce^{4+} are

Substituting these concentrations into equation 9.3 gives a potential of

$$E = +1.70\ \text{V} - 0.05916\log\frac{4.55 \times 10^{-2}\ \text{M}}{9.09 \times 10^{-3}\ \text{M}} = +1.66\ \text{V}$$

Note

Step 4: Calculate the potential at the equivalence point.

At the titration's equivalence point, the potential, E_{eq}, in equation 12.2 and equation 12.3 are identical. Adding the equations together to gives

$$2E_{eq} = E^{o}_{Fe^{3+}/Fe^{2+}} + E^{o}_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

Because $[Fe^{2+}] = [Ce^{4+}]$ and $[Ce^{3+}] = [Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767\text{ V} + 1.70\text{ V}}{2} = 1.23\text{ V}$$

Additional results for this titration curve are shown in Table 12.1 and Figure 1.

Table 12.1 Data for the Titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}

Volume of Ce^{4+} (mL)	***E* (V)**	**Volume Ce^{4+} (mL)**	***E* (V)**
10.0	0.731	60.0	1.66
20.0	0.757	70.0	1.68
30.0	0.777	80.0	1.69
40.0	0.803	90.0	1.69
50.0	1.23	100.0	1.70

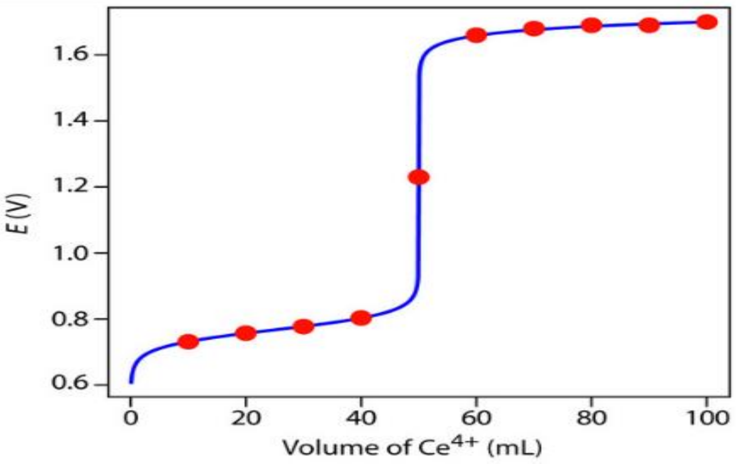


Figure 1 Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The red points correspond to the data in Table 12.1. The blue line shows the complete titration curve.

Practice Exercise 1

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq)$$

Sketching a Redox Titration Curve

To evaluate the relationship between a titration’s equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a redox titration curve. Our goal is to sketch the titration curve quickly, using as few calculations as possible. Let's use the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$.

Note

This is the same example that we used in developing the calculations for a redox titration curve. You can review the results of that calculation in Table 12.1 and Figure 1.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 50.0 mL. Next, we draw our axes, placing the potential, *E*, on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 50.0 mL of Ce^{4+}. Figure.2 a shows the result of the first step in our sketch.

Before the equivalence point, the potential is determined by a redox buffer of Fe^{2+} and Fe^{3+}. Although we can easily calculate the potential using the Nernst equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a redox buffer operates over a range of potentials that extends approximately ±(0.05916/*n*) unit on either side of $E^o_{Fe}{}^{3+}/Fe^{2+}$. The potential is at the buffer's lower limit

$$E = E^o_{Fe3+\,/\,Fe2+} - 0.05916$$

when the concentration of Fe^{2+} is 10× greater than that of Fe^{3+}. The buffer reaches its upper potential

$$E = E^o_{Fe3+\,/Fe2+} + 0.05916$$

when the concentration of Fe^{2+} is 10× smaller than that of Fe^{3+}. The redox buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

Figure b shows the second step in our sketch. First, we superimpose a ladder diagram for Fe^{2+} on the *y*-axis, using its $E^o_{Fe}{}^{3+}/Fe^{2+}$ value of 0.767 V and including the buffer's range of potentials. Next, we add points representing the pH at 10% of the equivalence point volume (a potential of 0.708 V at 5.0 mL) and at 90% of the equivalence point volume (a potential of 0.826 V at 45.0 mL).

Note

We used a similar approach when sketching the acid–base titration curve for the titration of acetic acid with NaOH.

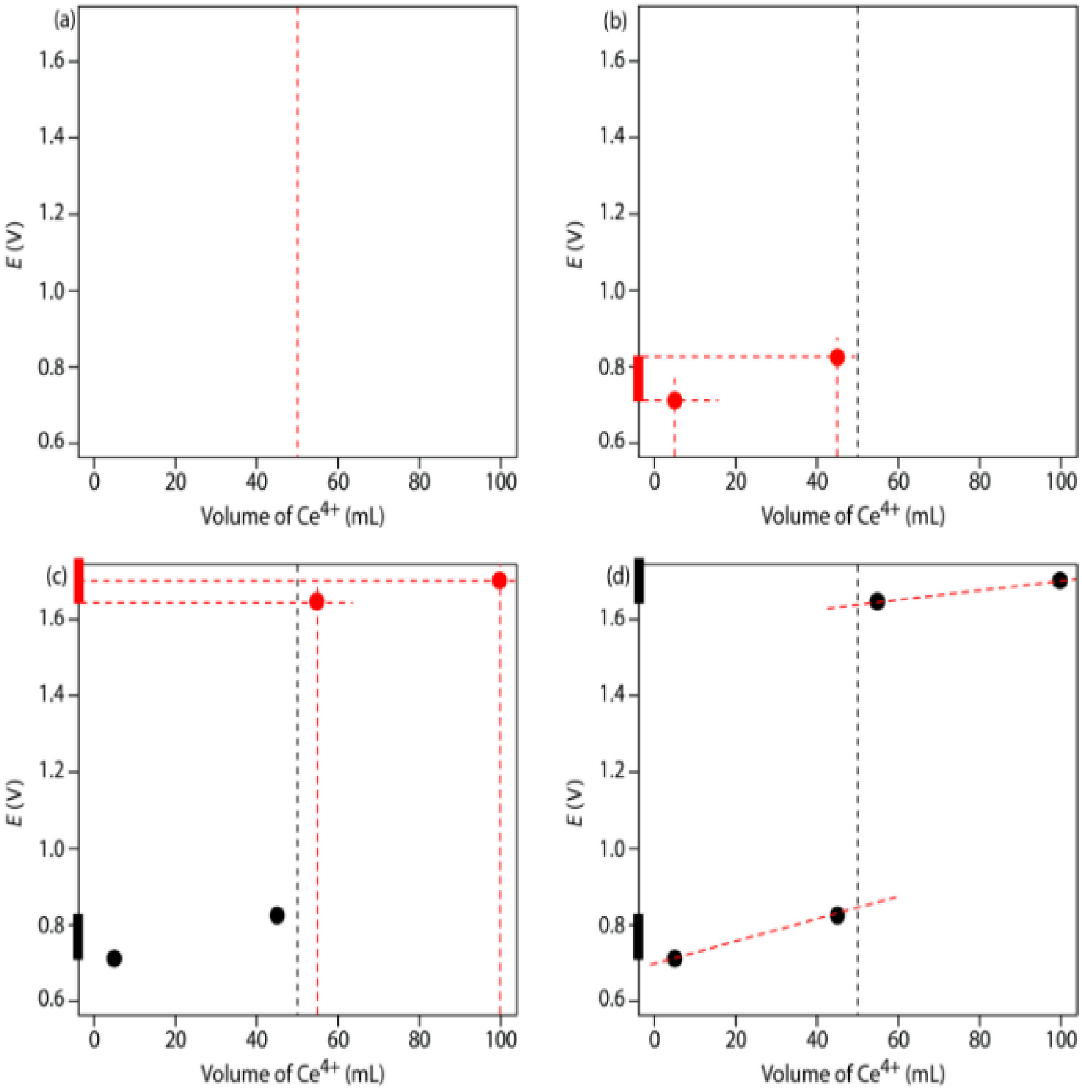
The third step in sketching our titration curve is to add two points after the equivalence point. Here the potential is controlled by a redox buffer of Ce^{3+} and Ce^{4+}.The redox buffer is at its lower limit of $E = E^o_{Ce}{}^{4+}/_{Ce}{}^{3+} - 0.05916$ when the titrant reaches 110% of the equivalence point volume and the potential is $E^o_{Ce}{}^{4+}/Ce^{3+}$ when the volume of Ce^{4+} is $2\times V_{eq}$.

Figure c shows the third step in our sketch. First, we add a ladder diagram for Ce^{4+}, including its buffer range, using its $E^{o}_{Ce^{4+}/Ce^{3+}}$ value of 1.70 V. Next, we add points representing the potential at 110% of V_{eq} (a value of 1.66 V at 55.0 mL) and at 200% of V_{eq} (a value of 1.70 V at 100.0 mL).

Note

We used a similar approach when sketching the complexation titration curve for the titration of Mg^{2+} with EDTA.

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure e). A comparison of our sketch to the exact titration curve (Figure f) shows that they are in close agreement.



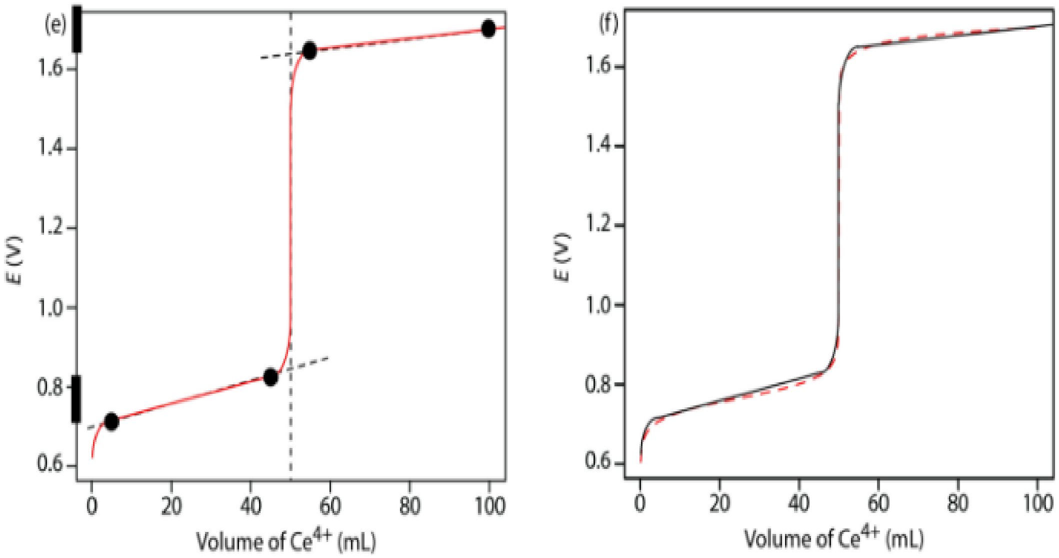


Figure 2 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M $HClO_4$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

Practice Exercise 2

Sketch the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{4+} with 0.100 M Tl^{+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq)$$

Compare your sketch to your calculated titration curve from **Practice Exercise 1**

Practice Exercise 1

The volume of Tl^{3+} needed to reach the equivalence point is

$$V_{eq} = V_{Tl} = \frac{M_{Sn}V_{Sn}}{M_{Tl}} = \frac{(0.050\ \text{M})(50.0\ \text{mL})}{0.100\ \text{M}} = 25.0\ \text{mL}$$

Before the equivalence point, the concentration of unreacted Sn^{2+} and the concentration of Sn^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Sn^{4+}/Sn^{2+} half-reaction.For example, the concentrations of Sn^{2+} and Sn^{4+} after adding 10.0 mL of titrant are

$$[\mathrm{Sn^{2+}}] = \frac{(0.050\ \mathrm{M})(50.0\ \mathrm{mL}) - (0.100\ \mathrm{M})(10.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 10.0\ \mathrm{mL}} = 0.0250\ \mathrm{M}$$

$$[\mathrm{Sn^{4+}}] = \frac{(0.100\ \mathrm{M})(10.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 10.0\ \mathrm{mL}} = 0.0167\ \mathrm{M}$$

and the potential is

$$E = +0.139\ \mathrm{V} - \frac{0.05916}{2}\log\frac{0.0250\ \mathrm{M}}{0.0167\ \mathrm{M}} = +0.134\ \mathrm{V}$$

After the equivalence point, the concentration of Tl^+ and the concentration of excess Tl^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Tl^{3+}/Tl^+ half-reaction. For example, after adding 40.0 mL of titrant, the concentrations of Tl^+ and Tl^{3+} are

$$[\mathrm{Tl^{+}}] = \frac{(0.0500\ \mathrm{M})(50.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 40.0\ \mathrm{mL}} = 0.0278\ \mathrm{M}$$

$$[\mathrm{Tl^{3+}}] = \frac{(0.100\ \mathrm{M})(40.0\ \mathrm{mL}) - (0.0500\ \mathrm{M})(50.0\ \mathrm{mL})}{50.0\ \mathrm{mL} + 40.0\ \mathrm{mL}} = 0.0167\ \mathrm{M}$$

and the potential is

$$E = +0.77\ \mathrm{V} - \frac{0.05916}{2}\log\frac{0.0278\ \mathrm{M}}{0.0167\ \mathrm{M}} = +0.76\ \mathrm{V}$$

At the titration’s equivalence point, the potential, E_{eq}, potential is

$$E_{eq} = \frac{0.139\ \mathrm{V} + 0.77\ \mathrm{V}}{2} = 0.45\ \mathrm{V}$$

Some additional results are shown here.

Vol. of Tl^{3+} (mL)	E (V)	Vol. of Tl^{3+} (mL)	E (V)
5	0.121	30	0.75
10	0.134	35	0.75
15	0.144	40	0.76
20	0.157	45	0.76
25	0.45	50	0.76

References

- Modern Analytical Chemistry by David Harvey (DePauw University)
- Fundametal of Analytical Chemistry by Skoog

Lecture - 13

Gravimetric Methods of Analysis

13.1.1 Using Mass as an Analytical Signal

Suppose you are to determine the total suspended solids in the water released by a sewage-treatment facility. Suspended solids are just that—solid matter that has yet to settle out of its solution matrix. The analysis is easy. After collecting a sample, you pass it through a preweighed filter that retains the suspended solids, and dry the filter and solids to remove any residual moisture. The mass of suspended solids is the difference between the filter's final mass and its original mass. We call this a **direct analysis** because the analyte—the suspended solids in this example—is the species that is weighed.

Note : Method 2540D in *Standard Methods for the Examination of Waters and Wastewaters*, 20th Edition (American Public Health Association, 1998) provides an approved method for determining total suspended solids. The method uses a glass-fiber filter to retain the suspended solids. After filtering the sample, the filter is dried to a constant weight at 103–105^{o}C

What if our analyte is an aqueous ion, such as Pb^{2+}? Because the analyte is not a solid, we cannot isolate it by filtration. We can still measure the analyte's mass directly if we first convert it into a solid form. If we suspend a pair of Pt electrodes in the sample and apply a sufficiently positive potential between them for a long enough time, we can force the following reaction to completion.

$$Pb^{2+}(aq) + 4H_2O(l) \rightleftharpoons PbO_2(s) + H_2(g) + 2H_3O^+(aq)$$

Oxidizing Pb^{2+} deposits PbO_2 on the Pt anode. If we weigh the anode before and after applying the potential, the change in its mass gives the mass of PbO_2 and, from the reaction's stoichiometry, the amount of Pb^{2+} in the sample. This is a direct analysis because PbO_2 contains the analyte.

Sometimes it is easier to remove the analyte and let a change in mass serve as the analytical signal. Suppose you need to determine a food's moisture content. One approach is to heat a sample of the food to a temperature that vaporizes the water, capturing it in a preweighed absorbent trap. The change in the absorbent's mass provides a direct determination of the amount of water in the sample. An easier approach is to weigh the sample of food before and after heating, using the change in its mass as an indication of the amount of water originally present. We call this an **indirect analysis** because we determine the analyte using a signal that is proportional its disappearance.

Note: Method 925.10 in *Official Methods of Analysis*, 18th Edition (AOAC International, 2007) provides an approved method for determining the moisture content of flour. A preweighed sample is heated for one hour in a 130^{o}C oven and transferred to a desiccator while it cools to room temperature. The loss in mass gives the amount of water in the sample.

13.1.2 Types of Gravimetric Methods

In the previous section we used four examples to illustrate the different ways that mass can serve as an analytical signal. These examples also illustrate the four gravimetric methods of analysis.

1- When the signal is the mass of a precipitate, we call the method **precipitation gravimetry.** The indirect determination of $PO3^{3-}$ by precipitating Hg_2Cl_2 is a representative example, as is the direct determination of Cl^- by precipitating AgCl.

2- In **electrogravimetry** the analyte is deposited as a solid film on one electrode inan electrochemical cell. The oxidation of Pb^{2+}, and its deposition as PbO_2 on a Pt anode is one example of electrogravimetry. Reduction also may be used in electrogravimetry. The electrodeposition of Cu on a Pt cathode, for example, provides a direct analysis for Cu^{2+}.

3- When thermal or chemical energy is used to remove a volatile species, we call the method **volatilization gravimetry**. In determining the moisture content of food, thermal energy vaporizes the H_2O. The amount of carbon in an organic compound may be determined by using the chemical energy of combustion to convert C to CO_2

4- Finally, in **particulate gravimetry** the analyte is determined following its removal from the sample matrix by filtration or extraction. The determination of suspended solids is one example of particulate gravimetry.

13.1.3 Conservation of Mass

An accurate gravimetric analysis requires that the analytical signal—whether it is a mass or a change in mass—be proportional to the amount of analyte in our sample. For all gravimetric methods this proportionality involves a **conservation of mass**. If the method relies on one or more chemical reactions, then the stoichiometry of the reactions must be known. Thus, for the analysis of PO_3^{3-} described earlier, we know that each mole of Hg_2Cl_2 corresponds to a mole of PO_3^{3-} in our sample. If we remove the analyte from its matrix, then the separation must be selective for the analyte. When determining the moisture content in bread, for example, we know that the mass of H_2O in the bread is the difference between the sample's final mass and its initial mass.

Note : We will return to this concept of applying a conservation of mass later in the chapter when we consider specific examples of gravimetric methods.

13.1.4 Why Gravimetry is Important

Except for particulate gravimetry, which is the most trivial form of gravimetry, you probably will not use gravimetry after you complete this course. Why, then, is familiarity with gravimetry still important? The answer is that gravimetry is one of only a small number of **definitive techniques** whose measurements require only base SI units, such as mass or the mole, and defined constants, such as Avogadro's number and the mass of ^{12}C. Ultimately, we must be able to trace the result of an analysis to a definitive technique, such as gravimetry, that we can relate to fundamental physical properties.[2] Although most analysts never use gravimetry to validate their results, they often verifying an analytical method by analyzing a standard reference material whose composition is traceable to a definitive technique.

Note : Other examples of definitive techniques are coulometry and isotope-dilution mass spectrometry. Coulometry is discussed in Chapter 11. Isotope-dilution mass spectrometry is beyond the scope of an introductory textbook; however, you will find some suggested readings in this chapter's Additional Resources.

13.2: Precipitation Gravimetry

In precipitation gravimetry an insoluble compound forms when we add a precipitating reagent, or **precipitant**, to a solution containing our analyte. In most methods the precipitate is the product of a simple metathesis reaction between the analyte and the precipitant; however, any reaction generating a precipitate can potentially serve as a gravimetric method.

13.2.1 Theory and Practice

All precipitation gravimetric analysis share two important attributes. First, the precipitate must be of low solubility, of high purity, and of known composition if its mass is to accurately reflect the analyte's mass. Second, the precipitate must be easy to separate from the reaction mixture.

Solubility Considerations

To provide accurate results, a precipitate's solubility must be minimal. The accuracy of a total analysis technique typically is better than ±0.1%, which means that the precipitate must account for at least 99.9% of the analyte. Extending this requirement to 99.99% ensures that the precipitate's solubility does not limit the accuracy of a gravimetric analysis.

Note : A total analysis technique is one in which the analytical signal—mass in this case—is proportional to the absolute amount of analyte in the sample.

We can minimize solubility losses by carefully controlling the conditions under which the precipitate forms. This, in turn, requires that we account for every equilibrium reaction affecting the precipitate's solubility. For example, we can determine Ag^+ gravimetrically by adding NaCl as a precipitant, forming a precipitate of AgCl.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl_{(s)} \qquad (8.1)$$

If this is the only reaction we consider, then we predict that the precipitate's

$$S_{AgCl} = [Ag^+] = \frac{K_{sp}}{[Cl^-]} \qquad (8.2)$$

Equation 8.2 suggests that we can minimize solubility losses by adding a large excess of Cl^-. In fact, as shown in Figure 8.1, adding a large excess of Cl^- increases the precipitate's solubility.

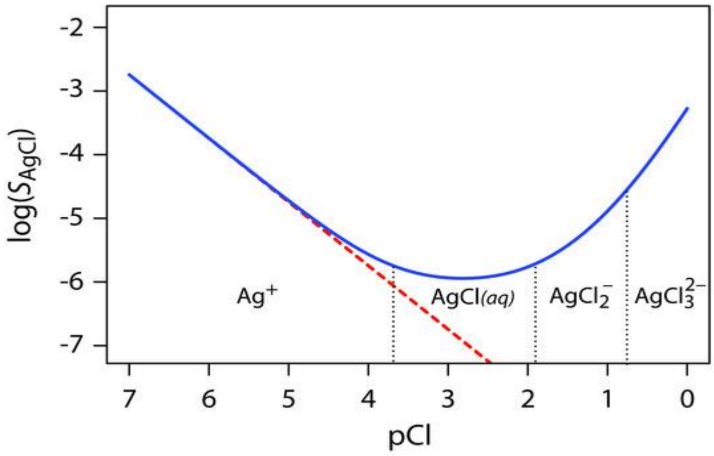


Figure 13.1 Solubility of AgCl as a function of pCl. The dashed red line shows our prediction for S_{AgCl} if we incorrectly assume that only reaction 8.1 and equation 8.2 affect silver chloride's solubility. The solid blue curve is calculated using equation 8.7, which accounts for reaction 8.1 and reactions 8.3–8.5. Because the solubility of AgCl spans several orders of magnitude, S_{AgCl} is displayed on the *y*-axis in logarithmic form.

To understand why the solubility of AgCl is more complicated than the relationship suggested by equation 8.2, we must recognize that Ag^+ also forms a series of soluble silver-chloro metal–ligand complexes.

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(aq) \qquad \log K_1 = 3.70 \qquad (8.3)$$

$$AgCl(aq) + Cl^-(aq) \rightleftharpoons AgCl_2^-(aq) \qquad \log K_2 = 1.92 \qquad (8.4)$$

$$AgCl_2^-(aq) + Cl^-(aq) \rightleftharpoons AgCl_3^{2-}(aq) \qquad \log K_3 = 0.78 \qquad (8.5)$$

The actual solubility of AgCl is the sum of the equilibrium concentrations for all soluble forms of Ag^+, as shown by the following equation.

$$S_{AgCl} = [Ag^+] + [AgCl(aq)] + [AgCl_2^-] + [AgCl_3^{2-}] \qquad (8.6)$$

By substituting into equation 8.6 the equilibrium constant expressions for reaction 8.1 and reactions 8.3–8.5, we can define the solubility of AgCl as

$$S_{AgCl} = \frac{K_{sp}}{[Cl^-]} + K_1K_{sp} + K_1K_2K_{sp}[Cl^-] + K_1K_2K_3K_{sp}[Cl^-]^2 \qquad (8.7)$$

Note : Problem 1 in the end-of-chapter problems asks you to show that equation 8.7 is correct by completing the derivation.

Equation 8.7 explains the solubility curve for AgCl shown in Figure 8.1. As we add NaCl to a solution of Ag^+, the solubility of AgCl initially decreases because of reaction 8.1. Under these conditions, the final three terms in equation 8.7 are small and equation 8.1 is sufficient to describe AgCl's solubility. At higher concentrations of $Cl^–$, reaction 8.4 and reaction 8.5 increase the solubility of AgCl. Clearly the equilibrium concentration of chloride is important if we want to determine the concentration of silver by precipitating AgCl. In particular, we must avoid a large excess of chloride.

Note : The predominate silver-chloro complexes for different values of pCl are shown by the ladder diagram along the *x*-axis in Figure 8.1 Note that the increase in solubility begins when the higher-order soluble complexes, $AgCl_2^–$ and $AgCl_3^{2–}$, become the predominate species.

Another important parameter that may affect a precipitate's solubility is pH. For example, a hydroxide precipitates such as $Fe(OH)_3$ is more soluble at lower pH levels where the concentration of $OH^–$ is small. Because fluoride is a weak base, the solubility of calcium fluoride, S_{CaF2}, also is pH-dependent. We can derive an equation for S_{CaF2} by considering the following equilibrium reactions

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = 3.9\times10^{-11} \qquad (8.8)$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K_a = 6.8\times10^{-4} \qquad (8.9)$$

and the following equation for the solubility of CaF_2.

$$S_{CaF_2} = [Ca^{2+}] = \frac{1}{2}\{[F^-] + [HF]\} \qquad (8.10)$$

Note : Be sure that equation 8.10 makes sense to you. Reaction 8.8 tells us that the dissolution of CaF_2 produces one mole of Ca^{2+} for every two moles of $F^–$, which explains the term of 1/2 in equation 8.10. Because $F^–$ is a weak base, we need to account for both of its chemical forms in solution, which explains why we include HF.

Substituting the equilibrium constant expressions for reaction 8.8 and reaction 8.9 into equation 8.10 defines the solubility of CaF_2 in terms of the equilibrium concentration of H_3O^+.

$$S_{CaF_2} = [Ca^{2+}] = \left\{ \frac{K_{sp}}{4} \left(1 + \frac{[H_3O^+]}{K_a} \right)^2 \right\}^{1/3} \tag{8.11}$$

Note : Problem 4 in the end-of-chapter problems asks you to show that equation 8.11 is correct by completing the derivation.

Figure 8.2 shows how pH affects the solubility of CaF_2. Depending on the solution's pH, the predominate form of fluoride is either HF or F^-. When the pH is greater than 4.17, the predominate species is F^- and the solubility of CaF_2 is independent of pH because only reaction 8.8 occurs to an appreciable extent. At more acidic pH levels, the solubility of CaF_2 increases because of the contribution of reaction 8.9.

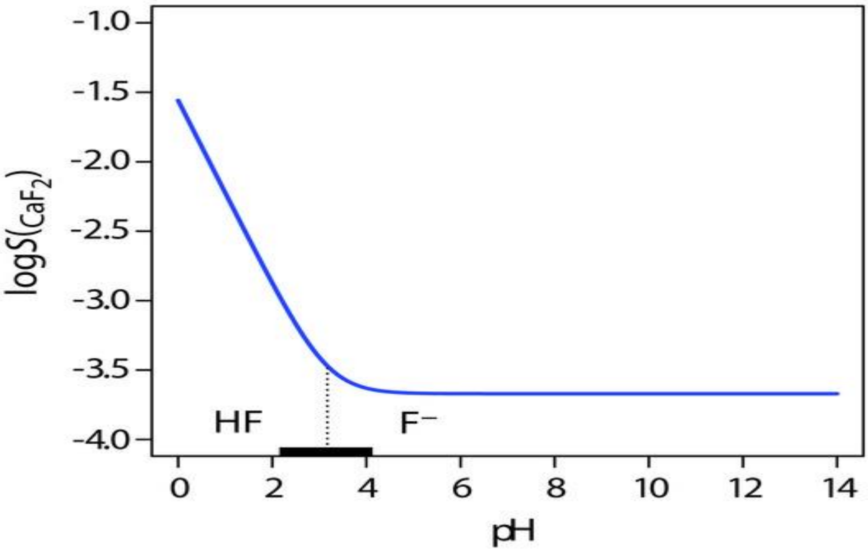


Figure 13.2 Solubility of CaF_2 as a function of pH. The solid blue curve is a plot of equation 8.11. The predominate form of fluoride in solution is shown by the ladder diagram along the *x*-axis, with the black rectangle showing the region where both HF and F^- are important species. Note that the solubility of CaF_2 is independent of pH for pH levels greater than 4.17, and that its solubility increases dramatically at lower pH levels where HF is the predominate species. Because the solubility of CaF_2 spans several orders of magnitude, its solubility is shown in logarithmic form.

When solubility is a concern, it may be possible to decrease solubility by using a non-aqueous solvent. A precipitate's solubility is generally greater in an aqueous solution because of water's ability to stabilize ions through solvation. The poorer solvating ability of non-aqueous solvents, even those which are polar, leads to a smaller solubility product. For example, the K_{sp} of $PbSO_4$ is 2×10^{-8} in H_2O and 2.6×10^{-12} in a 50:50 mixture of H_2O and ethanol.

Practice Exercise 13.1

You can use a ladder diagram to predict the conditions for minimizing a precipitate's solubility. Draw a ladder diagram for oxalic acid, $H_2C_2O_4$, and use it to establish a suitable range of pH values for minimizing the solubility of CaC_2O_4. Relevant equilibrium constants may be found in the appendices.

Solution

The solubility reaction for CaC_2O_4 is

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

To minimize solubility, the pH needs to be basic enough that oxalate, $C_2O_4^{2-}$, does not react to form $HC_2O_4^-$ or $H_2C_2O_4$. The ladder diagram for oxalic acid, including approximate buffer ranges, is shown in Figure 8.17. Maintaining a pH greater than 5.3 ensures that $C_2O_4^{2-}$ is the only important form of oxalic acid in solution, minimizing the solubility of CaC_2O_4.

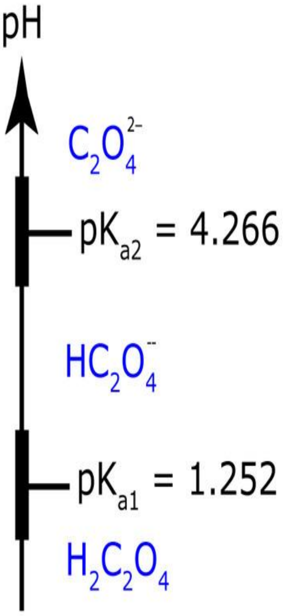


Figure 13.17 pH ladder diagram for oxalic acid, $H_2C_2O_4$.

Avoiding Impurities

In addition to having a low solubility, the precipitate must be free from impurities. Because precipitation usually occurs in a solution that is rich in dissolved solids, the initial precipitate is often impure. We must remove these impurities before determining the precipitate's mass.

The greatest source of impurities is the result of chemical and physical interactions occurring at the precipitate’s surface. A precipitate is generally crystalline—even if only on a microscopic scale—with a well-defined lattice of cations and anions. Those cations and anions at the precipitate’s surface carry, respectively, a positive or a negative charge because they have incomplete coordination spheres. In a precipitate of AgCl, for example, each silver ion in the precipitate’s interior is bound to six chloride ions. A silver ion at the surface, however, is bound to no more than five chloride ions and carries a partial positive charge (Figure 8.3). The presence of these partial charges makes the precipitate’s surface an active site for the chemical and physical interactions that produce impurities.

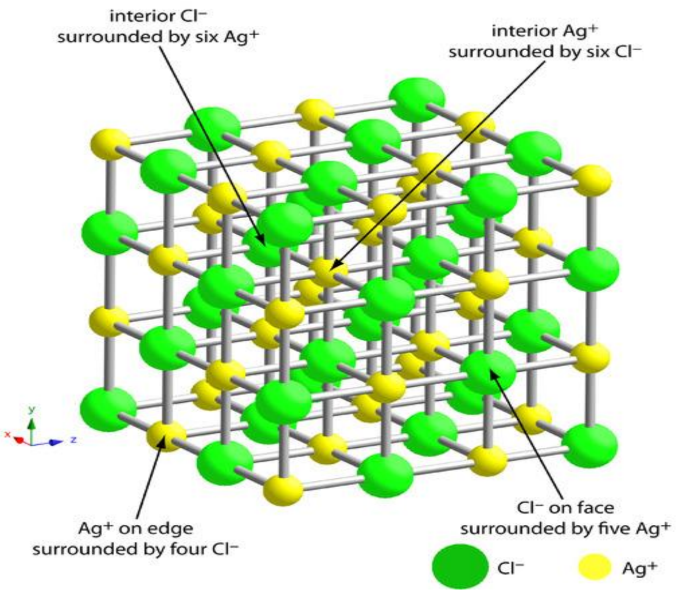


Figure 13.3 Ball-and-stick diagram showing the lattice structure of AgCl. Each silver ion in the lattice’s interior binds with six chloride ions, and each chloride ion in the interior binds with six silver ions. Those ions on the lattice’s surface or edges bind to fewer than six ions and carry a partial charge. A silver ion on the surface, for example, carries a partial positive charge. These charges make the surface of a precipitate an active site for chemical and physical interactions.

One common impurity is an **inclusion**. A potential interfering ion whose size and charge is similar to a lattice ion, may substitute into the lattice structure, provided that the interferent precipitates with the same crystal structure (Figure 8.4a). The probability of forming an inclusion is greatest when the concentration of the interfering ion is substantially greater than the lattice ion’s concentration. An inclusion does not decrease the amount of analyte that precipitates, provided that the precipitant is present in sufficient excess. Thus, the precipitate’s mass is always larger than expected.

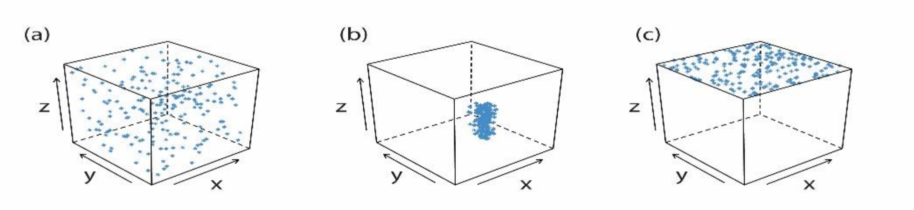


Figure 13.4 Three examples of impurities that may form during precipitation. The cubic frame represents the precipitate and the blue marks are impurities: (a) inclusions, (b) occlusions, and (c) surface adsorbates. Inclusions are randomly distributed throughout the precipitate. Occlusions are localized within the interior of the precipitate and surface adsorbates are localized on the precipitate's exterior. For ease of viewing, in (c) adsorption is shown on only one surface.

An inclusion is difficult to remove since it is chemically part of the precipitate's lattice. The only way to remove an inclusion is through **reprecipitation**. After isolating the precipitate from its supernatant solution, we dissolve it by heating in a small portion of a suitable solvent. We then allow the solution to cool, reforming the precipitate. Because the interferent's concentration is less than that in the original solution, the amount of included material is smaller. We can repeat the process of reprecipitation until the inclusion's mass is insignificant. The loss of analyte during reprecipitation, however, can be a significant source of error.

Note : Suppose that 10% of an interferent forms an inclusion during each precipitation. When we initially form the precipitate, 10% of the original interferent is present as an inclusion. After the first reprecipitation, 10% of the included interferent remains, which is 1% of the original interferent. A second reprecipitation decreases the interferent to 0.1% of the original amount.

Occlusions form when interfering ions become trapped within the growing precipitate. Unlike inclusions, which are randomly dispersed within the precipitate, an occlusion is localized, either along flaws within the precipitate's lattice structure or within aggregates of individual precipitate particles (Figure 8.4b). An occlusion usually increases a precipitate's mass; however, the mass is smaller if the occlusion includes the analyte in a lower molecular weight form than that of the precipitate.

We can minimize occlusions by maintaining the precipitate in equilibrium with its supernatant solution for an extended time. This process is called a **digestion**. During digestion, the dynamic nature of the solubility–precipitation equilibrium, in which the precipitate dissolves and reforms, ensures that the occlusion is reexposed to the supernatant solution. Because the rates of dissolution and reprecipitation are slow, there is less opportunity for forming new occlusions.

After precipitation is complete the surface continues to attract ions from solution (Figure 8.4c). These **surface adsorbates** comprise a third type of impurity. We can minimize surface adsorption by decreasing the precipitate's available surface area. One benefit of digesting a precipitate is that it increases the average particle size. Because the probability of a particle completely dissolving is inversely proportional to its size, during digestion larger particles increase in size at the expense of smaller particles. One consequence of forming a smaller number of larger particles is an overall decrease in the precipitate's surface area. We also can remove surface adsorbates by washing the precipitate, although the potential loss of analyte can not be ignored.

I**nclusions**, **occlusions,** and **surface adsorbates** are examples of **coprecipitates**—otherwise soluble forms an independent precipitate under the conditions of the analysis. For example, the species that form within the precipitate containing the analyte. Another type of impurity is an interferent that precipitation of nickel dimethylglyoxime requires a slightly basic pH. Under these conditions, any Fe^{3+} in the sample precipitates as $Fe(OH)_3$. In addition, because most precipitants are rarely selective toward a single analyte, there is always a risk that the precipitant will react with both the analyte and an interferent.

Note : In addition to forming a precipitate with Ni^{2+}, dimethylglyoxime also forms precipitates with Pd^{2+} and Pt^{2+}. These cations are potential interferents in an analysis for nickel.

We can minimize the formation of additional precipitates by carefully controlling solution conditions. If an interferent forms a precipitate that is less soluble than the analyte's precipitate, we can precipitate the interferent and remove it by filtration, leaving the analyte behind in solution. Alternatively, we can mask the analyte or the interferent to prevent its precipitation.

Both of the above-mentioned approaches are illustrated in Fresenius' analytical method for determining Ni in ores containing Pb^{2+}, Cu^{2+}, and Fe^{3+} (see Figure 1.1). Dissolving the ore in the presence of H_2SO_4 selectively precipitates Pb^{2+} as $PbSO_4$. Treating the supernatant with H_2S precipitates the Cu^{2+} as CuS. After removing the CuS by filtration, adding ammonia precipitates Fe^{3+} as $Fe(OH)_3$. Nickel, which forms a soluble amine complex, remains in solution.

Controlling Particle Size

Size matters when it comes to forming a precipitate. Larger particles are easier to filter, and, as noted earlier, a smaller surface area means there is less opportunity for surface adsorbates to form. By carefully controlling the reaction conditions we can significantly increase a precipitate's average particle size.

Precipitation consists of two distinct events: nucleation, the initial formation of smaller stable particles of precipitate, and particle growth. Larger particles form when the rate of particle growth exceeds the rate of nucleation. Understanding the conditions favoring particle growth is important when designing a gravimetric method of analysis.

We define a solute's **relative supersaturation**, *RSS*, as

$$RSS = \frac{Q - S}{S} \qquad 8.12$$

where *Q* is the solute's actual concentration and *S* is the solute's concentration at equilibrium.[4] The numerator of equation 8.12, *Q* – *S*, is a measure of the solute's supersaturation. A solution with a large, positive value of *RSS* has a high rate of nucleation, producing a precipitate with many small particles. When the *RSS* is small, precipitation is more likely to occur by particle growth than by nucleation.

Note : A supersaturated solution is one that contains more dissolved solute than that predicted by equilibrium chemistry. The solution is inherently unstable and precipitates solute to reach its equilibrium position. How quickly this process occurs depends, in part, on the value of *RSS*.

Examining equation 8.12 shows that we can minimize *RSS* by decreasing the solute's concentration, *Q*, or by increasing the precipitate's solubility, *S*. A precipitate's solubility usually increases at higher temperatures, and adjusting pH may affect a precipitate's solubility if it contains an acidic or a basic ion. Temperature and pH, therefore, are useful ways to increase the value of *S*. Conducting the precipitation in a dilute solution of analyte, or adding the precipitant slowly and with vigorous stirring are ways to decrease the value of *Q*.

There are practical limitations to minimizing *RSS*. Some precipitates, such as $Fe(OH)_3$ and PbS, are so insoluble that *S* is very small and a large *RSS* is unavoidable. Such solutes inevitably form small particles. In addition, conditions favoring a small *RSS* may lead to a relatively stable supersaturated solution that requires a long time to fully precipitate. For example, almost a month is required to form a visible precipitate of $BaSO_4$ under conditions in which the initial *RSS* is 5.

A visible precipitate takes longer to form when *RSS* is small both because there is a slow rate of nucleation and because there is a steady decrease in *RSS* as the precipitate forms. One solution to the latter problem is to generate the precipitant in situ as the product of a slow chemical reaction. This maintains the *RSS* at an effectively constant level. Because the precipitate forms under conditions of low *RSS*, initial nucleation produces a small number of particles. As additional precipitant forms, particle growth supersedes nucleation, resulting in larger precipitate particles. This process is called **homogeneous precipitation**.

Two general methods are used for homogeneous precipitation. If the precipitate's solubility is pH-dependent, then we can mix the analyte and the precipitant under conditions where precipitation does not occur, and then increase or decrease the pH by chemically generating OH^- or H_3O^+. For example, the hydrolysis of urea is a source of OH^-.

$$CO(NH_2)_2(aq) + H_2O(l) \rightleftharpoons 2NH_3(aq) + CO_2(g)$$

$$NH_3(aq)+H_2O(l)\rightleftharpoons OH^-(aq)+NH_4^+ (aq)$$

Because the hydrolysis of urea is temperature-dependent—it is negligible at room temperature—we can use temperature to control the rate of hydrolysis and the rate of precipitate formation. Precipitates of CaC_2O_4, for example, have been produced by this method. After dissolving the sample containing Ca^{2+}, the solution is made acidic with HCl before adding a solution of 5% w/v $(NH_4)_2C_2O_4$. Because the solution is acidic, a precipitate of CaC_2O_4 does not form. The solution is heated to approximately 50°C and urea is added. After several minutes, a precipitate of CaC_2O_4 begins to form, with precipitation reaching completion in about 30 min.

In the second method of homogeneous precipitation, the precipitant is generated by a chemical reaction. For example, Pb^{2+} is precipitated homogeneously as $PbCrO_4$ by using bromate, BrO_3^-, to oxidize Cr^{3+} to CrO_4^{2-}.

$6BrO_3^-(aq) + 10Cr^{3+}(aq) + 22H_2O(l) \rightleftharpoons 3Br_2(aq) + 10CrO_4^{2-}(aq) + 44H^+(aq)$

Figure 8.5 shows the result of preparing $PbCrO_4$ by the direct addition of $KCrO_4$ (Beaker A) and by homogenous precipitation (Beaker B). Both beakers contain the same amount of $PbCrO_4$. Because the direct addition of $KCrO_4$ leads to rapid precipitation and the formation of smaller particles, the precipitate remains less settled than the precipitate prepared homogeneously. Note, as well, the difference in the color of the two precipitates.

Figure 13.5 Two precipitates of $PbCrO_4$. In Beaker A, combining 0.1 M $Pb(NO_3)_2$ and 0.1 M K_2CrO_4 forms the precipitate under conditions of high *RSS*. The precipitate forms rapidly and consists of very small particles. In Beaker B, heating a solution of 0.1 M $Pb(NO_3)_2$, 0.1 M $Cr(NO_3)_3$, and 0.1 M $KBrO_3$ slowly oxidizes Cr^{3+} to CrO_4^{2-}, precipitating $PbCrO_4$ under conditions of low *RSS*. The precipitate forms slowly and consists of much larger particles.

Note: The effect of particle size on color is well-known to geologists, who use a streak test to help identify minerals. The color of a bulk mineral and its color when powdered are often different. Rubbing a mineral across an unglazed porcelain plate leaves behind a small streak of the powdered mineral. Bulk samples of hematite, Fe_2O_3, are black in color, but its streak is a familiar rust-red. Crocite, the mineral $PbCrO_4$, is red-orange in color; its streak is orange-yellow.

A homogeneous precipitation produces large particles of precipitate that are relatively free from impurities. These advantages, however, are offset by requiring more time to produce the precipitate and a tendency for the precipitate to deposit as a thin film on the container's walls. The latter problem is particularly severe for hydroxide precipitates generated using urea.

An additional method for increasing particle size deserves mention. When a precipitate's particles are electrically neutral they tend to coagulate into larger particles that are easier to filter. Surface adsorption of excess lattice ions, however, provides the precipitate's particles with a net positive or a net negative surface charge. Electrostatic repulsion between the particles prevents them from coagulating into larger particles.

Let's use the precipitation of AgCl from a solution of $AgNO_3$ using NaCl as a precipitant to illustrate this effect. Early in the precipitation, when NaCl is the limiting reagent, excess Ag^+ ions chemically adsorb to the AgCl particles, forming a positively charged primary adsorption layer (Figure 8.6a). The solution in contact with this layer contains more inert anions, NO_3^- in this case, than inert cations, Na^+, giving a secondary adsorption layer with a negative charge that balances the primary adsorption layer's positive charge. The solution outside the secondary adsorption layer remains electrically neutral. **Coagulation** cannot occur if the secondary adsorption layer is too thick because the individual particles of AgCl are unable to approach each other closely enough.

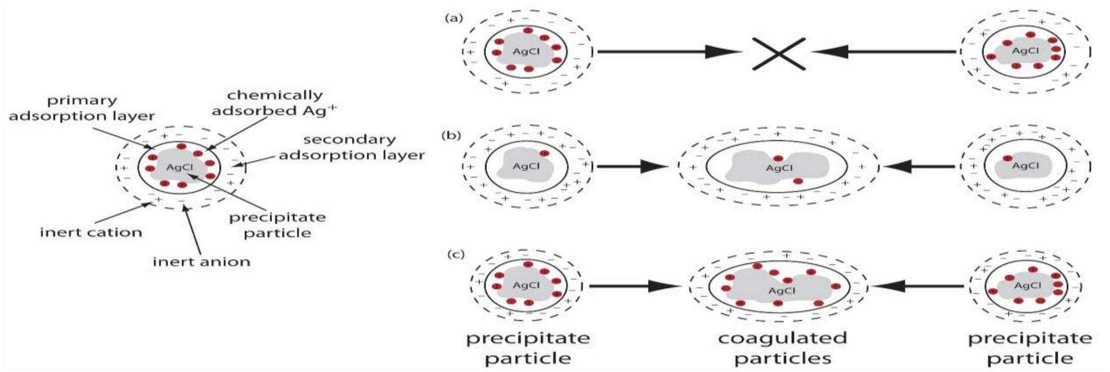


Figure 8.6 Two methods for coagulating a precipitate of AgCl. (a) Coagulation does not happen due to the electrostatic repulsion between the two positively charged particles. (b) Decreasing the charge within the primary adsorption layer, by adding additional NaCl, decreases the electrostatic repulsion, allowing the particles to coagulate. (c) Adding additional inert ions decreases the thickness of the secondary adsorption layer. Because the particles can approach each other more closely, they are able to coagulate.

We can induce coagulation in three ways: by decreasing the number of chemically adsorbed Ag^+ ions, by increasing the concentration of inert ions, or by heating the solution. As we add additional NaCl, precipitating more of the excess Ag^+, the number of chemically adsorbed silver ions decreases and coagulation occurs (Figure 8.6b). Adding too much NaCl, however, creates a primary adsorption layer of excess Cl^- with a loss of coagulation.

Note: The coagulation and decoagulation of AgCl as we add NaCl to a solution of $AgNO_3$ can serve as an endpoint for a titration. SeeChapter 9 for additional details.

A second way to induce coagulation is to add an inert electrolyte, which increases the concentration of ions in the secondary adsorption layer. With more ions available, the thickness of the secondary absorption layer decreases. Particles of precipitate may now approach each other more closely, allowing the precipitate to coagulate. The amount of electrolyte needed to cause spontaneous coagulation is called the critical coagulation concentration.

Heating the solution and precipitate provides a third way to induce coagulation. As the temperature increases, the number of ions in the primary adsorption layer decreases, lowering the precipitate's surface charge. In addition, heating increases the particles' kinetic energy, allowing them to overcome the electrostatic repulsion that prevents coagulation at lower temperatures.

Filtering the Precipitate

After precipitating and digesting the precipitate, we separate it from solution by filtering. The most common filtration method uses filter paper, which is classified according to its speed, its size, and its ash content on ignition. Speed, or how quickly the supernatant passes through the filter paper, is a function of the paper's pore size. A larger pore allows the supernatant to pass more quickly through the filter paper, but does not retain small particles of precipitate. Filter paper is rated as fast (retains particles larger than 20–25 μm), medium–fast (retains particles larger than 16 μm), medium (retains particles larger than 8 μm), and slow (retains particles larger than 2–3 μm). The proper choice of filtering speed is important. If the filtering speed is too fast, we may fail to retain some of the precipitate, causing a negative determinate error. On the other hand, the precipitate may clog the pores if we use a filter paper that is too slow.

Note: A filter paper's size is just its diameter. Filter paper comes in many sizes, including 4.25 cm, 7.0 cm, 11.0 cm, 12.5 cm, 15.0 cm, and 27.0 cm. Choose a size that fits comfortably into your funnel. For a typical 65-mm long-stem funnel, 11.0 cm and 12.5 cm filter paper are good choices.

Because filter paper is hygroscopic, it is not easy to dry it to a constant weight. When accuracy is important, the filter paper is removed before determining the precipitate's mass. After transferring the precipitate and filter paper to a covered crucible, we heat the crucible to a temperature that coverts the paper to CO_2(g) and H_2O(g), a process called **ignition**.

Note: Igniting a poor quality filter paper leaves behind a residue of inorganic ash. For quantitative work, use a low-ash filter paper. This grade of filter paper is pretreated with a mixture of HCl and HF to remove inorganic materials. Quantitative filter paper typically has an ash content of less than 0.010% w/w.

Gravity filtering is accomplished by folding the filter paper into a cone and placing it in a long-stem funnel (Figure 8.7). A seal between the filter cone and the funnel is formed by dampening the paper with water or supernatant, and pressing the paper to the wall of the funnel. When properly prepared, the funnel's stem fills with the supernatant, increasing the rate of filtration.

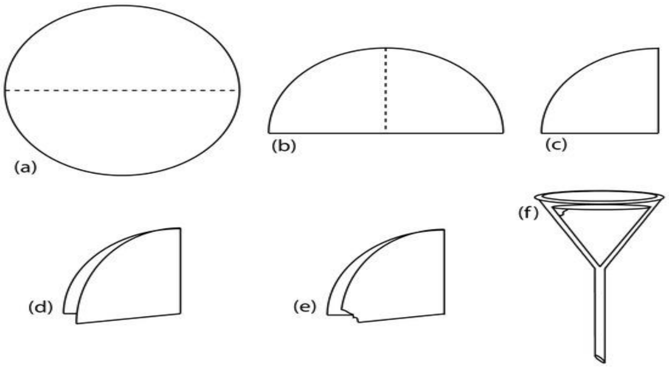


Figure 13.7 Preparing a filter paper cone. The filter paper circle in (a) is folded in half (b), and folded in half again (c). The folded filter paper is parted (d) and a small corner is torn off (e). The filter paper is opened up into a cone and placed in the funnel (f).

The precipitate is transferred to the filter in several steps. The first step is to decant the majority of the **supernatant** through the filter paper without transferring the precipitate (Figure 8.8). This prevents the filter paper from clogging at the beginning of the filtration process. The precipitate is rinsed while it remains in its beaker, with the rinsings decanted through the filter paper. Finally, the precipitate is transferred onto the filter paper using a stream of rinse solution. Any precipitate clinging to the walls of the beaker is transferred using a rubber policeman (a flexible rubber spatula attached to the end of a glass stirring rod).

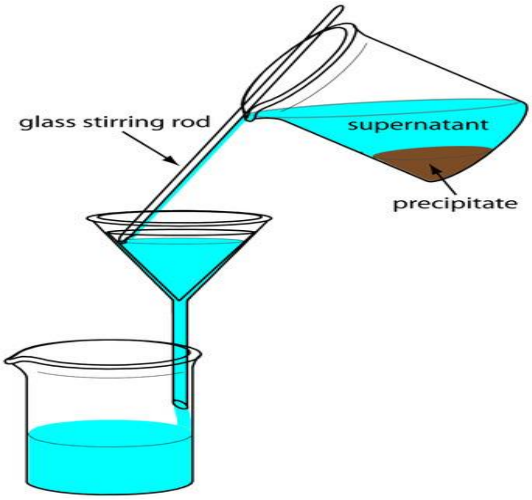


Figure 8.8 Proper procedure for transferring the supernatant to the filter paper cone.

An alternative method for filtering a precipitate is a filtering crucible. The most common is a fritted-glass crucible containing a porous glass disk filter. Fritted-glass crucibles are classified by their porosity: coarse (retaining particles larger than 40–60 μm), medium (retaining particles greater than 10–15 μm), and fine (retaining particles greater than 4–5.5 μm). Another type of filtering crucible is the Gooch crucible, which is a porcelain crucible with a perforated bottom. A glass fiber mat is placed in the crucible to retain the precipitate. For both types of crucibles, the precipitate is transferred in the same manner described earlier for filter paper. Instead of using gravity, the supernatant is drawn through the crucible with the assistance of suction from a vacuum aspirator or pump (Figure 8.9).

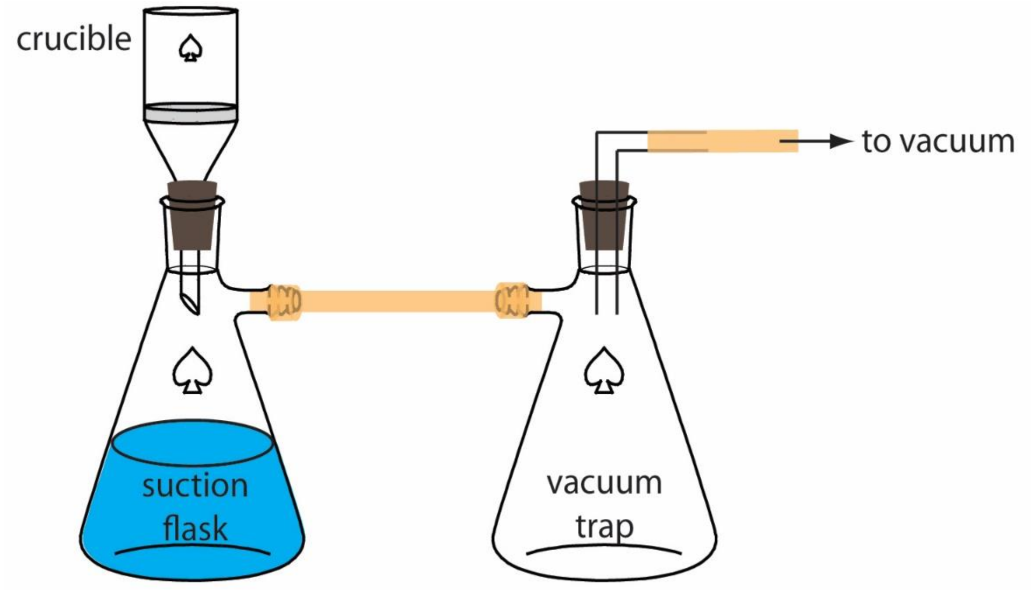


Figure 8.9 Procedure for filtering a precipitate through a filtering crucible. The trap prevents water from an aspirator from back-washing into the suction flask.

Rinsing the Precipitate

Because the supernatant is rich with dissolved inert ions, we must remove any residual traces of supernatant to avoid a positive determinate error without incurring solubility losses. In many cases this simply involves the use of cold solvents or rinse solutions containing organic solvents such as ethanol. The pH of the rinse solution is critical if the precipitate contains an acidic or basic ion. When coagulation plays an important role in determining particle size, adding a volatile inert electrolyte to the rinse solution prevents the precipitate from reverting into smaller particles that might pass through the filter. This process of reverting to smaller particles is called **peptization**. The volatile electrolyte is removed when drying the precipitate.

In general, we can minimize the loss of analyte by using several small portions of rinse solution instead of a single large volume. Testing the used rinse solution for the presence of impurities is another way to guard against over rinsing the precipitate. For example, if Cl^- is a residual ion in the supernatant, we can test for its presence using $AgNO_3$. After collecting a small portion of the rinse solution, we add a few drops of $AgNO_3$ and look for the presence or absence of a precipitate of AgCl. If a precipitate forms, then we know that Cl^- is present and continue to rinse the precipitate. Additional rinsing is not needed if the $AgNO_3$ does not produce a precipitate.

Drying the Precipitate

After separating the precipitate from its supernatant solution, the precipitate is dried to remove residual traces of rinse solution and any volatile impurities. The temperature and method of drying depend on the method of filtration and the precipitate's desired chemical form. Placing the precipitate in a laboratory oven and heating to a temperature of 110^oC is sufficient when removing water and other easily volatilized impurities. Higher temperatures require a muffle furnace, a Bunsen burner, or a Meker burner, and are necessary if we need to thermally decompose the precipitate before weighing.

Because filter paper absorbs moisture, we must remove it before weighing the precipitate. This is accomplished by folding the filter paper over the precipitate and transferring both the filter paper and the precipitate to a porcelain or platinum crucible. Gentle heating first dries and then chars the filter paper. Once the paper begins to char, we slowly increase the temperature until all traces of the filter paper are gone and any remaining carbon is oxidized to CO_2.

Fritted-glass crucibles can not withstand high temperatures and must be dried in an oven at temperatures below 200^oC. The glass fiber mats used in Gooch crucibles can be heated to a maximum temperature of approximately 500^oC.

Composition of the Final Precipitate

For a quantitative application, the final precipitate must have a well-defined composition. Precipitates containing volatile ions or substantial amounts of hydrated water, are usually dried at a temperature that completely removes these volatile species. For example, one standard gravimetric method for the determination of magnesium involves its precipitation as $MgNH_4PO_4{\bullet}6H_2O$. Unfortunately, this precipitate is difficult to dry at lower temperatures without losing an inconsistent amount of hydrated water and ammonia. Instead, the precipitate is dried at temperatures above 1000^oC where it decomposes to magnesium pyrophosphate, $Mg_2P_2O_7$.

An additional problem is encountered if the isolated solid is nonstoichiometric. For example, precipitating Mn^{2+} as $Mn(OH)_2$ and heating frequently produces a nonstoichiometric manganese oxide, MnO_x, where x varies between one and two. In this case the nonstoichiometric product is the result of forming of a mixture of oxides with different oxidation state of manganese. Other nonstoichiometric compounds form as a result of lattice defects in the crystal structure.

Note : The best way to appreciate the theoretical and practical details discussed in this section is to carefully examine a typical precipitation gravimetric method. Although each method is unique, the determination of Mg^{2+} in water and wastewater by precipitating $MgNH_4PO_4 \bullet 6H_2O$ and isolating $Mg_2P_2O_7$ provides an instructive example of a typical procedure. The description here is based on Method 3500-Mg D in *Standard Methods for the Examination of Water and Wastewater*, 19th Ed., American Public Health Association: Washington, D. C., 1995. With the publication of the 20th Edition in 1998, this method is no longer listed as an approved method.

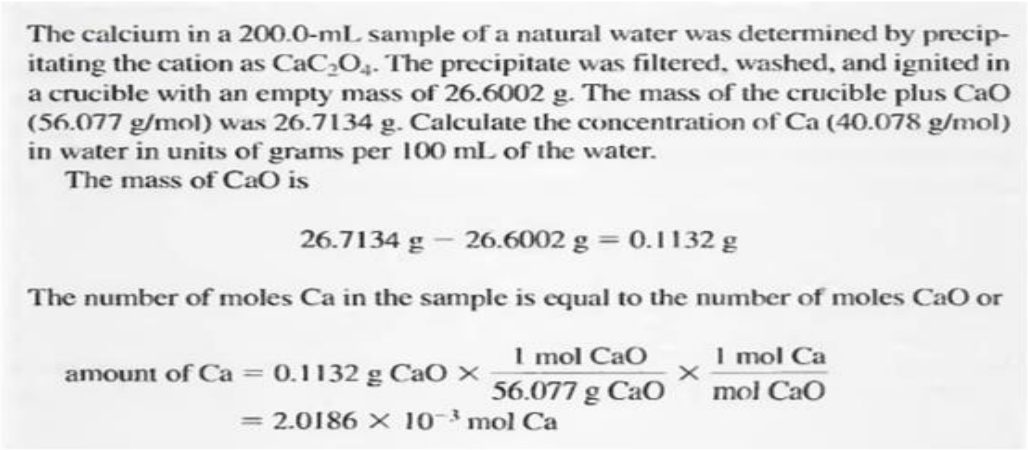
Lecture – 14

Calculation of Results From Gravimetric Data

The results of a gravimetric analysis are generally computed from two experimental measurements: the mass of sample and the mass of aproduct of known composition. The examples that follow illustrate how such computations are carried out.

∗ Tutorial: Calculating Percentage of a Compound in a Sample Using Production of a Different Compound

Example 13-1



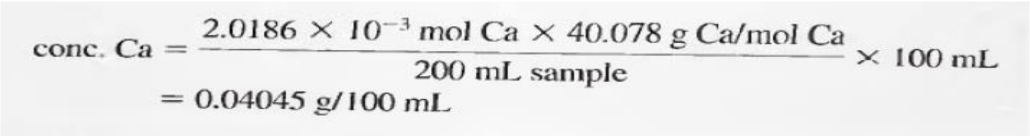
The calcium in a 200.0-mL sample of a natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26.6002 g. The mass of the crucible plus CaO (56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g/mol) in water in units of grams per 100 mL of the water.

The mass of CaO is

$$26.7134\ \text{g} - 26.6002\ \text{g} = 0.1132\ \text{g}$$

The number of moles Ca in the sample is equal to the number of moles CaO or

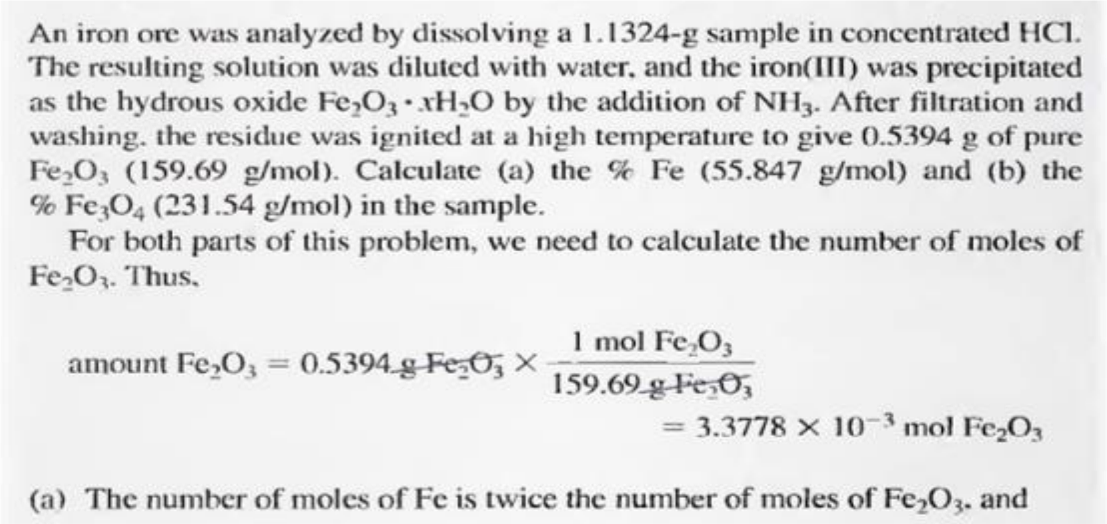
$$\begin{aligned}\text{amount of Ca} &= 0.1132\ \text{g CaO} \times \frac{1\ \text{mol CaO}}{56.077\ \text{g CaO}} \times \frac{1\ \text{mol Ca}}{\text{mol CaO}}\\ &= 2.0186 \times 10^{-3}\ \text{mol Ca}\end{aligned}$$



$$\begin{aligned}\text{conc. Ca} &= \frac{2.0186 \times 10^{-3}\ \text{mol Ca} \times 40.078\ \text{g Ca/mol Ca}}{200\ \text{mL sample}} \times 100\ \text{mL}\\ &= 0.04045\ \text{g/100 mL}\end{aligned}$$

Tutorial : Calculated Gravimetric Factors.

Example 13-2

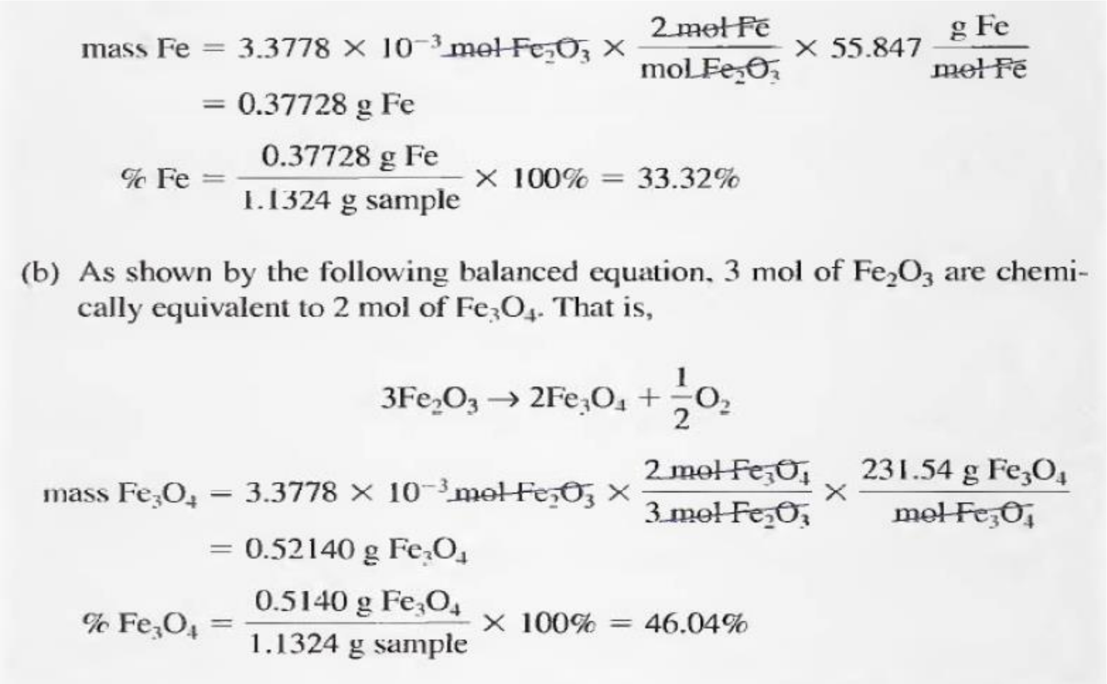


An iron ore was analyzed by dissolving a 1.1324-g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $Fe_2O_3 \cdot xH_2O$ by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g/mol). Calculate (a) the % Fe (55.847 g/mol) and (b) the % Fe_3O_4 (231.54 g/mol) in the sample.

For both parts of this problem, we need to calculate the number of moles of Fe_2O_3. Thus,

$$\text{amount } Fe_2O_3 = 0.5394\,\cancel{\text{g } Fe_2O_3} \times \frac{1 \text{ mol } Fe_2O_3}{159.69\,\cancel{\text{g } Fe_2O_3}}$$
$$= 3.3778 \times 10^{-3} \text{ mol } Fe_2O_3$$

(a) The number of moles of Fe is twice the number of moles of Fe_2O_3, and



$$\text{mass Fe} = 3.3778 \times 10^{-3}\,\cancel{\text{mol } Fe_2O_3} \times \frac{2\,\cancel{\text{mol Fe}}}{\text{mol}\,\cancel{Fe_2O_3}} \times 55.847\,\frac{\text{g Fe}}{\cancel{\text{mol Fe}}}$$
$$= 0.37728 \text{ g Fe}$$

$$\% \text{ Fe} = \frac{0.37728 \text{ g Fe}}{1.1324 \text{ g sample}} \times 100\% = 33.32\%$$

(b) As shown by the following balanced equation, 3 mol of Fe_2O_3 are chemically equivalent to 2 mol of Fe_3O_4. That is,

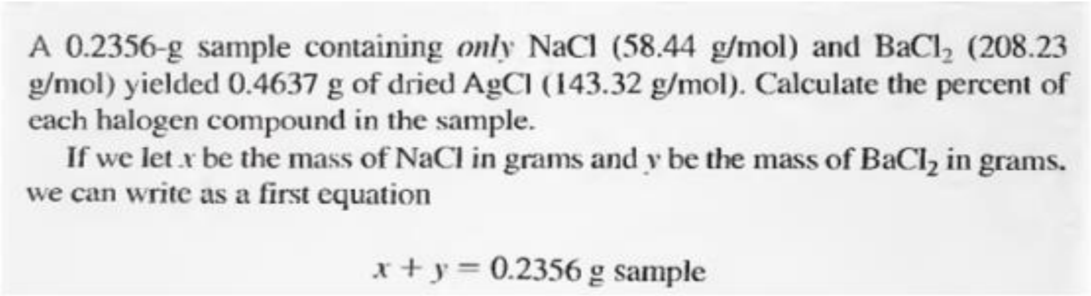
$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$$

$$\text{mass } Fe_3O_4 = 3.3778 \times 10^{-3}\,\cancel{\text{mol } Fe_2O_3} \times \frac{2\,\cancel{\text{mol } Fe_3O_4}}{3\,\cancel{\text{mol } Fe_2O_3}} \times \frac{231.54 \text{ g } Fe_3O_4}{\cancel{\text{mol } Fe_3O_4}}$$
$$= 0.52140 \text{ g } Fe_3O_4$$

$$\% \, Fe_3O_4 = \frac{0.5140 \text{ g } Fe_3O_4}{1.1324 \text{ g sample}} \times 100\% = 46.04\%$$

Tutorial: Using Gravimetric Analysis for Determining Percent in a Mixture.

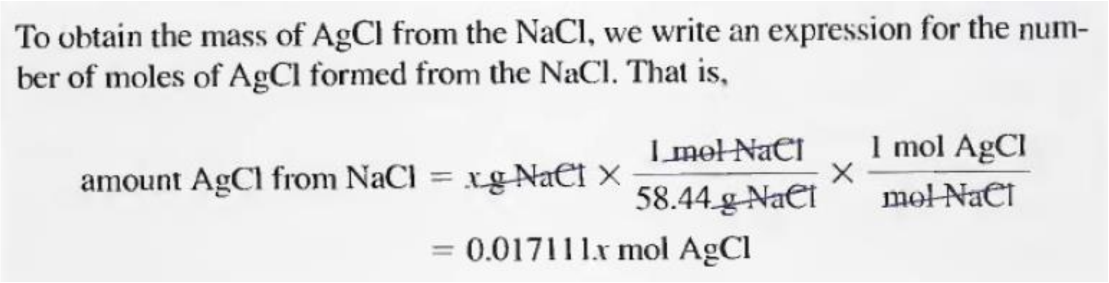
Example 13-3



A 0.2356-g sample containing *only* NaCl (58.44 g/mol) and $BaCl_2$ (208.23 g/mol) yielded 0.4637 g of dried AgCl (143.32 g/mol). Calculate the percent of each halogen compound in the sample.

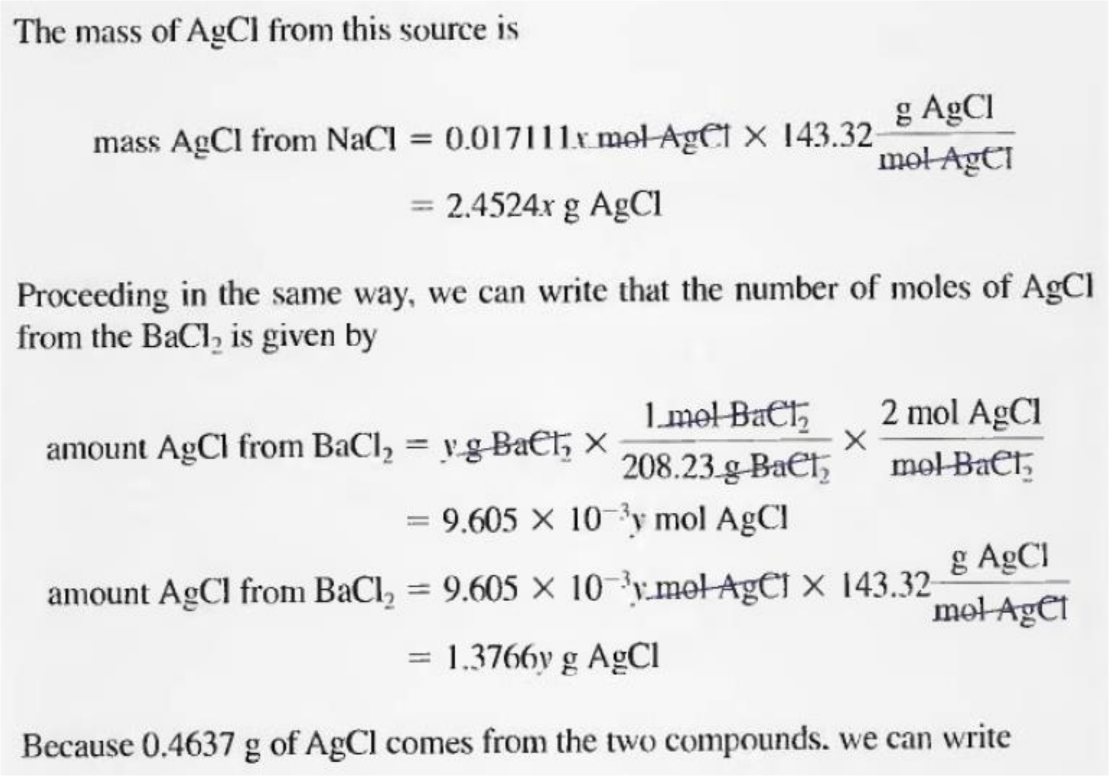
If we let x be the mass of NaCl in grams and y be the mass of $BaCl_2$ in grams, we can write as a first equation

$$x + y = 0.2356 \text{ g sample}$$



To obtain the mass of AgCl from the NaCl, we write an expression for the number of moles of AgCl formed from the NaCl. That is,

$$\text{amount AgCl from NaCl} = x\,\cancel{\text{g NaCl}} \times \frac{1\,\cancel{\text{mol NaCl}}}{58.44\,\cancel{\text{g NaCl}}} \times \frac{1\text{ mol AgCl}}{\cancel{\text{mol NaCl}}}$$
$$= 0.017111x \text{ mol AgCl}$$



The mass of AgCl from this source is

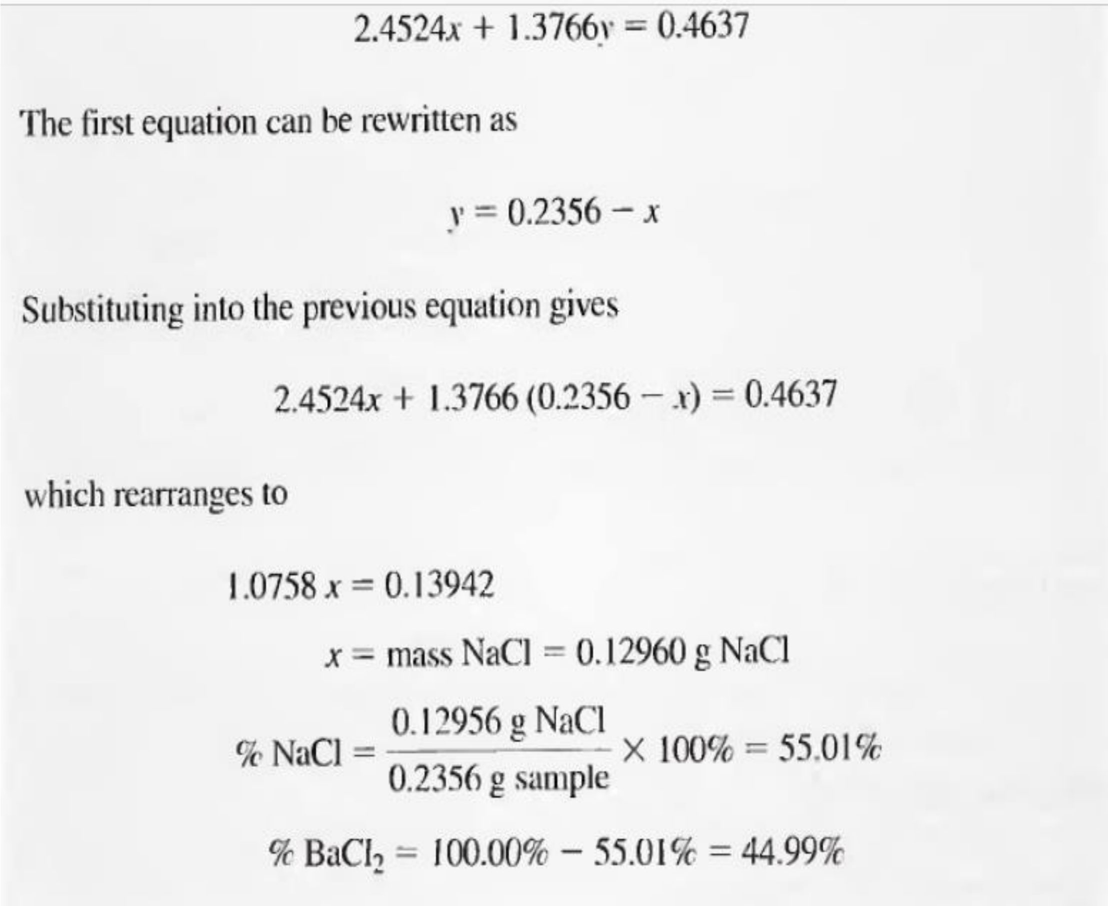
$$\text{mass AgCl from NaCl} = 0.017111x\,\cancel{\text{mol AgCl}} \times 143.32\frac{\text{g AgCl}}{\cancel{\text{mol AgCl}}}$$
$$= 2.4524x \text{ g AgCl}$$

Proceeding in the same way, we can write that the number of moles of AgCl from the $BaCl_2$ is given by

$$\text{amount AgCl from BaCl}_2 = y\,\cancel{\text{g BaCl}_2} \times \frac{1\,\cancel{\text{mol BaCl}_2}}{208.23\,\cancel{\text{g BaCl}_2}} \times \frac{2\text{ mol AgCl}}{\cancel{\text{mol BaCl}_2}}$$
$$= 9.605 \times 10^{-3}y \text{ mol AgCl}$$
$$\text{amount AgCl from BaCl}_2 = 9.605 \times 10^{-3}y\,\cancel{\text{mol AgCl}} \times 143.32\frac{\text{g AgCl}}{\cancel{\text{mol AgCl}}}$$
$$= 1.3766y \text{ g AgCl}$$

Because 0.4637 g of AgCl comes from the two compounds, we can write

(*Continued*)



$$2.4524x + 1.3766y = 0.4637$$

The first equation can be rewritten as

$$y = 0.2356 - x$$

Substituting into the previous equation gives

$$2.4524x + 1.3766\,(0.2356 - x) = 0.4637$$

which rearranges to

$$1.0758\,x = 0.13942$$

$$x = \text{mass NaCl} = 0.12960 \text{ g NaCl}$$

$$\%\ \text{NaCl} = \frac{0.12956 \text{ g NaCl}}{0.2356 \text{ g sample}} \times 100\% = 55.01\%$$

$$\%\ \text{BaCl}_2 = 100.00\% - 55.01\% = 44.99\%$$

Example 13-4

An ore containing magnetite, Fe_3O_4, was analyzed by dissolving a 1.5419-g sample in concentrated HCl, giving a mixture of Fe^{2+} and Fe^{3+}. After adding HNO_3 to oxidize any Fe^{2+} to Fe^{3+}, the resulting solution was diluted with water and the Fe^{3+} precipitated as $Fe(OH)_3$ by adding NH_3. After filtering and rinsing, the residue was ignited, giving 0.8525 g of pure Fe_2O_3. Calculate the %w/w Fe_3O_4 in the sample.

SOLUTION

This is an example of a direct analysis since the iron in the analyte, Fe_3O_4, is part of the isolated precipitate, Fe_2O_3. Applying a conservation of mass to Fe, we write

$$3 \times \text{moles } Fe_3O_4 = 2 \times \text{moles } Fe_2O_3$$

Using formula weights, FW, to convert from moles to grams in the preceding equation leaves us with

$$\frac{3 \times \text{g } Fe_3O_4}{\text{FW } Fe_3O_4} = \frac{2 \times \text{g } Fe_2O_3}{\text{FW } Fe_2O_3}$$

which can be solved for grams of Fe_3O_4 and %w/w Fe_3O_4 in the sample.

$$\frac{2 \times \text{g Fe}_2\text{O}_3 \times \text{FW Fe}_3\text{O}_4}{3 \times \text{FW Fe}_2\text{O}_3} = \frac{2 \times 0.8525 \text{ g} \times 231.54 \text{ g/mol}}{3 \times 159.69 \text{ g/mol}} = 0.82405 \text{ g Fe}_3\text{O}_4$$

$$\frac{\text{g Fe}_3\text{O}_4}{\text{g sample}} \times 100 = \frac{0.82405 \text{ g}}{1.5419 \text{ g}} \times 100 = 53.44\% \text{ w/w Fe}$$

Example 13-5

A 0.6113-g sample of Dow metal, containing aluminum, magnesium, and other metals, was dissolved and treated to prevent interferences by the other metals. The aluminum and magnesium were precipitated with 8-hydroxyquinoline. After filtering and drying, the mixture of $Al(C_9H_6NO)_3$ and $Mg(C_9H_6NO)_2$ was found to weigh 7.8154 g.The mixture of dried precipitates was then ignited, converting the precipitate to a mixture of Al_2O_3 and MgO. The weight of this mixed solid was found to be 1.0022 g. Calculate the %w/w Al and %w/w Mg in the alloy.

SOLUTION:

This is an example of a direct analysis in which the two analytes are determined without a prior separation. The weight of the original precipitate and the ignited precipitate are given by the following two equations ;

$$\text{g } Al(C_9H_6NO)_3 + \text{g } Mg(C_9H_6NO)_2 = 7.8154$$

$$\text{g } Al_2O_3 + \text{g } MgO = 1.0022$$

containing four unknown terms. To solve this pair of equations, we must find two additional equations relating the four unknowns to one another. These additional equations describe the stoichiometric relationships between the two compounds containing aluminum and the two compounds containing magnesium and are based on the conservation of Al and Mg. Thus, for Al we have

$$2 \times \text{moles } Al_2O_3 = \text{moles } Al(C_9H_6NO)_3$$

Converting from moles to grams and solving yields an equation relating the grams of Al_2O_3 to the grams of $Al(C_9H_6NO)_3$

(Continued)

$$\frac{2 \times \text{g Al}_2\text{O}_3}{\text{FW Al}_2\text{O}_3} = \frac{\text{g Al(C}_9\text{H}_6\text{NO)}_3}{\text{FW Al(C}_9\text{H}_6\text{NO)}_3}$$

$$\text{g Al}_2\text{O}_3 = \frac{\text{g Al(C}_9\text{H}_6\text{NO)}_3 \times \text{FW Al}_2\text{O}_3}{2 \times \text{FW Al(C}_9\text{H}_6\text{NO)}_3} = \frac{\text{g Al(C}_9\text{H}_6\text{NO)}_3 \times 101.96\ \text{g/mol}}{2 \times 459.45\ \text{g/mol}}$$

$$= 0.11096 \times \text{g Al(C}_9\text{H}_6\text{NO)}_3$$

For Mg we have

$$\text{Moles MgO} = \text{moles Mg(C}_9\text{H}_6\text{NO)}_2$$

$$\frac{\text{g MgO}}{\text{FW MgO}} = \frac{\text{g Mg(C}_9\text{H}_6\text{NO)}_2}{\text{FW Mg(C}_9\text{H}_6\text{NO)}_2}$$

$$\text{g MgO} = \frac{\text{g Mg(C}_9\text{H}_6\text{NO)}_2 \times \text{FW MgO}}{\text{FW Mg(C}_9\text{H}_6\text{NO)}_2} = \frac{\text{g Mg(C}_9\text{H}_6\text{NO)}_2 \times 40.304\ \text{g/mol}}{312.61\ \text{g/mol}}$$

$$= 0.12893 \times \text{g Mg(C}_9\text{H}_6\text{NO)}_2$$

Substituting the equations for g MgO and g Al_2O_3 into the equation for the combined weights of MgO and Al_2O_3 leaves us with two equations and two **unknowns.**

$$\text{g Al(C}_9\text{H}_6\text{NO)}_3 + \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 7.8154$$

$$0.11096 \times \text{g Al(C}_9\text{H}_6\text{NO)}_3 + 0.12893 \times \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 1.0022$$

Multiplying the first equation by 0.11096 and subtracting the second equation Gives

$$-0.01797 \times \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = -0.1350$$

which can be solved for the mass of $Mg(C_9H_6NO)_2$.

$$\text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 7.5125\ \text{g}$$

The mass of $Al(C_9H_6NO)_3$ can then be calculated using the known combined mass of the two original precipitates.

$$7.8154\ \text{g} - \text{g Mg(C}_9\text{H}_6\text{NO)}_2 = 7.8154\ \text{g} - 7.5125\ \text{g} = 0.3029\ \text{g Al(C}_9\text{H}_6\text{NO)}_3$$

Using the conservation of Mg and Al, the % w/w Mg and % w/w Al in the sample can now be determined as in Example 5, where AW is an atomic weight

(***Continued***)

$$\text{Moles Mg} = \text{moles Mg}(C_9H_6NO)_2$$

$$\frac{\text{g Mg}}{\text{AW Mg}} = \frac{\text{g Mg}(C_9H_6NO)_2}{\text{FW Mg}(C_9H_6NO)_2}$$

$$\text{g Mg} = \frac{\text{g Mg}(C_9H_6NO)_2 \times \text{AW Mg}}{\text{FW Mg}(C_9H_6NO)_2}$$

$$= \frac{7.5125 \text{ g} \times 24.305 \text{ g/mol}}{312.61 \text{ g/mol}}$$

$$= 0.5841 \text{ g}$$

$$\%\text{Mg} = \frac{\text{g Mg}}{\text{g sample}} \times 100$$

$$\frac{0.5841 \text{ g}}{0.6113 \text{ g}} \times 100 = 95.55\% \text{ w/w Mg}$$

$$\text{Moles Al} = \text{moles Al}(C_9H_6NO)_3$$

$$\frac{\text{g Al}}{\text{AW Al}} = \frac{\text{g Al}(C_9H_6NO)_3}{\text{FW Al}(C_9H_6NO)_3}$$

$$\text{g Al} = \frac{\text{g Al}(C_9H_6NO)_3 \times \text{AW Al}}{\text{FW Al}(C_9H_6NO)_3}$$

$$= \frac{0.3029 \text{ g} \times 26.982 \text{ g/mol}}{459.45 \text{ g/mol}}$$

$$= 0.0178 \text{ g}$$

$$\%\text{Al} = \frac{\text{g Al}}{\text{g sample}} \times 100$$

$$\frac{0.0178 \text{ g}}{0.6113 \text{ g}} \times 100 = 2.91\% \text{ w/w Al}$$

Lecture – 15

Volatilization Gravimetry

A second approach to gravimetry is to thermally or chemically decompose a solid sample. The volatile products of the decomposition reaction may be trapped and weighed to provide quantitative information. Alternatively, the residue remaining when decomposition is complete may be weighed. In thermogravimetry, which is one form of volatilization gravimetry, the sample's mass is continuously monitored while the applied temperature is slowly increased.

Theory and Practice

Whether the analysis is direct or indirect, volatilization gravimetry requires that the products of the decomposition reaction be known. This requirement is rarely a problem for organic compounds for which volatilization is usually accomplished by combustion and the products are gases such as CO_2, H_2O, and N_2. For inorganic compounds, however, the identity of the volatilization products may depend on the temperature at which the decomposition is conducted.

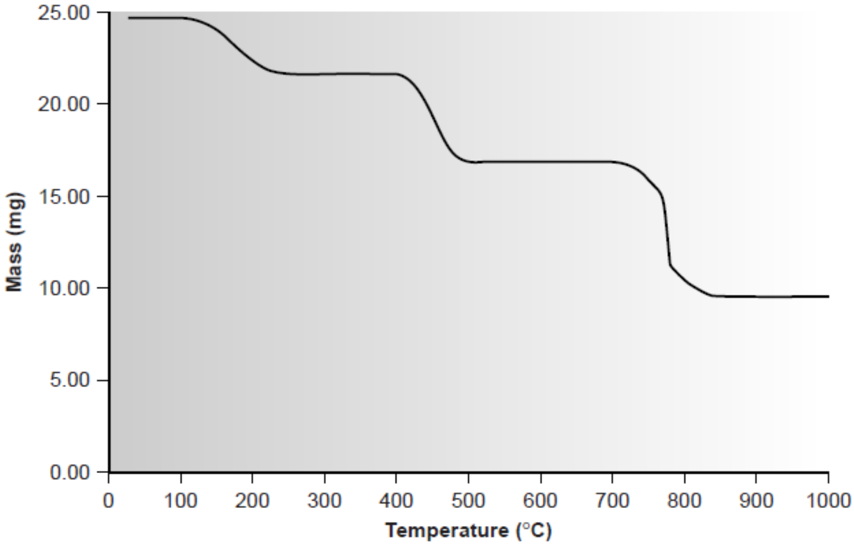


Figure.15.1 Thermogram for $CaC_2O_4.H_2O$

Thermogravimetry: The products of a thermal decomposition can be deduced by monitoring the sample's mass as a function of applied temperature. (Figure 15.1). The loss of a volatile gas on thermal decomposition is indicated by a step in the **thermogram**. As shown in Example 15.1, the change in mass at each step in a thermogram can be used to identify both the volatilized species and the solid residue.

EXAMPLE 15.1

The thermogram in Figure 15.1 shows the change in mass for a sample of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$. The original sample weighed 24.60 mg and was heated from room temperature to 1000 °C at a rate of 5 °C min. The following changes in mass and corresponding temperature ranges were observed:

Loss of 3.03 mg from 100–250 °C
Loss of 4.72 mg from 400–500 °C
Loss of 7.41 mg from 700–850 °C

Determine the identities of the volatilization products and the solid residue at each step of the thermal decomposition.

SOLUTION:

The loss of 3.03 mg from 100–250 °C corresponds to a 12.32% decrease in the original sample's mass.

$$\frac{3.03\text{ mg}}{24.60\text{ mg}} \times 100 = 12.32\%$$

In terms of $CaC_2O_4 \cdot H_2O$, this corresponds to a loss of 18.00 g/mol.

$0.1232 \times 146.11\text{ g/mol} = 18.00\text{ g/mol}$

The product's molar mass, coupled with the temperature range, suggests that this represents the loss of H_2O. The residue is CaC_2O_4.
The loss of 4.72 mg from 400–500 °C represents a 19.19% decrease in the original mass of 24.60 g, or a loss of

$0.1919 \times 146.11\text{ g/mol} = 28.04\text{ g/mol}$

This loss is consistent with CO as the volatile product, leaving a residue of $CaCO_3$.
Finally, the loss of 7.41 mg from 700–850 °C is a 30.12% decrease in the original mass of 24.60 g. This is equivalent to a loss of

$0.3012 \times 146.11\text{ g/mol} = 44.01\text{ g/mol}$

suggesting the loss of CO_2. The final residue is CaO.

Once the products of thermal decomposition have been determined, an analytical procedure can be developed. For example, the thermogram in Figure 15.1 shows that a precipitate of $CaC_2O_4 \cdot H_2O$ must be heated at temperatures above 250 °C, but below 400 °C if it is to be isolated as CaC_2O_4. Alternatively, by heating the sample to 1000 °C, the precipitate can be isolated as CaO. Knowing the identity of the volatilization products also makes it possible to design an analytical method in which one or more of the gases are trapped. Thus, a sample of $CaC_2O_4 \cdot H_2O$ could be analyzed by heating to 1000 °C and passing the volatilized gases through a trap that selectively retains H_2O, CO, or CO_2.

Practice Exercise

Under the same conditions as Figure 8.9, the thermogram for a 22.16 mg sample of $MgC_2O_4•H_2O$ shows two steps: a loss of 3.06 mg from 100–250°C and a loss of 12.24 mg from 350–550°C. For each step, identify the volatilization product and the solid residue that remains.

Solution

From 100–250°C the sample loses 13.8% of its mass, or a loss of

$$0.138 \times 130.35 \text{g/mol} = 18.0 \text{g/mol}$$

consistent with the loss of H_2O(*g*), leaving a residue of MgC_2O_4. From 350–550°C the sample loses 55.23% of its original mass, or a loss of

$$0.5523 \times 130.35 \text{g/mol} = 71.99 \text{g/mol}$$

This weight loss is consistent with the simultaneous loss of CO(*g*) and CO_2(*g*), leaving a residue of MgO.

References:

- Modern of Analytical Chemistry by David Harvey (DePauw University)