



**Benha University
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Chemistry Department**

Physical chemistry

(CHE125)

المستوى الأول – شعبة رياضيات باللغة الإنجليزية

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content	page
Chapter 1: solutions	3
1.1 Nature of Solutions	3
1.2 The Solution Process	4
1.3 Hydrated Ions	6
1.5 Effect of Temperature and Pressure on Solubility	8
1.6 Concentrations of Solutions	10
1.7 Vapor Pressure of Solutions	15
1.8 Boiling Point and Freezing Point of Solutions	18
1.9 osmosis	21
CHAPTER 2: CHEMICAL EQUILIBRIUM	29
2.3 Equilibrium Constants	32
2.4. Le Chatelier's Principle	38
Chapter 3: Ionic Equilibrium	42
3.1 Weak Electrolytes	43
3.2. The Ionization of Water	46
3.3. pH	48
3.4 Indicators	51
3.5 The Common-Ion Effect	53
3.6 Buffers	54
3.7 Polyprotic Acids	60
3.8 Ions That Function as Acids and Bases	65
3.9 Acid-Base Titrations	70
Chapter 4 : Solubility product	76

CHAPTER1: SOLUTIONS

Solutions are homogeneous mixtures. They are usually classified according to their physical state; gaseous, liquid, and solid solutions can be prepared. Dalton's law of partial pressures describes the behavior of gaseous solutions, of which air is the most common example. Certain alloys are solid solutions; coinage silver is copper dissolved in silver, and brass is a solid solution of zinc in copper. Not all alloys are solid solutions, however. Some are heterogeneous mixtures, and some are intermetallic compounds. Liquid solutions are the most common and are probably the most important to the chemist.

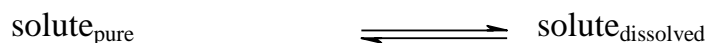
1.1 Nature of Solutions

The component of a solution that is present in greatest quantity is usually called the solvent, and all other components are called solutes.

Certain pairs of substances will dissolve in each other in all proportions. Complete miscibility is characteristic of the components of all gaseous solutions and some pairs of components of liquid and solid solutions. For most materials, however, there is a limit on the amount of the substance that will dissolve in a given solvent. The solubility of a substance in a particular solvent at a specified temperature is the maximum amount of the solute that will dissolve in a definite amount of the solvent and produce a stable system.

For a given solution, the amount of solute dissolved in an amount of solvent given is the concentration of the solute. Solutions containing a relatively low concentration of solute are called dilute solutions; those of relatively high concentrations are called concentrated solutions.

If an excess of solute (more than will normally dissolve) is added to a quantity of a liquid solvent, an equilibrium is established between the pure solute and the dissolved solute:



The pure solute may be a solid, liquid, or gas. At equilibrium in such a system, the rate at which the pure solute dissolves equals the rate at which the dissolved solute comes out of solution. The concentration of the dissolved solute, therefore, is a constant. A solution of this type is called a saturated solution, and its concentration is the solubility of the solute in question.

That such dynamic equilibria exist has been shown experimentally. If small crystals of a solid solute are placed in contact with a saturated solution of the solute, the crystals are observed to change in size and shape. Throughout this experiment, however, the concentration of the saturated solution does not change, nor does the quantity of excess solute decrease or increase.

An **unsaturated solution** has a lower concentration of solute than a saturated solution. On the other hand, it is sometimes possible to prepare a supersaturated solution, one in which the concentration of solute is higher than that of a saturated solution. A supersaturated solution, however, is metastable, and if a very small amount of pure solute is added to it, the solute that is in excess of that needed to saturate the solution will precipitate.

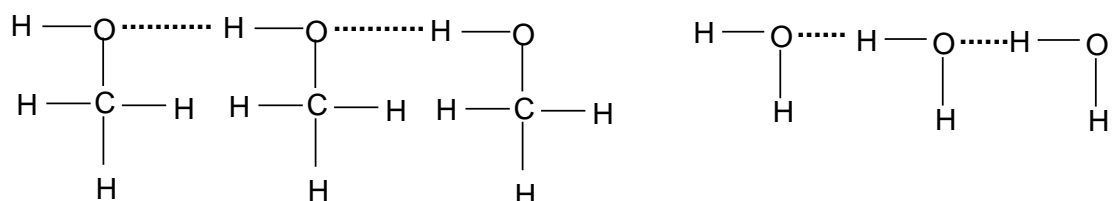
1.2 The Solution Process

London forces are the only intermolecular forces between nonpolar covalent molecules. On the other hand, the intermolecular attractions between polar covalent molecules are due to dipole-dipole forces as well as to London forces. In substances in which there is hydrogen bonding the intermolecular forces are unusually strong.

Nonpolar substances and polar substances are generally insoluble in one another. Carbon tetrachloride (a nonpolar substance) is insoluble in water (a polar substance). The attraction of one water molecule for another water molecule is much greater than an attraction between a carbon tetrachloride molecule and a water molecule. Hence, carbon tetrachloride molecules are "squeezed out," and these two substances form a two-liquid-layer system.

Iodine, a nonpolar material, is soluble in carbon tetrachloride. The attractions between I_2 molecules in solid iodine are approximately of the same type and magnitude as those between CCl_4 molecules in pure carbon tetrachloride. Hence, significant iodine-carbon tetrachloride attractions are possible, and iodine molecules can mix with carbon tetrachloride molecules.

Methyl alcohol, CH_3OH , like water, consists of polar molecules that are highly associated. In both pure liquids the molecules are attracted to one another through hydrogen bonding:



Methyl alcohol and water are miscible in all proportions. In solutions of methyl alcohol in water, CH_3OH and H_2O molecules are associated through hydrogen bonding:

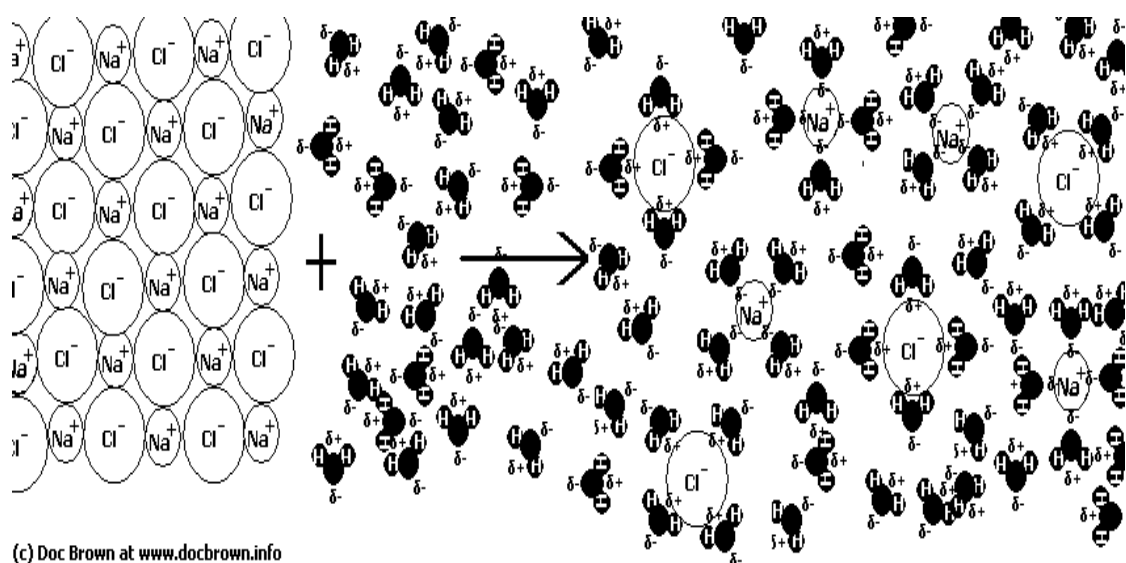
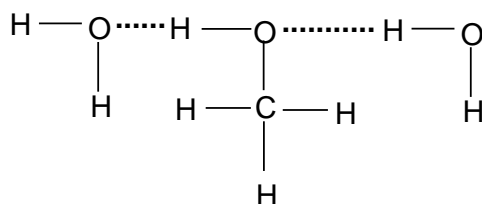


Figure 1.1 Solution of an ionic crystal in water

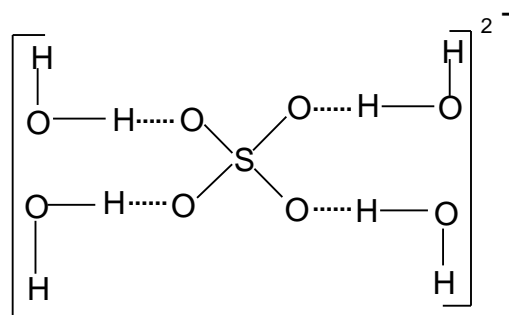
In general, polar materials dissolve only in polar solvents, and nonpolar substances are soluble in nonpolar solvents. This is the first rule of solubility: "like dissolves like."

Polar liquids (water, in particular) can function as solvents for many ionic compounds. The ions of the solute are electrostatically attracted by the polar solvent molecules—negative ions by the positive poles of the solvent molecules, positive ions by the negative poles of the solvent molecules. These ion-dipole attractions can be relatively strong.

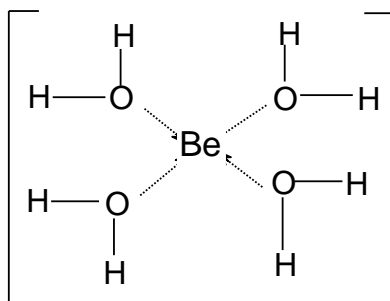
Figure 1 diagrams the solution of an ionic crystal in water. The ions in the center of the crystal are attracted equally in all directions by the oppositely charged ions of the crystal. The electrostatic attractions on the ions of the surface of the crystal, however, are unbalanced. Water molecules are attracted to these surface ions, the positive ends of the water molecules to the anions and the negative ends of the water molecules to the cations. The ion-dipole attractions formed in this way allow the ions to escape from the crystal and drift into the liquid phase. The dissolved ions are hydrated and move through the solution surrounded by a sheath of water molecules. All ions are hydrated in water solution.

1.3 Hydrated Ions

Negative ions are hydrated in water solution by means of attractions between the ion and the hydrogen atoms of the water molecule. In some cases (the sulfate ion, for example) these attractions may be one or more hydrogen bonds:



Positive ions are hydrated by means of attractions between the ion and the unshared electron pairs of the oxygen atom of the water molecule. These attractions are strong. In many cases, each cation is hydrated by a definite number of H₂O molecules:



What factors lead to the formation of strong interactions between the ion and water molecules?

1. Ions with *high charges* strongly attract the H or O atoms of the H₂O molecule.
2. *Small ions* are more effective than large ones because the charge is more highly concentrated in small ions.

The formation of a bond always liberates energy, and the breaking of a bond always requires energy. The energy *released* by a hypothetical process in which hydrated ions are formed from gaseous ions is called the enthalpy of hydration of the ions. For example,



The value of an enthalpy of hydration gives an indication of the strength of the attractions between the ions and the water molecules that hydrate them. A large negative value (which indicates a large quantity of energy evolved) shows that the ions are strongly hydrated.

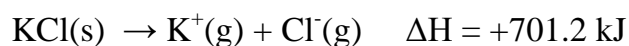
1.4 Enthalpy of Solution

The enthalpy change associated with the process in which a solute dissolves in a solvent is called the enthalpy of solution. The value of an enthalpy of solution (given in kJ/mol of solute) depends upon the concentration

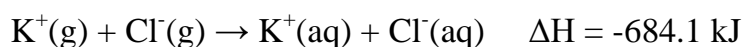
of the final solution in the same way that an enthalpy of hydration does. Unless otherwise noted, an enthalpy of solution is considered to apply to the preparation of a solution that is infinitely dilute. The enthalpy of solution is virtually constant for all the dilute solutions of a given solute-solvent pair.

The enthalpy change observed when a solution is prepared is the net result of the energy *required* to break apart certain chemical bonds or attractions (solute-solute and solvent-solvent) and the energy *released* by the formation of new ones (solute-solvent). The enthalpy of solution for the preparation of a solution of KCl in water, for example, can be considered to be the sum of two enthalpy changes:

1. The energy required to break apart the KCl crystal lattice and form gaseous ions:



2. The *enthalpy of hydration* of KCl, which is the energy released when the gaseous ions are hydrated:

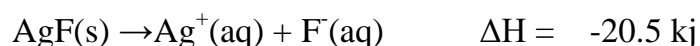
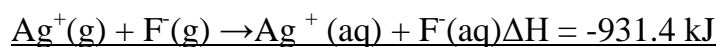


This enthalpy change is actually the sum of two enthalpy changes: the energy required to break the hydrogen bonds between some of the water molecules and the energy released when these water molecules hydrate the ions. It is, however, difficult to investigate these two effects separately.

In this example, the overall process is endothermic. The enthalpy of solution is positive because more energy is required in step I than is released in step 2:



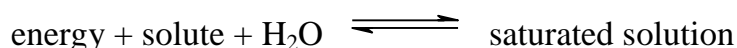
Some enthalpies of solution are negative because more energy is liberated by the hydration of the ions of the solute than is required to break apart the crystal lattice:



Gases generally dissolve in liquids with the evolution of heat. Since no energy is required to separate the molecules of a gas, the predominant enthalpy change of such a solution process is the solvation of the gas molecules; the process, therefore, is exothermic.

1. 5 Effect of Temperature and Pressure on Solubility

The effect of a temperature change on the solubility of a substance depends upon whether heat is absorbed or evolved *when a saturated solution is prepared*. Suppose that a small quantity of solute dissolves in a nearly saturated solution with the absorption of heat. We can represent the equilibrium between excess solid solute and the saturated solution as



The effect of a temperature change on this system can be predicted by means of a principle proposed by Henri Le Chatelier in 1884. Le Chatelier's principle states that a system in equilibrium reacts to a stress in a way that counteracts the stress and establishes a new equilibrium state.

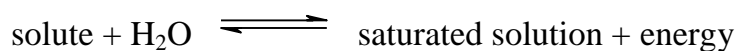
Suppose that we have a beaker containing a saturated solution of the type previously described together with some excess solid solute in equilibrium with it. What will be the effect if we raise the temperature? According to Le Chatelier's principle, the system will react in a way that lowers the temperature. We conclude that increasing the temperature increases the solubility of this particular solute.

What will happen if we lower the temperature? Le Chatelier's principle predicts that the system will react in a way that raises the temperature a way that liberates energy.

The solubilities of substances that *absorb heat* when they dissolve in nearly saturated solutions *increase* with *increasing temperature*. Most ionic solutes behave in this way.

The enthalpy of solution of many ionic compounds for solutions that are *infinitely dilute* are *exothermic*.

When a substance dissolves in a nearly saturated solution with the evolution of heat,



Le Chatelier's principle indicates that the solubility of the solute increases when the temperature is lowered, and the solubility decreases when the temperature is raised. In addition, the solubility of all gases decreases as the temperature is raised. Warming a soft drink causes bubbles of carbon dioxide gas to come out of solution.

Changes in pressure ordinarily have little effect upon the solubility of solid and liquid solutes. However, increasing or decreasing the pressure on a solution that contains a dissolved gas has a definite effect. William Henry in 1803 discovered that the amount of a gas that dissolves in a given quantity of a liquid at constant temperature is directly proportional to the partial pressure of the gas above the solution. Henry's law is valid only for dilute solutions and relatively low pressures. Gases that are extremely soluble generally react chemically with the solvent (for example, hydrogen chloride gas in water reacts to produce hydrochloric acid); these solutions do not follow Henry's law.

1.6 Concentrations of Solutions

The concentration of a solute in a solution can be expressed in several different ways.

- 1. The percentage by mass of a solute** in a solution is 100 times the mass of the solute divided by the *total mass* of the solution. A 10% aqueous solution of sodium chloride contains 10 g of NaCl and 90 g of H₂O.
- 2. The mole fraction, X ,** of a component of a solution is the ratio of the number of moles of that component to the *total number* of moles of all the substances present in the solution:

$$X_A = \frac{n_A}{n_A + n_B + n_C + \dots} \quad (1.1)$$

where X_A is the mole fraction of A and n_A, n_B, n_C, \dots , are the number of moles of A, B, C, The sum of the mole fractions of all the components present in the solution must equal one.

Example 1.1

A gaseous solution contains 2.00 g of He and 4.00 g of O₂. What are the mole fractions of He and O₂ in the solution?

Solution

We first find the number of moles of each component present in the solution:

$$? \text{ mol He} = 2.00 \text{ g He} \left(\frac{1 \text{ mol He}}{4.00 \text{ g He}} \right) = 0.500 \text{ mol He}$$

$$? \text{ mol O}_2 = 4.00 \text{ g O}_2 \left(\frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \right) = 0.125 \text{ mol O}_2$$

We use these values to find the mole fractions:

$$X_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{He}} + n_{\text{O}_2}} = \frac{0.500 \text{ mol}}{0.500 \text{ mol} + 0.125 \text{ mol}} = \frac{0.500 \text{ mol}}{0.625 \text{ mol}} = 0.800$$

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{He}} + n_{\text{O}_2}} = \frac{0.125 \text{ mol}}{0.625 \text{ mol}} = 0.200$$

Notice that the sum of the mole fraction is equal to one.

3. The molarity, M , of a solution is the number of moles of solute per liter of *solution* (see Section 2.9). Thus, 1 liter of a 6 M solution of sodium chloride is prepared by taking 6 mol of NaCl and adding sufficient water to make exactly 1 liter of solution.



Figure 1.2 Volumetric flask

Notice that the definition is based on the *total volume of the solution*. When a liquid solution is prepared, the volume of the solution rarely equals the sum of the volumes of the pure components. Molar solutions are generally prepared by the use of the volumetric flasks (Figure 1.2).

It is a simple matter to calculate the quantity of solute present in a given volume of a solution when the concentration of the solution is expressed in terms of molarity.

Example 1.2

- (a) How many grams of concentrated nitric acid solution should be used to prepare 250 ml of 2.00 M HNO₃? The concentrated acid is 70.0% HNO₃.
- (b) If the density of the concentrated nitric acid solution is 42 g/ml, what volume should be used?

Solution

- (a) The factors used to solve the problem are derived from the following facts (in order):

1. Since the desired solution is 2.00 M, there must be 2.00 mol HNO₃ in 1000 ml.
2. The molecular weight of HNO₃ is 63.0.
3. In 100.0 g of concentrated nitric acid (70.0% HNO₃) there are 70.0 g of HNO₃:

? g conc HNO₃ = 250 ml sol'n

$$= \left(\frac{2 \text{ mol HNO}_3}{1000 \text{ ml sol'n}} \right) \left(\frac{63.0 \text{ g HNO}_3}{1 \text{ mol HNO}_3} \right) \left(\frac{1000 \text{ g conc HNO}_3}{70.0 \text{ g HNO}_3} \right) = 45.0 \text{ g conc HNO}_3$$

- (b) The density of the concentrated acid is used to convert the answer to part (a) into ml of concentrated HNO₃:

$$? \text{ ml conc HNO}_3 = 45.0 \text{ g conc HNO}_3 \left(\frac{1000 \text{ ml conc HNO}_3}{1.42 \text{ g conc HNO}_3} \right)$$

Example 1.3

What is the molarity of concentrated HCl if the solution contains 37.0% HCl by mass and if the density of the solution is 1.18 g/ml ?

Solution

In order to find the molarity of the solution, we must determine the number of moles of HCl in 1 liter of solution. The problem can be solved by using factors derived in the following way :

1. The mass of 1 liter of the solution is found by means of the density.
2. The mass of pure HCl in this quantity of solution is obtained by use of the percent composition.
3. The molecular weight of HCl (36.5) is used to convert the mass of HCl into moles of HCl:

$$\begin{aligned} ? \text{ mol HCl} &= 1000 \text{ ml sol'n} \left(\frac{1.18 \text{ g sol'n}}{1 \text{ ml sol'n}} \right) \left(\frac{37.0 \text{ g HCl}}{100.0 \text{ g sol'n}} \right) \left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) \\ &= 12.0 \text{ mol HCl} \end{aligned}$$

Since 1 liter of the solution contains 12.0 mol HCl, the solution is 12.0 M.

The number of moles of solute in a sample of a solution may be obtained by multiplying the volume of the solution (V_1 in liters) by the molarity of the solution (M_1 ; the number of moles of solute in 1 liter):

$$\text{number of moles of solute} = V_1 M_1$$

When the solution is diluted to a new volume, V_2 , *it still contains the same number of moles of solute*. The concentration has decreased to M_2 but the product $V_2 M_2$ equals the same number of moles. Therefore,

$$V_1 M_1 = V_2 M_2 \quad (1.2)$$

Since a volume term is found on both sides of this equation, any volume unit can be used to express V_1 and V_2 provided the same unit is used for each. Note that this equation is used for dilution problems only.

Example 1.4

What volume of concentrated HCl should be used to prepare 500 ml of a 3.00 M HCl solution?

Solution

From Table 1.1 (as well as from Example 10.3) we note that concentrated HCl is 12.0 M:

$$V_1 M_1 = V_2 M_2$$

$$V_1(12.0 M) = (500 \text{ ml})(3.00 M)$$

$$V_1 = 125 \text{ ml}$$

4. The molality of a solution, m , is defined as the number of moles of solute dissolved in 1 kg of *solvent*. A 1 m solution of urea, $\text{CO}(\text{NH}_2)_2$, is made by dissolving 1 mol of urea (60.06 g) in 1000 g of water. Notice that the definition is *not* based on the total volume of solution. The final volume of a molal solution is of no importance. One molal solutions of different solutes, each containing 1000g of water, will have different volumes. All these solutions, however, will have the same mole fractions of solute and solvent (see Example 10.5).

Example 1.5

What are the mole fractions of solute and solvent in a 1.00 m aqueous solution?

Solution

The molecular weight of H_2O is 18.0. We find the number of moles of water in 1000g of H_2O :

$$? \text{ mol } \text{H}_2\text{O} = 1000 \text{ g } \text{H}_2\text{O} \left(\frac{1 \text{ mol } \text{H}_2\text{O}}{18.0 \text{ g } \text{H}_2\text{O}} \right) = 55.6 \text{ mol } \text{H}_2\text{O}$$

A 1.00 m aqueous solution contains

$$n_{\text{solute}} = 1.0 \text{ mol}$$

$$\frac{n_{\text{H}_2\text{O}} = 55.6 \text{ mol}}{n_{\text{total}} = 55.6 \text{ mol}}$$

The mole fractions are

$$X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{total}}} = \frac{1.0 \text{ mol}}{55.6 \text{ mol}} = 0.018$$

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{total}}} = \frac{55.6 \text{ mol}}{55.6 \text{ mol}} = 0.982$$

These mole fractions pertain to all 1.00 m aqueous solutions.

The molality of a given solution does not vary with temperature since the solution is prepared on the basis of the masses of the components; mass does not vary with temperature changes. The molality of a very dilute aqueous solution is approximately the same as the molarity of the solution since 1000 g of water occupies approximately 1000ml.

5. The normality of a solution, N , is the number of *equivalent weights* per liter of solution. Normal concentrations, like molar concentrations, are based on the *total volume* of solution. Consequently, volumetric flasks are used in the preparation of normal solutions, and the normality of a solution, like the molarity, varies slightly with temperature.

1:7 Vapor Pressure of Solutions

The vapor pressure of any solution (P_{total}) is the sum of the partial pressures of the components of the solution (p_A, p_B, \dots). For a solution of two components, A and B,

$$P_{\text{total}} = P_A + P_B \quad (1.3)$$

The partial pressures in this equation are given by a relationship known as **Raoult's law**, which describes what is called an **ideal solution**. The partial pressure of A, p_A , for example, is given by the equation

$$P_A = X_A P_A^\circ \quad (1.4)$$

where X_A is the mole fraction of A in the solution and P_A° is the vapor pressure of *pure* A at the temperature of the experiment.

Suppose that we prepare a solution from 4 mol of A and 1 mol of B. Since the total number of moles in the solution is 5, the mole fraction of A is 4/5. The partial pressure of A, therefore, is 4/5 the vapor pressure of pure A.

The partial pressure of B can be found by use of a similar equation:

$$P_B = X_B P_B^\circ \quad (1.5)$$

where Y_B is the mole fraction of B in the solution and P_B° is the vapor pressure of *pure* B at the temperature of the experiment. In our hypothetical solution, the

mole fraction of B is 1/5. The partial pressure of B, therefore, is 1/5 the vapor pressure of pure B.

The vapor pressure of the solution is equal to the sum of the two partial pressures, according to Equation 10.3:

$$P_{\text{total}} = X_A P_A^\circ + X_B P_B^\circ \quad (1.6)$$

In Figure 1.3, the partial pressures of A and B as well as the total vapor pressure of solutions of A and B are plotted against solution concentration. The total vapor pressure curve is the sum of the two partial pressure curves.

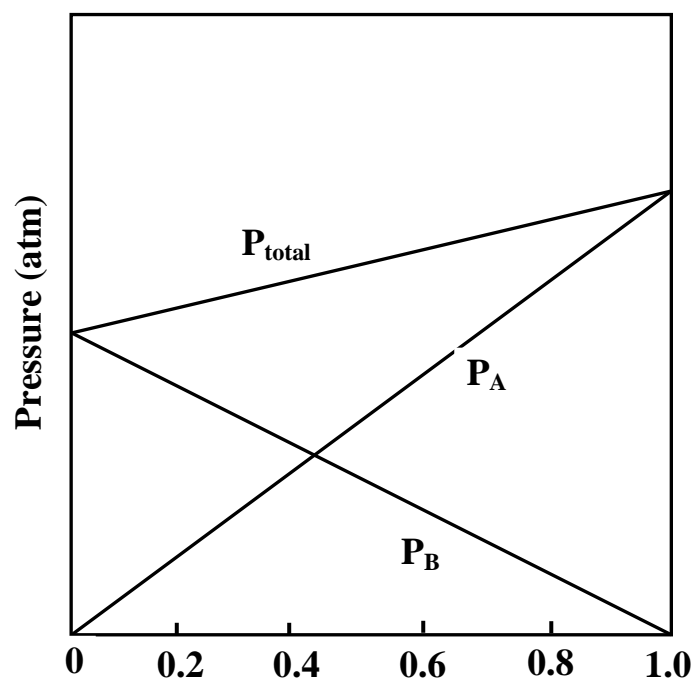


Figure 1.3 Typical total and partial vapor pressures for solutions that follow Raoult's law

Actually, a solution containing A and B will be ideal only if the intermolecular attractive forces between A and B molecules are similar to those between molecules of the pure components (A and A, B and B).

Few solutions are ideal. Two types of deviations from Raoult's law are observed:

- 1. Positive deviations.** The partial pressures of A and B and the total vapor pressure are *higher* than predicted (Figure 1.4). This type of deviation is observed when the attractive forces between A and B molecules are *weaker* than those between two A molecules or two B molecules. In such a situation, A molecules find it easier to escape from the liquid and the partial pressure of A is higher than predicted. The behavior of B molecules is similar.
- 2. Negative deviations.** The partial pressures of A and B and the total vapor pressure are *lower* than predicted (Figure 1.5). The A—B attractions are *stronger* than A—A or B—B attractions. The A molecules find it more difficult to leave the liquid, and the partial pressure of A is lower than predicted. The behavior of B molecules is similar.

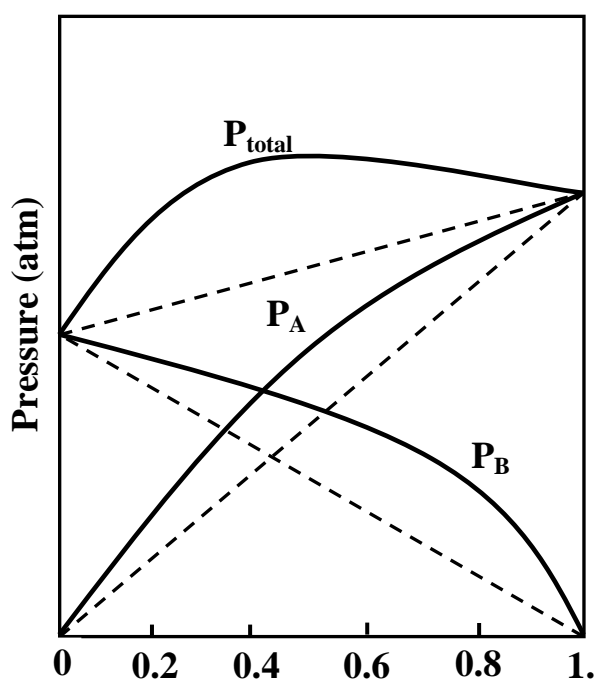


Figure 1.4 Partial vapor pressure curves for solutions that show positive deviations from Raoult's law. (dashed lines are based on Raoult's law.)

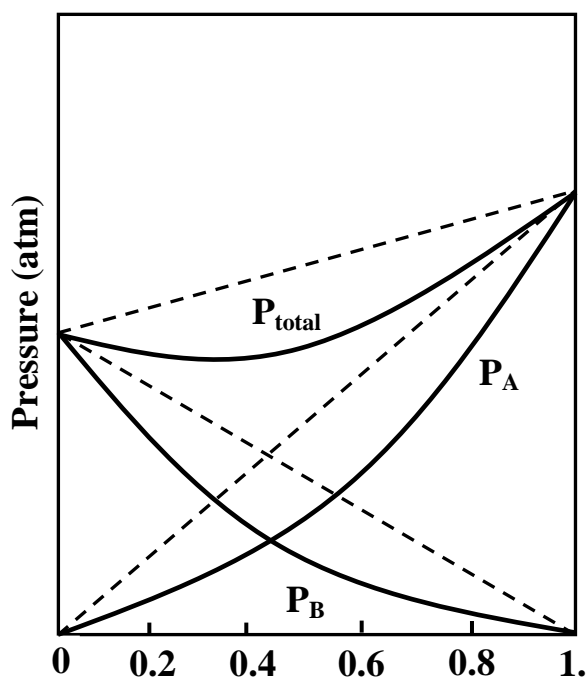


Figure 1.5 Partial vapor pressure curves for solutions that show negative deviations from Raoult's law. (dashed lines are based on Raoult's law.)

Example 1.6

Heptane (C_7H_{16}) and octane (C_8H_{18}) form ideal solutions. What is the vapor pressure at 40°C of a solution that contains 3.00 mol of heptane and 5.00

mol of octane? At 40°C, the vapor pressure of heptane is 0.121 atm and the vapor pressure of octane is 0.041 atm.

Solution

The total number of moles is 8.00. Therefore,

$$X_{\text{heptanes}} = \frac{3.00 \text{ mol}}{8.00 \text{ mol}} = 0.375$$

$$X_{\text{octane}} = \frac{5.00 \text{ mol}}{8.00 \text{ mol}} = 0.625$$

The vapor present is

$$P_{\text{total}} = X_{\text{heptane}} P^{\circ}_{\text{heptane}} + X_{\text{octane}} P^{\circ}_{\text{octane}}$$

The vapor pressure is

$$\begin{aligned} P_{\text{total}} &= P_{\text{heptane}} P^{\circ}_{\text{heptane}} + X_{\text{octane}} P^{\circ}_{\text{octane}} \\ &= 0.375(0.121 \text{ atm}) + 0.625(0.041 \text{ atm}) \\ &= 0.045 \text{ atm} + 0.026 \text{ atm} = 0.071 \text{ atm} \end{aligned}$$

Example 1.7

Assuming ideality, calculate the vapor pressure of a 1.00 *m* solution of a nonvolatile, nondissociating solute in water at 50°C. The vapor pressure of water at 50°C is 0.122 atm.

Solution

The mole fraction of water in a 1.00 *m* solution is 0.982 (from Example 10.5).

The vapor pressure of a 1.00 *m* solution of this type at 50°C is

$$\begin{aligned} P_{\text{total}} &= X_{\text{H}_2\text{O}} P^{\circ}_{\text{H}_2\text{O}} \\ &= (0.982)(0.122 \text{ atm}) \\ &= 0.120 \text{ atm} \end{aligned}$$

1.8 Boiling Point and Freezing Point of Solutions

The boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid is equal to the prevailing atmospheric pressure. Boiling points measured under 1 atmosphere pressure are called normal boiling points. Since the addition of a nonvolatile solute decreases the vapor pressure of a liquid, a solution will not boil at the normal boiling point of the solvent. It

is necessary to increase the temperature above this point in order to attain a vapor pressure over the solution of 1 atmosphere. The boiling point of a solution containing a nonvolatile molecular solute, therefore, is higher than that of the pure solvent. The elevation is proportional to the concentration of solute in the solution.

This effect is illustrated by the vapor pressure curves plotted in Figure 1.6. The extent to which the vapor pressure curve of the solution lies below the vapor pressure curve of the solvent is proportional to the mole fraction of solute in the solution. The elevation of the boiling point, Δt_b , reflects this displacement of the vapor pressure curve. For a given solvent the elevation is a constant for all solutions of the same concentration.

Concentrations are customarily expressed in molalities, rather than mole fractions, for problems involving boiling-point elevations. The boiling point of a 1 *m* aqueous solution, for example, is 0.512°C higher than the boiling point of water.

Thus, the boiling-point elevation, Δt_b , of a solution can be calculated by multiplying the molal boiling-point elevation constant of the solvent, k_b , by the molality of the solution, m :

$$\Delta t_b = mk_b(1.10)$$

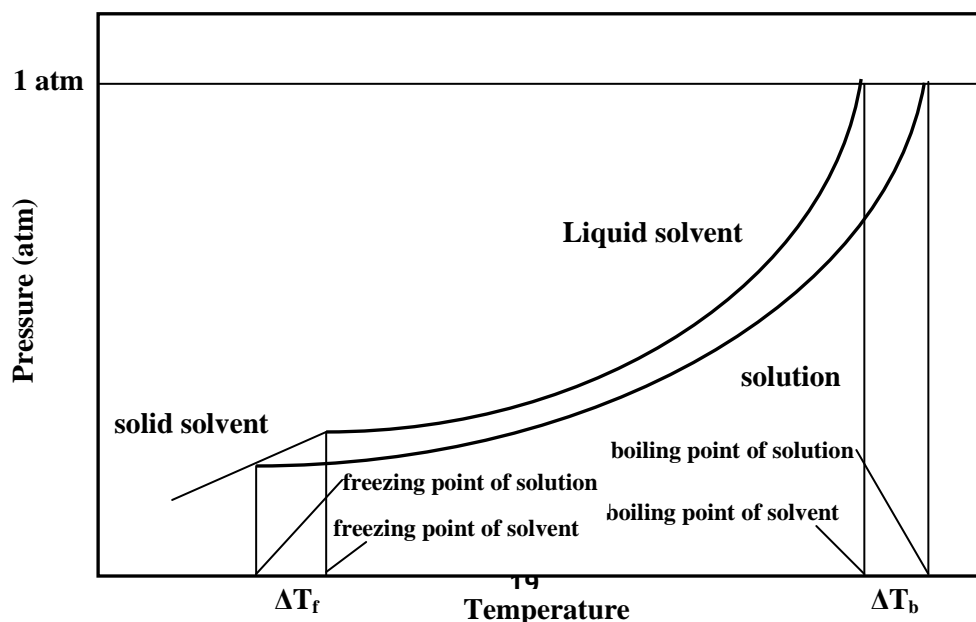


Figure 1.6: Vapor pressure curves of a pure solvent and a solution of a nonvolatile solute. (Not drawn to scale.)

The freezing point of the solution is lower than that of the pure solvent. As in the case of boiling-point elevations, freezing-point depressions depend upon the concentration of the solution and the solvent employed. The freezing-point depression, Δt_f , of a solution can be calculated from the molality of the solution and the constant for the solvent k_f :

$$\Delta t_f = m k_f \quad (1.11)$$

Example 1.8

What are the boiling point and freezing point of a solution prepared by dissolving 2.40 g of biphenyl ($C_{12}H_{10}$) in 75.0 g of benzene? The molecular weight of biphenyl is 154.

Solution

The molality of the solution is the number of moles of biphenyl dissolved in 1000 g of benzene:

$$\begin{aligned} \text{mol } C_{12}H_{10} &= 1000 \text{ g benzene} \left(\frac{2.40 \text{ g } C_{12}H_{10}}{75.0 \text{ g benzene}} \right) \left(\frac{1 \text{ mol } C_{12}H_{10}}{154 \text{ g } C_{12}H_{10}} \right) \\ &= 0.208 \text{ mol } C_{12}H_{10} \end{aligned}$$

The molal boiling-point elevation constant for benzene solutions is $+2.53^\circ\text{C}/m$ (Table 10.2):

$$\begin{aligned} \Delta t_b &= m k_b \quad (10.10) \\ &= (0.208 \text{ m})(+2.53^\circ\text{C}/m) \\ &= +0.526^\circ\text{C} \end{aligned}$$

The normal boiling point of benzene is 80.1°C (Table 1.2). The boiling point of the solution, therefore, is

$$80.1^\circ\text{C} + 0.5^\circ\text{C} = 80.6^\circ\text{C}$$

The molal freezing-point depression constant for benzene solutions is $-5.12^\circ\text{C}/m$ (Table 1.2):

$$\begin{aligned}\Delta t_f &= mk_f(10.11) \\ &= (0.208\text{m})(-5.12^\circ\text{C/m}) \\ &= -1.06^\circ\text{C}\end{aligned}$$

The normal freezing point of benzene is 5.5°C (Table 1.2). The freezing point of the solution, therefore, is

$$5.5^\circ\text{C} - 1.1^\circ\text{C} = 4.4^\circ\text{C}$$

Example 1.9

A solution prepared by dissolving 0.300 g of an unknown nonvolatile solute in 30.0 g of carbon tetrachloride has a boiling point that is 0.392°C higher than that of pure CCl_4 . What is the molecular weight of the solute?

Solution

For CCl_4 solutions, k_b is $+5.02^\circ\text{C/m}$ (Table 1.2). We find the molality of the solution from the boiling-point elevation:

$$\begin{aligned}\Delta t_b &= mk_b & (1.10) \\ +0.392^\circ\text{C} &= m(+5.02^\circ\text{C/m}) \\ m &= 0.0781\text{ m}\end{aligned}$$

Next, we find the number of grams of solute dissolved in 1 000 g of CCl_4

$$? \text{ g solute} = 1000 \text{ g CCl}_4 \left(\frac{0.300 \text{ g solute}}{300 \text{ g CCl}_4} \right) = 10.0 \text{ g solute}$$

Since the solution is 0.0781 m, 10.0 g of solute is 0.0781 mol of solute:

$$? \text{ g solute} = 1 \text{ mol solute} \left(\frac{10.0 \text{ g solute}}{0.0781 \text{ mol solute}} \right) = 128 \text{ g solute}$$

1.9 Osmosis

The properties of solutions that depend principally upon the concentration of dissolved particles, rather than upon the nature of these particles, are called colligative properties. For solutions of nonvolatile solutes these properties include: vapor-pressure lowering, freezing-point depression, boiling-point elevation, and osmotic pressure. The last of these, osmotic pressure, is the topic of this section.

A membrane, such as cellophane or parchment, that permits some molecules or ions, but not all, to pass through it is called a semipermeable membrane. Figure 10.7 shows a membrane that is permeable to water but not to sucrose (cane sugar) placed between pure water and a sugar solution. Water molecules, but not sugar molecules, can go through the membrane in either direction. However, there are more water molecules per unit volume on the left side (the side containing pure water) than on the right. The rate of passage through the membrane from left to right, therefore, exceeds the rate in the opposite direction.

As a result, the number of water molecules on the right increases, the sugar solution becomes more dilute, and the height of the solution in the right arm of the U tube increases. This process is called osmosis. The difference in height between the levels of the liquids in the two arms of the U tube is a measure of the osmotic pressure.

The increased hydrostatic pressure on the right tends to force water molecules through the membrane from right to left, so that ultimately the rate of passage to the left equals the rate of passage to the right. The final condition, therefore, is an equilibrium state with equal rates of passage of water molecules through the membrane in both directions.

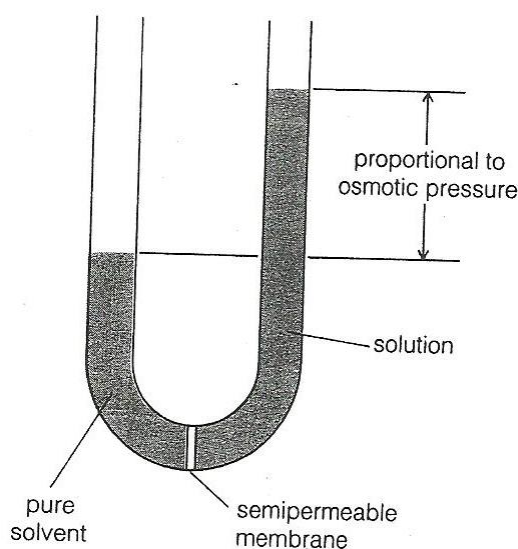


Figure 1.7 Osmosis

If a pressure that is higher than the equilibrium pressure is applied to the solution in the right arm, water is forced in a direction contrary to that normally observed. This process, called reverse osmosis, is used to secure pure water from salt water.

Similarities exist between the behavior of water molecules in osmosis and the behavior of gas molecules in diffusion. In both processes molecules diffuse from regions of high concentrations to regions of low concentration. In 1887 Jacobus van't Hoff discovered the relation

$$\pi V = nRT \quad (1.12)$$

where π is the osmotic pressure (in atm), n is the number of moles of solute dissolved in volume V (in liters), T is absolute temperature, and R is the gas constant (0.08206 liter atm/K mol). The similarity between this equation and the equation of state for an ideal gas is striking. The equation may be written in the form

$$\pi = \left(\frac{n}{V}\right) RT \quad (1.13)$$

$$\pi = MRT \quad (1.14)$$

where M is the molarity of the solution. Osmosis plays an important role in plant and animal physiological processes; the passage of substances through the semipermeable walls of a living cell, the action of the kidneys, and the rising of sap in trees are prime examples.

Example 1.10

Find the osmotic pressure of blood at body temperature (37°C) if the blood behaves as if it were a 0.296 M solution of a nonionizing solute.

Solution

$$\pi = MRT$$

$$= (0.296 \text{ mol/liter})(0.0821 \text{ liter atm/K mol})(310 \text{ K})$$

$$= 7.53 \text{ atm}$$

Example 1.11

One liter of an aqueous solution contains 30.0 g of a protein. The osmotic pressure of the solution is 0.0167 atm at 25°C. What is the approximate molecular weight of the protein?

Solution

We use the van't Hoff equation to find the number of moles of protein present in the solution :

$$\pi = \left(\frac{n}{V}\right) RT \quad (1.3)$$

$$0.0167 \text{ atm} = \frac{n}{1 \text{ liter}} [0.0821 \text{ liter atm/(K mol)}] (298 \text{ K})$$

$$n = 6.83 \times 10^{-4} \text{ mol}$$

Since there are 30.0 g of protein in the solution,

30.0 g protein

$$? \text{ g protein} = 1 \text{ mol protein} \frac{30.0 \text{ g protein}}{6.83 \times 10^{-4} \text{ mol protein}}$$

$$= 4.39 \times 10^4 \text{ g protein}$$

The molecular weight of the protein is approximately 43,900.

Since proteins have high molecular weights, the molal and molar concentrations of saturated solutions of proteins are very low. For the solution described in this example, the following effects can be calculated:

vapor pressure lowering 0.000000385 atm

boiling-point elevation 0.000350°C

freezing-point depression - 0.00127°C

osmotic pressure 0.0167 atm

Clearly, the first three are too small for accurate measurement. The osmotic pressure of this solution, however, would make the difference in the height of the two columns shown in Figure 10.7 approximately 17 cm, an amount which is easily measured.

1.11 Solutions of Electrolytes

If an aqueous solution contains ions, it will conduct electricity. Pure water itself is slightly ionized and is a poor conductor:



The solute of an aqueous solution that is a better electrical conductor than pure water alone is called an electrolyte. An electrolyte is wholly or partly ionized in water solution. Covalent solutes that are exclusively molecular in solution and therefore do nothing to enhance the conductivity of the solvent are called non-electrolytes; sucrose (cane sugar) is an example.

Electrolytes can be further divided into two groups:

1. Strong electrolytes are virtually completely ionic in water solution.
2. Weak electrolytes are polar covalent substances that are incompletely dissociated in water solution. The conductivity of a 1*m* solution of a weak electrolyte is lower than the conductivity of a 1 *m* solution of a strong electrolyte.

The boiling-point elevations and freezing-point depressions of dilute solutions of electrolytes are different from those of solutions of nonelectrolytes with the same concentrations. Since 1 mol of NaCl contains 2 mol of ions (1 mol of Na⁺ and 1 mol of Cl⁻) and since colligative properties depend upon the number of dissolved particles and not their nature, we would expect the freezing-point depression of a 1 *m* solution of NaCl to be twice that of a 1 *m* solution of a non-electrolyte. We would also expect the freezing-point depression of a solution of K₂SO₄ (which contains 3 mol of ions per mole of K₂SO₄) to be three times that of a solution that has the same concentration and that contains a solute that does not dissociate into ions.

The observed freezing-point depressions listed in Table 1.3 agree approximately with these predictions. The observed values agree best with the calculated values when the solutions are most dilute. Data such as these, together with data from electrical conductivity experiments led Svante Arrhenius to propose his "chemical theory of electrolytes" in 1887. The boiling-point elevations of solutions of electrolytes are proportionately higher than the boiling-point elevations of solutions of nonelectrolytes with the same concentrations.

1.12 Interionic Attractions in Solution

The van't Hoff factor, i , is defined as the ratio of the observed freezing-point depression of a solution, Δt_f to the depression calculated on the basis that the solute does not dissociate:

Table 1.3: Freezing point depression

Solute	Concentration of Solution		
	0.001 m	0.01 m	0.1 m
nonelectrolyte	0.00186°C	0.0186°C	0.186°C
sucrose	0.00186	0.0186	0.188
2 ions/formula	0.00372	0.0372	0.372
NaCl	0.00366	0.0360	0.348
3 ions/formula	0.00558	0.0558	0.558
K ₂ SO ₄	0.00528	0.0501	0.432
4 ions/formula	0.00744	0.0744	0.744
K ₃ [Fe(CN) ₆]	0.00710	0.0626	0.530

Calculated on the assumptions that K_f for water is -1.86°C/moal over the entire range of concentrations, the salts are 100% ionic in solution, and the ions act independently of one another in their effect on the freezing point of the solution.

Table 1.4: The i values of different solutes

Electrolyte	Concentration of Solution		
	0.001 m	0.01	0.1 m
NaCl	1.97	1.94	1.87
MgSO ₄	1.82	1.53	1.21
K ₃ SO ₄	2.84	2.69	2.32
K ₃ [Fe(CN) ₆]	3.82	3.36	2.85

$$i = \frac{\Delta t_f}{mk_f} \quad (1.16)$$

The preceding equation can be rearranged to

$$\Delta t_f = imk_f \quad (1.16)$$

When dissociation of a solute occurs, it is necessary to correct the molality of the solution for calculations involving colligative properties. The i factor will do just that. Since 1 mol of NaCl dissociates into 2 mol of ions in solution (1 mol of Na^+ and 1 mol of Cl^-), the i factor for a solution of NaCl is theoretically 2. If we assume that each ion acts independently, the effective concentration of a 0.001 m solution of NaCl would be 0.002 m . In other words, $i = 2$, $m = 0.001$ *in*, and

$$\Delta t_f = 2(0.001 \text{ } m)k_f$$

Inspection of the i values recorded in Table 1.4 reveals that the i factors do not exactly equal the number of ions per formula unit for each of the strong electrolytes listed. Thus, for 0.001 m solutions, the factor for NaCl is 1.97 (not 2), for K_2SO_4 is 2.84 (not 3), and for $\text{K}_3[\text{Fe}(\text{CN})_6]$ is 3.28 (not 4). Furthermore, the i value changes with concentration of the solution and approaches the value expected for complete dissociation as the solution becomes more dilute.

Interionic attractions occur in solutions of electrolytes and the ions are not completely independent of one another in the way that uncharged solute molecules are. The electrical forces that operate between oppositely charged ions reduce the effectiveness of these ions. As a solution is diluted, the ions spread farther and farther apart, their influence on one another diminishes, and the i factor approaches its limiting value. Notice that the interionic attractions in solutions of MgSO_4 produce a stronger effect than those in solutions of NaCl, even though both solutes contain two moles of ions per mole of compound. For 0.001 *in* MgSO_4 , $i = 1.82$, whereas for 0.001 m NaCl, $i = 1.97$. Both the ions of MgSO_4 are doubly charged (Mg^{2+} , SO_4^{2-}), whereas the ions of NaCl are singly charged (Na^+ , Cl^-). The interionic attractions are stronger in solutions of magnesium sulfate.

Some characteristics of solutes are summarized in Table 1.5. The van't Hoff factor, i , is used in calculations of freezing-point depression, boiling-point elevation, and osmotic pressure when the solute is an electrolyte.

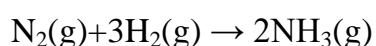
Table 1.5: Characteristics of different solutes

Solute	Form of solute in 1 m solution	Van't Hoff factor for Δt_f Dilute solutions of molality, m $\Delta t_f = i k_f m$	Examples
nonelectrolytes	molecules	$i = 1$	$C_{12}H_{22}O_{11}$ (sucrose) CON_2H_4 (urea) $C_3H_5(OH)_3$ (glycerol)
strong electrolytes	ions	$i \approx n^a$	NaCl KOH
weak electrolytes	molecules and ions	$1 < i < n^*$	$HC_2H_3O_2$ NH_3 $HgCl_2$

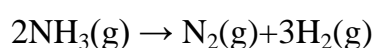
* n = number of moles of ions per mole of solute.

CHAPTER 2: CHEMICAL EQUILIBRIUM

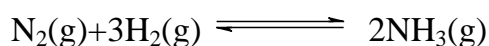
Under suitable conditions, nitrogen and hydrogen react to form ammonia:



On the other hand, ammonia decomposes at high temperatures to yield nitrogen and hydrogen:



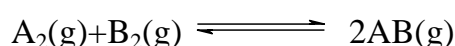
The reaction is reversible, and the equation for the reaction can be written



The double arrow (\rightleftharpoons) indicates that the equation can be read in either direction. For a reversible chemical reaction, an equilibrium state is attained when the rate at which a chemical reaction is proceeding equals the rate at which the reverse reaction is proceeding. Equilibrium systems that involve reversible chemical reactions are the topic of this chapter.

2.1 Reversible Reactions and Chemical Equilibrium

Consider a hypothetical reversible reaction



This equation may be read either forward or backward. If A_2 and B_2 are mixed, they will react to produce AB. A sample of pure AB, on the other hand, will decompose to form A_2 and B_2 .

Suppose that we place a mixture of A_2 and B_2 in a container. They will react to produce AB, and their concentrations will gradually decrease as the forward reaction occurs {see Figure 2.1). Since the concentrations of A_2 and B_2 decrease, the rate of the forward reaction decreases.

At the start of the experiment, the reverse reaction cannot occur since there is no AB present. As soon as the forward reaction produces some AB, however, the reverse reaction begins. The reverse reaction starts slowly (since the concentration of AB is low) and gradually picks up speed.

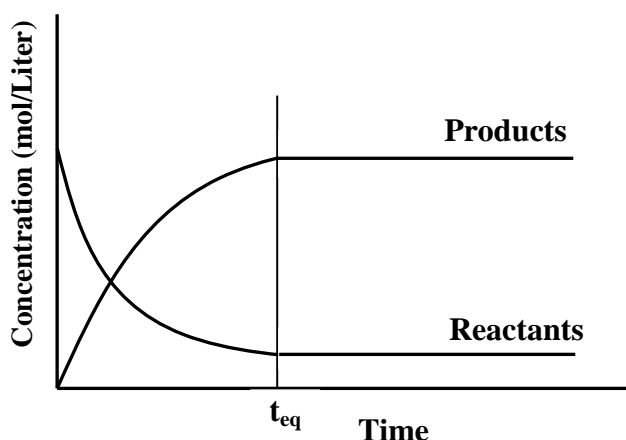


Figure 2.1: Curves showing changes in concentrations of materials with time for the reaction $A_2 + B_2 \rightleftharpoons 2 AB$. Equilibrium is attained at time t_e .

As time passes, the rate of the forward reaction decreases and the rate of the reverse reaction increases until the two rates are equal. At this point, chemical equilibrium is established. An equilibrium condition is one in which the rates of two opposing tendencies are equal.

At equilibrium, the concentrations of all the substances are constant. The concentration of AB is constant since AB is produced by the forward reaction at the same rate that it is used by the reverse reaction. In like manner, A_2 and B_2 are being made (by the reverse reaction) at the same rate that they are being used (by the forward reaction). It is important to note that the concentrations are constant because the rates of the opposing reactions are equal and *not* because all activity has stopped. Data for the experiment are plotted in Figure 13.1. Equilibrium is attained at time t_e .

If we assume that the forward and reverse reactions occur by simple one-step mechanisms, the rate of the forward reaction is

$$\text{rate}_f = k_f [A_2][B_2]$$

and the rate of the reverse reaction is

$$\text{rate}_r = k_r [AB]^2$$

At equilibrium, these two rates are equal, and therefore

$$\text{rate}_f = \text{rate}_r$$

$$k_f [A_2][B_2] = k_r [AB]^2$$

This equation can be rearranged to

$$\frac{k_f}{k_r} = \frac{[AB]^2}{[A_2][B_2]}$$

The rate constant of the forward reaction, k_f , divided by the rate constant of the reverse reaction, k_r , is equal to a third constant, which is called the equilibrium constant, K

$$\frac{k_f}{k_r} = K \quad (2.1)$$

Therefore,

$$K = \frac{[AB]^2}{[A_2][B_2]}$$

The numerical value of K varies with temperature. There are an unlimited number of possible equilibrium systems for this reaction. The concentrations, however, of A_2 , B_2 , and AB for any system in equilibrium at a given temperature will, when expressed in the preceding manner, equal the same value of K .

In general, for any reversible reaction

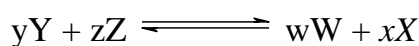


at equilibrium,

$$K = \frac{[Y]^y[Z]^z}{[W]^w[X]^x} \quad (2.3)$$

By convention, the concentration terms for the materials on the right of the chemical equation are written in the numerator of the expression for the equilibrium constant.

If the equation is written in the reverse form,



The expression for the equilibrium constant (which we will indicate as K') is

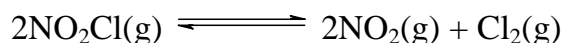
$$K = \frac{[W]^w[X]^x}{[Y]^y[Z]^z}$$

Notice that K' is the reciprocal of K :

$$K' = \frac{1}{K}$$

In our derivation, we assumed that the forward and reverse reactions occurred by mechanisms each consisting of a single step. **Does the law of chemical equilibrium hold for reactions that occur by mechanisms of more than one step?** The answer to the question is that it does.

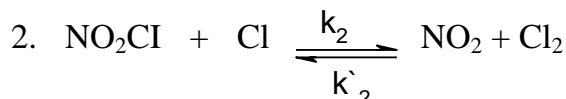
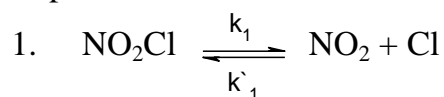
Consider the reaction



for which the expression for the equilibrium constant is

$$K = \frac{[NO_2]^2[Cl_2]}{[NO_2Cl]^2}$$

The reaction is believed to occur by means of a mechanism consisting of two steps:



Symbols for the rate constants appear above and below the arrows in these equations. The symbol k is used for the rate constant of the forward reaction, and k' is used for the reverse reaction. The subscripts of these symbols designate the steps.

Since the overall reaction is reversible, each step of the mechanism must also be reversible. When equilibrium is established for the overall reaction, each step of the mechanism must be in equilibrium. Therefore,

$$K_1 = \frac{k_1}{k'_1} = \frac{[\text{NO}_2][\text{Cl}]}{[\text{NO}_2\text{Cl}]}$$

and

$$K_2 = \frac{k_2}{k'_2} = \frac{[\text{NO}_2][\text{Cl}_2]}{[\text{NO}_2\text{Cl}][\text{Cl}]}$$

The product of these expressions is

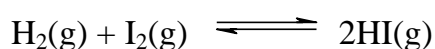
$$K_1 K_2 = \frac{k_1 k_2}{k'_1 k'_2} = \frac{[\text{NO}_2][\text{Cl}]}{[\text{NO}_2\text{Cl}]} \frac{[\text{NO}_2][\text{Cl}_2]}{[\text{NO}_2\text{Cl}][\text{Cl}]} = \frac{[\text{NO}_2]^2 [\text{Cl}_2]}{[\text{NO}_2\text{Cl}]^2}$$

which is the same as the expression for the equilibrium constant that we derived directly from the equation for the overall change. In this case, the equilibrium constant for the overall change is the product of the equilibrium constants of each of the steps:

$$K = K_1 K_2$$

3.2 Equilibrium Constants

For the reaction



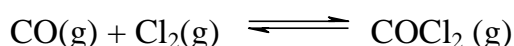
the equilibrium constant at 425°C is

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

The numerical value of K must be determined experimentally. If the concentrations of the materials (in mol/Liter) present in any equilibrium mixture at 425°C are substituted into the expression for the equilibrium constant, the result will equal 54.8. If any value other than 54.8 is obtained, the mixture is not in equilibrium.

The equilibrium condition may be approached from either direction. That is, an equilibrium mixture can be obtained by mixing hydrogen and iodine, by allowing pure hydrogen iodide to dissociate, or by mixing all three materials.

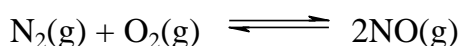
The magnitude of the value of the equilibrium constant gives an indication of the position of equilibrium. Recall that the concentration terms of substances on the right of the equation are written in the numerator of the expression for the equilibrium constant. For the reaction



at 100°C ,

$$K = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = 4.57 \times 10^9 \text{ liter/mol}$$

From this relatively large value of K , we conclude that equilibrium concentrations of CO and Cl_2 are small and that the synthesis of COCl_2 is virtually complete. In other words, the reaction to the right is fairly complete at equilibrium. For the reaction



at 2000°C ,

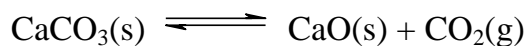
$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 4.08 \times 10^{-4}$$

We conclude from this small value of K that NO is largely dissociated into N_2 and O_2 at equilibrium. The reaction to the left is fairly complete.

Equilibria between substances in two or more phases are called **heterogeneous equilibria**. The concentration of a pure solid or a pure liquid is constant when the temperature and pressure are constant. For any heterogeneous equilibrium, therefore, the values of the concentrations of solids

or liquids involved are included in the value of K , and concentration terms for these substances do not appear in the expression for the equilibrium constant.

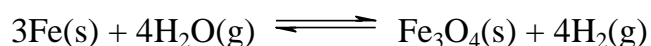
For example, for the reaction



the values for the concentrations of CaO and CaCO₃ are included in the value of K , and the expression for the equilibrium constant is

$$K = [\text{CO}_2]$$

Hence, at any fixed temperature the equilibrium concentration of CO₂ over a mixture of the solids is a definite value. The equilibrium constant for the reaction



is expressed in the following terms:

$$K = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

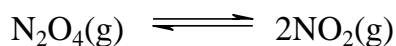
Some facts dealing with expressions for equilibrium constants may be summarized as follows:

1. The concentration terms for substances that appear on the *right side* of the chemical equation are written in the *numerator* of the expression for K . The concentration terms for substances that appear on the *left side* are written in the *denominator*.
2. No concentration terms are included for pure solids or pure liquids. The value of K includes these terms.
3. The value of K for a given equilibrium is constant if the equilibrium temperature does not change. At a different temperature, the value of K is different.
4. The magnitude of K for a given equilibrium indicates the position of equilibrium. **A large value of K** indicates that the reaction to the right is fairly complete. **A small value of K** indicates that the reaction to the left is fairly complete. A value of K that is neither very large nor very small indicates an intermediate situation.

The following examples illustrate how some simple problems involving equilibrium constants may be solved.

Example 2.1

For the reaction



the concentrations of the substances present in an equilibrium mixture at 25°C are

$$[\text{N}_2\text{O}_4] = 4.27 \times 10^{-2} \text{ mol/liter}$$

$$[\text{NO}_2] = 1.41 \times 10^{-2} \text{ mol/liter}$$

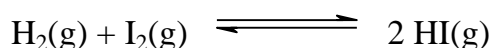
What is the value of K for this temperature?

Solution

$$\begin{aligned} K &= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \\ &= \frac{(1.41 \times 10^{-2} \text{ mol/liter})^2}{(4.27 \times 10^{-2} \text{ mol/liter})} \\ &= 4.66 \times 10^{-3} \text{ mol/liter} \end{aligned}$$

Example 2.2

K for the HI equilibrium at 425°C is 54.8:



A quantity of HI(g) is placed in a 1.00 liter container and allowed to come to equilibrium at 425°C. What are the concentrations of H₂(g) and I₂(g) in equilibrium with 0.50 mol/liter of HI(g)?

Solution

The concentrations of H₂(g) and I₂(g) must be equal since they are produced in equal amounts by the decomposition of HI(g). Therefore, let

$$[\text{H}_2] = [\text{I}_2] = x$$

We are told that the equilibrium concentration of HI is

$$[\text{HI}] = 0.50 \text{ mol/liter}$$

We substitute these values into the equation for the equilibrium constant and solve for x :

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 54.8$$

$$\frac{(0.50 \text{ mol/liter})^2}{x^2} = 54.8$$

$$54.8x^2 = 0.25 \text{ mol}^2/\text{liter}^2$$

$$x^2 = 0.00456 \text{ mol}^2/\text{liter}^2$$

$$x = 0.068 \text{ mol/liter}$$

The equilibrium concentrations are

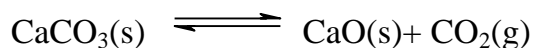
$$[\text{HI}] = 0.50 \text{ mol/liter}$$

$$[\text{H}_2] = [\text{I}_2] = 0.068 \text{ mol/liter}$$

2.3 Equilibrium Constants Expressed in Pressures

The partial pressure of a gas is a measure of its concentration. Equilibrium constants for reactions involving gases, therefore, may be written in terms of the partial pressures of the reacting gases. An equilibrium constant of this type is given the designation K_p .

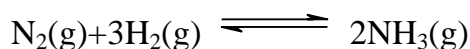
For the calcium carbonate equilibrium



the equilibrium constant in terms of partial pressures is

$$K_p = P_{\text{CO}_2}$$

For the equilibrium



The K_p is

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

There is a simple relation between the K_p for a reaction and the equilibrium constant derived from concentrations. Consider the reaction



If *all* these materials are **gases**,

$$K_p = \frac{(P_y)^y (P_z)^z}{(P_w)^w (P_x)^x} \quad (2.5)$$

Assume that each of the gases follows the ideal gas law

$$PV = nRT$$

Then the partial pressure of any gas, p , is

$$P = \frac{n}{V}RT$$

The concentration of a gas in mol/liter is equal to n/V . Therefore, for gas W

$$P_w = [W] RT \quad (2.6)$$

$$(P_w)^w = [W]^w (RT)^w \quad (2.7)$$

If we substitute expressions such as Equation 2.7 for the partial pressure terms in the expression for K_p (Equation 2.5), we get

$$K_p = \frac{[Y]^y (RT)^y [Z]^z (RT)^z}{[W]^w (RT)^w [X]^x (RT)^x}$$

$$\frac{[Y]^y [Z]^z}{[W]^w [X]^x} (RT)^{+y+z-w-x} \quad (2.8)$$

The fractional term in the last equation is equal to K :

$$K_p = (RT)^{+y+z-w-x} \quad (2.9)$$

If we read the chemical equation for the reaction



in molar quantities,

$y + z$ = number of moles of gases on the right

$w + x$ = number of moles of gases on the left

We let Δn equal the change in the number of moles of gases when the equation is read from left to right:

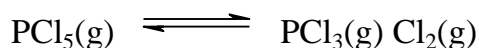
$$\Delta n = (y + z) - (w + x) = +y + z - w - x \quad (2.10)$$

Therefore,

$$K_p = K(RT)^{\Delta n} \quad (2.11)$$

Partial pressures are expressed in atmospheres, concentrations are expressed in moles per liter, R is 0.08206 liter atm/(K • mol), T is the absolute temperature in K.

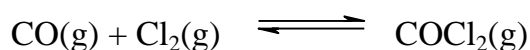
For the reaction



Δn is + 1. Therefore,

$$K_p = K(RT)^{+1}$$

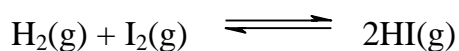
For the reaction



$\Delta n = -1$. Therefore,

$$K_p = K(RT)^{-1} \text{ or } K_p = \frac{K}{(RT)}$$

For the reaction

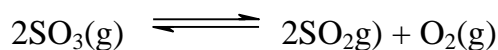


$\Delta n = 0$. Therefore,

$$K_p = K(RT)^0 \text{ or } K_p = K$$

Example 2.3

At 1100 K, the equilibrium constant for the reaction



is 0.0271 mol/liter. What is K_p at this temperature?

Solution

Two moles of $\text{SO}_3\text{(g)}$ produce a total of 3 mol of gases. Therefore,

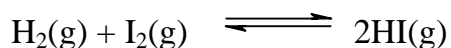
$$\Delta n = +1$$

$$\begin{aligned} K_p &= K(RT)^{+1} \\ &= (0.0271 \text{ mol/liter}) \{ [0.0821 \text{ liter} \cdot \text{atm}/(\text{K} \cdot \text{mol})](1100 \text{ K}) \} \\ &= 2.45 \text{ atm} \end{aligned}$$

2.4. Le Chatelier's Principle

What happens to an equilibrium system if an experimental conditions (such as temperature or pressure) is changed? The effects of such changes were summarized in 1884 by Henri Le Chatelier's. Le Chatelier's principle states that a system in equilibrium reacts to a stress in a way that counteracts the stress and establishes a new equilibrium state. This important generalization is very simple to apply:

1. Concentration changes. If the concentration of a substance is *increased*, the equilibrium will shift in a way that will *decrease* the concentration of the substance that was added. Suppose that we have a system in equilibrium.

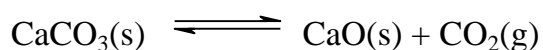


and we *increase* the concentration of H_2 by adding more H_2 to the system. The equilibrium is upset, and the system will react in a way that will *decrease* the concentration of H_2 . It can do that by using up some of the H_2 (and some I_2 as well) to form more HI . When equilibrium is established again, the concentration of HI will be higher than it was initially. The position of equilibrium is said to have shifted to the right.

If the concentration of HI is increased by adding HI to the system, the position of equilibrium -will shift to the left. In this way some HI will be used up. When equilibrium is established again, the concentrations of H_2 and I_2 will be higher than they were initially.

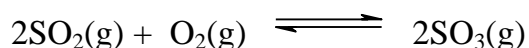
Removal of one of the substances from an equilibrium system will also cause the position of equilibrium to shift. If, for example, HI could be removed, the position of equilibrium would shift to the right. Additional HI would be produced and the concentrations of H_2 and I_2 would decrease.

By the continuous removal of a product it is possible to drive some reversible reactions "to completion," Complete conversion of $\text{CaCO}_3(\text{s})$ into $\text{CaO}(\text{s})$:



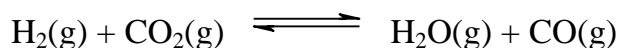
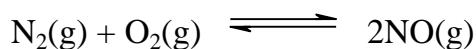
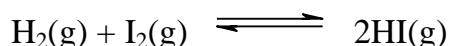
can be accomplished by removing the CO_2 gas as fast as it is produced.

2. Pressure changes. Le Chatelier's principle may also be used to make qualitative predictions of the effect of pressure changes on systems in equilibrium. Consider the effect of a pressure increase on an equilibrium mixture of SO_2 , O_2 , and SO_3 :



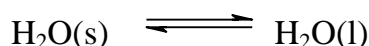
In the forward reaction two gas molecules (2SO_3) are produced by the disappearance of three gas molecules ($2\text{SO}_2 + \text{O}_2$). Two gas molecules do not exert as high a pressure as three gas molecules. When the pressure on an equilibrium mixture is increased (or the volume of the system decreased), the position of equilibrium shifts to the right. In this way the system counteracts the change. Alternatively, decreasing the pressure (or increasing the volume) causes the position of this equilibrium to shift to the left.

For reactions in which $\Delta n = 0$, pressure changes have no effect on the position of equilibria. Equilibria involving the systems



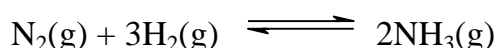
are not influenced by changing the pressure since there is no difference in the total volume in either the forward or reverse direction for any one of these reactions.

For a system that involves only liquids and solids, the effect of pressure on the position of equilibrium is slight and may usually be ignored for ordinary changes in pressure. Large pressure changes, however, can significantly alter such equilibria; and at times, even slight changes in such equilibria are of interest. For example, the position of equilibrium



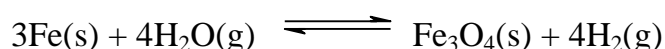
is forced to the right by an increase in pressure because a given quantity of water occupies a smaller volume in the liquid state than in the solid state (its density is higher in the liquid state).

Pressure changes affect equilibria involving gases to a much greater degree. For example, a high pressure would favor the production of a high yield of ammonia from the equilibrium



Hence, Le Chatelier's principle is of practical importance as an aid in determining favorable reaction conditions for the production of a desired substance.

For heterogeneous equilibria the effect of pressure is predicted by counting the number of moles of *gas* indicated on each side of the equation. For example, the position of equilibrium

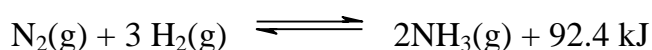


is virtually unaffected by pressure because there are four moles of gas indicated on each side of the equation.

3. Temperature changes. In order to predict the effect of a temperature change on a system in equilibrium, the nature of the heat effect that accompanies the reaction must be known. At 25°C, the thermochemical equation for the synthesis of ammonia is

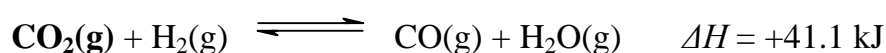


Since ΔH is negative, the reaction to the right evolves heat. We can write the equation to indicate heat as a product:

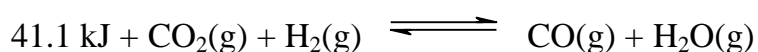


The forward reaction is *exothermic*, and the reverse reaction is *endothermic*. In other words, the forward reaction produces heat, and the reverse reaction uses heat. If heat is added (the temperature of the system is raised), the position of equilibrium will shift to the left — the direction in which heat is absorbed. If the mixture is cooled, the position of equilibrium will shift to the right — the direction in which heat is evolved. The highest yields of NH_3 will be obtained at the lowest temperatures. Unfortunately, if the temperature is too low, the reaction will be extremely slow. High pressures and temperatures around 500°C are employed in the commercial process.

Consider the reaction



Since ΔH is positive, the forward reaction is endothermic. We write the equation



Increasing the temperature *always* favors the endothermic change, and decreasing the temperature *always* favors the exothermic change. In this case, the reaction is forced to the right by an increase in temperature. A decrease in temperature causes the position of equilibrium to shift to the left.

The numerical value of the equilibrium constant changes when the temperature is changed. The reaction of CO_2 and H_2 is shifted to the right by an increase in temperature. The concentrations of the substances on the right are increased by this shift. The terms for the concentrations of these substances appear in the numerator of the expression for K . As the temperature is

increased, therefore, the value of K increases. For this reaction, at 700°C , $K = 0.63$, and at 1000°C , $K = 1.66$.

4. Addition of a catalyst. The presence of a catalyst has no effect on the position of a chemical equilibrium since a catalyst affects the rates of the forward and reverse reactions equally (see Section 12.7). A catalyst will, however, cause a system to attain equilibrium more rapidly than it otherwise would.

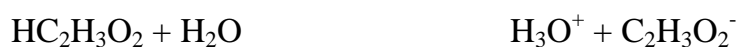
Chapter 3: Ionic Equilibrium

Part I: Ionic Equilibrium

The principles of chemical equilibrium can be applied to equilibrium systems that involve molecules and ions in water solution. In pure water, H_3O^+ and OH^- ions exist in equilibrium with H_2O molecules from which they are derived. Other molecular substances (weak electrolytes) are partially ionized in water solution and exist in equilibrium with their ions. An understanding of these systems is important to the study of analytical chemistry.

3.1 Weak Electrolytes

Strong electrolytes are completely ionized in water solution. A 0.01 M solution of CaCl_2 , for example, contains Ca^{2+} ions (at a concentration of 0.01M), Cl^- ions (at a concentration of 0.02 M) and no CaCl_2 molecules at all. Weak electrolytes, however, are incompletely ionized in water solution. Dissolved molecules exist in equilibrium with their ions in such solutions. The following chemical equation represents the dissociation of acetic acid in water:



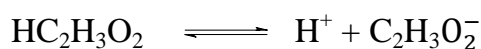
The equilibrium constant \rightleftharpoons for this reaction as written is

$$\frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2][\text{H}_2\text{O}]} = K_A$$

In dilute solutions, the concentration of water may be considered to be a constant. The number of moles of water used in forming H_3O^+ (which is about 0.001 mol in 1 liter of a 0.1 M solution of acetic acid) is very small in comparison to the large number of moles of water present (which is about 55.5 mol in 1 liter of the solution). If we combine $[\text{H}_2\text{O}]$ with K'_a , we get

$$\frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K'_a = K_a$$

We shall follow the practice of representing the concentration of hydronium ion, $[\text{H}_3\text{O}^+]$, by the symbol $[\text{H}^+]$. The simplified expression for the equilibrium constant K_a , sometimes called an acid dissociation constant, and the corresponding simplified chemical equation are



$$\frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K_a$$

By convention, the ions are written on the right of the chemical equation for a reversible ionization. Consequently, the terms for the concentrations of the ions appear in the numerator of the expression for K_a

The degree of dissociation, α , of a weak electrolyte in water solution is the fraction of the total concentration of the electrolyte that is in ionic form at equilibrium. These values are frequently given in terms of percent ionized, which is 100α

Example 3.1

At 25°C, a 0.1000 M solution of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) is 1.34% ionized. What is the ionization constant, K_a for acetic acid?

Solution

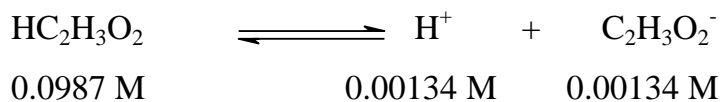
Let us assume that we have 1 liter of solution. Since the acid is 1.34% ionized, the number of moles of $\text{HC}_2\text{H}_3\text{O}_2$ in ionic form is

$$(0.0134)(0.1000 \text{ mol HC}_2\text{H}_3\text{O}_2) = 0.00134 \text{ mol HC}_2\text{H}_3\text{O}_2$$

We subtract this number from the total number of moles of $\text{HC}_2\text{H}_3\text{O}_2$ to get the number of moles of acid in molecular form:

$$(0.1000 \text{ mol HC}_2\text{H}_3\text{O}_2) - (0.00134 \text{ mol HC}_2\text{H}_3\text{O}_2) = 0.0987 \text{ mol HC}_2\text{H}_3\text{O}_2$$

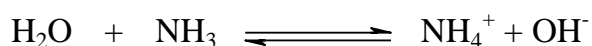
According to the chemical equation for the ionization, 1 mol of H^+ and 1 mol of $\text{C}_2\text{H}_3\text{O}_2^-$ are produced for every 1 mol of $\text{HC}_2\text{H}_3\text{O}_2$ that ionizes. Therefore, the concentrations at equilibrium are



These concentrations may be used to find the numerical value of the equilibrium constant:

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \\ &= \frac{(0.00134)(0.00134)}{(0.0987)} \\ &= 1.82 \times 10^{-5} \end{aligned}$$

In alkaline solutions,



The expression for the equilibrium constant (a base dissociation constant) for this reaction,

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]}$$

simplifies to the following if the concentration of water is assumed to be a

constant: $K_b = K'_b[\text{H}_2\text{O}] = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$

	Weak Acids	
Acetic	$\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HC}_2\text{H}_3\text{O}_2^-$	1.8×10^{-5}
Benzoic	$\text{HC}_7\text{H}_5\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HC}_7\text{H}_5\text{O}_2^-$	6.0×10^{-5}
Chlorous	$\text{HClO}_2 \rightleftharpoons \text{H}^+ + \text{ClO}_2^-$	1.1×10^{-2}
Cyanic	$\text{HOCN} \rightleftharpoons \text{H}^+ + \text{OCN}^-$	1.2×10^{-4}
Formic	$\text{HCHO}_2 \rightleftharpoons \text{H}^+ + \text{CHO}_2^-$	1.8×10^{-4}
Hydrazoic	$\text{HN}_3 \rightleftharpoons \text{H}^+ + \text{N}_3^-$	1.9×10^{-5}
Hydrocyanic	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$	4.0×10^{-10}
Hydrofluoric	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	6.7×10^{-4}
Hypobromous	$\text{HOBr} \rightleftharpoons \text{H}^+ + \text{BRO}^-$	2.1×10^{-9}
Hypochlorous	$\text{HOCl} \rightleftharpoons \text{H}^+ + \text{ClO}^-$	3.2×10^{-8}
Nitrous	$\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	4.5×10^{-4}
	Weak Bases	
Ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	4.6×10^{-10}
Dimethylamine	$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	7.4×10^{-4}
hydrazine	$\text{N}_2\text{H}_4 + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OH}^-$	9.8×10^{-7}
Methylamine	$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$	5.0×10^{-4}

Pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{N H}^+ + \text{OH}^-$	1.5×10^{-9}
Trimethylamine	$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	7.4×10^{-5}

Table 3.1 lists the ionization constants for some compounds that function as weak acids and some that function as weak bases. Certain ions also can function as weak acids and others as weak bases. These systems are discussed in later sections of this chapter.

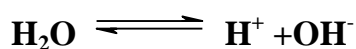
The values of ionization constants change with temperature. At 25°C, K_a for acetic acid is 1.8×10^{-5} ; at 100°C, K_a for this weak acid is 1.1×10^{-5} . Ionization constants are usually reported for equilibrium systems at 25°C.

3.2. The Ionization of Water

Pure water is itself a very weak electrolyte and ionizes according to the equation



In simplified form this equation is



The expression for the ionization constant derived from the simplified equation is

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

In dilute solutions the concentration of water is virtually a constant, and we may combine $[\text{H}_2\text{O}]$ with the constant K . Thus,

$$K[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

This constant, $K[\text{H}_2\text{O}]$, is called the ion product of water, or the water dissociation constant, and is given the symbol K_w . At 25°C,

$$K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-] \quad (3.1) \text{ In pure}$$

water,

$$[\text{H}^+] = [\text{OH}^-] = x$$

$$[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7} \text{ M}$$

The concentrations of both of the ions of water are equal to 1.0×10^{-7} M in pure water or in any neutral solution at 25°C. In 1 liter, only 10^{-7} mol of water is in ionic form out of a total of approximately 55.5 mol.

Both $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ exist in any aqueous solution. In an acid solution the concentration of $\text{H}^+(\text{aq})$ is larger than 1.0×10^{-7} M and larger than the $\text{OH}^-(\text{aq})$ concentration. In an alkaline solution the $\text{OH}^-(\text{aq})$ concentration is larger than 1.0×10^{-7} M and larger than the $\text{H}^+(\text{aq})$ concentration.

Example 3.2

What are $[\text{H}^+]$ and $[\text{OH}^-]$ in a 0.020 M solution of HCl?

Solution

The quantity of $\text{H}^+(\text{aq})$ ion obtained from the ionization of water is negligible compared to that derived from the hydrochloric acid. Since HCl is a strong electrolyte, $[\text{H}^+] = 0.020$ M:

$$\begin{aligned} [\text{H}^+][\text{OH}^-] &= 1.0 \times 10^{-14} \\ (2.0 \times 10^{-2})[\text{OH}^-] &= 1.0 \times 10^{-14} \\ [\text{OH}^-] &= \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-2}} \\ [\text{OH}^-] &= 5.0 \times 10^{-13} \text{ M} \end{aligned}$$

Notice that $[\text{OH}^-]$ is extremely small. In this solution there would be one OH^- ion for every 40 billion H^+ ions.

Example 3.3

What are $[\text{H}^+]$ and $[\text{OH}^-]$ in a 0.0050 M solution of NaOH?

Solution

Sodium hydroxide is a strong electrolyte, and therefore $[\text{OH}^-] = 5.0 \times 10^{-3}$ M:

$$\begin{aligned} [\text{H}^+][\text{OH}^-] &= 1.0 \times 10^{-14} \\ [\text{H}^+](5.0 \times 10^{-3}) &= 1.0 \times 10^{-14} \\ [\text{H}^+] &= \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-3}} \\ [\text{H}^+] &= 2.0 \times 10^{-12} \text{ M} \end{aligned}$$

3.3. pH

The concentration of $H^+(aq)$ in a solution may be expressed in terms of the pH scale. The pH of a solution is defined as

$$pH = \log \frac{1}{[H^+]} = -\log [H^+]$$

The common logarithm of a number is the power to which 10 must be raised in order to get the number (see the appendix). If.

$$a = 10^n$$

then

$$\log a = n$$

Therefore, if

$$a = 10^{-3}$$

then

$$\log a = -3$$

The pH is the negative logarithm of the hydrogen ion concentration.

Therefore, if

$$[H^+] = 10^{-3} \text{ M}$$

$$\log[H^+] = -3$$

$$pH = -\log[H^+] = 3$$

For a neutral solution, therefore,

$$[H^+] = 1.0 \times 10^{-7} \text{ M}$$

$$pH = -\log(10^{-7}) = -(-7)$$

$$pH = 7$$

The pOH of a solution is defined in the same terms:

$$pOH = -\log [OH^-] \quad (3.3)$$

The relationship between pH and pOH can be derived from the water constant:

$$[H^+][OH^-] = 10^{-14}$$

We take the logarithm of each term:

$$\log[H^+] + \log [OH^-] = \log (10^{-14})$$

and multiply through by — 1

$$-\log[H^+] - \log[OH^-] = -\log(10^{-14})$$

or

$$\text{pH} + \text{pOH} = 14 \quad (3.4)$$

For a 0.01 M solution of NaOH, which is a strong base,

$$[\text{OH}^-] = 10^{-2} \text{M}$$

$$\text{pOH} = -\log [\text{OH}^-] = 2$$

Since the sum of the pH and pOH of a solution at 25°C equals 14,

$$\text{pH} = 12$$

Example 3.4

What is the pH of a solution that is 0.050 M in H^+ ?

Solution

$$[\text{H}^+] = 5.0 \times 10^{-2} \text{M}$$

$$\log [\text{H}^+] = \log 5.0 + \log 10^{-2}$$

The logarithm of 5.0 can be found in the logarithm table that appears in the appendix :

$$\text{Log} [\text{H}^+] = 0.70 - 2.00 = -1.30$$

$$\text{pH} = 1.30$$

It should be kept in mind that pH relates to a power of 10. Hence, a solution of $\text{pH} = 1$ has a H^+ (aq) concentration 100 times that of a solution of $\text{pH} = 3$ (not three times). The lower the pH value, the larger the concentration of H^+ (aq). At $\text{pH} = 7$, a solution is neutral. Solutions with pH's below 7 are acidic. Those with pH's above 7 are alkaline. These relationships are summarized in the following Table.

The ionization constant of a weak acid or a weak base can be determined by measuring the pH of a solution of known concentration of the weak electrolyte.

pH	(H^+)	(H^-)	
14	10^{-14}	10^0	↑
13	10^{-13}	10^{-1}	
12	10^{-12}	10^{-2}	
11	10^{-11}	10^{-3}	increasing alkalinity
10	10^{-10}	10^{-4}	

9	10^{-9}	10^{-5}	
8	10^{-8}	10^{-6}	
7	10^{-7}	10^{-7}	neutrality
6	10^{-6}	10^{-8}	
5	10^{-5}	10^{-9}	
4	10^{-4}	10^{-10}	
3	10^{-3}	10^{-11}	Increasing acidity
2	10^{-2}	10^{-12}	↓
1	10^{-1}	10^{-13}	
0	10^0	10^{-14}	

Example 3.5

The pH of a 0.10 M solution of a weak acid HX is 3.30. What is the ionization constant of HX?

Solution



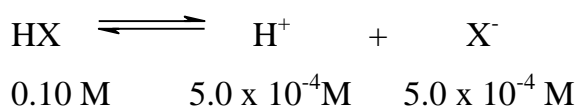
$$\text{pH} = 3.30$$

$$\log[\text{H}^+] = -3.30$$

$$[\text{H}^+] = 10^{-3.30} = 5.0 \times 10^{-4} \text{ M}$$

Since the solution was prepared from HX alone, $[\text{H}^+] = [\text{X}^-] = 5.0 \times 10^{-4} \text{ M}$

The concentration of HX in the solution is for all practical purposes equal to 0.10 M. The small quantity of HX that dissociated need not be considered. The equilibrium concentrations, therefore, are



The value of the ionization constant is

$$K = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

$$= \frac{(5.0 \times 10^{-4})^2}{1.0 \times 10^{-1}} = \frac{25 \times 10^{-8}}{1.0 \times 10^{-1}}$$

$$K = 2.5 \times 10^{-6}$$

3.4 Indicators

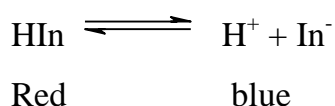
Indicators are organic compounds of complex structure that change color in solution as the pH changes. Methyl orange, for example, is red in solutions of pH below 3.1 and yellow in solutions of pH above 4.5. The color of this indicator is a varying mixture of yellow and red in the pH range between 3.1 and 4.5. Many indicators have been described and used. A few are listed in Table 3.4.

The pH of a solution is usually determined by use of a pH meter, but indicators may also be used for this purpose.

Indicators are weak acids or weak bases. Since they are intensely colored, only a few drops of a dilute solution of an indicator need be employed in any determination. Hence, the acidity of the solution in question is not significantly altered by the addition of the indicator.

If we let the symbol HIn stand for the litmus molecule (which is red) and the symbol In⁻ stand for the anion (which is blue) derived from the weak acid, the equation for the litmus equilibrium may be written

Indicator	Acid color	Ph range of color change	Alkaline color
Thymol blue	Red	1.2-2.8	Yellow
Methyl orange	Red	3.1-4.5	Yellow
Bromcresol green	Yellow	3.8-5.5	Blue
Methyl red	Red	4.2-6.3	Yellow
Litmus	Red	5.0-8.0	Blue
Bromthymol blue	Yellow	6.0-7.6	blue
Thymol blue	Yellow	8.0-9.6	Blue
Phenolphthalein	Colorless	8.3-10.0	Red
Alizarin yellow	Yellow	10.0-12.1	Lavender



According to the principle of Le Chatelier, increasing the concentration of H^+ shifts the equilibrium to the left, and the red (or acid) color of HIn is observed. On the other hand, addition of OH^- decreases the concentration of H^+ . The equilibrium shifts to the right, and the blue (or alkaline) color of In^- is observed. The ionization constant for litmus is approximately equal to 10^{-7} :

$$10^{-7} = \frac{[H^+][In^-]}{[HIn]}$$

We may rearrange this expression in the following manner:

$$\frac{10^{-7}}{[H^+]} = \frac{[In^-]}{[HIn]}$$

At a pH of 5 or below, the red color of litmus is observed. If we substitute $[H^+] = 10^{-5}$, which corresponds to pH = 5, into the preceding expression, we get

$$\frac{10^{-7}}{10^{-5}} = \frac{1}{100} \frac{[In^-]}{[HIn]} \quad \begin{matrix} \leftarrow \text{blue} \\ \leftarrow \text{red} \end{matrix}$$

Thus, the mixture appears red to the eye when the concentration of the red HIn is 100 times (or more) that of the blue In^- .

The blue color of litmus is observed in solutions of pH = 8 or higher. If $[H^+] = 10^{-8}$

$$\frac{10^{-7}}{10^{-8}} = \frac{10}{1} \frac{[In^-]}{[HIn]} \quad \begin{matrix} \leftarrow \text{blue} \\ \leftarrow \text{red} \end{matrix}$$

When the concentration of the blue In^- ion is 10 times that of the red HIn , or approximately 91% of the indicator is in ionic form, the blue color of the In^- ions completely masks the red color of the HIn molecules, and the mixture appears blue.

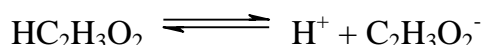
Thus, the blue color predominates when the concentration of the blue species is 10 times that of the red, whereas the red color predominates only when the concentration of the red form is 100 times that of the blue. This difference is not surprising since the blue color of litmus is a much stronger color than the red. Only when $[H^+] = K = 10^{-7}$ will the factor $K/[H^+] = 1$ and $[In^-] = [HIn]$. Hence, at pH = 7, litmus exhibits its "neutral" color (purple).

The pH range over which a given indicator changes color depends, therefore, upon the ionization constant of the indicator. For indicators that are

weak acids, the smaller the value of K , the higher is the pH range of the color change.

3.5 The Common-Ion Effect

In a 0.1 M solution of acetic acid, methyl orange assumes its acid color, red. If sodium acetate is added to this solution, the color changes to yellow, showing that the addition causes the acidity of the solution to decrease. This experimental observation is readily explained on the basis of Le Chatelier's principle. The equilibrium



is shifted to the left by the addition of the acetate ion from the sodium acetate, and the concentration of H^+ (aq) correspondingly decreases. Since acetic acid and sodium acetate have the acetate ion in common, this phenomenon is called the common-ion effect.

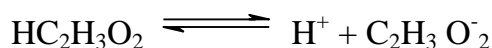
The concentration of H^+ (aq) in a solution of acetic acid to which acetate ion has been added can be calculated by means of the ionization constant of acetic acid.

Example 3.6

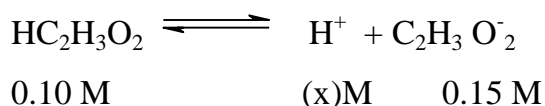
What is the concentration of H^+ in a 0.10 M solution of acetic acid that has been made 0.15 M in sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$)?

Solution

Sodium acetate is a strong electrolyte. Therefore, the concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ from this source is 0.15 M. The addition of this excess $\text{C}_2\text{H}_3\text{O}_2^-$ shifts the acetic acid equilibrium to the left:



Consequently, the concentration of $\text{HC}_2\text{H}_3\text{O}_2$ may be taken as equal to the total $\text{HC}_2\text{H}_3\text{O}_2$ concentration (0.10 M) since so little is ionized. The concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ may be taken as equal to the concentration of $\text{C}_2\text{H}_3\text{O}_2^-$ from the $\text{NaC}_2\text{H}_3\text{O}_2$ (0.15 M) since very little is supplied by the ionization of $\text{HC}_2\text{H}_3\text{O}_2$:



$$1.8 \times 10^{-5} \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

$$= \frac{[\text{H}^+]^{(0.15)}}{(0.10)}$$

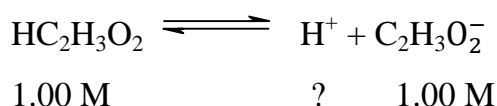
$$[\text{H}^+] = 1.2 \times 10^{-5} \text{ M}$$

The concentration of H^+ in a 0.10M solution of pure $\text{HC}_2\text{H}_3\text{O}_2$ is $1.3 \times 10^{-3} \text{ Af}$ (see Table 15.1).

3.6 Buffers

It is sometimes necessary that a solution with a definite pH be prepared and stored. The preservation of such a solution is even more difficult than its preparation. If the solution comes in contact with the air, it will absorb carbon dioxide (an acid anhydride) and become more acidic. If the solution is stored in a glass bottle, alkaline impurities leached from the glass may alter the pH. Buffer solutions are capable of maintaining their pH at some fairly constant value even when small amounts of acid or base are added.

A buffer solution based on a weak acid contains relatively high concentrations of both the weak acid and a salt of the acid. Consider an acetic acid-acetate buffer in which the concentration of acetic acid and the concentration of acetate ion (from sodium acetate) are both 1.00 M:



$$\frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}$$

Since $[\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-]$:

$$[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$$

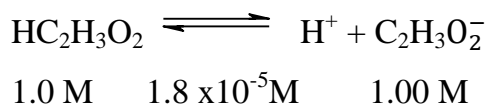
$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

The pK of a weak electrolyte may be defined in a manner analogous to pH :

$$\text{pK} = -\log K \quad (3.5)$$

A solution of a weak acid in which the concentration of the anion is the same as the concentration of the undissociated acid has a pH equal to the pK_a of the acid. In a sample of the buffer previously described, the quantities of

$\text{HC}_2\text{H}_3\text{O}_2$ and $\text{C}_2\text{H}_3\text{O}_2^-$ (aq) are much larger than the quantity of H^+ (aq) present — approximately 50,000 times larger :



If a small quantity of H^+ (aq) ion is added, the large reserve of acetate ion will quickly convert it to acetic acid. If a small amount of OH^- (aq) ion is added to the buffer, it will neutralize H^+ (aq) ion, but the large quantity of acetic acid present will by dissociation replace any H^+ (aq) ion removed and maintain the pH at a fairly constant value:

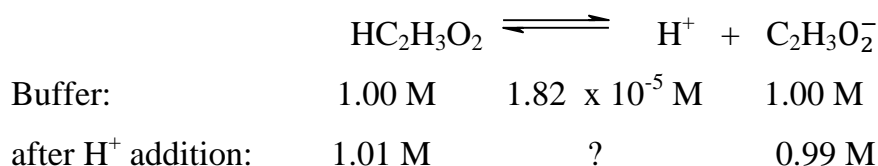
Buffers cannot withstand the addition of large amounts of acids or alkalis. The addition of 0.01 mol per liter of H^+ (aq) or OH^- (aq) is about the maximum that any buffer can be expected to withstand. How successfully a buffer withstands such an addition is illustrated in the following example.

Example 3.7

The ionization constant of acetic acid to three significant figures is 1.82×10^{-5} . A buffer containing 1.00 M concentrations of acetic acid and sodium acetate has a pH of 4.742. (a) What is the pH of the solution after 0.01 mol of HCl has been added to 1 liter of the buffer? (b) What is the pH of the solution after the addition of 0.1 mol of NaOH?

Solution

(a) The 0.01 mol of H^+ from HCl converts an equivalent amount of acetate ion into acetic acid. Thus, the concentrations are



$$\frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.82 \times 10^{-5}$$

$$\frac{[\text{H}^+](0.99)}{(1.01)} = 1.82 \times 10^{-5}$$

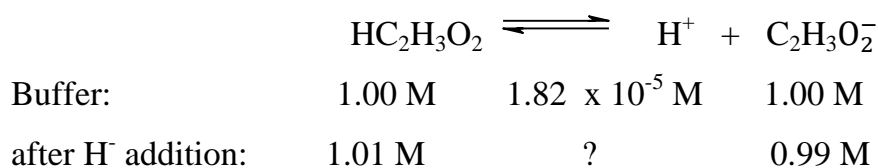
$$[\text{H}^+] = 1.82 \times 10^{-5} \frac{(1.01)}{(0.99)}$$

$$= 1.86 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.731$$

Thus, the addition causes the pH to change 0.009 pH units. A similar addition to pure water would change the pH from 7.0 to 2.0 -a change of 5.0 pH units.

(b) The addition of 0.0100 mol of OH^- would change the concentration of acetate ion to 1.01 M and the concentration of acetic acid to 0.99 M. Thus, the concentrations are



$$\frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.82 \times 10^{-5}$$

$$\frac{[\text{H}^+](1.01)}{(0.99)} = 1.82 \times 10^{-5}$$

$$[\text{H}^+] = 1.82 \times 10^{-5} \frac{(0.99)}{(1.01)}$$

$$= 1.78 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.749$$

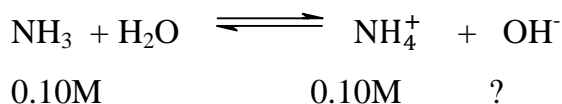
A similar addition to water would cause the pH to rise from 7.0 to 12.0.

Alkaline buffers may also be prepared. If the base and its derived ion are present in equal concentrations,

$$\text{pOH} = \text{pK}_b$$

$$\text{pH} = 14.00 - \text{pK}_b$$

A solution with $[\text{NH}_3] = 0.10 \text{ M}$ and $[\text{NH}_4^+] = 0.10 \text{ M}$ is an example of this type of buffer:



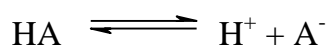
$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

$$[\text{OH}^-] = 1.8 \times 10^{-5} \text{ M}$$

$$\text{pOH} = 4.74$$

$$\text{pH} = 9.26$$

Buffers may also be prepared in which the ratio of the concentration of weak electrolyte to the concentration of common ion is not 1:1; this technique may be used to obtain a buffer that has a pH (or pOH) different from the pK_a of the weak acid (or pK_b of the weak base). Let us assume that a buffer is to be prepared from a hypothetical weak acid, HA:



for which

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a$$

The logarithm of this expression is

$$\text{Log} \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \log K_a$$

which can be also written

$$\log [\text{H}^+] + \log \frac{[\text{A}^-]}{[\text{HA}]} = -\log K_a$$

If we multiply both sides of the equation by -1 , we get

$$-\log [\text{H}^+] - \log \frac{[\text{A}^-]}{[\text{HA}]} = -\log K_a$$

or

$$\text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{pK}_a$$

Upon rearrangement, we get what is called the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (3.6)$$

In general, the ratio of ionic species to molecular species for an effective buffer should be between 1/10 and 10/1. This concentration range is equivalent to the following pH range :

$$\text{pH} = \text{pK}_a + \log \frac{1}{10} = \text{pK}_a + \log 10^{-1}$$

$$= \text{pK}_a - 1$$

$$\text{pH} = \text{pK}_a + \log \frac{10}{1}$$

$$= \text{pK}_a + 1$$

A buffer, therefore, can be prepared with a pH of any value between ($\text{pK}_a + 1$) and ($\text{pK}_a - 1$). An acetic acid-acetate buffer, for example, can be prepared that has any desired pH between 3.74 and 5.74 since the pK_a of acetic acid is 4.74.

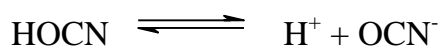
Example 3.8

What concentration should be used to prepare a cyanic acid-cyanate buffer with a pH of 3.50?

Solution

$$\text{pH} = 3.50$$

$$[\text{H}^+] = 3.2 \times 10^{-4} \text{ M}$$



$$\frac{[\text{H}^+][\text{OCN}^-]}{[\text{HOCN}]} = 1.2 \times 10^{-4}$$

$$\frac{(3.2 \times 10^{-4})[\text{OCN}^-]}{[\text{HOCN}]} = 1.2 \times 10^{-4}$$

$$\frac{[\text{OCN}^-]}{[\text{HOCN}]} = \frac{1.2 \times 10^{-4}}{3.2 \times 10^{-4}}$$

$$\frac{[\text{OCN}^-]}{[\text{HOCN}]} = 0.38$$

Any solution in which $[\text{OCN}^-]/[\text{HOCN}]$ is 0.38 will have a pH of 3.50. For example, if $[\text{OCN}^-] = 0.38 \text{ M}$, then $[\text{HOCN}]$ must be 1.00 M ; or if $[\text{OCN}^-] = 0.76 \text{ M}$, $[\text{HOCN}] = 2.00 \text{ M}$.

An alternative solution utilizes the Henderson-Haselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{OCN}^-]}{[\text{HOCN}]}$$

$$3.50 = 3.92 + \log \frac{[\text{OCN}^-]}{[\text{HOCN}]}$$

$$\log \frac{[\text{OCN}^-]}{[\text{HOCN}]} = -0.42$$

$$\frac{[\text{OCN}^-]}{[\text{HOCN}]} = 0.38$$

Example 3.9

What is the pH of a solution made by mixing 100 ml of 0.15 M HCl and 200 ml of 0.20 M aniline ($C_6H_5NH_2$)? Assume that the volume of the final solution is 300 ml.

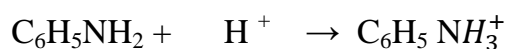
Solution

The number of moles of HCl used and the number of moles of aniline used are

$$? \text{ mol HCl} = 0.015 \text{ mol HCl}$$

$$? \text{ mol aniline} = 0.040 \text{ mol aniline}$$

One mole of aniline reacts with one mole of H^+ . Thus,



$$\text{before reaction: } 0.040 \text{ mol} \quad 0.015 \text{ mol} \quad -$$

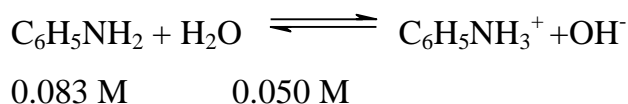
$$\text{after reaction: } 0.025 \text{ mol} \quad - \quad 0.015 \text{ mol}$$

The molar concentrations in the final solution are

$$\begin{aligned} ? \text{ mol } C_6H_5NH_3^+ &= 1000 \text{ ml sol'n} \left(\frac{0.015 \text{ mol } C_6H_5NH_3^+}{300 \text{ ml sol'n}} \right) \\ &= 0.050 \text{ mol } C_6H_5NH_3^+ \end{aligned}$$

$$\begin{aligned} ? \text{ mol } C_6H_5NH_2 &= 1000 \text{ ml sol'n} \frac{0.025 \text{ mol } C_6H_5NH_2}{300 \text{ ml sol'n}} \\ &= 0.083 \text{ mol } C_6H_5NH_2 \end{aligned}$$

Therefore, the concentrations in the solution are



$$\frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = 4.6 \times 10^{-10}$$

$$\frac{(0.050)[OH^-]}{(0.083)} = 4.6 \times 10^{-10}$$

$$[OH^-] = 7.6 \times 10^{-10} \text{ M}$$

$$[H^+] = 1.3 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.89$$

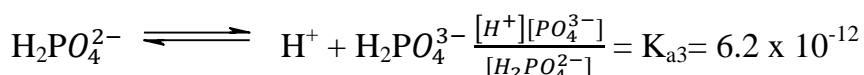
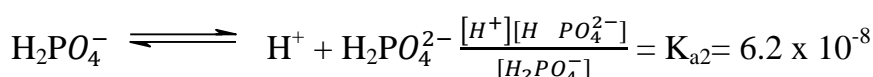
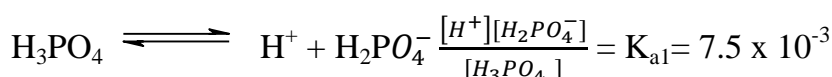
The use of buffers is an important part of many industrial processes. Examples are electroplating and the manufacture of leather, photographic materials, and dyes. In bacteriological research, culture media are generally buffered to maintain the pH required for the growth of the bacteria being

studied. Buffers are used extensively in analytical chemistry and are used to calibrate pH meters. Human blood is buffered to a pH of 7.4 by means of bicarbonate, phosphate, and complex protein systems.

3.7 Polyprotic Acids

Polyprotic acids are acids that contain more than one acid hydrogen per molecule. Examples include sulfuric acid (H_2SO_4), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), phosphoric acid (H_3PO_4), and arsenic acid (H_3AsO_4). Polyprotic acids ionize in a stepwise manner, and there is an ionization constant for each step. Numbers are added to the subscripts of the symbol K_a in order to specify the step to which the constant applies.

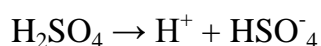
Phosphoric acid is triprotic and ionizes in three steps:



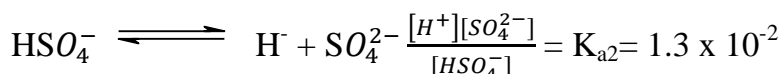
Thus, in a solution of phosphoric acid three equilibria occur together with the water equilibrium.

The ionization of phosphoric acid is typical of all polyprotic acids in that the primary ionization is stronger than the secondary, and the secondary ionization is stronger than the tertiary. This trend in the value of the ionization constant is consistent with the nature of the particle that releases a proton in each step. One would predict that a proton would be released more readily by an uncharged molecule than by an uninegative ion and more, readily by a uninegative ion than by a binegative ion.

No polyprotic acid is known for which all ionizations are complete. The primary ionization of sulfuric acid is essentially complete:



but the secondary ionization is not:

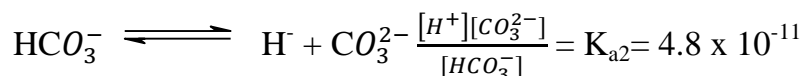


Solutions of carbon dioxide are acidic. Carbon dioxide reacts with water to form carbonic acid, H_2CO_3 . The reaction, however, is not complete most of the carbon dioxide exists in solution as CO_2 molecules. Therefore, we shall indicate the primary ionizations as

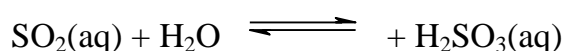


arsenic	$\text{H}_3\text{AsO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{AsO}_4^-$	$K_{a1} = 2.5 \times 10^{-4}$
	$\text{H}_2\text{AsO}_4^- \rightleftharpoons \text{H}^+ + \text{HAsO}_4^{2-}$	$K_{a2} = 5.6 \times 10^{-8}$
	$\text{HAsO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{AsO}_4^{3-}$	$K_{a3} = 3 \times 10^{-13}$
carbonic	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	$K_{a1} = 4.2 \times 10^{-7}$
	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$K_{a2} = 4.8 \times 10^{-11}$
hydrosulfuric	$\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$	$K_{a1} = 1.1 \times 10^{-7}$
	$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$	$K_{a2} = 1.0 \times 10^{-14}$
oxalic	$\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{H}^+ + \text{HC}_2\text{O}_4^-$	$K_{a1} = 5.9 \times 10^{-2}$
	$\text{HC}_2\text{O}_4^- \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4^{2-}$	$K_{a2} = 6.4 \times 10^{-5}$
phosphoric.	$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	$K_{a1} = 4.8 \times 10^{-3}$
	$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$	$K_{a2} = 7.5 \times 10^{-8}$
	$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$	$K_{a3} = 6.2 \times 10^{-12}$
phosphorus (diprotic)	$\text{H}_3\text{PO}_3 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_3^-$	$K_{a1} = 1.6 \times 10^{-2}$
	$\text{H}_2\text{PO}_3^- \rightleftharpoons \text{H}^+ + \text{HPO}_3^{2-}$	$K_{a2} = 7 \times 10^{-7}$
sulfuric	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	Strong
	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$K_{a2} = 1.3 \times 10^{-2}$
sulfurous	$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$K_{a1} = 1.3 \times 10^{-2}$
	$\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$K_{a2} = 5.6 \times 10^{-8}$

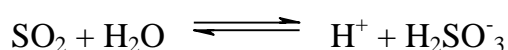
where the symbol $[\text{CO}_2]$ is used to represent the total concentration of $\text{CO}_2(\text{aq})$ and H_2CO_3 . The second ionization step is



An analogous situation exists for solutions of sulfur dioxide in water. The acidity of aqueous SO_2 has been attributed to the ionization of sulfurous acid, H_2SO_3 . However, H_2SO_3 has never been isolated in pure form. In solution it apparently exists in equilibrium with $\text{SO}_2(\text{aq})$:



We shall represent the primary ionization of sulfurous acid as



The ionization constants of some polyprotic acids are listed in previous Table.

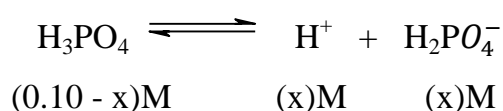
Polyprotic acids form more than one salt. Depending upon the stoichiometric ratio of reactants, the reaction of NaOH and H_2SO_4 yields either the normal salt Na_2SO_4 (sodium sulfate) or the acid salt NaHSO_4 (sodium hydrogen sulfate or sodium bisulfate). Three salts may be derived from phosphoric acid: NaH_2PO_4 (sodium dihydrogen phosphate), Na_2HPO_4 (sodium hydrogen phosphate), and Na_3PO_4 (sodium phosphate).

Example 3.10

Calculate $[\text{H}^+]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{HPO}_4^{2-}]$, $[\text{PO}_4^{3-}]$, and $[\text{H}_3\text{PO}_4]$ in a 0.10 M solution of phosphoric acid.

Solution

The principal source of H^+ is the primary ionization. The H^+ produced by the other ionizations, as well as that from the ionization of water, is negligible in comparison. Furthermore, the concentration of H_2PO_4^- derived from the primary ionization is not significantly diminished by the secondary ionization. Thus, we write



The problem must be solved by means of the quadratic formula since x is not negligible in comparison to 0.10 M:

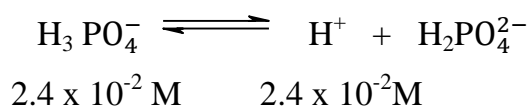
$$\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$\frac{x^2}{(0.10-x)} = 7.5 \times 10^{-3}$$

$$x = [H^+] - [H_2PO_4^-] = 2.4 \times 10^{-2} \text{ M}$$

$$(0.10 - x) - [H_3PO_4] = 7.6 \times 10^{-2} \text{ M}$$

The $[H^+]$ and $[H_2PO_4^-]$ apply to the secondary ionization. Therefore,

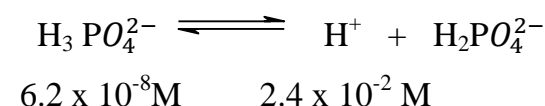


$$\frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$\frac{(2.4 \times 10^{-2})[HPO_4^{2-}]}{(2.4 \times 10^{-2})} = 6.2 \times 10^{-8}$$

$$[HPO_4^{2-}] = 6.2 \times 10^{-8} \text{ M}$$

In any solution of H_3PO_4 that does not contain ions derived from another electrolyte, the concentration of the secondary ion is equal to K_{a2} . For the tertiary ionization,



$$\frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 1 \times 10^{-12}$$

$$\frac{(2.4 \times 10^{-2})[PO_4^{3-}]}{(6.2 \times 10^{-8})} = 1 \times 10^{-12}$$

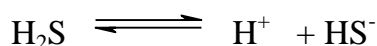
$$[PO_4^{3-}] = 3 \times 10^{-18} \text{ M}$$

Example 3.11

What are $[H^+]$, $[HS^-]$, $[S^{2-}]$, and $[H_2S]$ in a 0.10 M solution of H_2S ?

Solution

K_{a1} for H_2S is 1.1×10^{-7} . Therefore, the small amount of H_2S that ionizes is negligible in comparison with the original concentration of H_2S . In addition, the concentrations of H^+ and HS^- are not significantly altered by the secondary ionization ($K_{a2} = 1.0 \times 10^{-14}$). Thus:



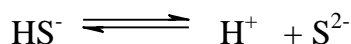
$$0.10\text{M} \quad (x)\text{M} \quad (x)\text{M}$$

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 1.1 \times 10^{-7}$$

$$\frac{x^2}{0.10} = 1.1 \times 10^{-7}$$

$$x = [\text{H}^+] = [\text{HS}^-] = 1.0 \times 10^{-4}\text{M}$$

These concentrations also apply to the secondary ionization:



$$1.0 \times 10^{-4}\text{M} \quad 1.0 \times 10^{-4}\text{M} \quad ?$$

$$\frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = 1.0 \times 10^{-14}$$

$$\frac{(1.0 \times 10^{-4})[\text{S}^{2-}]}{(0.10^{-4})} = 1.0 \times 10^{-14}\text{M}$$

$$[\text{S}^{2-}] = 1.0 \times 10^{-14}\text{M}$$

The concentration of the secondary ion is equal to K_{a2} in any solution of H_2S that does not contain ions derived from another electrolyte;

The product of the expressions for the two ionizations of H_2S is

$$\left(\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \right) \left(\frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} \right) = K_{a1} K_{a2}$$

$$\frac{[\text{H}^+][\text{S}^{2-}]}{[\text{H}_2\text{S}]} = (1.1 \times 10^{-7})(1.0 \times 10^{-14}) = 1.1 \times 10^{-21}$$

This very convenient relationship can be misleading. Superficially it looks as though it applies to a process in which one sulfide ion is produced for every two H^+ ions. However, the ionization of H_2S does not proceed in this manner. In any solution of H_2S , the concentration of $\text{H}^+(\text{aq})$ is much larger than the concentration of sulfide ion (see Example 15.17). The majority of the H_2S molecules that ionize do so only to the HS^- stage, and S^{2-} ions result only from the small ionization of the secondary ion.

At 25°C a saturated solution of H_2S is 0.10 M. For a saturated solution, therefore,

$$\frac{[H^+]^2[S^{2-}]}{(0.10)} = 1.1 \times 10^{-21}$$

$$[H^+]^2[S^{2-}] = 1.1 \times 10^{-22}$$

This relation can be used to calculate the sulfide ion concentration of a solution of known pH that has been saturated with H₂S.

Example 3.11

What is the sulfide ion concentration of a dilute HCl solution that has been saturated with H₂S if the pH of the solution is 3.00?

Solution

Since the pH = 3.00,

$$[H^+] = 1.0 \times 10^{-3} M$$

Therefore,

$$[H^+]^2[S^{2-}] = 1.1 \times 10^{-22}$$

$$(1.0 \times 10^{-3})^2[S^{2-}] = 1.1 \times 10^{-22}$$

$$[S^{2-}] = 1.1 \times 10^{-16} M$$

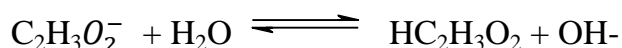
In a saturated solution of pure H₂S (see Example 15.17), $[S^{2-}] = 1.0 \times 10^{-14}$ M. In the H₂S solution described in this problem, the common ion, H⁺, has repressed the ionization of H₂S. In addition, since the solution contains H⁺ ions from a source other than H₂S, [H⁺] does not equal [HS⁻], and consequently [S²⁻] does not equal K_{a2}.

3.8 Ions That Function as Acids and Bases

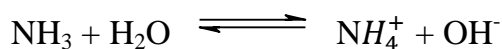
That the anions of polyprotic acids (such as H₂PO₄⁻ and HS⁻) have acidic properties is not surprising. What is perhaps unexpected, however, is that certain ions derived from normal salts (such as C₂H₃O₂⁻, NO₂⁻, NH₄⁺, and Fe³⁺) form acidic or basic solutions:

1. Anions derived from weak acids (such as C₂H₃O₂⁻ and NO₂⁻) form basic solutions.
2. Cations derived from weak bases (such as NH₄⁺ and Fe³⁺) form acidic solutions.

We will consider the anions of weak acids first. In water solution, the acetate ion reacts with water to increase the concentration of OH⁻ ions:

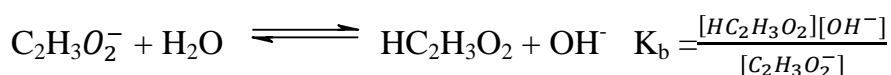
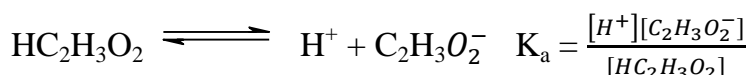


This reaction of the acetate ion is similar to that of any other weak base, such as NH_3 , with water:



The fact that the acetate ion has a charge and the ammonia molecule does not is unimportant. Both species are bases, and both equilibria have corresponding K_b values. The reaction of an ion with water, however, is sometimes called a hydrolysis reaction.

According to the Brønsted theory (see Section 14.3), the acetate ion is the conjugate base of acetic acid. The chemical equations for the two equilibria and corresponding expressions for the equilibrium constants are



The two constants are related in the following way. The product of K_a and K_b is

$$K_a K_b = \left(\frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right) \left(\frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} \right)$$

$$K_a K_b = [\text{H}^+][\text{OH}^-]$$

Since $[\text{H}^+][\text{OH}^-]$ is equal to the water dissociation constant, K_w

$$K_a K_b = K_w. \quad (3.7)$$

This relation provides a convenient way to obtain the value of K_b for the anion derived from a weak acid:

$$K_b = K_w / K_a \quad (3.8)$$

In the case of the K_b for the hydrolysis of the acetate ion,

$$K_b = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$$

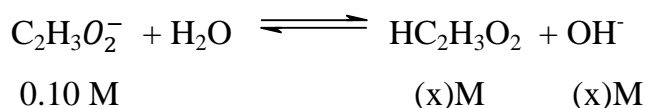
Anions derived from strong acids (such as Cl^- from HCl) and cations derived from strong bases (such as Na^+ from NaOH) do not react with water to affect the pH. An equilibrium of this type (a hydrolysis equilibrium) results only when the ion can form a molecule or ion that is a weak electrolyte in the reaction with water. Strong acids and bases do not exist as molecules in water solution.

Example 3.12

What is the pH of a 0.10 M solution of $\text{NaC}_2\text{H}_3\text{O}_2$?

Solution

The salt $\text{NaC}_2\text{H}_3\text{O}_2$ completely dissociates into Na^+ and $\text{C}_2\text{H}_3\text{O}_2^-$ ions in water solution. The Na^+ ion does not react with H_2O . Let x equal the equilibrium concentration of $\text{HC}_2\text{H}_3\text{O}_2$ that results from the hydrolysis of $\text{C}_2\text{H}_3\text{O}_2^-$ ions:



Since the value of K_b is very small (5.6×10^{-10}), x is small and $[\text{C}_2\text{H}_3\text{O}_2^-]$ may be assumed to be equal to 0.10 M rather than $(0.10 - x)$ M:

$$\frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = K_b$$

$$\frac{x^2}{0.10} = 5.6 \times 10^{-10}$$

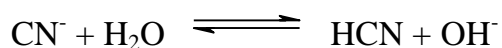
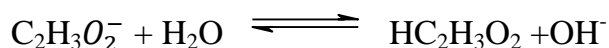
$$x^2 = 5.6 \times 10^{-11}$$

$$x = [\text{HC}_2\text{H}_3\text{O}_2] = [\text{OH}^-] = 7.5 \times 10^{-6} \text{ M}$$

$$\text{pOH} = -\log(7.5 \times 10^{-6}) = 5.12$$

$$\text{pH} = 14.00 - 5.12 = 8.88$$

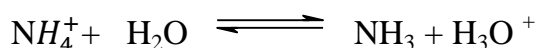
The weaker the electrolyte from which an ion is derived, the more extensive is its reaction with water. A 0.1 M solution of sodium acetate has a pH of 8.9, and the pH of a 0.1 M solution of sodium cyanide is 11.2. In each case it is the hydrolysis of the anion that causes the solution to be alkaline. The sodium ion does not undergo hydrolysis ;



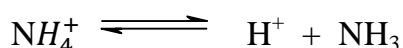
Since HCN ($K_a = 4.0 \times 10^{-10}$) is a weaker electrolyte than $\text{HC}_2\text{H}_3\text{O}_2$ ($K_a = 1.8 \times 10^{-5}$), HCN does a better job of tying up protons than $\text{HC}_2\text{H}_3\text{O}_2$ does. Therefore, the hydrolysis of CN^- is more complete than that of $\text{C}_2\text{H}_3\text{O}_2^-$, and the concentration of OH^- is higher in the NaCN solution than in the $\text{NaC}_2\text{H}_3\text{O}_2$ solution. Note, however, that in both of these systems the position of equilibrium is such that the reverse reaction, which may be regarded as a

neutralization, proceeds to a greater extent than the forward reaction since H_2O is a weaker electrolyte than either HCN or $\text{HC}_2\text{H}_3\text{O}_2$.

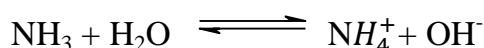
A cation derived from a weak base reacts with water to form an acidic solution. Consider the reaction of the ammonium ion:



This reaction of NH_4^+ is similar to the ionization of any other weak acid such as $\text{HC}_2\text{H}_3\text{O}_2$. If we represent the acid dissociation of NH_4^+ ion our customary way, we get



The equilibrium constant for this system, a K_a , can be derived by using the K_b for the base dissociation of NH_3 , which is the conjugate base of NH_4^+ :



According to the relation

$$K_a K_b = K_w$$

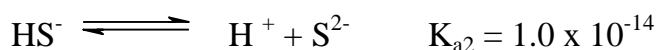
the acid dissociation constant may be found by substitution into

$$K_a = K_w / K_b \quad (3.9)$$

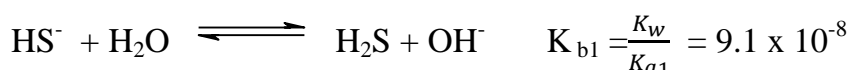
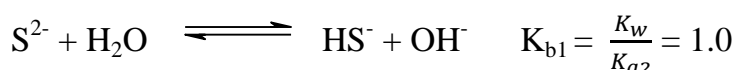
For the $\text{NH}_4^+ / \text{NH}_3$ system,

$$K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$$

The hydrolysis of an anion derived from a weak polyprotic acid proceeds in several steps. The acid dissociation constants for H_2S are



Therefore, the base dissociation constants for the ions are



Notice that the first base dissociation constant is obtained by dividing the water constant by the second acid dissociation constant of H_2S .

In solutions of a soluble sulfide the first step of the hydrolysis of the sulfide ion is so nearly complete that it far overshadows the second, and the

acidity of the solution may be calculated by neglecting the hydrolysis of the HS^- ion.

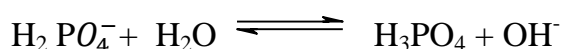
The **pH of a solution** of a normal salt can be predicted on the basis of the strengths of the acid and base from which the salt is derived:

1. **Salt of a strong base and a strong acid.** Examples are: NaCl , KNO_3 , and $\text{Ba}(\text{ClO}_3)_2$. Neither cation nor anion hydrolyzes. The solution has a pH of 7.
2. **Salt of a strong base and a weak acid.** Examples are: KNO_2 , $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, and NaCN . The anion hydrolyzes to produce OH^- ions. The solution has a pH that is higher than 7.
3. **Salt of a weak base and a strong acid.** Examples are: NH_4NO_3 , FeBr_2 , and AlCl_3 . The cation hydrolyzes to produce H_3O^+ ions. The pH of the solution is below 7.
4. **Salt of a weak base and a weak acid.** Examples are: $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, NH_4CN , and $\text{Cu}(\text{NO}_2)_2$. Both cation and anion hydrolyze. The pH of the solution depends upon the extent to which each ion hydrolyzes. The pH of a solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is 7 since NH_3 ($K_b = 1.8 \times 10^{-5}$) and $\text{HC}_2\text{H}_3\text{O}_2$ ($K_a = 1.8 \times 10^{-5}$) are equally weak. The pH of a solution of NH_4CN , on the other hand, is above 7 because HCN ($K_a = 4.0 \times 10^{-10}$) is a weaker acid than NH_3 ($K_b = 1.8 \times 10^{-5}$) is a base. As a consequence, the CN^- hydrolyzes to a greater extent (producing OH^-) than the NH_4 does (producing H_3O^+).

The pH of a solution of an acid salt (such as NaHS , NaH_2PO_4 , Na_2HPO_4 , and NaHCO_3) is affected not only by the hydrolysis of the anion but also by the acid dissociation of the anion. Solutions of these salts may be acidic or alkaline. The two important equilibria in solutions of NaH_2PO_4 , for example, are the acid dissociation of the H_2PO_4^- ion:



and the hydrolysis of the H_2PO_4^- ion:



$$K_{b3} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12}$$

Since the equilibrium constant for the dissociation (which produces H^+) is larger than the equilibrium constant for the hydrolysis (which produces OH^-), a solution of NaH_2PO_4 is acidic.

On the other hand, a solution of Na_2HPO_4 is alkaline. The two pertinent equilibria are



The base dissociation occurs to a greater extent than the acid dissociation, and the pH of the solution is higher than 7.

3.9 Acid-Base Titrations

We are now in a position to study acid-base titrations in some detail. Let us consider the titration of a 50.0 ml sample of 0.100 M HCl with a 0.100 M NaOH solution. Since both HCl and NaOH are strong electrolytes, the only equilibrium to be considered is the water equilibrium.

The concentration of $H^+(aq)$ in the original 50.0ml sample of acid in the titration flask is 0.100 M (or 10^{-1} M). The pH, therefore, is 1.00.

After the addition of 10.0 ml of 0.100 M NaOH from the buret, the equivalent of 40.0ml of 0.100 M HCl remains unneutralized. The number of moles of $H^+(aq)$ in the titration flask, therefore, is

$$? \text{ mol } H^+ = 40.0 \text{ ml } \frac{0.100 \text{ mol } H^+}{1000 \text{ ml}} = 4.00 \times 10^{-3} \text{ mol } H^+$$

The total volume of the solution after the addition is 60.0 ml (which is 6.00×10^{-2} liter), and, therefore,

$$[H^+] = \frac{4.00 \times 10^{-3} \text{ mol } H^+}{6.00 \times 10^{-2} \text{ liter}} = 6.67 \times 10^{-2} \text{ M}$$

$$\text{pH} = 1.18$$

When 50.0 ml of 0.100 M NaOH has been added from the buret, the equivalence point is reached. All the acid is neutralized, and the pH is 7.00.

As NaOH solution is added beyond the equivalence point, the solution in the titration flask becomes increasingly alkaline. When 60.0ml of 0.100 M

NaOH has been added, for example, the solution contains the equivalent of 10.0ml of 0.100 M NaOH:

$$? \text{ mol OH}^- = 10.0 \text{ ml} = \frac{0.100 \text{ mol OH}^-}{1000 \text{ ml}} = 1.00 \times 10^{-3} \text{ mol OH}^-$$

The total volume of the solution at this point is 110.0 ml (which is 1.10×10^{-1} liter), and, therefore,

$$[\text{OH}^-] = \frac{1.00 \times 10^{-3} \text{ mol OH}^-}{1.10 \times 10^{-1} \text{ liter}} = 9.09 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.04$$

$$\text{pH} = 11.96$$

The values in Table 15.6 were obtained from calculations such as these. The data of Table 15.6 are plotted in Figure 15.1. Notice that the curve rises sharply in the section around the equivalence point. Whereas the first 49.9 ml of NaOH solution added causes the pH to change by three units, the next 0.2 ml added causes a change of six units in the pH.

The color-change ranges of three indicators are shown in Figure 3.1. Each indicator exhibits its acid color at pH's below its range and its alkaline color at pH's above its range. In the course of the titration, the pH of the solution changes along the curve from left to right. The end point of the titration is signaled when the indicator changes to its alkaline color.

Any of the three indicators would be satisfactory to use for this titration. The color-change ranges of all three indicators fall in the straight portion of the pH curve where one drop of NaOH solution causes a sharp increase in the pH.

Let us now consider the titration of 50.0 ml of 0.100 M acetic acid - a weak acid - with 0.100 M sodium hydroxide. The concentration of H^+ in the original

Volume of 0.10 M NaOH Added (ml)	pH
0.0	1.00
10.0	1.18
20.0	1.37
30.0	1.60

40.0	1.96
49.0	3.00
49.9	4.00
50.0	7.00
50.1	10.00
51.0	11.00
60.0	11.96
70.0	12.22
80.0	12.36
90.0	12.46
100.0	12.52

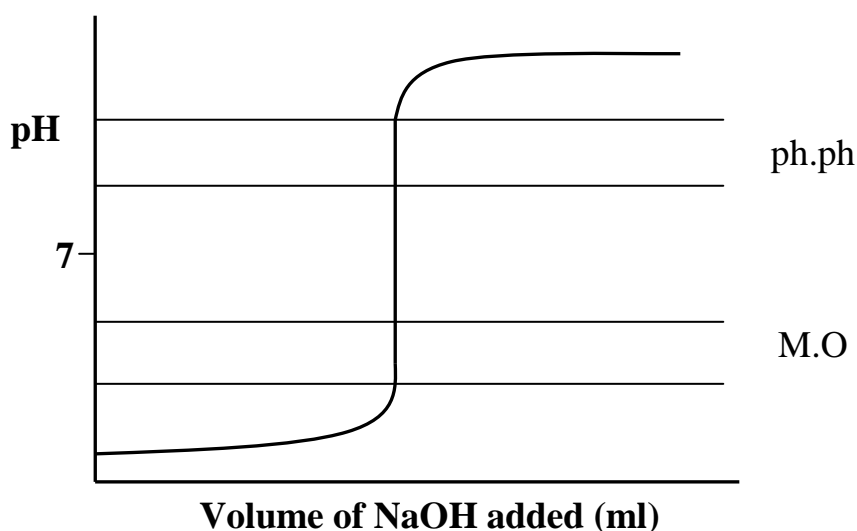


Figure 3.1 Titration of 50.0 ml of 0.100 M HCl with 0.100 M NaOH

50.0 ml sample of acid may be calculated by using the equilibrium constant of acetic acid (see Example 15.2). From Table 15.1 we see that $[H^+] = 1.34 \times 10^{-3}$ M. The pH of the solution is therefore 2.87.

The solution resulting from the addition of 10.0 ml of 0.100 M NaOH to the 50.0ml sample of 0.100 M $HC_2H_3O_2$ is, in effect, a buffer since it contains a mixture of $C_2H_3O_2^-$ ions, produced by the neutralization, together with un-neutralized $HC_2H_3O_2$. The pH of a buffer is conveniently calculated by the use of the relation

$$\text{pH} = \text{pK}_a + \log \frac{[A^-]}{[HA]} \quad (3.6)$$

which was derived in Section 15.6. For acetic acid the pK_a is 4.74 (the negative logarithm of 1.8×10^{-5}). The ratio $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$ is easily calculated. After 10.0 ml of NaOH is added, 10/50 of the acid of the original 50.0 ml sample has been neutralized; it has, in effect, been converted into the salt sodium acetate. Since 40/50 of the acid remains unneutralized, the ratio is 1 to 4. Thus,

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log \left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right) \\ &= 4.74 + \log(1/4) \\ &= 4.14 \end{aligned}$$

At the equivalence point all of the acid has been neutralized, and the solution (100 ml) is effectively 0.0500 M in sodium acetate. The calculation of the pH of

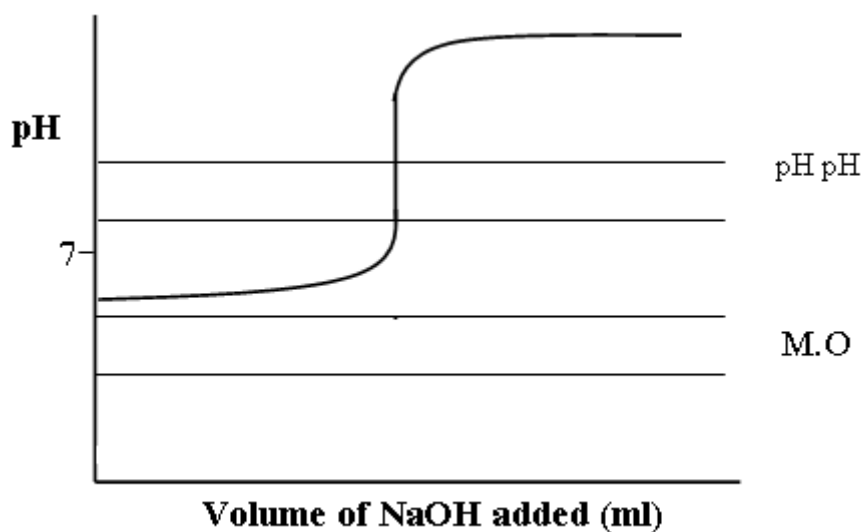
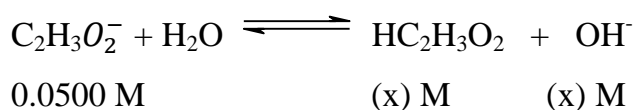


Figure 3.2 Titration of 50.0 ml of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.100 M NaOH

this solution must take into account the hydrolysis of the $\text{C}_2\text{H}_3\text{O}_2^-$ ion (see Example 15.19):



$$\frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = 5.56 \times 10^{-10}$$

$$\frac{x^2}{5.00 \times 10^{-2}} = 5.56 \times 10^{-10}$$

$$x = [\text{OH}^-] = 5.27 \times 10^{-6}$$

$$\text{pOH} = 5.28$$

$$\text{pH} = 8.72$$

Notice that the equivalence point in this titration does not occur at a pH of 7.

After the equivalence point the addition of NaOH causes the solution to become increasingly alkaline. The added OH^- shifts the hydrolysis equilibrium to the left. The effect of the hydrolysis on the pH is negligible. Thus, the calculations from this point on are identical to those for the HCl-NaOH titration.

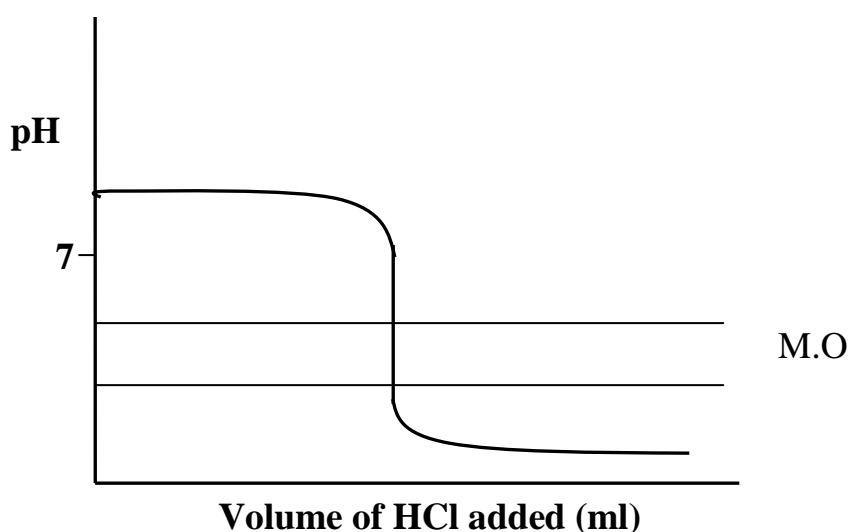


Figure 3.3: Titration of 50.0 ml of 0.100 M NH_3 with 0.100 M HCl

the curve around the equivalence point is reduced in length. From the curve of Figure 15.2 we can see that methyl orange is not a suitable indicator for this titration. Neither is bromthymol blue suitable, since its color change would start after 47.34ml of NaOH has been added and continue until 49.97 ml has been added, which would hardly constitute a sharp end point for a titration. Phenolphthalein, however, would be a satisfactory indicator to employ.

Other titration curves may be drawn following the general line of approach outlined here. Figure 3.3 represents the titration curve for the titration

of 50.0 ml of 0.100 M NH_3 with 0.100 M HCl . In this instance methyl orange could be used as the indicator. Figure 3.4 is the titration curve for the titration of 50.0 ml of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.100 M NH_3 ; both solutes are weak electrolytes. No indicator can be found that would function satisfactorily for this titration, and such titrations - between weak electrolytes - are not usually run.

Titration may be conducted potentiometrically. For example, a titration may be performed with the electrodes of a pH meter immersed in the solution being analyzed. The pH of the solution is determined after successive additions of reagent. The equivalence point of the titration is indicated by an abrupt change in the pH, but additions and readings are continued beyond this point. The equivalence point may be determined by graphing the data and estimating the volume corresponding to the midpoint of the steeply rising portion of the titration curve.

The potentiometric titration of a weak electrolyte serves as an important method of determining the dissociation constant of the electrolyte. Since

$$\text{pH} = \text{pK}_a + \log ([\text{A}^-] / [\text{HA}]) \quad (3.6)$$

the pK_a of the electrolyte is equal to the pH of the solution at half neutralization

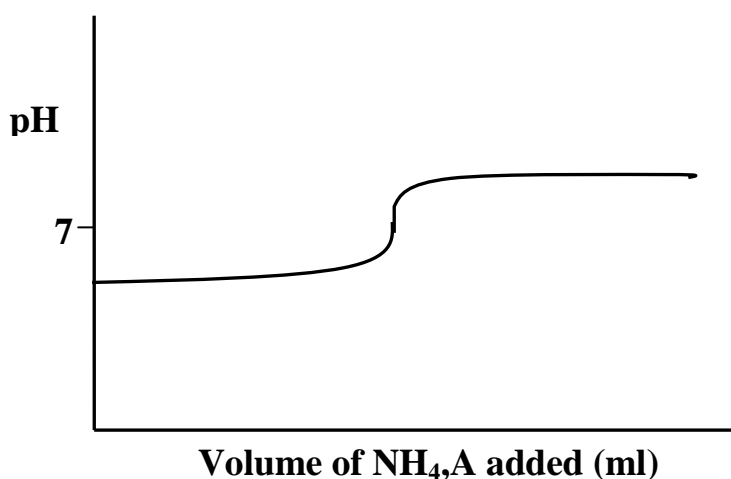


Figure 3.4: Titration of 50.0 ml of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.100 M NH_3 (where $[\text{A}^-] = [\text{HA}]$), but the pK_a , and hence the K_a itself, may be determined from any point on the titration curve.

Example 3.13

The equivalence point in the titration of 40.00 ml of a solution of a weak monoprotic acid occurs when 35.00 ml of a 0.100 M NaOH solution has been added. The pH of the solution is 5.75 after 20.00 ml of the NaOH solution has been added. What is the dissociation constant of the acid?

Solution

Since 35.00ml of NaOH solution is required for complete neutralization, the acid is 20/35 neutralized after 20.00 ml of NaOH has been added. In other words, 15/35 of the acid is in the form HA, and 20/35 is in the form A^- . The ratio $[\text{A}^-]/[\text{HA}]$ is therefore 20 to 15, or 1.33;

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$$5.75 = \text{pK}_a + \log(1.33)$$

$$\text{pK}_a = 5.63$$

$$\text{K}_a = 2.4 \times 10^{-6}$$

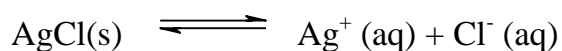
CHAPTER 4

Part II: Ionic Equilibrium

Homogeneous, aqueous equilibrium systems involving weak acids and bases were discussed in part I, Chapter 3. This chapter begins with a study of **heterogeneous systems** in which slightly soluble solids are in equilibrium with their constituent ions in solution. Equilibrium principles apply to the precipitation of such solids in the qualitative or quantitative determinations of dissolved ions. Several additional types of homogeneous systems are also considered, including the equilibria that occur in the formation of complex ions in solution and equilibria associated with amphoteric substances.

4.1 The Solubility Product

Most substances are soluble in water to at least some slight extent. If an "insoluble" or "slightly soluble" material is placed in water, an equilibrium is established when the rate of dissolution of ions from the solid equals the rate of precipitation of ions from the saturated solution. Thus, equilibrium exists between solid silver chloride and a saturated solution of silver chloride:



The equilibrium constant is

$$K' = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

Since the concentration of a pure solid is a constant, $[\text{AgCl}]$ may be combined with K' to give

$$K_{\text{sp}} = K[\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$$

The constant K_{sp} is called a solubility product. The ionic concentrations of the expression are those for a saturated solution at the reference temperature. Since the solubility of a salt usually varies widely with temperature, the numerical value for K_{sp} for a salt changes with temperature. A table of solubility products at 25°C is given in the appendix.

The numerical value of K_{sp} for a salt may be found from the molar solubility of the salt.

Example 4.1

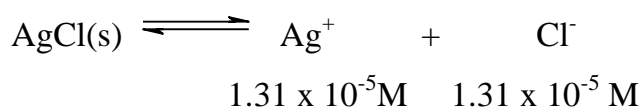
At 25°C, 0.00188 g of AgCl dissolves in 1 liter of water. What is the K_{SP} of AgCl?

Solution

The molar solubility of AgCl (molecular weight, 143) is

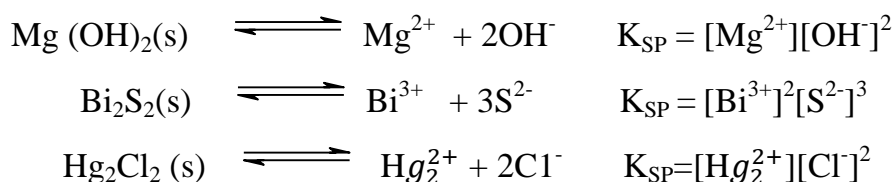
$$\begin{aligned} ? \text{ mol AgCl} &= 0.00188 \text{ g AgCl} \frac{1 \text{ mol AgCl}}{143 \text{ g AgCl}} \\ &= 1.31 \times 10^{-5} \text{ mol AgCl} \end{aligned}$$

For each mole of AgCl dissolving, 1 mol of Ag^+ and 1 mol of Cl^- are formed:



$$\begin{aligned} K_{sp} &= [\text{Ag}^+][\text{Cl}^-] \\ &= (1.31 \times 10^{-5})^2 \\ &= 1.7 \times 10^{-10} \end{aligned}$$

For salts that have more than two ions per formula unit, the ion concentrations must be raised to the powers indicated by the coefficients of the balanced chemical equation:



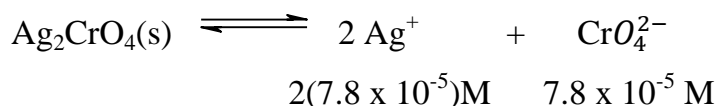
For a salt of this type the calculation of the A''_{SP} from the molar solubility requires that the chemical equation representing the dissociation process be carefully interpreted.

Example 4.2

At 25°C, 7.8×10^{-5} mol of silver chromate dissolves in 1 liter of water. What is the K_{SP} of Ag_2CrO_4 ?

Solution

For each mole of Ag_2CrO_4 that dissolves, 2 mol of Ag^+ and 1 mol of CrO_4^{2-} are formed. Therefore,

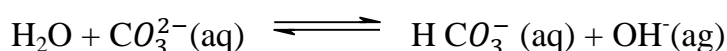


$$\begin{aligned}
 K_{sp} &= [Ag^+]^2[CrO_4^{2-}] \\
 &= (1.56 \times 10^{-4})^2(7.8 \times 10^{-5}) \\
 &= 1.9 \times 10^{-12}
 \end{aligned}$$

The solubilities of some salts in water are slightly higher than those predicted by calculations based on the K_{sp} values. Consider the barium carbonate system

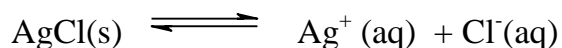


The carbonate ion in this solution undergoes hydrolysis since it is a weak base.

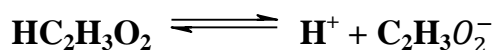


The concentration of the CO_3^{2-} ion is reduced by this reaction with water, the $BaCO_3$ equilibrium is forced to the right, and more $BaCO_3$ dissolves than would otherwise be the case. A calculation of molar solubility based on the K_{sp} for $BaCO_3$ would give the concentration of CO_3^{2-} that must be present in the solution at equilibrium. More than the corresponding amount of $BaCO_3$ must dissolve, however, in order to provide not only this concentration of CO_3^{2-} but also the CO_3^{2-} that is converted into HCO_3^- by hydrolysis. In the solutions of some salts (PbS , for example) both cation and anion hydrolyze.

The salt effect is another factor that may cause a calculated solubility to be in error. The solubility of a salt is increased by the addition of another electrolyte to the solution. Silver chloride, for example, is about 20% more soluble in 0.02 M KNO_3 solutions than it is in pure water:



The K^+ and NO_3^- ions help create an ionic atmosphere in the solution so that Ag^+ and Cl^- ions are surrounded by ions of opposite charges. As a result, the Ag^+ and Cl^- ions are held in solution more firmly and are less apt to recombine to form $AgCl(s)$. The net effect is that the solubility equilibrium shifts to the right. Other types of ionic equilibria are influenced by the salt effect. A 0.10 M solution of acetic acid in pure water is 1.3% ionized:



A 0.10 M solution of acetic acid in 0.10 M NaCl is 1.7% ionized.

Interionic attractions, therefore, make a solution behave as though its ion concentrations were less than they actually are. The activity of an ion, its "effective concentration," is obtained by correcting the actual ion concentration to take interionic attractions into account. Equilibrium constants are properly expressed in terms of activities, rather than concentrations.

4.2 Precipitation and the Solubility Product

The numerical value of the K_{SP} of a salt is a quantitative statement of the limit of solubility of the salt. When the values for the concentrations of the ions of a salt solution are substituted into an expression similar to that for the K_{SP} of the salt, the result is called the ion product of the solution. The K_{SP} is the ion product of a saturated solution.

We can calculate an ion product for a test solution and compare the result to the K_{SP} for the salt under consideration. Three types of comparisons are possible:

1. **The ion product is less than the K_{SP} .** This solution is unsaturated.

Additional solid can be dissolved in it up to the limit described by the K_{SP} .

2. **The ion product is greater than the K_{SP} .** The solution is momentarily supersaturated. Precipitation will occur until the ion product equals the K_{SP} .

3. **The ion product equals the K_{SP} .** This solution is saturated.

The following examples illustrate the application of this method.

Example 4.3

Will a precipitate form if 10 ml of 0.010 M AgNO_3 and 10 ml of 0.00010 M NaCl are mixed? Assume that the final volume of the solution is 20 ml. For AgCl ,

$$K_{SP} = 1.7 \times 10^{-10}.$$

Solution

Diluting a solution to twice its original volume reduces the concentrations of ions in the solution to half their original value. If there were no reaction, the ion concentrations would be

$$[\text{Ag}^+] = 5.0 \times 10^{-3} \text{ M}$$

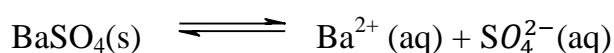
$$[\text{Cl}^-] = 5.0 \times 10^{-5} \text{ M}$$

The ion product is

$$(5.0 \times 10^{-3})(5.0 \times 10^{-5}) = 2.5 \times 10^{-7}$$

Since the ion product is larger than the K_{sp} (1.7×10^{-10}), precipitation of AgCl should occur.

The common-ion effect pertains to solubility equilibria. As an example, consider the system



The addition of sulfate ion, from sodium sulfate, to a saturated solution of barium sulfate will cause the equilibrium to shift to the left; the concentration of Ba^{2+} will decrease, and BaSO_4 will precipitate. Since the product $[\text{Ba}^{2+}][\text{SO}_4^{2-}]$ is a constant, increasing $[\text{SO}_4^{2-}]$ will cause $[\text{Ba}^{2+}]$ to decrease.

The amount of barium ion in a solution may be determined by precipitating the Ba^{2+} as BaSO_4 . The precipitate is then removed by filtration and is dried and weighed. The concentration of Ba^{2+} left in solution after the precipitation may be reduced to a very low value if excess sulfate ion is employed in the precipitation. As a general rule, however, too large an excess of the common ion should be avoided. At high ionic concentrations the salt effect increases the solubility of a salt, and for certain precipitates the formation of a complex ion may lead to enhanced solubility.

Example 4.4

At 25°C a saturated solution of BaSO_4 is $3.9 \times 10^{-5} \text{ M}$. The K_{sp} of BaSO_4 is 1.5×10^{-9} . What is the solubility of BaSO_4 in $0.050 \text{ M Na}_2\text{SO}_4$?

Solution

The SO_4^{2-} derived from the BaSO_4 is negligible in comparison to the $[\text{SO}_4^{2-}]$ already present in the solution ($5.0 \times 10^{-2} \text{ M}$):

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$$

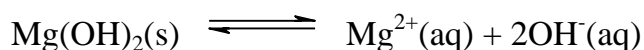
$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.5 \times 10^{-9}$$

$$[\text{Ba}^{2+}](5.0 \times 10^{-2}) = 1.5 \times 10^{-9}$$

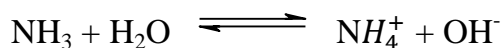
$$[\text{Ba}^{2+}] = 3.0 \times 10^{-8} \text{ M}$$

The solubility of BaSO_4 has been reduced from $3.9 \times 10^{-5} \text{ M}$ to $3.0 \times 10^{-8} \text{ M}$ by the common-ion effect.

At times, the common-ion effect is used to prevent the formation of a precipitate. Consider the precipitation of magnesium hydroxide from a solution that contains Mg^{2+} ions:



The precipitation can be prevented by holding the concentration of OH^{-} to a low value. If the hydroxide ion is supplied by the weak base ammonia



the concentration of OH^{-} can be controlled by the addition of NH_4^{+} . When the common ion NH_4^{+} is added, the ammonia equilibrium shifts to the left, which reduces the concentration of OH^{-} . In this way, the concentration of OH^{-} can be held to a level that will not cause $\text{Mg}(\text{OH})_2$ to precipitate.

Chapter 3

Thermochemistry

In the course of a chemical reaction, energy is either liberated or absorbed. Calculations relating to these energy changes are as important as those concerned with the masses of reacting substances. Thermochemistry is the study of the heat released or absorbed by chemical and physical changes. In succeeding chapters, calculations involving these energy changes will be frequently encountered. In this chapter, this type of calculation will be introduced.

3.1 Energy Measurement

It is common to think of force as the application of physical strength—as pushing. If the effects of friction are neglected, a body in motion remains in motion at a constant velocity, and a body at rest stays at rest (its velocity is zero). If these bodies are pushed, there will be a change in their velocities. The increase in velocity per unit time is called the acceleration.

Suppose, for example, that we have a body moving at a velocity of 1 m/s. Assume that this body is acted on by a constant force, that is, given a sustained push. The body will move faster and faster. At the end of 1 second it may be moving at the rate of 2 m/s. At the end of 2 s, its speed may be 3 m/s. If the body picks up speed at the rate of one meter per second in a second, its acceleration is said to be 1 m/s².

A force that gives a *one gram* body an acceleration of 1 m/s² is not so large as a force that gives a *one kilogram* body the same acceleration. The magnitude of a force (F), therefore, is proportional to the mass of the body (m) as well as to the acceleration (a) that the force produces:

$$F = ma$$

The SI unit of force is called the newton (symbol, N) and is derived from the base units of mass (the kilogram), length (the meter), and time (the second):

$$F = ma \quad (3.1)$$

$$1 \text{ N} = (1 \text{ kg})(1 \text{ m/s}^2)$$

$$1 \text{ N} = 1 \text{ kg}\cdot\text{m/s}^2$$

Work (W) is defined as the force times the distance through which the force acts (d).

$$W = Fd \quad (3.2)$$

In the International System, the unit of work is the joule (symbol, J). The joule is defined as the work done when a force of one newton acts through a distance of one meter:

$$W = Fd$$

$$1 \text{ J} = (1 \text{ N})(1 \text{ m})$$

$$= 1 \text{ N}\cdot\text{m}$$

$$= 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

Energy may be defined as the capacity to do work. There are many forms of energy, such as heat energy, electrical energy, and chemical energy. When one form of energy is converted into another form, energy is neither created nor destroyed. The SI unit of work, the joule, is the unit used for all energy measurements, including heat measurements. The unit is named in honor of James Joule (1818-1889), a student of John Dalton, who demonstrated that a given quantity of work always produces the same quantity of heat.

3.2 Temperature and Heat

Most liquids expand as the temperature increases. The mercury thermometer is designed to use the expansion of mercury to measure

temperature. The thermometer consists of a small bulb sealed to a tube that has a narrow bore (called a capillary tube). The bulb and part of the tube contain mercury, the space above the mercury is evacuated, and the upper end of the tube is sealed. When the temperature increases, the mercury expands and rises in the capillary tube.

The Celsius temperature scale, named for Anders Celsius, a Swedish astronomer, is employed in scientific studies and is part of the International System. The scale is based on the assignment of 0°C to the normal freezing point of water and 100°C to the normal boiling point of water. When a thermometer is placed in a mixture of ice and water, the mercury will stand at a height that is marked on the tube as 0°C . When the thermometer is placed in boiling water under standard atmospheric pressure, the mercury will rise to a position that is marked 100°C . The tube is marked between these two fixed points to indicate 100 equal divisions, each of which represents one degree. The thermometer is calibrated below 0°C and above 100°C by marking off degrees of the same size. The Celsius scale was formerly called the centigrade scale, derived from the Latin words *centum* (a hundred) and *gradus* (a degree).

On the Fahrenheit temperature scale (named for G. Daniel Fahrenheit, a German instrument maker) the normal freezing point of water is 32°F and the normal boiling point of water is 212°F . Since there are 100 Celsius degrees and 180 (212 minus 32) Fahrenheit degrees between these two fixed points, 5 Celsius degrees equal 9 Fahrenheit degrees.

The Fahrenheit temperature scale is not used in scientific work. Conversion of a temperature from the Fahrenheit scale (T_f) to the Celsius scale (t_c) can be accomplished in the following way:

1. Subtract 32 from the Fahrenheit reading. The value obtained tells how many Fahrenheit degrees the temperature is above the freezing point of water.

2. Since 5 Celsius degrees equal 9 Fahrenheit degrees, 5/9 of the value obtained is the number of Celsius degrees above the freezing point of water, which is 0°C.

Hence,

$$t_c = \frac{5^{\circ}\text{C}}{9^{\circ}\text{C}} (t_F - 32^{\circ}\text{F}) \quad (3.3)$$

In Figure 3.1, the two temperature scales are compared. The thermodynamic temperature scale, called the Kelvin scale, is described in Section 8.3,

Temperature is defined as the degree of hotness. Heat, on the other hand, is a form of energy. In the past, chemists have customarily measured heat in calories. The specific heat of a substance is defined as the amount of heat required to raise the temperature of 1 g of the substance by 1°C. The calorie was originally defined in terms of the specific heat of water. The one-degree temperature interval had to be specified, however, since the specific heat of water changes slightly as the temperature changes. For many years, the calorie was defined as the amount of heat required to raise the temperature of 1 g of water from 14.5°C to 15.5°C.

Very precise determinations of heat energy, in joules, can be made by electrical measurements. The joule, therefore, is a better primary standard of heat than the specific heat of water. The calorie is now defined by its joule equivalent:

$$1 \text{ cal} = 4.184 \text{ J (exactly)}$$

Several points should be noted:

1. The joule and the calorie are relatively small units for measurement of thermochemical values. Such values are frequently reported in kilojoules (a kJ is 1000 J) and kilocalories (a kcal is 1000 cal).

2. The International Committee of Weights and Measures recommends that all energy measurements be based on the joule and that the calorie no longer be used. In the past, however, thermochemical values have customarily been recorded in calories and kilocalories.

a. To convert a value given in *calories to joules*, multiply by (4.184J/1 cal).

b. To convert a value given in *kilocalories to kilojoules*, multiply by (4.184 kJ/1 kcal).

3. For our purposes, the specific heat of water can be considered to be a constant, 4.184J/(g°C) or 1.000cal/(g°C), over any temperature interval between the freezing point and boiling point of water.

3.3 Calorimetry

The heat capacity (C) of a given mass of a substance is the amount of heat required to raise the temperature of the mass by 1°C. Specific heat is the heat capacity of *one gram* of a substance the amount -of heat required to raise the temperature of 1 g of the substance by 1°C Therefore,

$$C = (\text{mass}) (\text{specific heat}) \quad (3.4)$$

Since the specific heat of water is 4.184 J/(g°C), the heat capacity of 500 g of water is

$$C = [500\text{g}][4.18\text{J}/(\text{g}^\circ\text{C})]$$

$$= 2090 \text{ J}/^\circ\text{C} = 2.09 \text{ kJ}/^\circ\text{C}$$

This sample absorbs 2.09 kJ of heat for each degree that the temperature increases. Twice this amount of heat would be required to raise the temperature by 2°C. In general,

$$q = C(t_2 - t_1)$$

where q is the heat absorbed by the sample, C is the heat capacity of the sample, t_2 is the final temperature, and t_1 is the initial temperature. The

heat absorbed by a 500-g sample of water when it is heated from 20.00°C to 25.00°C can be calculated in the following way:

$$\begin{aligned}
 q &= C(t_2 - t_1) & (3.5) \\
 &= (2.09 \text{ kJ/}^\circ\text{C})(25.00^\circ\text{C} - 20.00^\circ\text{C}) \\
 &= (2509 \text{ kJ/}^\circ\text{C})(5.00^\circ\text{C}) \\
 &= 10.4 \text{ kJ}
 \end{aligned}$$

A device called a calorimeter is used to measure the heat changes that accompany chemical reactions. A calorimeter consists of a vessel, in which the reaction is conducted, submerged in a weighed quantity of water in a well-insulated container. The reaction is run using known quantities of reactants, and the heat evolved by the reaction increases the temperature of the water and the calorimeter. The amount of heat liberated by the reaction can be calculated from the increase in temperature if the total heat capacity of the calorimeter and its contents is known.

Example 3.1

A bomb type of calorimeter (Figure 3.2) is used to measure the heat evolved by the combustion of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$:



A 3.00-g sample of glucose is placed in the bomb, which is then filled with oxygen gas under pressure. The bomb is placed in a well-insulated calorimeter vessel that is filled with 1.20 kg of water. The initial temperature of the assembly is 19.00°C. The reaction mixture is ignited by the electrical heating of a wire within the bomb. The reaction causes the temperature of the calorimeter and its contents to increase to 25.50°C. The heat capacity of the calorimeter is 2.21 kJ/°C. The molecular weight of glucose is 180. How much heat is evolved by the combustion of 1 mol of glucose?

Solution

Since 1200 g of water is employed and the specific heat of water is 4.13 J/(g°C), the heat capacity of the water in the calorimeter, $C_{\text{H}_2\text{O}}$, is

$$\begin{aligned} C &= (\text{mass})(\text{specific heat}) \\ C_{\text{H}_2\text{O}} &= [1200\text{g}][4.18\text{J}/(\text{g}^\circ\text{C})] \\ &= 5016 \text{ J}/^\circ\text{C} = 5.02 \text{ kJ}/^\circ\text{C} \end{aligned}$$

The heat capacity of the calorimeter, C_{cat} , is 2.21 kJ/°C. The total heat capacity, C_{total} is . .

$$\begin{aligned} C_{\text{total}} &= C_{\text{H}_2\text{O}} + C_{\text{cal}} \\ &= 5.02\text{kJ}/^\circ\text{C} + 2.21 \text{ kJ}/^\circ\text{C} \\ &= 7.23 \text{ kJ}/^\circ\text{C} \end{aligned}$$

Thus, 7.23 kJ of heat is needed to raise the temperature of the assembly by 1°C. The amount of heat *absorbed* by the calorimeter and the water is

$$\begin{aligned} q &= C(t_2 - t_1) \\ &= (7.23 \text{ kJ}/^\circ\text{C})(25.50^\circ\text{C} - 19.00^\circ\text{C}) \\ &= (7.23 \text{ kJ}/^\circ\text{C})(6.50^\circ\text{C}) \\ &= 47.0 \text{ kJ} \end{aligned}$$

This quantity (47.0 kJ) is also the amount of heat *evolved* by the combustion of 3.00 g of glucose. Therefore,

$$47.0 \text{ kJ} = 3.00\text{g } \text{C}_6\text{H}_{12}\text{O}_6$$

For a mol of glucose (180 g of glucose), the quantity of heat evolved is

$$? \text{kJ} = 180\text{g } \text{C}_6\text{H}_{12}\text{O}_6 \left(\frac{47.0 \text{ kJ}}{3.00\text{g } \text{C}_6\text{H}_{12}\text{O}_6} \right) = 2.82 \times 10^3 \text{ kJ}$$

3.4 Thermochemical Equations

If a reaction that produces a gas is run in a closed container, the pressure inside the container will increase. Most reactions, however, are run in containers that are open to the atmosphere. For these reactions, the pressure is constant whether gases are produced or not.

The heat liberated or absorbed by reactions that are conducted under constant pressure can be related to a property that is called enthalpy and is given the symbol H . Every pure substance is assumed to have an enthalpy (which is also called a heat content). A given set of reactants, therefore, has a definite total enthalpy, $H_{\text{reactants}}$. The corresponding set of products also has a definite total enthalpy, H_{products} . The heat of reaction is the difference between these enthalpies and is therefore given the symbol ΔH . The upper case Greek delta, Δ , is used to indicate a difference:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Reactions that liberate heat are called exothermic reactions. For reactions of this type, the products have a lower enthalpy than the reactants; ΔH is a negative value. When the reaction occurs, the products replace the reactants **in** the system. The enthalpy of the reaction system declines (ΔH is negative), and the difference is given off as heat (see Figure 3).

Reactions that absorb heat are called endothermic reactions. For reactions of this type, the enthalpy of the products is higher than the enthalpy of the reactants, and ΔH is positive. When the reaction occurs, heat must be supplied in order to raise the enthalpy of the system (see Figure 4).

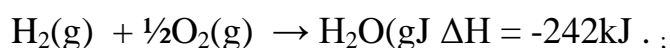
The enthalpies of chemical substances depend upon temperature and pressure. By convention, ΔH values are usually reported for reactions run at 25°C and standard atmospheric pressure. If any other conditions are employed, they are noted.

Thermochemical data may be given by writing a chemical equation for the reaction under consideration and listing beside it the ΔH value for the reaction *as it is written*. The appropriate value of ΔH is the one required when the equation is read in molar quantities. Contrary to usual practice, fractional coefficients may be used to balance the chemical equation. A fractional coefficient simply indicates a fraction of a mole of a substance. Thus,



When 1 mol of hydrogen gas reacts with 1 mol of oxygen gas to produce 1 mol of liquid water, 286 kJ of heat is evolved.

The state of each substance in the reaction must be indicated in the equation. A designation, such as (g) for gas, (s) for solid, (l) for liquid, or (aq) for "in aqueous solution," is placed after each formula. The need for this convention can be demonstrated by comparing the following equation with the preceding one:



Notice that 44 kJ less heat is liberated by the second reaction than by the first reaction. This quantity of heat is used to convert 1 mol of $\text{H}_2\text{O}(\text{l})$ to 1 mol of $\text{H}_2\text{O}(\text{g})$.

When an equation is reversed, the sign of ΔH is changed. A reaction that is endothermic in one direction is exothermic in the opposite direction:



If the coefficients of the substances in a chemical equation are multiplied by a factor, the ΔH value must be multiplied by the same factor. For example, if the

Last equation is multiplied through by 2, the ΔH value must also be multiplied by 2:



In like manner, the coefficients of an equation and the ΔH value can be divided by the same number.

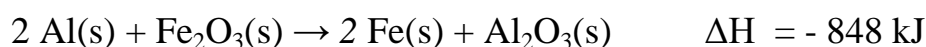
The conventions for writing thermochemical equations can be summarized as follows:

1. For exothermic reactions (the reaction system loses heat), ΔH is negative. For endothermic reactions (the reaction system absorbs heat), ΔH is positive.
2. Unless otherwise noted, ΔH values are given for reactions run at 25°C and standard atmospheric pressure.
3. Designations such as (g), (s), (l), and (aq) are placed behind the formulas in the equation to indicate the physical state of each substance.
4. The coefficients of the substances of the chemical equation indicate the number of moles of each substance involved in the reaction (fractions may be used), and the ΔH value given corresponds to these quantities of materials.
5. If the coefficients in the chemical equation are multiplied or divided by a factor, the ΔH value must be multiplied or divided by the same factor,
6. When a chemical equation is reversed, the sign but not the magnitude of the ΔH value is changed.

Thermochemical problems are solved in much the same way that simple stoichiometric problems are solved.

Example 3.2

The thermite reaction is highly exothermic:



How much heat is liberated when 36.0 g of Al reacts with excess Fe_2O_3 ?

Solution

The equation and ΔH value show that

$$-848 \text{ kJ} = 2 \text{ mol Al}$$

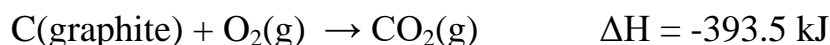
Since the atomic weight of Al is 27.0,

$$? \text{ kJ} = 36.0 \text{ g Al} \left(\left(\frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \right) \left(\frac{-848 \text{ kJ}}{2 \text{ mol Al}} \right) \right) = -565 \text{ kJ}$$

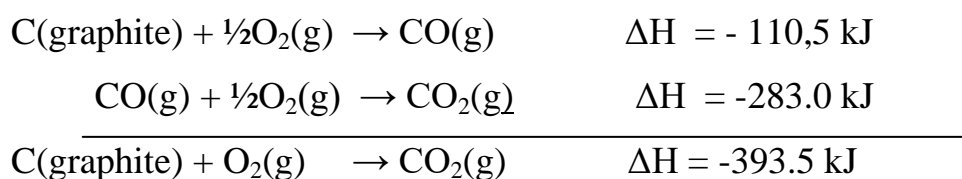
3.5 The Law of Hess

The basis of many thermochemical calculations is the law of constant heat summation, which was established experimentally by G. H. Hess in 1840. This law of Hess states that the change in enthalpy for any chemical reaction is constant, whether the reaction occurs in one step or in several steps. Thermochemical data, therefore, may be treated algebraically.

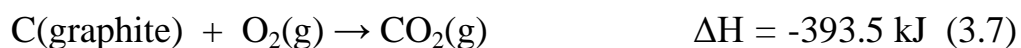
Consider, for example, the reaction of graphite with oxygen that produces carbon dioxide gas:



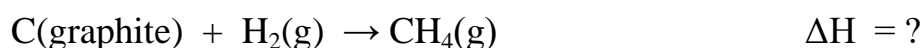
This transformation also can occur in two steps: the reaction of graphite with O_2 that forms CO followed by the reaction of the CO with O_2 that forms CO_2 . Addition of the equations for the steps gives a result that is identical with the equation for the direct reaction (see Figure 3.5).



Since thermochemical data can be treated algebraically, it is possible to derive an enthalpy of reaction from measurements made on other reactions. Suppose, for example, that the following thermochemical equations are given:



These relations can be used to find the ΔH for the reaction in which methane, CH_4 , is prepared from carbon and hydrogen. This enthalpy change cannot be measured directly:



Since 1 mol of C(graphite) appears on the left of equation (3.7) and *also* on the left of the desired equation, equation (3.7) is written as previously given:



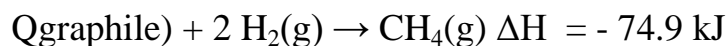
Two moles of $\text{H}_2(\text{g})$ appear on the left of the desired equation and only 1 mol of $\text{H}_2(\text{g})$ appears on the left of equation (3.8). Equation (3.8), therefore, is multiplied through by 2, and the ΔH value is multiplied by 2:



One mole of $\text{CH}_4(\text{g})$ appears on the *right* side of the desired equation. Therefore, equation (3.9) is reversed, and the sign of the ΔH value is changed:



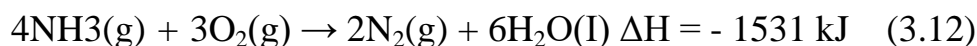
Equations (3.7), (3.10), and (3.11) are added. Terms common to both sides of the final equation (2O_2 , CO_2 , and $2\text{H}_2\text{O}$) are canceled.

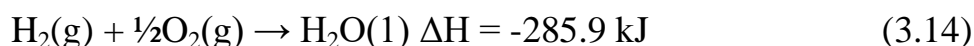
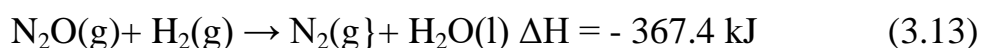


The resulting ΔH value is the enthalpy of reaction that was sought.

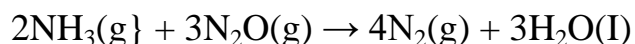
Example 3.3

Given the following thermochemical equations:



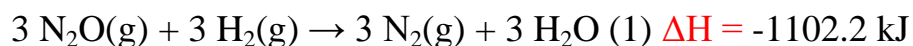
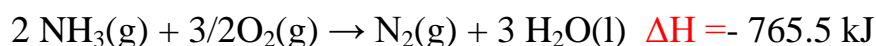


Find the value of ΔH for the reaction

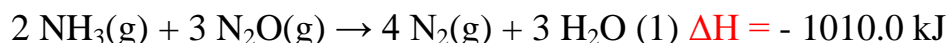


Solution

Since the desired equation has 2 mol of NH_3 on the left, we divide equation (3.12) by 2 and the ΔH value by 2. We multiply equation (3.13) and the corresponding ΔH value by 3 so that the coefficient of N_2O in the final equation will be 3. To eliminate the 3 $\text{H}_2(\text{g})$ added to the left by the last step, we reverse equation (3.14) and multiply it by 3; the ΔH value is multiplied by 3 and its sign changed:



The equations and ΔH values are added. Terms common to both sides of the final equation ($\frac{3}{2}\text{O}_2$, 3 H_2 , and 3 H_2O) are canceled:



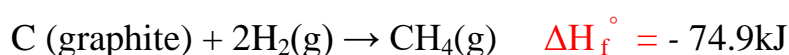
3.6 Enthalpies of Formation

The enthalpy of an element or compound depends upon the temperature and pressure. If we wish to compare ΔH values, the conditions under which they have been measured must be identical. The standard state of a substance is the state in which the substance is stable at 1 atm pressure and 25°C. The symbol ΔH is used to indicate standard enthalpy changes, which apply to reactions involving only materials in their standard states. The standard enthalpy of formation, ΔH°_f of a compound is the enthalpy change for the reaction in which 1 mol of the compound in its standard

state is made from its elements in their standard states. Enthalpy of formation, therefore, is a specific type of enthalpy change. The ΔH values for the reactions shown in Figures 3 and 4 are in reality the ΔH values of $H_2O(l)$ and $HI(g)$, respectively:



Enthalpies of formation are either measured directly or calculated from other thermochemical data by applying the law of Hess. The result of the calculation of this type given in Section 3.5,



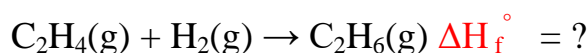
is the enthalpy of formation of $CH_4(g)$. Some enthalpies of formation are listed in Table 3.1

Table 1: Enthalpies of formation of some compounds.

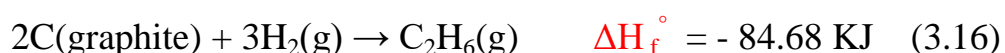
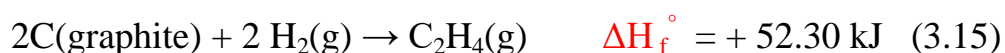
Compound	ΔH_f° (kJ/mol)	Compound	ΔH_f° (kJ/mol)
$H_2O(g)$	-241.8	$COCl_2(g)$	-223.
$H_2O(l)$	-285.9	$SO_2(g)$	-296.9
$HF(g)$	-269	$CO(g)$	-110.5
$HCl(g)$	-92.30	$CO_2(g)$	-393.5
$HBr(g)$	-36.2	$NO(g)$	+ 90.37
$HI(g)$	+ 25.9	$NO_2(g)$	+ 33.8
$H_2S(g)$	-20.2	$HNO_3(l)$	-173.2
$HCN(g)$	+ 130.5	$NH_4NO_3(s)$	-365.1
$NH_3(g)$	-46.19	$NaCl(s)$	-411.0
$PH_3(g)$	+ 9.25	$MgO(s)$	-601.83
$CH_4(g)$	-74.85	$CaO(s)$	-635.5

C ₂ H ₆ (g)	-84.68	Ca(OH) ₂ (s)	-986.59
C ₂ H ₄ (g)	+ 52.30	CaCO ₃ (s)	-1206.9
C ₂ H ₂ (g)	+ 226.7	Ca ₃ P ₂ (s)	-504.17
C ₆ H ₆ (l)	+ 49.04	BaO(s)	-583.1
CH ₃ OH(g)	-201.2	BaCO ₃ (s)	-1218.
CH ₃ OH(l)	-238.6	Al ₂ O ₃ (s)	- 1669.8
CH ₃ NH ₂ (g)	-28	Fe ₂ O ₃ (s)	-822.2
NF ₃ (g)	-113	AgCl (s)	- 127.0
CF ₄ (g)	-913.4	HgBr ₂ (s)	-169
CHCl ₃ (l)	-132	ZnO(s)	-348.0

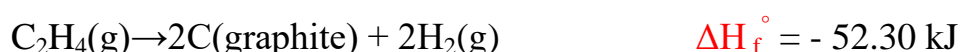
The enthalpy change for a reaction can be calculated from the enthalpies of formation of the compounds involved in the reaction. For example, the enthalpy change for the reaction

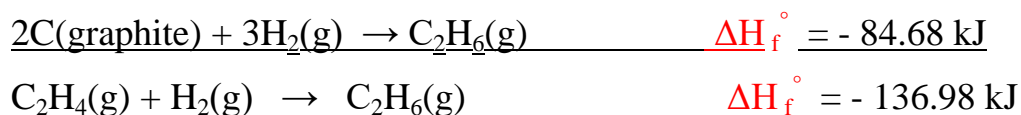


can be calculated from the enthalpies of formation of ethylene, C₂H₄(g), and ethane, C₂H₆(g):



The reverse of equation (3.15) indicates a transformation in which C₂H₄(g) breaks down into its elements. The appropriate value of the enthalpy change for the reversed reaction is ΔH_f° (C₂H₄) or -52.30 kJ. The elements from the decomposition of C₂H₄(g) plus an additional mole of H₂(g) can be imagined to form C₂H₆(g); equation (3.16) is written as shown. When these two equations are added, the desired thermochemical expression is obtained:





The ΔH of the reaction is, therefore, $\Delta H_f^\circ (\text{C}_2\text{H}_6) - \Delta H_f^\circ (\text{C}_2\text{H}_4)$.

In general, a ΔH° value for a reaction may be obtained by subtracting the sum of the enthalpies of formation of the reactants from the sum of the enthalpies of formation of the products:

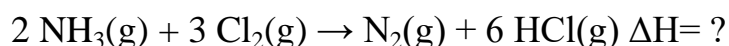
$$\Delta H^\circ = \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants})$$

The uppercase Greek sigma, Σ , indicates a sum. By reversing the sign of (reactants), we indicate a process in which the reactants are broken down into the elements. The formation of the products from these elements is indicated by the term $\Sigma \Delta H_f^\circ$ (products).

Two factors frequently cause trouble in the use of this approach for the calculation of ΔH° values.

1. Enthalpies of formation are given in kilojoules per *mole*. The chemical equation that corresponds to a value listed in Table 3.1 pertains to the formation of only *one* mole of the compound. If more than one mole (or less than one mole) of the compound is involved in the reaction being studied, the ΔH_f° value must be multiplied by the number of moles involved.
2. The enthalpy of formation of an *element* in its standard state is zero (the enthalpy change when an element is prepared from itself). No terms for elements are added into the sums $\Sigma \Delta H^\circ$ (products) and $\Sigma \Delta H^\circ$ (reactants),

Consider the reaction



The enthalpy change for the reaction can be calculated in the following way:

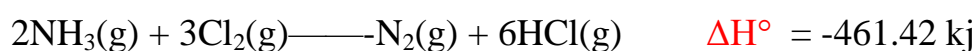
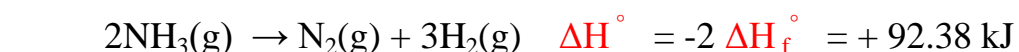
$$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ (Products)} - \Sigma \Delta H_f^\circ \text{ (reactants)}$$

$$= 6 \Delta H_f^\circ(\text{HCl}) - 2 \Delta H_f^\circ(\text{NH}_3)$$

$$= 6(-92.30\text{kJ}) - 2(-46.19\text{ kJ})$$

$$= -553.80\text{kJ} + 92.38\text{ kJ} = -461.42\text{kJ}$$

This calculation may be checked by the addition of the appropriate thermochemical equations. Since 6 mol of HCl(g) are prepared, the equation for the formation of HCl(g) is multiplied through by 6 and the enthalpy of formation of HCl(g) is multiplied by 6. Two moles of NH₃(g) are *consumed* in the reaction. The equation for the *formation* of NH₃(g) is multiplied through by 2 and *reversed*; the value of ΔH° is multiplied by 2 and the sign changed. These two thermochemical expressions are added. No separate equations are introduced for the elements that are involved in the reaction (Cl₂ and N₂):



The terms "3H₂(g)" cancel in the addition. Notice that "3Cl₂(g)" and "N₂(g)" appear in the final equation even though no special provision was made for their introduction.

Example 3.4

Use enthalpies of formation to calculate the ΔH° of the reaction Fe₂O₃(s) + 3CO(g) → 2Fe(s) + 3CO₂(g)

Solution

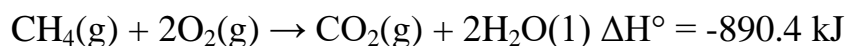
The values needed can be found in Table 3.1

$$\Delta H^\circ = \Sigma \Delta H_f^\circ \text{ (Products)} - \Sigma \Delta H_f^\circ \text{ (reactants)}$$

$$\begin{aligned}
&= 3\Delta H^\circ (\text{CO}_2) - [3\Delta H^\circ(\text{Fe}_2\text{O}_3) + 33\Delta H^\circ (\text{CO})] \\
&= 3(- 393.5 \text{ kJ}) - [(- 822.2 \text{ U}) + 3(- 110.5 \text{ kJ})] \\
&= -1180.5 \text{ kJ} + 11 53.7 \text{ kJ} = -26.8 \text{ kJ}
\end{aligned}$$

Example 3.5

Given the following data;



the enthalpy of formation of $\text{CO}_2(\text{g})$ is $- 393.5 \text{ kJ/mol}$, the enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ is -285.9 kJ/mol . Calculate the enthalpy of formation of $\text{CH}_4(\text{g})$.

Solution

In this case, the value of ΔH for a reaction is known and a ΔH° value for one of the reactants is sought.

$$\Delta H^\circ = \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants})$$

$$\begin{aligned}
\Delta H^\circ &= \Delta H_f^\circ (\text{CO}_2) + 2\Delta H_f^\circ (\text{H}_2\text{O}) - \Delta H_f^\circ (\text{CH}_4) \\
&= -890.4 \text{ kJ} - (-393.5 \text{ kJ}) + 2(-285.9 \text{ kJ}) - \Delta H_f^\circ (\text{CH}_4) \\
&= -890.4 \text{ kJ} = -965.3 \text{ kJ} - \Delta H^\circ (\text{CH}_4)
\end{aligned}$$

$$\Delta H_f^\circ (\text{CH}_4) = - 74.9 \text{ kJ}$$

Using Enthalpies of Formation to derive ΔH Values

1. Write the chemical equation for the reaction.

2. Substitute in the equation:

$$\Delta H^\circ = \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants})$$

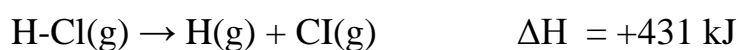
(a) The term $\Sigma \Delta H^\circ$ (products) is the sum of the enthalpies of formation, of the *compounds* that appear on the *right* side of the chemical equation..

(b) The term $\Sigma \Delta H^\circ$ (reactants) is the sum of the enthalpies of formation of *the compounds* that appear on the *left* side of the chemical equation.

To obtain either of these sums, multiply the enthalpy of formation of each compound by the number of moles of that compound involved in the reaction (given by the appropriate coefficient of the chemical equation). No enthalpy terms are introduced for *elements* that appear in the chemical

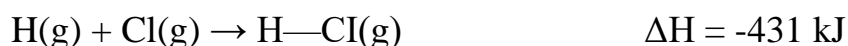
3.7 Bond Energies

Atoms are held together in molecules by chemical bonds. The energy required to *break* the bond that holds two atoms together in a diatomic molecule is called the bond dissociation energy. These values are reported in kilojoules per mole of bonds. In the following equations, which illustrate this process, dashes are used to represent the bonds between atoms; H₂, for example, appears as H—H:



Each of these ΔH values is *positive*, which indicates that energy is *absorbed* in each process. The bond in the H₂ molecule is the strongest of the three. It takes the most energy to pull the atoms of the H₂ molecule apart.

If one of these equations is reversed, the sign of the ΔH value must be changed;



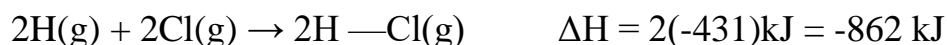
When a bond forms, energy is *released* the same amount that is *required* to break the bond.

Bond energies may be used to determine ΔH values. Consider the reaction



The ΔH for this reaction is twice the enthalpy of formation of HCl(g) since the equation indicates the formation of two moles of HCl(g). We can derive this ΔH value from bond energies in the following way. The enthalpy change is the sum of the energy *required* to break 1 mol of H—

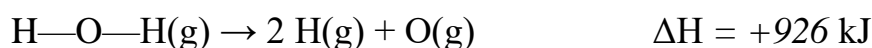
H bonds, the energy *required* to break 1 mol of Cl—Cl bonds, and the energy *evolved* by the formation of 2 mol of H—Cl bonds.



The sum of these equations is

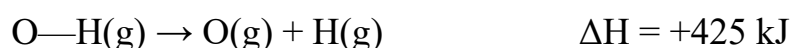


A molecule that contains more than two atoms, such as H_2O , is called a polyatomic molecule. Molecules of this type contain more than one bond. There are, for example, two H—O bonds in the H_2O molecule. The AH for



refers to a process in which *two* moles of H—O bonds are broken. The average bond energy of the H—O bond, therefore, is +926 kJ/mol, or +463 kJ/mol.

In the H_2O molecule, the H—O bonds are equivalent. If the bonds were broken one at a time, however, the AH values would not be the same.



The average of the AH values for the steps is +463 kJ/mol, which is the average bond energy. In general, the second bond of a molecule such as H_2O is easier to break than the first. The fragment remaining after one H has been removed ($\text{O}-\text{H}$) is not as stable as the original molecule ($\text{H}-\text{O}-\text{H}$).

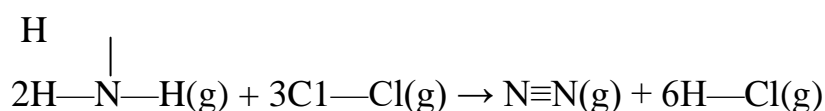
The bond energy of a given type of bond is not the same in all molecules containing that bond. The H—O bond energy in $\text{H}-\text{O}-\text{H}$ is different from the H—O bond energy in $\text{H}-\text{O}-\text{Cl}$. The values listed in Table 3.2 for diatomic molecules are bond dissociation energies. The other values

listed are average bond energies, and each of these values is an average derived from a large number of cases. Since average bond energies are approximations, a ΔH value obtained by use of these values must be regarded as an estimate.

In some molecules, two atoms are bonded together by more than one bond. Two nitrogen atoms, for example, can be joined by a single bond (N—N), a double bond (N=N), or a triple bond (N≡N), depending on the molecule. Multiple bonds are indicated in Table 3.2.

Example 3.6

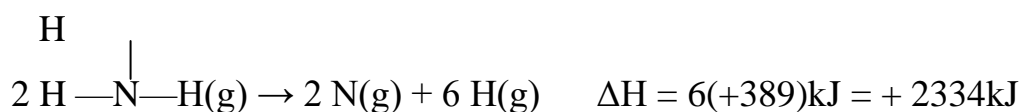
Use average bond energies to calculate the value of ΔH for the reaction



Solution

We can imagine the reaction to take place by a series of steps. Energy is absorbed (ΔH is positive) when a bond is broken, and energy is evolved (ΔH is negative) when a bond is formed.

Six N—H bonds are broken:



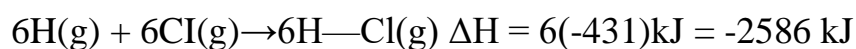
Three Cl—Cl bonds are broken:



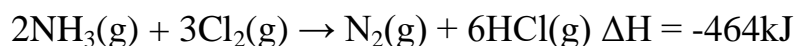
One N≡N bond is formed: .



Six H—Cl bonds are formed:



The sum of these steps is the answer to the problem:



In Section 3.6, enthalpies of formation were used to calculate the value of ΔH for this reaction. The value obtained in this way (— 461 kJ) is a more reliable value than the one derived from bond energies (— 464 kJ).

Table 2: Average bond energy for various bonds.

Bond	Average Bond Energy (kJ/mol)	Bond	Average Bond Enprgy
H—H	435	P—H	318
H—F	565	N—Cl	20
H—Cl	431	P—Cl	329
H—Br	364	C—C	347
H—I	297	C=C	619
F—F	155	C≡C	812
Cl—Cl	243	C—H	414
Br—Br	193	C—O	335
I—I	151	C=O	707
O—O	138	C—F	485
O ₂ ^b	494	C—C	326
O—H	463	C—N	283
O—F	184	C=N	616

O—Cl	205	C≡N	879
N—N	159	S—H	339
N=N	418	S—S	213
N≡N	941	S—Cl	276
N—H	389		

* Reactants and products in gaseous state.

* **Double bond of molecular oxygen.**

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