Equilibrium

Equilibrium

INTRODUCTION

The term "equilibrium" is used in many branches of science. For physicists, equilibrium is a balancing act, much like the balance of force holding up the Leaning Tower of Pisa. In general, equilibrium is a state in which there are no observable changes as time goes by. In physical equilibrium, such as liquid–vapor equilibrium, the vapor pressure exerted by the vapor of the liquid evaporating in a closed container acquires a constant value because the number of molecules leaving the liquid state equals the number of molecules returning to the liquid state from the vapor. When a chemical reaction has reached the equilibrium state (chemical equilibrium), the concentrations of reactants as well as products remain constant over time, and there are no visible changes in the system because the forward and reverse rates are equal. However, there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules. This dynamic situation, a characteristic of chemical equilibrium, is also observed in physical equilibrium, e.g., in liquid–vapor equilibrium, the molecules continue to escape from the liquid surface (evaporation) to form the corresponding vapor while an equal number of molecules continue to enter into the liquid state from the vapor (condensation).

Essential Requirement for Attaining Equilibrium

1. The system should be closed (either it should have fixed walls or should be fitted with a movable piston).
2. The system should undergo simultaneously two exactly opposite changes such as evaporation and condensation.

At equilibrium, two exactly opposite changes take place at the same rate and the macroscopic properties of the system (temperature, pressure, concentration, etc.) do not change with time.

Types of Equilibria

There are two types of equilibria depending on the nature of changes occurring in the system at equilibrium:

Physical equilibrium: The equilibrium achieved with the help of two opposing physical changes such as evaporation and condensation.

Chemical equilibrium: The equilibrium achieved with the help of two opposing chemical changes like the forward and backward changes of a reversible chemical reaction.

Reversible physical changes

$$\text{Solid} \underset{\text{Freezing}}{\overset{\text{Melting}}{\rightleftharpoons}} \text{Liquid}$$

$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapor}$$

$$\text{Solid} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \text{Aqueous solution}$$

$$\text{Gas} \underset{\text{Effervescence}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \text{Aqueous solution}$$

Reversible chemical reactions

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$

$Fe^{3+}(aq.) + SCN^-(aq.) \rightleftharpoons FeSCN^{2+}(aq.)$

Irreversible chemical reactions

$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

$2KClO_3(g) \longrightarrow 2KCl(s) + 3O_2(g)$

$BaCl_2(aq.) + Na_2SO_4(aq.) \longrightarrow BaSO_4(s) + NaCl(aq.)$
$AgNO_3(aq.) + NaCl(aq.) \longrightarrow AgCl(s) + NaNO_3(aq.)$

7.1 EQUILIBRIUM IN PHYSICAL PROCESSES

By examining physical processes such as phase transformations, we can easily understand the characteristics of a system at equilibrium.

7.1.1 Solid–Liquid Equilibrium

Water placed in a perfectly insulated thermos flask at 273 K and 1 atm pressure exists in two physical states: solid (ice) and liquid (water) which are in equilibrium because the mass of ice and water do not change with time and the temperature of the system remains constant. This is possible an account of no exchange of heat between the system and its surroundings.

This equilibrium state is not static as the H_2O molecules from liquid water collide against the surface of ice and stick to it while an equal number of H_2O molecules from ice escape into liquid phase. As the rates of transfer of H_2O molecules from ice into liquid water and of reverse transfer from liquid water into ice are equal at 273 K and 1 atm pressure, there is no change in the mass of ice and liquid water at equilibrium.

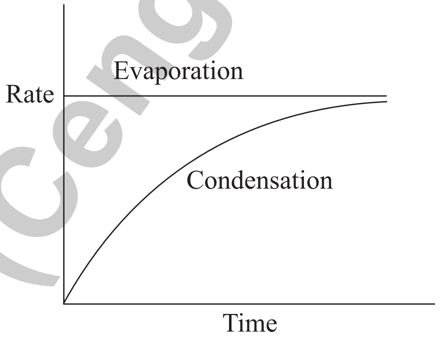
$$H_2O(s) \rightleftharpoons H_2O(l)$$

It is significant to note that ice and liquid water are in dynamic equilibrium (i.e., both the opposing processes of melting and freezing occur simultaneously at the same rate) at atmospheric pressure only at a particular temperature called the normal melting point or normal freezing point of water.

> The temperature at which the solid and the liquid phases of any pure substance are at equilibrium at 1 atm pressure is called the normal melting point or normal freezing point of the substance.

7.1.2 Liquid–Vapor Equilibrium

If water is taken in a transparent dry container fitted with a mercury manometer, then we observe that mercury level in the right limb of manometer slowly increases and finally attains a constant height. This happens because the evaporation of water increases the pressure inside the box. At constant temperature, the rate of evaporation is constant. However, due to the condensation of water vapor into liquid water, the rate of increase in pressure decreases with time.



Finally, an equilibrium condition is attained when there is no net evaporation as well as condensation because the rate of evaporation is equal to the rate of condensation.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

At a given temperature, the pressure exerted by the water molecules at equilibrium becomes constant and is called the *equilibrium vapor pressure* of water (or just, the *vapor pressure* of water). With the increase of temperature, the vapor pressure of water increases because more and more H_2O molecules acquire high kinetic energy and escape from the surface of liquid water. *The temperature at which the vapor pressure of liquid water becomes equal to the atmospheric pressure is called the boiling point of water*. The boiling point of water is 100°C at 1.013 bar pressure (1 atm pressure). Thus, liquid water and water vapor are in equilibrium position at 1 atm pressure (1.013 bar) and at 100°C in a closed container.

For any pure liquid at atmospheric pressure, the temperature at which the liquid and vapor are at equilibrium is called the boiling point of the liquid. Its value depends upon the magnitude of the atmospheric pressure. For example, the boiling point of a pure liquid changes with the altitude of the place; it decreases with the increase of altitude.

7.1.3 Solid–Vapor Equilibrium

This kind of physical equilibrium can be established by placing sublimable solids in a closed container. Such solids such as iodine, camphor, and ammonium chloride directly convert into their vapor without forming the liquid. If we place solid iodine in a closed transparent container, it gets filled up with violet vapor of iodide. The intensity of violet color increases with time and becomes constant after certain time. At this stage, solid iodine sublimes to give iodine vapor and iodine vapor condenses to give solid iodine at equal rate, i.e., the rate of sublimation is equal to the rate of condensation.

$$I_2(s) \rightleftharpoons I_2(g)$$

This is definitely the equilibrium state.

7.1.4 Solid–Solution Equilibrium

At room temperature, we can dissolve only a limited amount of sugar ($C_{12}H_{22}O_{11}$) in a given amount of liquid water. Once we get a saturated solution, no more of sugar can be dissolved in it at a given temperature. Thus, if we add more of sugar to the saturated solution, it does not dissolve and settles down at the bottom of the container. If we keep this system closed for any length of time, we notice that the concentration of aqueous solution of sugar as well as the mass of undissolved sugar do not change with time. This is because a dynamic equilibrium exists between the sugar molecules present in the aqueous solution and those present in the undissolved sugar:

$$\text{Sugar(aq.)} \rightleftharpoons \text{Sugar(s)}$$

At this stage, the rate of dissolution of sugar becomes equal to the rate of crystallization of sugar.

With the help of radioactive sugar (sugar containing ^{14}C, an isotope of C), we can confirm the dynamic nature of equilibrium as well as the equality of the two rates. If we add some radioactive sugar to the saturated solution of ordinary nonradioactive sugar, then after certain time, both the solution and the undissolved sugar show the sign of radioactivity. This can only be explained by the dynamic nature of equilibrium which involves an exchange between the radioactive and the nonradioactive sugar molecules between the two phases (i.e., aqueous solution and solid). Initially there were no radioactive sugar molecules in the solution, but due to the exchange, the ratio of the radioactive to the nonradioactive sugar molecules in the aqueous solution increases till it attains a constant value—a sign of equilibrium state.

7.1.5 Gas–Solution Equilibrium

If we place CO_2(g) and liquid water in a closed container, an equilibrium is established between the CO_2 molecules in the gaseous state and the CO_2 molecules in the aqueous solution:

$$CO_2(g) \rightleftharpoons CO_2(aq.)$$

At equilibrium, the rate of dissolution is equal to the rate of effervescence. At any given temperature, the amount of CO_2(g) dissolved in liquid water at equilibrium depends upon the pressure of undissolved CO_2(g) present above the surface of aqueous solution and is governed by *Henry's law* which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is directly proportional to the pressure of the undissolved gas above the solution:

$$m \propto p$$

$$m = Kp \tag{7.1}$$

where K, a proportionality constant, is called Henry's constant. Its value depends upon the nature of the gas, the nature of the liquid solvent, and the temperature. Its value increases with increase of temperature, i.e., the solubility of gases dissolved in any given solvent at any given pressure decreases with the increase of temperature.

In soda water bottle, the solubility of CO_2 in water is very high because the bottle is sealed under high pressure of CO_2. As soon as the soda water bottle is opened, some of the undissolved CO_2(g) present above the liquid solution fizzes out rapidly. To reach a new equilibrium condition required for the lower pressure (i.e., partial pressure of CO_2 in the atmosphere), some of the dissolved CO_2 gas escapes. This is how the soda water in bottle turns "flat" when the sealed bottle is left open to the atmosphere for some time.

7.1.6 General Characteristics of Equilibrium Involving Physical Processes

Following characteristics are common to the system at physical equilibrium:

1. Equilibrium is possible only in an isolated system (closed and perfectly insulated) at a given temperature. If a liquid–vapor equilibrium system is open to the atmosphere, the rate of evaporation remains constant but the molecules in the vapor phase are dispersed into the large volume of the room. Consequently, the rate of condensation from vapor to liquid state is much less from the rate of evaporation. Thus, it is not possible to reach equilibrium in an open system.
2. There is a dynamic but stable condition because both the opposing processes (such as evaporation and condensation) occur simultaneously but at the same rate.
3. All measurable physical properties of the system at equilibrium are constant. For example, for solid $\rightleftharpoons$ liquid equilibrium, the melting point is fixed at constant atmospheric pressure. The mass of the two phases also remains constant.
4. The establishment of physical equilibrium is always characterized by the constant value of one of the parameters at a given temperature. For example, as evaporation and condensation occur simultaneously in liquid–vapor system, the vapor pressure increases with time but acquires a constant value the moment equilibrium is attained. Table 7.1 lists such parameters for different systems.

Table 7.1 At physical equilibrium, some observable property of the system becomes constant at the given temperature.

Equilibrium process	**Constant observable property**
Solid $\rightleftharpoons$ Liquid	Mass of the two phases and the melting point
Liquid $\rightleftharpoons$ Vapor	Vapor pressure at a given temperature
Solid $\rightleftharpoons$ Aqueous solution	Solubility, i.e., [solid (solution)] is constant at a given temperature.
Gas $\rightleftharpoons$ Aqueous solution	Solubility, i.e., [gas(aq.)] is constant at a given temperature.

5. The extent to which the process has proceeded before attaining equilibrium is measured by the magnitude of the characteristic parameter mentioned in Table 7.1. For example, higher the vapor pressure at a given temperature for the liquid $\rightleftharpoons$ vapor equilibrium, the greater the conversion of liquid into vapor.

Follow-up Test 1

1. When a volatile liquid is introduced into an evacuated closed vessel at a particular temperature, both evaporation and condensation take place simultaneously. The system reaches equilibrium state when
   (1) the liquid is completely transformed into the corresponding vapor
   (2) equal amounts of liquid and vapor are present in the system
   (3) the rate of evaporation becomes equal to the rate of condensation
   (4) liquid cannot be converted into vapor and vice versa.

2. Which of the following equilibrium is dynamic?
   (1) Solid $\rightleftharpoons$ Liquid (2) Liquid $\rightleftharpoons$ Vapor
   (3) Solid $\rightleftharpoons$ Vapor (4) All of these
3. Which of the following is not true for solid–liquid equilibrium?
   (1) It can be established at any given temperature.
   (2) The mass of solid does not change with time.
   (3) The mass of liquid does not change with time.
   (4) There is no exchange of heat between the system and its surroundings.
4. The vapor pressures of water, acetone, and ethanol at 293 K are 2.34, 12.36, and 5.85 kPa, respectively. Which of the following statements is correct?
   (1) Acetone has the lowest boiling point.
   (2) Water has the highest boiling point.
   (3) Water evaporates the least in a sealed container at 293 K before equilibrium is established.
   (4) All of these.
5. Which of the following substances can be placed in a closed vessel to establish solid$\rightleftharpoons$vapor equilibrium?
   (1) Ammonium chloride (2) Camphor
   (3) Iodine (4) All of these
6. Which of the following solutions kept in contact with undissolved solute is an example of solid–solution equilibrium?
   (1) Aqueous solution (2) Saturated solution
   (3) Unsaturated solution (4) Nonaqueous solution
7. 0.200 g of iodine is stirred in 100 mL of water at 298 K till equilibrium is reached:
   $[I_2(aq.)]_{\text{Equilibrium}} = 0.0011 \text{ mol L}^{-1}$ at 298 K
   What will be the mass of iodine found in solution?
   (1) 0.028 g (2) 0.28 g
   (3) 0.0028 g (4) 2.8 g
8. Refer to Q.7. 0.200 g of iodine is stirred in 100 mL of water. After equilibrium is reached, we add 150 mL of water to the system. How much iodine will be left undissolved?
   (1) 1.3 g (2) 0.130 g
   (3) 0.013 g (4) 13 g
9. Refer to Q.8. What will be the concentration of iodine in solution?
   (1) 1.1 M (2) 0.011 M
   (3) 0.0011 M (4) 0.11 M
10. Which of the following is correct regarding the gas–solution equilibrium?
    (1) The solubility of the dissolved gas increases with the increase of pressure and decreases with the increase of temperature.
    (2) The solubility of the dissolved gas increases with the increase of pressure as well as temperature.
    (3) The solubility of the dissolved gas decreases with the increase of pressure and increases with the increase of temperature.
    (4) The solubility of the dissolved gas decreases with the increase of pressure as well as temperature.

7.2 EQUILIBRIUM IN CHEMICAL PROCESSES

Equilibrium between two different phases of the same substance is called *physical equilibrium* because the changes that occur are physical processes. On the other hand, a chemical equilibrium involves different substances as reactants and products.

To achieve physical equilibrium, we need to perform two exactly opposing physical processes simultaneously. The equilibrium is attained when these opposing processes occur at the same rate. Similarly, to achieve chemical equilibrium, we need to perform two exactly opposing chemical processes simultaneously. This can be achieved by running a reversible chemical reaction in a closed vessel if gaseous substances are involved.

A few chemical reactions proceed in only one direction. Such reactions are called *irreversible reactions*. Most chemical reactions (at least to some extent) are *reversible reactions* which proceed not only in the forward direction but also in the backward direction under identical conditions. Such reactions do not go to completion, that is, when the reactants are mixed in stoichiometric quantities, they are not completely converted to the products.

> Chemical reactions that do not go to completion and that can occur in either direction are called reversible reactions.

At the start of a reversible process, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reversible process, i.e., the formation of reactant molecules from product molecules begins to take place.

When the rates of the forward and the reverse reactions become equal and the concentrations of the reactants and the products no longer change with time, the stage of chemical equilibrium is attained.

Like physical equilibrium, chemical equilibrium is a dynamic process. This actually implies that at equilibrium, there is the occurrence of forward reaction in which the reactant molecules yield the product molecules as well as the occurrence of reverse reaction in which the product molecules yield the original reactant molecules. But there is no net reaction as both the reactions proceed at equal rates. As a result, the concentrations of different substances at equilibrium remain constant.

Reversible chemical reactions can be represented in general terms as follows:

$$aA + bB \rightleftharpoons cC + dD$$

where the capital letters represent formulas of the reacting species and the lowercase letters represent the stoichiometric coefficients in the balanced equation. The double arrow ($\rightleftharpoons$) indicates that the reaction is reversible, i.e., both the forward and the reverse reactions occur simultaneously.

> The terms “reactants” and “products” may cause confusion while dealing with reversible reactions, since any substance serving as a reactant for the forward reaction serves also as a product for the reverse reaction. In other words, every substance in a reversible reaction can play the role of a reactant as well as product. To avoid such confusion, the substances that appear on the left side of the double arrow are called the reactants and those on the right side are called the products.

When A and B react to form C and D at the same rate at which C and D react to from A and B, the system is at equilibrium, that is, chemical equilibrium exists when two opposing chemical reactions occur simultaneously at the same rate.

In a system at equilibrium, the equilibrium is said to lie toward the right if more C and D are present than A and B, and is said to lie toward the left if more A and B are present.

Typical examples of reversible chemical reactions that can be carried out in closed vessels to attain equilibrium are as follows:

(1) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(2) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(3) $N_2O_4(g) + \rightleftharpoons 2NO_2(g)$
(4) $3Fc(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
(5) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
(6) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(7) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Reversible reactions carried out in closed vessels never go to completion because a state of equilibrium is reached at some point. The ultimate outcome is an equilibrium mixture of all the reactants and products.

In contrast, an irreversible reaction always goes to completion because an irreversible reaction cannot take place in the reverse direction, i.e., the products formed do not react to give back the reactants under the same experimental conditions. The irreversible reaction can be represented in general terms as follows:

$$aA + bB \longrightarrow cC + dD$$

The single arrow ($\longrightarrow$) indicates that the reaction is irreversible, i.e., the reaction can proceed only in the forward direction. Typical examples of irreversible reactions are as follows:

1. $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$
2. $BaCl_2(aq.) + Na_2SO_4(aq.) \longrightarrow BaSO_4(s) + 2NaCl(aq.)$
3. $AgNO_3(aq.) + NaC1\ (aq.) \longrightarrow AgC1(s) + NaNO_3(aq.)$

A reversible reaction can become irreversible if one of the gaseous products is allowed to escape out. For example, the decomposition of limestone ($CaCO_3$) becomes an irreversible reaction if $CO_2(g)$ is allowed to escape out.

Consider a case in which the coefficients in the equation for a reversible reaction are all 1.

$$A + B \rightleftharpoons C + D$$

To establish chemical equilibrium through this reversible reaction, we have either the option of starting the forward reaction or the backward reaction in the beginning. For example, if we mix A and B in (1 : 1) ratio in a closed vessel, then in the beginning (when time is zero), there is only forward reaction and its rate is at its maximum value as both the reactants are about to react. The rate of backward reaction is zero as there is no C and D. When the substances A and B react, the rate of the forward reaction (R_f) decreases as time passes because the concentrations of A and B decrease:

$$A + B \longrightarrow C + D$$

As the concentrations of C and D build up, they start to re-form A and B:

$$C + D \longrightarrow A + B$$

As more C and D molecules are formed, more can react, and so the rate of the backward reaction R_b (i.e., reaction between C and D) increases with time. Eventually, the two reactions occur at the same rate (i.e., the rate of the forward reaction becomes equal to the rate of the backward reaction) and the system is at equilibrium (Figure 7.1). At this stage, the concentrations of all the substance (A, B, C, D) present in the equilibrium mixture become constant (Figure 7.2).

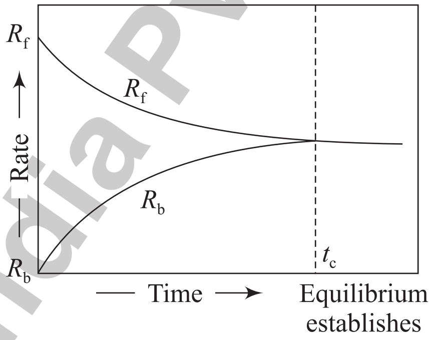


Figure 7.1

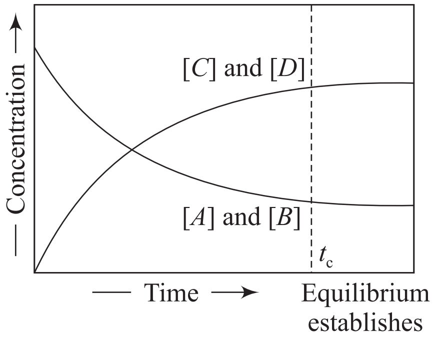


Figure 7.2

It is significant to note that at equilibrium, the rate of forward reaction (or rate of backward reaction) is not zero. However, both the rates are equal to each other. Further, note that at equilibrium, the concentrations of all the substances present in the equilibrium mixture become constant but that does not essentially mean that they are equal to one another.

The same state of chemical equilibrium is reached even if we start with C and D, i.e., no A and B being present initially. If a reaction begins with only C and D present, the rate of backward reaction ($C + D \longrightarrow A + B$) decreases with time and the rate of forward reaction ($A + B \longrightarrow C + D$) increases with time until the two rates are equal.

Chemical equilibrium can be reached by carrying out a reversible chemical reaction from either direction.

The dynamic nature of chemical equilibrium can be proved experimentally by inserting radioactive atoms into a small percentage of molecules and following them through the reaction. Even when the initial mixture is at equilibrium, radioactive atoms eventually appear in both reactant and product molecules.

7.2.1 General Characteristics of Equilibria involving Chemical System

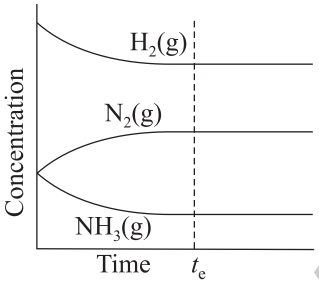
1. It takes a finite time to reach equilibrium (also true for physical systems).
2. The equilibrium is dynamic (also true for physical system) in the sense that at equilibrium, the rate of forward reaction is equal to the rate of backward reaction and that such bidirectional conversions are taking place all the time.
3. At equilibrium, the concentration of each of the substances becomes constant at a given temperature.
4. At equilibrium, the measurable properties of the system (e.g., temperature, pressure) remain constant.
5. The state of equilibrium can be attained from either direction (also true for physical system).
6. At equilibrium, the free energy change of the system is zero, i.e., $\Delta G = 0$ (also true for physical system).

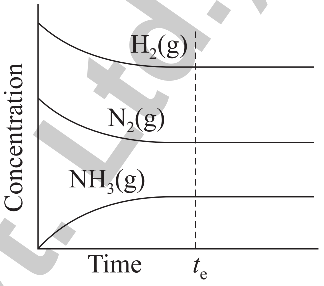
Follow-Up Test 2

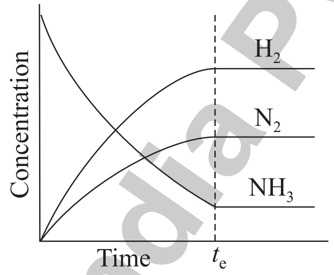
1. A reversible chemical reaction is said to be at equilibrium when
   (1) equal amounts of reactants and products are present
   (2) reactants are completely converted into products
   (3) the rates of the forward and backward reactions become equal
   (4) products cannot be converted into reactants and vice versa.
2. Chemical equilibrium is a dynamic equilibrium because
   (1) the rate of forward reaction is nonzero
   (2) the rate of backward reaction is nonzero
   (3) concentrations of reactants and products always keep changing
   (4) Both forward and backward reactions occur simultaneously at the rate which is nonzero.
3. An example of a reversible reaction is.
   (1) $2Na(s) + H_2O(l) \longrightarrow 2NaOH(aq.) + H_2(g)$
   (2) $AgNO_3(aq.) + HCl(aq.) \longrightarrow AgCl(s) + HNO_3(aq.)$
   (3) $KNO_3(aq.) + NaCl(aq.) \longrightarrow KCl(aq.) + NaNO_3(aq.)$
   (4) $Pb(NO_3)_2(aq.) + 2NaI(aq.) \longrightarrow PbI_2(s) + 2NaNO_3(aq.)$
4. The reaction which proceeds in the forward direction is.
   (1) $SnCl_4 + Hg_2Cl_2 \longrightarrow SnCl_2 + 2HgCl_2$
   (2) $2CuI + I_2 + 4K^+ \longrightarrow 2Cu^{2+} + 4KI$
   (3) $NH_3 + H_2O + NaCl \longrightarrow NH_4Cl + NaOH$
   (4) $Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$
5. Which of the following correctly depicts the attainment of equilibrium for the reaction:

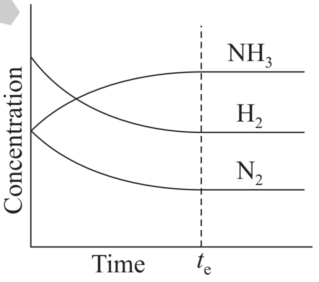
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

beginning with stoichiometric amounts of $N_2(g)$ and $H_2(g)$ and no $NH_3(g)$.



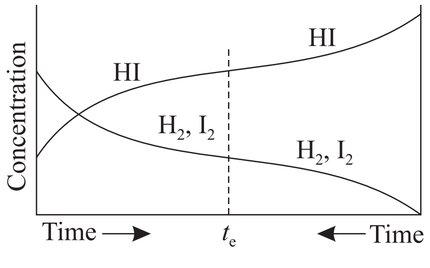




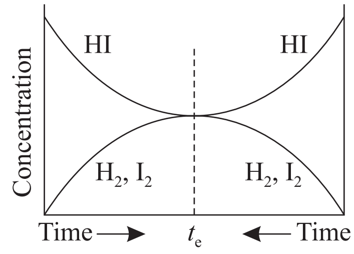


6. Equilibrium mixture (I) consists of N_2, H_2, and NH_3. Equilibrium mixture (II) consists of N_2, D_2, and ND_3. Which of the following observations is correct if both the mixtures (I and II) are mixed together and left for a while?
   (1) The concentration of NH_3 is just the same as before.
   (2) Ammonia and all deuterium-containing forms of ammonia (NH_2D, NHD_2, and ND_3) are present.
   (3) Dihydrogen and all deutrated forms (HD and D_2) are present.
   (4) All of these.
7. Which of the following correctly depicts the fact that identical chemical equilibrium can be attained through reversible reaction $H_2 + I_2 \rightleftharpoons 2HI$ from either direction?

(1)



(2)



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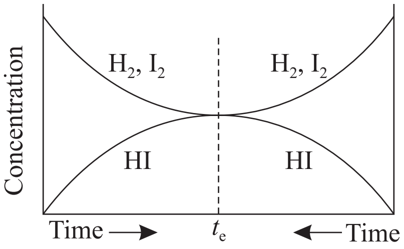
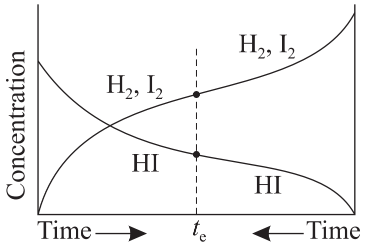


(4)



7.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

To describe the equilibrium state of a reversible chemical reaction by a quantitative relation between the equilibrium concentrations of reactants and products, we take the help of the law of mass action, first proposed by Cato Guldberg and Peter Waage. *It is significant to note that the law of mass action is applicable to only elementary reactions, i.e., simple reactions which take place in a single step only.*

The law of mass action states that the rate of an elementary chemical reaction at any given temperature is directly proportional to the product of the active masses of the reactants each being raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation. The active mass of a substance is usually represented by putting the formula of the substance in square brackets. Hence, for the most general reaction,

$$lL + mM + \cdots \longrightarrow rR + sS + \cdots$$

$$\text{Rate of reaction} \propto [L]^l[M]^m\cdots$$

or $$\text{Rate of reaction} = K\,[L]^l[\text{M}]^m\cdots \tag{7.2}$$

where K is the constant of proportionality and is called s*pecific reaction rate* or just *rate constant*. It is equal to the rate of reaction when the active mass of each of the reactants is unity.

7.3.1 How to Express the Active Mass?

1. For pure liquids and pure solids, active masses are expressed through their densities. Since the density of a pure liquid or a pure solid at any given temperature is essentially constant, the active mass of a pure liquid or of a pure solid is always constant.
2. For gases, active masses are usually expressed through their partial pressures in atmospheres, although sometimes the concentrations of gases in moles per liter or mole fractions of gases are used.
3. Active masses for solutes are usually expressed in the units of concentration such as moles per liter (molarity) of the solution.

Suppose the following reversible reaction occurs via a mechanism consisting of a single elementary step in both the forward and the reverse directions:

$$aA + bB \underset{K_r}{\overset{K_f}{\rightleftharpoons}} cC + dD$$

Applying the law of mass action, the rate of the forward reaction is given by

$$\text{Rate}_f = K_f\,[A]^a[B]^b$$

and the rate of the reverse reaction is given by

$$\text{Rate}_r = K_r\,[C]^c[D]^D$$

where K_f and K_r are the *specific rate constants* for the forward and the reverse reactions, respectively. By definition, the two rates are equal at equilibrium:

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

or $$K_f\,[A]^a_{eq}\,[B]^b_{eq} = K_r[C]^c_{eq}\,[D]^d_{eq}$$

Note that the subscript "eq" is used for equilibrium.

Collecting like terms on the same side gives

$$\frac{K_f}{K_r} = \frac{[C]^c_{eq}\,[D]^d_{eq}}{[A]^a_{eq}\,[B]^b_{eq}} \tag{7.3}$$

According to chemical kinetics (Arrhenius equation), at any specific temperature, the rate constant of a reaction is constant. Since both K_f and K_r are constants at a given temperature, their ratio (K_f/K_r) is also a constant. Because this constant value corresponds to the equilibrium situation, this ratio is given a special name and symbol: the *equilibrium constant*, K_{eq}.

$$K_{eq} = \frac{K_f}{K_r} \tag{7.4}$$

Substituting Eq. (7.4) in Eq. (7.3) gives

$$K_{eq} = \frac{[C]^c_{eq}\;[D]^d_{eq}}{[A_{eq}]\;[B_{eq}]} \tag{7.5}$$

This equality is called the law of chemical equilibrium'or, the equilibrium law, which states that at any given temperature, the equilibrium constant (K_{eq}) is defined as the product of the equilibrium active masses of the reaction products, each raised to the power that corresponds to its stoichiometric coefficient in the balanced chemical equation, divided by the product of the equilibrium active masses of reactants, each raised to the power that corresponds to its coefficient in the balanced equation.

For simplicity, we can use the term "concentration" in place of "active mass." Generally, the subscript "eq" (used for equilibrium) is omitted from the concentration term. It is taken for granted that the concentrations in the expression for K_{eq} are equilibrium values. We, therefore, write

$$K_{eq} = \frac{[C]^c\;[D]^d}{[A]^a\;[B]^b} \tag{7.6}$$

So, at any given temperature K_{eq} is always a constant regardless of the equilibrium concentrations (as well as initial concentrations) of the reacting species because it is always equal to K_f/K_r, the quotient of two quantities that are themselves constant at a given temperature. Because rate constants are temperature dependent, it follows that the equilibrium constant must also change with temperature.

Even if the overall reversible reaction occurs by a multistep mechanism, we can show that the equilibrium constant is the product and ratio of the rate constants for each step of the mechanism:

$$K_{eq} = \frac{K_f K'_f K''_f \cdots}{K_r K'_r K''_r \cdots} \tag{7.7}$$

Regardless of the mechanism by which this reversible reaction occurs, the concentrations of reaction intermediates cancel out and the equilibrium constant expression has the same form, i.e., whether a reaction, in general terms,

$$\underbrace{aA + bB}_{\text{Reactants}} \rightleftharpoons \underbrace{cC + bD}_{\text{Products}}$$

occurs in a single step or in multiple steps, the equilibrium constant can always be written as follows:

$$K_{eq} = \frac{[C]^c_{eq}\,[D]^d_{eq}}{[A]^a_{eq}\,[B]^b_{eq}} \begin{matrix} \leftarrow \text{Products} \\ \leftarrow \text{Reactants} \end{matrix}$$

In general, the numerical values for K_{eq} can come only from experiments. We have used the subscript "eq" to emphasize that the concentrations in the equilibrium constant expression are those at equilibrium. For the remainder of the discussion, we will omit these subscripts, remembering that calculations with K_{eq} values always involve the equilibrium values of concentrations.

The concept of equilibrium constant is extremely important in chemistry. Equilibrium constants are the key to solving a wide variety of stoichiometry problems involving equilibrium systems. The thermodynamic definition of the equilibrium constant involves active masses (or activities) rather than concentrations. To use equilibrium constants, we must know how to express active masses in terms of the reactant and the product concentrations. Because the concentrations of the reactants and the products can be expressed in several types of units and because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the same reaction.

7.4 HOMOGENEOUS EQUILIBRIA

The term *homogeneous equilibrium* applies to equilibrium attained with the help of a reversible reaction in which all the reacting species (reactants) of forward as well as reverse reaction are in the same phase. An example of homogeneous gas-phase equilibrium is the synthesis of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

We can notice that all reactants and products are in the homogeneous gas phase.

Examples of homogeneous solution-phase equilibria are as follows:

$$CH_3COOC_2H_5(aq.) + H_2O(l) \rightleftharpoons CH_3COOH(aq.) + C_2H_5OH(aq.)$$

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

Here, all the reactants and products are in homogeneous solution-phase.

Consider the following reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Applying the law of chemical equilibrium, we can write the equilibrium constant expression in terms of the equilibrium active masses of reactants and products at a particular temperature as follows:

$$K_{eq} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

If we assume that every reacting species in the above equilibrium reversible reaction is in the gas phase, we can express the active masses in the equilibrium constant expression in three different ways to get three different equilibrium constants.

1. If the active masses of gases are expressed in molar concentration (molarity, mol L^{-1}), we get K_c, *concentration equilibrium constant*.

   $$K_c = \frac{C_C^c\,C_D^d}{C_A^a\,C_B^b} \tag{7.8}$$

   Note that the subscript c in K_c denotes that in this form of equilibrium constant, the active masses of the reacting species are expressed in moles per liter.

   Consider the ionization of acetic acid (CH_3COOH) in water as another example of homogeneous equilibrium:

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

   The concentration equilibrium constant is

   $$K_c = \frac{C_{CH_3COO^-}\;C_{H_3O^+}}{C_{CH_3COOH}\;C_{H_2O}}$$

   However, when the concentration of acid is low (≤ 1M) and/or the equilibrium constant is small (≤1), as it happens in this case, the amount of water consumed in this process is negligible in comparison to the total amount of water present. Thus, we may treat C_{H_2O} practically constant and rewrite the equilibrium constant as

   $$K'_c = \frac{C_{CH_3COO^-}\;C_{H_3O^+}}{C_{CH_3COOH}}$$

   where $K'_c = K_c C_{H_2O}$

HELP In 1 L or 1000 g of water, there are (1000 g/18 g mol^{-1}), or 55.5 mol of water. Therefore, the concentration of water, i.e., C_{H_2O} is 55.5 mol L^{-1} or 55.5 M.

2. It is often more convenient to measure pressures rather than the concentrations of gases. If we express the active masses of reactants and products in gaseous reactions in terms of their partial pressures, we get K_p, the *pressure equilibrium constant* (sometimes known as *thermodynamic equilibrium constant*):

   $$K_p = \frac{P_C^c\,P_D^d}{P_A^a\,P_B^b} \tag{7.9}$$

   where P_A, P_B, P_C, and P_D represent the equilibrium partial pressures of A, B, C, and D, respectively.

3. There is a third type of equilibrium constant, called the *mole fraction equilibrium constant* K_χ. It is much less in use and is obtained when the active masses of all the reacting gaseous species are expanded in terms of their mole fractions:

$$K_\chi = \frac{\chi_C^c\ \chi_D^d}{\chi_A^a\ \chi_B^b} \tag{7.10}$$

where χ_A, χ_B, χ_C, and χ_D are the mole fractions of A, B, C, and D in the equilibrium mixture, respectively.

7.4.1 Relationship between K_p and K_c

To find a suitable relationship between K_p and K_c, we must first find the relation between the partial pressure of a gas and its molar concentration. Solving the ideal gas equation, $PV = nRT$, for pressure gives

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

or

$$P = CRT\left(C = \frac{n}{V} \text{ is } \frac{\text{Number of moles}}{\text{L}}\right) \tag{7.11}$$

From Eq. (7.11), we see that at constant temperature, the partial pressure of a gas is directly proportional to its molar concentration C (n/V).

For reactions in which all the substances that appear in the equilibrium constant expression are gases, we sometimes prefer to express the equilibrium constant in terms of partial pressures in atmospheres (K_p) rather than in terms of concentrations (K_c). In general, K_p is not equal to K_c, since the partial pressures of reactants and products are not equal to their concentrations expressed in moles per liter. A simple relationship between K_p and K_c can be derived as follows: Assuming ideal gas behavior for every gaseous species, we can substitute Eq. (7.11) into the expression for K_p, Eq. (7.10), to obtain.

$$K_p = \frac{(C_CRT)^c\ (C_DRT)^d}{(C_ART)^a\ (C_BRT)^b} = \frac{C_C^c(RT)^c\ C_D^d(RT)^d}{C_A^a(RT)^a\ C_B^b(RT)^b}$$

$$= \frac{C_C^c\,C_D^d(RT)^{c+d}}{C_A^c\,C_B^b(RT)^{a+b}} = \frac{C_C^c\,C_D^d}{C_A^a\,C_B^b}(RT)^{(c+d)-(a+b)}$$

$$K_p = K_c(RT)^{\Delta n_g} \tag{7.12}$$

where K_c is the concentration equilibrium constant according to Eq. (7.8) and

$$\begin{aligned}\Delta n_g &= (c+d)-(a+b)\\ &= (n_{\text{gas prod}})-(n_{\text{gas react}})\\ &= (\text{Moles of gaseous products})\\ &\qquad -(\text{Moles of gaseous reactants})\end{aligned}$$

The subscript "g" in Δn_g reminds us that only gaseous moles must be considered. Rewriting Eq. (7.12), we obtain

$$K_c = K_p(RT)^{-\Delta n_g} \tag{7.13}$$

Depending upon the value of Δn_g, there are three types of homogeneous gas-phase equilibria:

(1) For reactions in which equal number of moles of gases appear on both sides of the equation, $\Delta n_g = 0$ and $K_p = K_c$:

$$H_2(g) + I_2\,(g) \rightleftharpoons 2HI(g)$$

(2) For reactions in which more number of moles of gases appear on the right side of the equation (i.e., $n_{\text{gas prod}} > n_{\text{gas react}}$), Δn_{gas} is +ve and $K_p > K_c$:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(3) For reactions in which more number of moles of gases appear on the left side of the equation (i.e., $n_{\text{gas react}} > n_{\text{gas prod}}$), Δn_{gas} is –ve and $K_p > K_c$:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Similarly, we can work out the relation between K_p and K_x by expressing the partial pressure of a gas in terms of its mole fraction ($p_{\text{gas}} = p_{\text{total}}\,\chi_{\text{gas}}$):

$$K_p = \frac{(P_C^c)(P_D^d)}{(P_A^a)(P_B^b)} = \frac{(\chi_C^c)(\chi_D^d)(P_t)^{c+d}}{(\chi_A^a)(\chi_B^b)(P_t)^{a+b}}$$

$$= K_\chi\,(P_t)^{(c+d)-(a+b)}$$

or

$$K_p = K_\chi(P_t)^{\Delta n_g} \tag{7.14}$$

Example 7.1 Write the expressions for K_p and K_c (whichever is applicable) for the following reversible reactions at equilibrium:

(i) $2H_2S(g) + 3O_2(g) \rightleftharpoons 2H_2O(g) + 2SO_2(g)$

(ii) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

(iii) $HF(aq.) + H_2O(l) \rightleftharpoons H_3O^+(aq.) + F^-(aq.)$

Strategy: For K_p, we express the equilibrium active masses in terms of partial pressures while for K_c, we express the equilibrium active masses in terms of molar concentrations. For reactions involving gases only, we can write both K_p and K_c.

Solution:

(i) $K_p = \dfrac{P_{H_2O}^2 P_{SO_2}^2}{P_{H_2S}^2 P_{O_2}^3}$, $\quad K_c = \dfrac{C_{H_2O}^2 C_{SO_2}^2}{C_{H_2S}^2 C_{O_2}^3}$

(ii) $K_p = \dfrac{P_{NO_2}^2}{P_{NO}^2\,P_{O_2}}$, $\quad K_c = \dfrac{C_{NO_2}^2}{C_{NO}^2 C_{O_2}}$

(iii) Since there are no gases present, K_p does not apply. We, thus, have only K_c:

$$K_c = \frac{C_{H_3O^+}C_{F^+}}{C_{HF}}$$

Note that HF is a weak acid. Thus, the amount of water consumed in acid ionization is negligible relative to the total amount of water present as solvent. Thus, C_{H_2O} (a constant value) does not appear in the expression for K_c as it is already absorbed in its numerical value ($K_c = K'_c\ C_{H_2O}$).

Example 7.2 ***Calculating K_c*:** Some nitrogen and hydrogen gas are placed in an empty 2.50 L container at 500°C. When equilibrium is established, 1.51 mol of N_2, 1.05 mol of H_2, and 0.283 mol of NH_3 are present. Calculate K_c for the following reaction at 500°C:

$$N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g)$$

Strategy: To calculate K_c, we need equilibrium concentrations, which are obtained by dividing the number of equilibrium moles of each reacting substance by the volume of the container.

Solution:

$$C = \frac{n}{V}$$

$$\therefore \quad C_{N_2} = \frac{n_{N_2}}{V} = \frac{1.51\ \text{mol}}{2.50\ \text{L}} = 0.604\ \text{M}$$

$$C_{H_2} = \frac{n_{H_2}}{V} = \frac{1.05\ \text{mol}}{2.50\ \text{L}} = 0.420\ \text{M}$$

$$C_{NH_3} = \frac{n_{NH_3}}{V} = \frac{0.283\ \text{mol}}{2.50\ \text{L}} = 0.113\ \text{M}$$

The equilibrium constant, K_c, is given by

$$K_c = \frac{C_{NH_3}^2}{C_{N_2} C_{H_2}^3}$$

Substituting the equilibrium concentrations, we find that

$$K_c = \frac{(0.113)^2}{(0.604)(0.420)^3}$$

$$= 0.285$$

> Remember that the active masses in K_c calculations are equilibrium values of molar concentrations. Also note that K_c is given without units.

Example 7.3 ***Calculating K_p*:** In an equilibrium mixture at 500°C, we find that $P_{NH_3} = 0.076$ atm, $P_{N_2} = 3.00$ atm, and $P_{H_2} = 1.85$ atm. Calculate K_p at 500°C for the following reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Strategy: Write the expression for K_p in terms of equilibrium partial pressures of all reacting substances and substitute partial pressures in atmospheres into it.

Solution: Equilibrium constant K_p is given by

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

Substituting the pressures, we find that

$$K_p = \frac{(0.076)^2}{(0.300)(1.85)^3} = 3.04 \times 10^{-4}$$

> One error that students sometimes make when solving K_p problems is to express pressures in torr or mmHg. Remember that these pressures must be expressed in atmospheres or bar.

Example 7.4 ***Calculating K_p from K_c*:** The equilibrium constant, K_c, for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

is 3.64×10^{-3} at 25°C. What is the value of K_p at this temperature?

Strategy: Use Eq. (7.12) to calculate K_p from K_c and use chemical equation to find Δn_g, i.e., the change in the number of moles of gas as the reaction proceeds from left to right.

Solution: From Eq. (7.12), we write

$$K_p = K_c(RT)^{\Delta n_g}$$

Since $K_c = 3.64 \times 10^{-3}$, $R = 0.081$ L atm K^{-1} mol^{-1}, $T = 298$ K, and $\Delta n_g = (2 - 1) = 1$, we have

$$K_p = (3.64 \times 10^{-3})\,(0.0821)\,(298)$$

$$= 0.089$$

> Note that K_p, like K_c, is treated as a dimensionless quantity. This example shows that we can get quite a different value for the equilibrium constant for the same reaction, depending on whether we express the active masses in mol L^{-1} or in atmospheres.

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>
> To decide which value of R to use when we convert between K_p and K_c, we can reason as follows: K_p involves pressures expressed in atm while K_c involves molar concentrations in mol L^{-1}. Thus, the most suitable value of R to use for these conversions must include these units. Thus, we use 0.0821 L atm K^{-1} mol^{-1}. If pressure is expressed in bar (note that standard pressure is 1 bar), then we use 0.0831 L bar K^{-1} mol^{-1}.

7.5 HETEROGENEOUS EQUILIBRIUM

Homogeneous equilibria involve species in a single phase while heterogeneous equilibria involve species in more than one phase. Thus, a reversible reaction involving reacting species that are in different phases (i.e., different physical states) leads to a heterogeneous equilibrium.

Examples of heterogeneous physical equilibria are as follows:

(1) Equilibrium between water vapor and liquid water in a closed container

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Equilibrium in this system has more than one phase—a liquid phase and a gas phase.

(2) Equilibrium between a solid and its saturated solution:

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

Pure solids or liquids are often involved in heterogeneous equilibrium. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure solid or a pure liquid by using the fact that active mass of a pure solid or pure liquid is constant (i.e., independent of the amount present) as it is expressed through its density.

> If a substance Z is involved in an equilibrium system, then [Z(s)] or [Z(l)] is constant irrespective of the amount of Z taken. On the other hand, [Z(aq.)] or [Z(g)] will change as the amount of Z in a given volume changes.

Let us consider the heterogeneous chemical equilibrium when calcium carbonate (heated in a closed vessel) undergoes thermal decomposition.

$$CaCO_3(s) \xrightleftharpoons{\Delta} CaO(s) + CO_2(g)$$

When equilibrium is established for this system, three separate phases (two solids and one gas) are present.

Applying the law of chemical equilibrium, we have

$$K_{eq} = \frac{[CaO][CO_2]}{[CaCO_3]} \tag{7.15}$$

The fundamental definition of equilibrium constant in thermodynamics is in terms of the activities of the substances involved. For any pure solid (or pure liquid), the active mass is directly proportional to its density (proportionality constant is called activity coefficient), which is constant at a given temperature, i.e., it does not depend on the quantity of substance present. For example, the density of gold (at 20°C) is 19.32 g cm^{-3}. It is the same, whether we have 1 g or 1 ton of the metal:

$$\frac{19.32\,\text{g}}{\text{cm}^3} \times \frac{1\,\text{mol}}{197\,\text{g}} = 0.0981\,\text{mol cm}^{-3} = 98.1\,\text{mol L}^{-1}$$

Because both $CaCO_3$ and CaO are pure solids, their active masses do not change as the reaction proceeds. Thus, we can express the equilibrium constant for the thermal decomposition of $CaCO_3$ in a different way.

Rearranging Eq. (7.15), we obtain

$$K_{eq}\,\frac{[CaCO_3]}{[CaO]} = [CO_2]$$

Since K_{eq} is an equilibrium constant and both $[CaCO_3]$ and [CaO] are constants, we can say that all the terms on the left-hand side of the equation are constants and can be replaced by a single constant. This simplifies the equation and helps us to write

$$K'_{eq} = [CO_2] \qquad (7.16)$$

where K'_{eq}, the modified equilibrium constant, is just expressed in terms of a single active mass, that of CO_2. Keep in mind that the value of K'_{eq} does not depend on how much $CaCO_3$ and CaO are present as long as some of each is present to maintain equilibrium.

What has been said about pure solids also applies to pure liquids. Thus, if a pure liquid is present as one of the reacting species in a reversible reaction, we can treat its active mass as constant and omit it from the equilibrium constant expression. In future discussion, we will write only the modified equilibrium constant.

> In simple terms, we can say that for any pure solid or pure liquid, the active mass (or the activity) is taken as 1. So terms for pure solids and pure liquids do not appear in the equilibrium constant expressions for heterogeneous equilibria.

Thus, for the thermal decomposition of $CaCO_3$, concentration equilibrium constant should be written in the modified form as:

$$K_c = C_{CO2} \qquad (7.17)$$

which shows that at a particular temperature, there is a constant concentration of CO_2 in equilibrium with CaO(s) and $CaCO_3$(s).

Alternatively, we can express the pressure equilibrium constant as

$$K_p = P_{CO2} \qquad (7.18)$$

i.e., the pressure equilibrium constant is numerically equal to the equilibrium pressure of the CO_2 gas, an easily measurable quantity. Experimentally, it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $CaCO_3$(s) and CaC(s) is 2.0×10^5 Pa. Therefore, pressure equilibrium constant at 1100 K for the thermal decomposition of $CaCO_3$ is

$$K_p = P_{CO2} = \frac{2.0 \times 10^5 \text{ Pa}}{10^5 \text{ Pa bar}^{-1}} = 2.0$$

As an another example of heterogeneous equilibrium, consider the following reversible reaction at 25°C.

$$2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$$

When equilibrium is established for this system, a solid, a liquid, and a gas are present. Equilibrium constant expressions are

$$K_c = C_{O_2} \text{ and } K_p = P_{O_2}$$

These equilibrium constant expressions indicate that equilibrium exists at a given temperature for one and only one concentration and one partial pressure of oxygen in contact with liquid mercury and solid mercury (II) oxide.

Example 7.5 ***K_c and K_p for heterogeneous equilibrium*:**
Write the equilibrium constant expressions K_c and K_p, if applicable, for each of the following heterogeneous system:

(i) $S(s) + H_2SO_3(aq.) \rightleftharpoons H_2S_2O_3(aq.)$
(ii) $2NH_3(g) + H_2SO_4(l) \rightleftharpoons (NH_4)_2SO_4(s)$
(iii) $P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$
(iv) $AgCl(s) \rightleftharpoons Ag^+(aq.) + Cl^-(aq.)$
(v) $(NH_4)_2Se(s) \rightleftharpoons 2NH_3(g) + H_2Se(g)$

Strategy: Apply the definitions of K_c and K_p to each reaction. Remember that in heterogeneous equilibrium, pure solids or pure liquids must be present (however, small it may be) for the equilibrium to exist, but their active masses do not appear in the expression of the equilibrium constant because they are incorporated into the value of equilibrium constant.

Solution:

(i) $K_c = \dfrac{C_{H_2S_2O_3}}{C_{H_2SO_3}}$, K_p cannot be defined as no gases are involved

(ii) $K_c = \dfrac{1}{C_{NH_3}}, \quad K_p = \dfrac{1}{P_{NH_3}}$

(iii) $K_c = \dfrac{1}{C^6_{Cl_2}}, \quad K_p = \dfrac{1}{P^6_{Cl_2}}$

(iv) $K_c = C_{Ag^+}\,C_{Cl^-}$, K_p undefined, no gases involved
(v) $K_c = C^2_{NH_3}C_{H_2Se}, \quad K_p = P^1_{NH_3}P_{H_2Se}$

> *Units of equilibrium constant*: The value of concentration equilibrium constant K_c is calculated by substituting the activities in mol L^{-1}, and for K_p (pressure equilibrium constant), partial pressure is substituted in Pa, kPa, bar, or atm. This results in the units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and the denominator are the same.
>
> Thus, for the reaction
>
> $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
>
> K_c and K_p have no units while for the reaction
>
> $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
>
> K_c has unit mol L^{-1} and K_p has unit bar.
>
> Note that it is a general practice not to include units for the equilibrium constant. In thermodynamics, K_{eq} is defined to have no units since the thermodynamic definition of the equilibrium constant involves activities rather than concentrations. Activities are dimensionless quantities because the activity of a component

of an ideal mixture is the ratio of its concentration or partial pressure to a standard concentration (1 M) or pressure (1 atm). In other words, K_{eq} (in thermodynamics) has no units since every concentration (molarity) or pressure (atmospheres) term is actually a ratio to a standard value, which is 1 M or 1 atm. This procedure eliminates all units but does not alter the numerical parts of the concentration or pressure. For example, a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number.

Because of the use of activities, the equilibrium constant has no units. The values we put into K_c are numerically equal to molar concentrations, but are dimensionless, that is, they have no units. Thus, the calculations involving equilibrium are frequently carried out without units.

The numerical value of equilibrium constant depends on the standard state chosen. Thus, both K_p and K_c are dimensionless quantities but have different numerical values due to different standard states.

7.6 THE FORM OF *K* AND THE EQUILIBRIUM EQUATION

For any balanced chemical equation, the value of K_{eq} is constant at a given temperature (changes if the temperature changes) and does not depend on the initial concentrations of the reacting species.

However, the value of K_{eq} depends on the form of the balanced equation for the reaction.

1. When the chemical equation for a reversible reaction is written in the opposite direction, the equilibrium constant is changed. The new equilibrium constant becomes the reciprocal of the original equilibrium constant.

   Thus, if we write the equation for the reaction of SO_2 and O_2 to form SO_3 as

   $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

   then

   $$K_{\text{eq}} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \tag{7.19}$$

   Suppose we write the equation for the same reversible reaction in reverse:

   $$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

   The equilibrium constant is now given by

   $$K'_{\text{eq}} = \frac{[SO_2]^2[O_2]}{[SO_3]^2} \tag{7.20}$$

   Comparing Eqs. (7.19) and (7.20), we can see that

   $$K'_{\text{eq}} = \frac{1}{K_{eq}} \tag{7.21}$$

   or $K'_{\text{eq}} \cdot K_{\text{eq}} = 1$

   i.e., K'_{eq}, the equilibrium constant for the reaction written in reverse, is the reciprocal of K_{eq}, the equilibrium constant for the original reaction.

   Either K_{eq} or K'_{eq} is a valid equilibrium constant, but it is meaningless to say that the equilibrium constant for the SO_2–O_2–SO_3 system is K_{eq} or K'_{eq} unless we also specify how the equilibrium equation is written.

2. The value of equilibrium constant also depends on how the equilibrium equation is balanced. Let us consider the following two ways of describing the same equilibrium equation:

   $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ K_{\text{eq}} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

   $$SO_2(g) + \frac{1}{2}\ O_2(g) \rightleftharpoons SO_3(g);\ K'_{\text{eq}} = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

   Comparing the two equilibrium constant expressions (looking at the exponents), we see that $K'_{\text{eq}} = (K_{\text{eq}})^{1/2}$ or $\sqrt{K_{\text{eq}}}$, i.e., K'_{eq} is the square root of K_{eq}.

According to the law of mass action, each activity term in the equilibrium constant expression is raised to a power equal to its stoichiometric coefficient. Thus, if we double a chemical equation throughout, the corresponding equilibrium will be the square of the original value. Similarly, if we triple the equation, the equilibrium constant will be the cube of the original value, and so on.

In general, if an equilibrium equation for a reaction is multiplied by any factor n, then the original value of K_{eq} is raised to the nth power. Through this outcome, we can also cover the previous case (1), because reversing an equation is the same as multiplying all coefficients by –1. This reverses the roles of reactants and products.

We must always write the particular balanced chemical equation to quote the numerical value of an equilibrium constant.

7.6.1 Multiple Equilibria

All the equilibrium systems we have considered so far are relatively simple. Now, we consider a relatively complicated situation in which the product molecules in one equilibrium system are involved in a second equilibrium process:

$$A + B \rightleftharpoons C + D$$
$$C + D \rightleftharpoons E + F$$

Note that the products formed in the first reaction, C and D, react further to form products E and F. Applying the law of chemical equilibrium to each of the reactions gives two separate equilibrium constants:

$$K_{\text{eq}} = \frac{[C][D]}{[A][B]}$$

and $$K'_{\text{eq}} = \frac{[E][F]}{[C][D]}$$

The overall reaction is given by the sum of the two reactions:

$$\begin{array}{lll} & A + B \rightleftharpoons C + D & K_{\text{eq}} \\ & \underline{C + D \rightleftharpoons E + F} & K'_{eq} \\ \text{Overall reaction:} & A + B \rightleftharpoons E + F & K''_{eq} \end{array}$$

Applying the law of chemical equilibrium, we get the equilibrium constant (K''_{eq}) for the overall reaction,

$$K''_{\text{eq}} = \frac{[E][F]}{[A][B]}$$

Note that we obtain the same expression if we take the product of the expressions for K_{eq} and K'_{eq}:

$$K_{\text{eq}}K'_{\text{eq}} = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]}$$

Hence, we can write

$$K''_{\text{eq}} = K_{\text{eq}}K'_{\text{eq}} \tag{7.22}$$

An important statement about multiple equilibrium can now be made: *If a reaction can be expressed as the sum of two or more reactions, then the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.*

Follow-up Test 3

1. According to the law of mass action, the rate of an elementary reaction is directly proportional to the _______ of the reactants.
   (1) mole fractions (2) molalities
   (3) normalities (4) molarities
2. According to the law of chemical equilibrium,
   (1) the rate of forward reaction becomes equal to the rate of backward reaction when the chemical system attains equilibrium
   (2) a system can achieve the equilibrium state through forward as well as backward reaction
   (3) both (1) and (2)
   (4) the equilibrium constant K_{eq} is defined as the product of the equilibrium active masses of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the equilibrium active masses of reactants, each raised to the power that corresponds to its coefficient in the balanced equation
3. K_f and K_b are the velocity constants of forward and backward reactions. The equilibrium constant K_{eq} of the reversible reaction will be
   (1) K_b/K_f (2) $K_f \times K_b$
   (3) K_f/K_b (2) $K_f - K_b$
4. In which of the following equilibrium equation, $K_p > K_c$?
   (1) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
   (2) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
   (3) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
   (4) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
5. For the equilibrium equation
   $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
   the units of K_p will be
   (1) $(\text{atm})^{-2}$ (2) $(\text{atm})^{2}$
   (3) $(\text{atm})^{3}$ (4) atm
6. The equilibrium constant of the equilibrium equation
   $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$
   is 0.44 at 1259 K. The value of equilibrium constant for the equilibrium equation
   $H_2(g) + 2CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$
   will be
   (1) –0.44 (2) –1/0.44
   (3) 1/0.44 (4) 0.44
7. For the reversible reaction
   $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
   the value of the equilibrium constant depends on the
   (1) pressure of the system
   (2) volume of the reaction vessel
   (3) initial concentrations of H_2 and I_2
   (4) temperature of the system
8. If the equilibrium constant of the reversible reaction $HI(g) \rightleftharpoons 1/2H_2(g) + 1/2I_2(g)$ is 7.4, the equilibrium constant for the reversible reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ will be
   (1) $\sqrt{7.4}$ (2) 54.76
   (3) 14.8 (4) 7.4
9. 1.7 g of $NH_3(g)$ is present in a 2-L flask. The active mass of $NH_3(g)$ is
   (1) 0.1 M (2) 0.02 M
   (3) 0.05 M (4) 0.5 M
10. The active mass for any pure liquid or pure solid
    (1) is always taken as 1
    (2) is always infinity
    (3) is always zero
    (4) would depend on the nature of the solid
11. The relation between K_p and K_x is
    (1) $K_p = K_x\left(\dfrac{P}{\sum n}\right)$ (2) $K_p = K_x(P)^{-\Delta n}$
    (3) $K_p = K_x(P)^{\Delta n}$ (4) $K_p = K_x(RT)^{\Delta n}$
12. If the equilibrium constant of the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 0.25, the equilibrium constant of the reaction
    $$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$
    will be
    (1) 2.0 (2) 4.0
    (3) 1.0 (4) 3.0
13. If $CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g)$, $K_1 = 60$
    $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$, $K_2 = 180$
    then the equilibrium constant of the reaction
    $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
    will be
    (1) 0.44 (2) 0.11
    (3) 0.22 (4) 0.33

7.7 APPLICATIONS OF EQUILIBRIUM CONSTANT

Before we deal with the applications of equilibrium constant, it would be better to summarize the important rules for writing equilibrium constant expression and the features of equilibrium constant.

1. Equilibrium constant expression can be written in terms of the active masses of reactants and products only when the system has attained the equilibrium state.
2. The active masses of pure solids, pure liquids (in heterogeneous equilibrium), and solvents (in homogeneous equilibrium) do not appear in the equilibrium constant expressions.
3. The active masses of the reacting species in the condensed phase are expressed in mol L^{-1}. In the gaseous phase, the active masses can be expressed in mol L^{-1} or in atm.
4. K_c is related to K_p by a simple equation: $K_p = K_c(RT)^{\Delta n_g}$.
5. The equilibrium constant (K_p or K_c) is treated as a dimensionless quantity.
6. The numerical value of equilibrium constant is independent of the initial concentrations of reactants and products.
7. In quoting a value for the equilibrium constant, we must specify the balanced equation and the temperature because equilibrium constant is temperature dependent having a unique value for a particular reaction represented by a balanced equation at a given temperature.
8. If a given reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

7.7.1 Predicting the Extent of a Reaction

The magnitude of equilibrium constant depends on the nature of the reaction and on the temperature. At constant temperature, the magnitude of K_{eq} varies greatly from one reaction to another. According to the law of chemical equilibrium, the magnitude of K_{eq} (K_c or K_p) is directly proportional to the active masses (concentrations) of the products (as they appear in the numerator of equilibrium constant expression) and inversely proportional to the active masses of the reactants (as they appear in the denominator). This implies that the value of K_{eq} tells us the relative quantities of reactants and products formed at equilibrium, and, hence, the yield of the reaction—a great practical importance.

> The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is significant to note that an equilibrium constant does not give any information about the rate at which the equilibrium is reached.

By considering three cases, we can make the following generalizations concerning the composition of equilibrium mixtures and get a sense of whether reactants or products are favored.

Case I: If K_{eq} is very large compared with 1 (any number > 10 is said to be much greater than 1 in this context), then products predominate over reactants and the reaction proceeds nearly to completion. Typical examples are:

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g);\ K_c = 5.4 \times 10^{18} \text{ (at 300 K)}$$

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g);\ K_c = 4.0 \times 10^{31} \text{ (at 300 K)}$$

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g);\ K_c = 2.4 \times 10^{47} \text{ (at 500 K)}$$

Consider the following system at 2300°C:

$$2O_3(g) \rightleftharpoons 3O_2(g)$$

$$K_{eq} = \frac{[O_2]^3}{[O_3]^2} = 2.54 \times 10^{12}$$

This implies that an equilibrium mixture of O_2 and O_3 at this temperature contains very little O_3 as compared with O_2.

Thus, if $[O_2] = 0.500$ M at equilibrium,

then $$[O_3]^2 = \frac{(0.500)^3}{(2.54\times10^{12})}$$

$$= 4.92 \times 10^{-14}$$

$$[O_3] = 2.22 \times 10^{-7}$$

Case II: If K_{eq} is very small compared with 1 (any number < 0.1 is considered much smaller than 1 in this context), then reactants predominate over products and the reaction rarely proceeds. Typical examples are

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g);\ K_c = 4.1 \times 10^{-48} \text{ (500 K)}$$

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g);\ K_c = 4.8 \times 10^{-31} \text{ (298 K)}$$

Consider the following equilibrium system at 25°C:

$$Cl_2(g) \rightleftharpoons 2Cl(g);\ K_{eq} = \frac{[Cl]^2}{[Cl_2]} = 1.4\times10^{-38}$$

This implies that an equilibrium mixture at this temperature will contain mostly Cl_2 molecules and very few Cl atoms. If $[Cl_2] =$ 0.76 M at equilibrium, then

$$[Cl]^2 = (0.76)\ (1.4 \times 10^{-38})$$

$$= 1.1 \times 10^{-38}$$

$$[Cl] = 1.0 \times 10^{-19} \text{ M}$$

i.e., the concentration of Cl atoms is very low compared with that of Cl_2 molecules.

Case III: If K_{eq} is neither very large nor very small compared with 1, then the quantities of reactants and products present at equilibrium will be comparable. Typical examples are:

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O;\ K_c = 4$$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g);\ K_c = 57.0 \text{ (at 700 K)}$$

Consider the following equilibrium system at 830°C:

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

$$K_{eq} = \frac{[H_2][CO_2]}{[CO][H_2O]} = 5.10$$

If [CO] = 0.200 M, $[H_2O] = 0.400$ M, and $[H_2] = 0.300$ M at equilibrium, then

$$[CO_2] = (5.10)\frac{(0.400)(0.200)}{(0.300)}$$

$$= 1.36 \text{ M}$$

7.7.2 Predicting the Direction of the Reaction

The equilibrium constant helps us to predict the direction in which a reaction mixture will proceed to achieve equilibrium. For this purpose, we calculate the reaction quotient (Q) and compare it with the equilibrium constant (K_{eq}).

The reaction quotient, Q, for the general reversible reaction

$$aA + bB \rightleftharpoons cC + dD$$

is given as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ not necessarily equilibrium concentrations}$$

It is significant to note that the reaction quotient (Q) has the same form as the equilibrium constant, but it involves specific values that are not necessarily equilibrium active masses. If they are equilibrium active masses, then $Q = K_{eq}$. Moreover, we can calculate the value of reaction quotient at any stage but we can calculate the value of equilibrium constant only when the system is at equilibrium.

Like equilibrium constant, reaction quotient may be concentration reaction quotient Q_c (if molar concentrations are used for the active masses) or pressure reaction quotient Q_p (if partial pressures are used for the active masses). *Thus, the quantity obtained by substituting the initial concentrations into the equilibrium constant expression is called the concentration reaction quotient* (Q_c).

We can think of the concentration reaction quotient (Q_c) as a measure of the progress of the reaction. When the mixture contains only reactants, the concentrations in the numerator are zero. So, $Q_c = 0$. As the reaction proceeds to the right, the product concentrations (numerator) increase and the reactant concentrations (denominator) decrease. So, Q increases to an infinitely large value when all the reactants have been consumed and only products remain. The value of K_c is a particular value of Q_c that represents equilibrium mixture for the reaction.

To determine in which direction the net reaction will proceed to achieve equilibrium, we compare the values of Q_c *and* K_c. Three possible outcomes are as follows:

$\boldsymbol{Q_c < K_c}$**:** If at any time $Q_c < K_c$, the forward reaction must occur to a greater extent than the reverse reaction ($r_f > r_b$) for equilibrium to be established. This is because when $Q_c < K_c$, the numerator of Q_c is too small and the denominator is too large, i.e., the ratio of initial concentrations of products to reactants is too small. To reach equilibrium, i.e., to increase the numerator and reduce the denominator, the reactants (A and B) must react to produce products (C and D). Thus, the system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.

> When the forward reaction occurs to a greater extent than the reverse reaction, we say that a net forward reaction has occurred.

$\boldsymbol{Q_c > K_c}$**:** If at any time $Q_c > K_c$, the reverse reaction must occur to a greater extent than the forward reaction ($r_b > r_f$) for equilibrium to be reached. This is because when $Q_c > K_c$, the ratio of initial concentrations of products to reactants is too large. Thus, to reach equilibrium, the products must be converted to reactants, i.e., the system proceeds from right to left (consuming products, forming reactants) to reach equilibrium. When the value of Q_c reaches the value of K_c, the system is at equilibrium. So no further net reaction occurs.

$\boldsymbol{Q_c = K_c}$**:** If at any time $Q_c = K_c$, the forward reaction as well as the backward reaction occur to the same extent because the initial concentrations are equilibrium concentrations. The system is at equilibrium.

> When $Q_c > K_c$, reverse reaction predominates until equilibrium is established. When $Q_c < K_c$, forward reaction predominates until equilibrium is established. When $Q_c = K_c$, system is at equilibrium.

Example 7.5 ***Reaction quotient:*** At a very high temperature, $K_c = 65.0$ for the following reversible reaction:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The following concentrations were detected in a mixture.

$$C_{HI} = 0.50 \text{ M}, C_{H_2} = 2.80 \text{ M, and } C_{I_2} = 3.40 \text{ M}$$

Is the system at equilibrium? If not, in which direction must the reaction proceed for equilibrium to be established?

Strategy: First substitute these concentrations (which could be present if we started with a mixture of HI, H_2, and I_2) into the expression for the reaction quotient to calculate Q_c. Next we compare Q_c with the known value of K_c to see whether the system is at equilibrium and also to predict the direction of the reaction that leads to equilibrium.

Solution:

$$Q_c = \frac{C_{H_2}C_{I_2}}{C_{HI}^2} = \frac{(2.80)\,(3.40)}{(0.50)^2} = 38.1$$

Since Q_c is smaller than K_c (65.0), the system is not at equilibrium, i.e., $r_f \neq r_b$. For equilibrium to be established, the value of Q_c must increase until it equals K_c. This can occur only if the numerator increases (i.e., an increase in the concentrations of H_2 and I_2) and the denominator decreases (i.e., a decrease in the concentration of HI). Thus, the forward (left-to-right) reaction must occur to a greater extent than the reverse reaction ($r_f > r_b$), i.e., some HI must dissociate to form more H_2 and I_2 to reach equilibrium.

7.7.3 Calculating Equilibrium Concentrations

We have discussed that the equilibrium constant for a given reaction can be calculated from known equilibrium concentrations. Once we know the value of the equilibrium constant, we can use the equilibrium constant expression to calculate unknown equilibrium concentrations from a knowledge of the initial concentrations. During this process, we must remember that the equilibrium constant is a constant only if the temperature does not change.

Depending on the information given, the calculation may be straightforward or complex. Let us consider the synthesis of ammonia, which has an equilibrium constant K_c at a certain temperature:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Suppose that we start our reaction with N_2 and H_2 having initial concentrations a and b mol L^{-1}, respectively. Let us discuss how do we calculate the concentrations of N_2, H_2, and NH_3 at equilibrium?

From the stoichiometry of the reaction, we see that for every mole of N_2 consumed, 3 mol of H_2 are consumed and 2 mol of NH_3 are formed. Let x be the concentration of N_2 in mol L^{-1} that must react with H_2 to reach equilibrium. Then equilibrium concentrations of N_2, H_2, and NH_3 must be $(a - x)$ mol L^{-1}, $(b - 3x)$ mol L^{-1}, and $2x$ mol L^{-1}, respectively. It is useful to summarize the changes in concentration as follows:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Initial (M):	a	b	0
Change (M):	$-x$	$-3x$	$+2x$
Equilibrium (M):	$(a - x)$	$(b - 3x)$	$+2x$

A positive (+) change represents an increase and a negative (–) change indicates a decrease in concentration at equilibrium. Thus, when the system attains equilibrium, we can see that there is a decrease of x mol L^{-1} in the initial concentration of N_2 and an increase of $2x$ mol L^{-1} in the concentration NH_3 which started as zero.

Next, we set up the equilibrium constant expression

$$K_c = \frac{C^2_{NH_3}}{C_{N_2}\, C^3_{H_2}}$$

$$= \frac{(2x)^2}{(a - x)\,(b - 3x)^3}$$

Having solved for x, we calculate the equilibrium concentrations of N_2, H_2, and NH_3 as follows:

$C_{N_2} = a - x$, $C_{N_2} = b - 3x$, and $C_{NH_3} = 2x$

Similarly, we can deal with the dissociation of a compound such as phosphorus pentachloride:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Initial (M):	a	o	o
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$(a - x)$	x	x

In such situations, we also talk in terms of degree of the dissociation (*alpha*, α) *which is defined as the fraction of one mole of the substance dissociated at equilibrium.* Thus,

$$\alpha = \frac{x}{a}$$

or $\quad x = a\,\alpha$

Equilibrium concentrations can also be expressed in terms of the degree of dissociation:

$C_{PCl_5} = a - a\alpha$, $C_{PCl_3} = C_{Cl_2} = a\alpha$

We summarize our approach to solving equilibrium constant problems as follows:

Step 1: Write the correct balanced equation for the equilibrium reaction.

Step 2: Under the balanced equation, make a table that lists for each substance involved in the reaction,

(i) the initial concentration,
(ii) the change in concentration establishing the equilibrium, and
(iii) the equilibrium concentration.

To construct this table, we define x as the molar concentration or partial pressure of one of the reactants that is consumed in establishing the equilibrium. Then we use the stoichiometry of the reaction to determine the concentration of the other substances in terms of x. Finally, we express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown which represents the change in concentration.

Step 3: Write the equilibrium constant expression and substitute the equilibrium concentrations into it. Knowing the value of the equilibrium constant, solve for X. If we are to solve a quadratic equation, then choose the mathematical solution that makes chemical sense.

Step 4: Having solved for x, calculate the equilibrium concentrations of all species (from the calculated value of x).

Step 5: Check the results by substituting them into the equilibrium constant expression.

Example 7.6 ***Finding equilibrium concentrations*****:** A mixture of 0.50 mol H_2 and 0.50 mol I_2 is placed in a 1.00 L stainless steel container at 400°C. The equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 54.3 at this temperature. Calculate the equilibrium concentrations of H_2, I_2, and HI.

Strategy: First we find the initial concentrations. Then we write the reaction summary and represent the equilibrium concentrations algebraically. Finally, we substitute the algebraic representations of equilibrium concentrations into the K_c expression and find the equilibrium concentrations.

Solution:

Step 1: The initial concentrations are

$$C_{H_2} = \frac{n_{H_2}}{V_L} = \frac{0.50\,\text{mol}}{1.00\text{ L}} = 0.50\text{ mol}^{-1}$$

$$C_{I_2} = \frac{n_{I_2}}{V_L} = \frac{0.50\text{ mol}}{1.00\text{ L}} = 0.50\text{ mol L}^{-1}$$

The reaction can only proceed to the right because only reactants are present. The reaction summary includes the values, or symbols for the values, of (i) initial concentrations, (ii) changes in concentrations, and (iii) concentrations at equilibrium.

Step 2: According to the stoichiometry of the reaction, 1 mol H_2 reacts with 1 mol I_2 to produce 2 mol HI. Let x be the decrease in concentration (mol L^{-1}) of either H_2 or I_2 at equilibrium. Then the equilibrium concentration of HI must be $2x$. Summarizing the changes in concentrations, we get

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Initial (M):	0.50	0.50	0.00
Change (M):	$-x$	$-x$	$+2x$
Equilibrium	$(0.50 - x)$	$(0.50 - x)$	$2x$

Step 2: According to the law of chemical equilibrium, the equilibrium constant is given by

$$K_c = \frac{C_{HI}^2}{C_{H_2} C_{I_2}}$$

Now, K_c is known but concentrations are not. But the equilibrium concentrations have all been expressed in terms of a single variable x. We substitute the equilibrium concentrations (not the initial ones) into the K_c expression and solve for x.
Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.50 - x)(0.50 - x)}$$

$$= \frac{(2x)^2}{(0.50 - x)^2}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{(0.50 - x)}$$

$$(7.37)(0.50 - x) = 2x$$
$$3.685 - 7.37x = 2x$$
$$3.685 = 2x + 7.37\,x = 9.37\,x$$
$$x = \frac{3.685}{9.37} = 0.393 \text{ M}$$

Step 3: Now, we know the value of x. So the equilibrium concentrations are

$C_{H_2} = (0.50 - 0.393)$ M $= 0.107$ M
$C_{I_2} = (0.50 - 0.393)$ M $= 0.107$ M
$C_{HI} = 2 \times 0.393$ M $= 0.786$ M

Step 4: To check our answers, we use the equilibrium concentrations to calculate Q_c and verify that its value is equal to K_c.

$$Q_c = \frac{C_{HI}^2}{C_{H_2} C_{I_2}} = \frac{(0.786)^2}{(0.107)(0.107)} = 54.0$$

Example 7.7 The equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.3 at 400°C. If the initial concentrations of H_2, I_2, and HI are 0.00623 M, 0.00414 M, and 0.0224 M, respectively, calculate the concentrations of these species at equilibrium.

Strategy: Proceed as we did in Example 7.6. The only difference is that now we have non-stoichiometric amounts of reactants. Also, find the value of Q_c to decide the direction of reaction.

Solution:

Step 1: Let x be the decrease in concentration (mol L^{-1}) for H_2 and I_2 at equilibrium. Then, according to the stoichiometry of the reaction, the increase in concentration for HI must be $2x$. Summarize the changes in concentrations as follows:

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial (M):	0.00623		0.00414		0.0224
Change (M):	$-x$		$-x$		$+2x$
Equilibrium (M):	$(0.00623 - x)$		$(0.00414 - x)$		$(0.0224 + 2x)$

Note that we have considered the net reaction in the forward direction because Q_c (19.45) is less than K_c (54.3).

Step 2: Writing the equilibrium constant expression

$$K_c = \frac{C_{HI}^2}{C_{H_2} C_{I_2}}$$

Substituting, we get

$$K_c = \frac{(0.0224 + 2x)^2}{(0.0063 - x)(0.00414 - x)}$$

It is not possible to solve this equation by the square root shortcut as the left side of this equation is not a perfect square, because the starting concentrations of H_2 and I_2 are unequal. Instead, we can arrange this quadratic equation into the standard form by carrying out the multiplications:

$$54.3\,(0.00623 - x)(0.00414 - x) = (0.0224 + 2x)^2$$
$$54.3\,(2.58 \times 10^{-5} - 0.0104\,x + x^2) = 5.02 \times 10^{-4} + 0.0896\,x + 4x^2$$

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$, which can be solved by the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, we have

$a = 50.3$, $b = -0.654$, and $c = 8.98 \times 10^{-4}$

Substituting these values gives

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4\,(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$$\Rightarrow \quad x = 0.0114 \text{ M} \quad \text{or} \quad x = 0.00156 \text{ M}$$

The first solution is physically impossible since the amounts of H_2 and I_2 reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving a quadratic equation of this type, one answer is always physically impossible. Thus, the choice of which value to use for x is easy to make.

Step 3: The equilibrium concentrations are

$C_{H_2} = (0.00623 - 0.00156)$ M $= 0.00467$ M
$C_{I_2} = (0.00414 - 0.00156)$ M $= 0.00258$ M
$C_{HI} = (0.0224 + 2 \times 0.00156)$ M $= 0.0255$ M

Follow-up Test 4

1. Equilibrium concentrations of A, B and C in a reversible reaction

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

   are 0.03, 0.01, and 0.008 mol L^{-1}. Calculate the initial concentration of A?

   (1) 0.014 (2) 0.042
   (3) 0.084 (4) 0.343

2. At 250°C, K_c for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 0.04. How many moles of PCl_5 must be added to a 3-L flask to obtain 0.15 M Cl_2 at equilibrium?

   (1) 2.1 mol (2) 1.7 mol
   (3) 0.9 mol (4) 3.5 mol

3. A large value of equilibrium constant shows that
   (1) the reaction is taking place at high temperature
   (2) the reaction is very little in the forward as well as backward direction
   (3) the reaction is less in the forward direction and more in the backward direction
   (4) the forward reaction occurs to a greater extent than the reverse reaction
4. The equilibrium constant K_p for the reaction
   $A \rightleftharpoons 2B$
   is related to the degree of dissociation (α) of A and total pressure P as
   (1) $\frac{4\alpha^2 P}{1-\alpha}$ (2) $\frac{4\alpha^2 P^2}{1-\alpha}$
   (3) $\frac{4\alpha^2 P}{1-\alpha^2}$ (4) $\frac{4\alpha^2 P^2}{1-\alpha^2}$
5. The partial pressures of NO, Br_2, and NOBr in a flask at 25°C are 0.01, 0.1, and 0.04 atm, respectively. If the equilibrium constant at 25°C for the reaction
   $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$
   is equal to 160 atm^{-1}, then we can say that
   (1) the partial pressure of NOBr finally will be 0.05 atm
   (2) there is equilibrium in the flask
   (3) the reaction will proceed in the forward direction
   (4) the reaction will proceed in the backward direction
6. The equilibrium for the formation of SO_3 was established at a certain temperature starting with one mole of O_2 and two moles of SO_2. If V is the volume of the vessel and $2x$ is the number of moles of SO_3 present at equilibrium, then equilibrium constant will be
   (1) $\frac{(1-x)^3}{2V}$ (2) $\frac{4x^2}{(2-x)(1-x)}$
   (3) $\frac{x^2}{(2-x)(1-x)}$ (4) $\frac{x^2 V}{(1-x)^3}$
7. The dissociation of ammonium hydrogen sulphide in a closed container produces a pressure of 10 atm at 200°C. The value of K_p is
   (1) 25 (2) 50
   (3) 100 (4) 75
8. If 1 : 3 (molar ratio) mixture of N_2 and H_2 yields 20% (by volume) of NH_3 at 30 atm, then the moles of N_2 converted into the product at equilibrium will be
   (1) 0.66 (2) 0.22
   (3) 0.33 (4) 0.44
9. The equilibrium pressure necessary to obtain 50% dissociation of PCl_5 at 250°C is numerically _____ of K_p.
   (1) six times (2) four times
   (3) five times (4) three times
10. 2 mol each of A and B are taken in a container to carry out the following reaction:
    $2A(g) + B(g) \rightleftharpoons 2C(g) + 2D(g)$
    When the system attains equilibrium, we have
    (1) $[A] < [B]$ (2) $[A] > [B]$
    (3) $[A] = [B]$ (4) $[A] = [B] = [C] = [D]$

7.8 RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT (K_{eq}), REACTION QUOTIENT (Q), AND GIBBS ENERGY (G)

For a reversible reaction, the value of K_c does not depend on the rate of the reaction. However, as discussed in Chapter 6 the value of K_c is directly related to the change in Gibbs energy (ΔG). We can recall that

1. If ΔG is negative, then the reaction under consideration is spontaneous and proceeds in the forward direction.
2. If ΔG is positive, then the reaction under consideration is nonspontaneous. Rather the reverse of the reaction would have a negative ΔG, and the products of the forward reaction would be converted to the reactants.
3. If $\Delta G = 0$, the reaction has reached the equilibrium stage. At this point, the driving force is zero because there is no longer any free energy left to drive the reaction.

   This thermodynamic view of chemical equilibrium can be described mathematically by the following equation

   $$\Delta G = \Delta G^\ominus + RT \ln Q_c \qquad (7.23)$$

   where $\Delta G^\ominus$ is the standard Gibbs energy change and Q_c is the reaction quotient for the reversible reaction.

   When the system attains equilibrium, we have

   $$\Delta G = 0 \text{ and } Q_c = K_c$$

   Substituting these results into Eq. (7.23), we get

   $$0 = \Delta G^\ominus + RT \ln K_c$$

   or $\Delta G^\ominus = -RT \ln K_c$ (7.24)

   or In $K_c = \frac{-\Delta G^\ominus}{RT}$

   Taking the antilog of both sides, we get

   $$K_c = e^{-\Delta G^\ominus/RT} \qquad (7.25)$$

Using Eq. (7.25), we can interpret the reaction spontaneity in terms of the magnitude of K_c:

(1) If $\Delta G^\ominus$ is negative (< 0), then $-\Delta G^\ominus/RT$ is positive and $e^{-\Delta G^\ominus/RT} > 1$, making $K_c > 1$. This implies that if K_c is greater than 1, then the reaction under consideration is spontaneous. Thus, the reaction under consideration proceeds in the forward direction to such an extent that the products are present predominantly at equilibrium.

(2) If $\Delta G^\ominus$ is positive (> 0), then $-\Delta G^\ominus/RT$ is negative and $e^{-\Delta G^\ominus/RT} < 1$, making $K_c < 1$. This implies that if K_c is less than 1, then the reaction under consideration is nonspontaneous. Such a reaction proceeds in the forward direction to such a small extent that only a very small amount of products is formed.

(3) Finally, we can say that if $K_c = 1$, then the quantities of reactants and products present at equilibrium will be comparable.

Follow-up Test 5

1. Which of the following expressions is correct?
   (1) $\Delta G = \Delta G^{\ominus} + RT \ln Q$
   (2) $\Delta G^{\ominus} = -RT \ln K_{eq}$
   (3) $K_{eq} = e^{-\Delta G^{\ominus}/RT}$
   (4) All of these
2. If for heterogeneous equilibrium,
   $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_{eq} = 1$ at 1 atm pressure, the corresponding temperature is given by
   (1) $T = \dfrac{\Delta G^{\ominus}}{\Delta H^{\ominus}}$ (2) $T = \dfrac{\Delta G^{\ominus}}{R}$
   (3) $T = \dfrac{\Delta S^{\ominus}}{\Delta H}$ (4) $T = \dfrac{\Delta H^{\ominus}}{\Delta S^{\ominus}}$
3. If for homogeneous equilibrium,
   $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $K_{eq} = 1$, then
   (1) the reaction is spontaneous in the forward direction
   (2) the reaction is spontaneous in the backward direction
   (3) the reaction is spontaneous in both the directions
   (4) the reaction is neither spontaneous in the forward direction nor spontaneous in the backward direction

7.9 FACTORS AFFECTING EQUILIBRIA

One of the main goals of every chemical synthesis is to achieve the maximum possible conversion of the reactants into products through minimum expenditure of energy, i.e., maximum yield of products under mild conditions of temperature and pressure. If it does not happen on its own, then the experimental conditions must be adjusted. For example, the annual world production of ammonia is about hundred million tonnes, primarily for use as fertilizers. Thus, the choice of experimental conditions is of real economic importance in the Haber process for the synthesis of ammonia from N_2 and H_2.

At any given temperature, the magnitude of equilibrium constant (K_{eq}) is independent of initial concentrations. Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. When we say that an equilibrium position shifts to the right, we mean that the net reaction is now from left to right.

> If a system at equilibrium is subjected to a change in the experimental conditions, then the system is no longer at equilibrium and, thus, a net reaction takes place in some direction until the system returns to equilibrium once again.

Once a reacting system has reached equilibrium, it remains at equilibrium until it is disturbed by some change of conditions. For this purpose, we can use any of the following experimentally controllable variables: concentration, pressure, volume, and temperature.

To decide what course the reaction adopts and to make a qualitative prediction about the effect of a change in experimental conditions on equilibrium, we use *Le Chatelier's* (pronounced "le-SHOT-lce-ay") *principle. The guiding principle states that if a change of conditions (external stress) is applied to a system at equilibrium, the system shifts in the direction that reduces the stress to move toward a new state of equilibrium*. In other words, whenever a system at equilibrium is subjected to an external stress such as change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium (i.e., $r_f \neq r_b$) and, thus, undergoes a net reaction in that direction which tends to nullify the applied stress. This principle is applicable to all physical and chemical equilibria.

> Le Chatelier's principle is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs.

7.9.1 Effect of Concentration Change

Consider the following system at equilibrium:

$$aA + bB \rightleftharpoons cC + dD$$

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

We can understand Le Chatelier's principle in the kinetic terms. According to the law of mass action, the rate of forward reaction is directly proportional to the reactant concentrations raised to powers equal to their stoichiometric coefficients:

$$\text{Rate}_f = K_f[A]^a[B]^b$$

When we add more A to an equilibrium mixture, the rate of forward reaction increases so that it no longer matches the rate of reverse reaction. As the net reaction proceeds to the right, consuming some A and B and forming more C and D, the forward rate diminishes and the reverse rate increases until they are again equal. At this point, a new equilibrium condition has been reached, with more C and D than were present in the original equilibrium mixture. However, not all of the added A has been consumed when the new equilibrium is reached.

> In case of the addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture.

If a reactant or product is removed from a system at equilibrium, the reaction that produces that substance occurs more rapidly and to a greater extent than its reverse.

The reaction quotient (Q_c) also helps us to predict the direction of shift. When more of any reactant or product is added to the system at equilibrium, the value of Q_c changes. So, it no longer matches K_c and the reaction is no longer at equilibrium. The stress due to the added substance is relieved by shifting the equilibrium in the direction that consumes some of the added substances, moving the value of Q_c back toward K_c. Let us consider the expression for Q_c,

$$Q_c = C_C^c\, C_D^d \,/\, C_A^a C_B^b$$

and compare it with K_c. The moment more of A or B is added, the C_A or C_B increases while C_C and C_D remain unchanged. Consequently, $Q_C < K_C$, and the forward reaction occurs more rapidly and to a greater extent than the reverse reaction until the equilibrium is reestablished. Similarly, if more C or D is added, $Q_C > K_C$, and the reverse reaction occurs more rapidly and to a greater extent until the equilibrium is reestablished.

On the other hand, if some A or B is removed, then $Q_C > K_C$, and the reverse reaction is favored until the equilibrium is reestablished. If some C or D is removed, then $Q_C < K_C$; the forward reaction is favoured. It is significant to note that adding or removing reactants or products changes the value of Q_C but does not change the value of K_C.

When we say that the equilibrium is "shifted to the left," we mean that the reaction to the left occurs to a greater extent than the reaction to the right.

The following table summarizes a lot of useful information. Study it carefully.

Stress	Q_c	Direction of shift $aA + bB \rightleftharpoons cC + dD$
Increase concentration of A or B	$Q_c < K_c$	$\longrightarrow$ right
Increase concentration of C or D	$Q_c > K_c$	left $\longleftarrow$
Decrease concentration of A or B	$Q_c > K_c$	left $\longleftarrow$
Decrease concentration of C or D	$Q_c < K_c$	$\longrightarrow$ right

1. The concentration stress of an added reactant/product is relieved by the net reaction in the direction that consumes the added substance, but note that the entire added substance is never consumed.
2. The concentration stress of a removed reactant/product is relieved by the net reaction in the direction that produces the removed substance, but note that the entire removed substance is never recovered.

When the new equilibrium condition is established,

1. the rates of the forward and backward (reverse) reactions are again equal; and
2, K_c is again satisfied by the new concentrations of reactants and products.

Practical applications of changes in concentration are of great economic importance. Removing a product of a reversible reaction forces the reaction to produce more product than could be obtained if the reaction were simply allowed to reach equilibrium. For example, in the manufacture of ammonia by the Haber process, ammonia (a volatile substance) is liquefied and removed from the reaction mixture so that the reaction keeps moving in forward direction. Similarly, in the large-scale production of CaO (used as important building material) from $CaCO_3$, the constant removal of CO_2 from the kiln drives the reaction to completion.

Continuous removal of a product maintains Q_C at a value less than K_C and reaction continues to move in the forward direction.

Example 7.8 ***Changes in concentration*:** Some hydrogen and iodine are mixed at 229°C in a 1.00-liter container. When equilibrium is established, the following concentrations are present: $C_{H_2} = 0.080$ M, $C_{I_2} = 0.060$ M, and $C_{HI} = 0.490$ M. If an additional 0.300 mol of HI is then added, what concentrations will be present when the new equilibrium is established?

Strategy: Use the initial equilibrium concentrations to calculate the value of K_c. Then determine the new concentrations after some HI has been added and calculate Q_c. The value of Q_c tells us which reaction is favored. Represent the new equilibrium concentrations, substitute these representations into the K_c expression, and solve for the new equilibrium concentrations.

Note that it is obvious that adding some HI favors the reaction to the left. If more than one substance is added to the reaction mixture, it might not be obvious which reaction will be favored. Calculating Q always lets us make the decision.

Solution:

Calculate the value of K_c from the first set of equilibrium concentrations:

$$K_c = \frac{C_{HI}^2}{C_{H_2} C_{I_2}} = \frac{(0.490)^2}{(0.080)(0.060)} = 50$$

When we add 0.300 mol of HI to the 1.00–L container, the concentration of HI instantaneously increases by 0.300 M:

	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$		
Equilibrium conc. (M)	0.080	0.060	0.490
Added conc. (M)	0	0	+ 0.300
New initial conc. (M)	0.080	0.060	0.790

Calculate the value of reaction quotient by substituting these new initial concentrations:

$$Q_c = \frac{C_{HI}^2}{C_{H_2} C_{I_2}} = \frac{(0.790)^2}{(0.080)(0.060)} = 130$$

Since $Q_c > K_c$, the net reaction proceeds to the left to establish a new equilibrium. To determine the new equilibrium concentrations, let us assume that $2x$ mol L^{-1} of HI is consumed. Then x mol L^{-1} of H_2 is formed and x mol L^{-1} of I_2 is formed. (Note that equal concentrations of H_2 and I_2 must be formed by the new progress of the reaction.)

	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$		
Initial (M)	0.080	0.060	0.790
Change (M)	$+x$	$+x$	$-2x$
New equilibrium (M)	$(0.80 + x)$	$(0.060 + x)$	$(0.790 - 2x)$

Calculate x by substituting these new equilibrium concentrations into the equilibrium constant expression:

$$K_c = 50 = \frac{C_{\mathrm{HI}}^2}{C_{\mathrm{H_2}}C_{\mathrm{I_2}}}$$

$$= \frac{(0.790 - 2x)^2}{(0.080 + x)\,(0.060 + x)}$$

$$= \frac{0.624 - 3.16x + 4x^2}{0.0048 + 0.14x + x^2}$$

$$0.24 + 7.0x + 50x^2 = 0.624 - 3.61x + 4x^2$$

$$46x^2 + 10.2x - 0.38 = 0$$

Using the quadratic formula provides

$$x = 0.032 \text{ and } -0.25$$

Because x cannot be less than zero in this case, $x = -0.25$ is the irrelevant root. Because the reaction is proceeding towards the left, it does not consume a negative quantity of HI. Thus, $x = 0.032$ is the root with physical meaning. Hence, the new equilibrium concentrations are

$$C_{\mathrm{H_2}} = (0.080 + 0.032)\text{ M} = 0.112\text{ M}$$

$$C_{\mathrm{I_2}} = (0.060 + 0.032)\text{ M} = 0.092\text{ M}$$

$$C_{\mathrm{HI}} = (0.790 - 0.064)\text{ M} = 0.726\text{ M}$$

Notice that some of the additional HI is consumed, but not all of it. More HI remains after the new equilibrium is established than was present before the stress was applied. However, the new equilibrium concentrations of H_2 and I_2 are substantially greater than the original equilibrium concentrations.

7.9.2 Effect of Pressure Change

Changes in pressure (by changing volume) have practically no effect on the concentrations of reacting species in condensed phases of heterogeneous equilibrium because liquids and solids are only slightly compressible. However, changes in pressure do cause significant changes in the concentration of gases. Therefore, a pressure change obtained by changing the volume can affect the value of Q and, hence, the yield of products in case of a reaction in which the total number of moles of gaseous reactants differs from the total number of moles of gaseous products.

For an ideal gas,

$$PV = nRT$$

or

$$P = \frac{nRT}{V} = \left(\frac{n}{V}\right)RT$$

At constant temperature, n, R, and T are constants. Thus, P and V are related to each other inversely: The greater the pressure, the smaller the volume and vice versa. Also, note that the term n/V represents the concentration of the gas in mol L^{-1}, and it varies directly with pressure.

Suppose that the equilibrium system

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is in a cylinder fitted with a moveable piston. Now, we increase the pressure on the gases by pushing down the piston at constant temperature. Since the volume decreases, the partial pressure of every gas (N_2, H_2, and NH_3) present in the container increases by the same amount. Consequently, the total pressure exerted by the gases in equilibrium increases and the system is no longer at equilibrium. The direction in which the net reaction takes place to reestablish the equilibrium can be predicted by applying the Le Chatelier's principle.

Since the total pressure of gases involved in equilibrium has increased, the equilibrium shifts in that direction (forward in this case) which decreases the total number of moles of gases because according to ideal gas equation, pressure is directly related to the number of moles of gas.

We can also understand this by using the concept of reaction quotient (Q_P):

$$Q_P = \frac{P_{\mathrm{NH_3}}^2}{P_{\mathrm{N_2}}P_{\mathrm{H_2}}^3}$$

At constant temperature, an increase in pressure (decrease in volume) increases the pressure (or concentration) of each gaseous component (N_2, H_2, and NH_3) present in the equilibrium system.

For this reaction, the numerator of the expression for Q_P includes a pressure term to the second power, while the denominator includes pressure terms to the fourth power. Since the pressure of each gas increases by a constant factor, the denominator of Q_P increases more than the numerator. Thus, $Q_P < K_P$ and the system is no longer at equilibrium. The net reaction must proceed from left to right (until $Q_P = K_P$) to reduce the value of the denominator of Q_P as the system moves to a new equilibrium state. Conversely, a decrease in pressure (increase in volume) would result in $Q_P > K_P$, and this equilibrium shifts to the left until $Q_P = K_P$.

A change in pressure (volume) does not always cause a system to move out of an equilibrium state. For example, the system represented by the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is not affected by change in pressure (volume), because the value of reaction quotient remains unchanged as the pressure terms of the numerator and denominator are raised to equal powers:

$$Q_P = K_P = \frac{P_{\mathrm{HI}}^2}{P_{\mathrm{H_2}}P_{\mathrm{I_2}}}$$

This happens because the number of moles of gas on each side of the chemical equation is the same.

In general, an increase in pressure (decrease in volume) favors the net reaction that decreases the total number of moles of gases [i.e., the backward direction, if Δn_g is positive: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; and the forward direction, if Δn_g is negative: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$]. A decrease in pressure (increase in volume) favors the net reaction that increases the total number of moles of gases (i.e., the forward direction, if Δn_g is positive; and the backward direction, if Δn_g is negative). For reactions in which there is no change in the number of moles of gases (i.e., Δn_g is zero), a pressure (or volume) change has no effect on the position of equilibrium.

Example 7.9 An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atm pressures, respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of each gas.

Strategy: Use the initial equilibrium pressures to calculate the value of K_p. When the volume of the container is doubled, the pressure exerted by each gas is halved and the equilibrium shifts to the right (Δn_g is +ve) until new equilibrium is established. Represent the new equilibrium pressures and substitute them into the K_p expression and solve for the new equilibrium pressures.

Solution:

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
Equilibrium (atm)	0.28	1.1

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(1.1)^2}{0.28} = \frac{1.21}{0.28} = 4.32$$

When the volume of the container is halved:

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
New initial pressure (atm)	0.14	0.55
Change	$-x$	$+2x$
New equilibrium pressure (atm)	$(0.14 - x)$	$(0.55 + 2x)$

Substitution of these values into K_p allows us to evaluate x

$$K_p = 4.32 = \frac{(0.55 + 2x)^2}{(0.14 - x)}$$

Solving the quadratic equation, we get

$$x = 0.045$$

$$\therefore \quad P_{N_2O_4} = 0.14 - x = 0.14 - 0.045 = 0.095 \text{ atm}$$

$$P_{NO_2} = 0.55 + 2x = 0.55 + 2 \times 0.045 = 0.64 \text{ atm}$$

7.9.3 Effect of Inert Gas Addition

An inert gas is any gas which does not take part in the reaction. Thus, whenever such a gas is added to the system at equilibrium, the number of moles of each of the reacting species in the equilibrium mixture remains unchanged.

Addition of an inert gas is done under two conditions:

Addition at constant volume: This implies that when the inert gas is added, the volume of the container holding the equilibrium mixture should not change. Suppose that the equilibrium system

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is contained in a stainless-steel vessel whose volume is constant. At equilibrium,

$$Q_P = K_P = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$

According to ideal gas equation, the partial pressure of each gas in equilibrium mixture is given as follows:

$$P = \frac{nRT}{V}$$

When we add an inert gas at constant volume at a given temperature, n, R, T, and V remain unchanged. Thus, the partial pressure of each gas (N_2, H_2, and NH_3) does not change and $Q_P = K_P$, i.e., the system is still at equilibrium.

Alternatively, adding inert gas (such as He) to the equilibrium mixture at constant volume increases the total gas pressure (due to increase in the number of moles of gas, $p = nRT/V$) and decreases the mole fractions of N_2, H_2, and NH_3. Thus the partial pressure of every gas given by the product of its mole fraction and total pressure does not change. Hence, the addition of an inert gas at constant volume does not affect the equilibrium in all the three cases: $\Delta n_g = 0$, $\Delta n_g > 0$ and $\Delta n_g < 0$.

It is possible to change the pressure of a system without changing its volume. We can increase the total pressure in the vessel by adding an inert gas to the equilibrium system.

Addition at constant pressure: This implies that when we add an inert gas to the equilibrium system, the total pressure in the container should not change. This can be achieved by moving the movable piston upward while adding the inert gas. As a result, the volume of the equilibrium system increases and the partial pressure of every gas in equilibrium mixture (N_2, H_2, and NH_3) decreases. This leads to a decrease in the pressure of equilibrium system and favors the net reaction that increases the total number of moles of gases in the equilibrium system. Thus, the addition of an inert gas at constant pressure shifts the equilibrium to the right (forward direction) if Δn_g is positive, shifts the equilibrium to the left (backward direction) if Δn_g is negative, and does not affect the equilibrium if Δn_g is zero.

7.9.4 Effect of Temperature

Consider the following exothermic reaction at equilibrium:

$$M + N \rightleftharpoons R + T + \text{Heat} \quad (\Delta_r H^\ominus \text{is negative})$$

Heat is produced by the forward (exothermic) reaction while heat is absorbed by the backward (endothermic) reaction. Suppose we increase the temperature at constant pressure by adding heat to the system. According to the Le Chatelier's principle, the equilibrium will shift in that direction which partially offsets the stress by consuming some of the supplied heat. This favors the reaction to the left, removing some of the extra heat. On the other hand, lowering the temperature at constant pressure by removing heat from the system favors the reaction to the right as the system replaces some of the heat that was removed.

By contrast, for an endothermic reaction at equilibrium,

$$A + B + \text{heat} \rightleftharpoons C + D \ (\Delta_r H^\ominus \text{is positive})$$

an increase in temperature at constant pressure (by adding heat to the system) favors the reaction to the right while a decrease in temperature (by removing heat) favors the reaction to the left.

We summarize the results with the following statement: *A temperature increase favors an endothermic reaction and a temperature decrease favors an exothermic reaction.*

Whenever an equilibrium system is disturbed by a change in concentration, pressure, or volume, the equilibrium position is altered, i.e., the composition of the equilibrium mixture changes because the reaction quotient (Q) no longer equals the equilibrium constant (K_{eq}). But it does not change the value of the equilibrium constant. On the other hand, whenever a change in temperature occurs, the value of equilibrium constant (K_{eq}) is changed. We can understand (quantitatively) the effect of temperature on the value of equilibrium constant by using the *van't Hoff equation*:

$$\log\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H^\ominus}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (7.26)$$

where K_1 is the equilibrium constant at temperature T_1, K_2 is the equilibrium constant at temperature T_2, $\Delta_r H^\ominus$ is the standard enthalpy of reaction, and R is the universal gas constant.

If $T_2 > T_1$, then $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is a negative quantity. For an exothermic reaction, $\Delta_r H^\ominus$ is negative. Thus, according to Eq. (7.26), $\log(K_2/K_1)$ is a negative quantity. This implies that $K_2/K_1 < 1$ or $K_2 < K_1$. *Thus, the magnitude of equilibrium constant for an exothermic equilibrium reaction decreases with increasing temperature.*

On the other hand, for an endothermic reaction, $\Delta_r H^\ominus$ is positive. Thus, according to Eq. (7.26), $\log(K_2/K_1)$ is a positive quantity. This implies that $K_2/K_1 > 1$ or $K_2 > K_1$. *Thus, the magnitude of equilibrium constant for an endothermic reaction increases with increasing temperature.*

Chemists have determined equilibrium constants for thousands of reactions. It would be an impossibly huge task to catalog such constants at every temperature of interest for each reaction. Fortunately, there is no need to do this, because if we know $\Delta_r H^\ominus$ for a reaction and K_{eq} at any given temperature, we can use the van't Hoff equation to calculate the value of K_{eq} at any other temperature.

HELP The K_{eq} values that appear in the van't Hoff equation represent the thermodynamic constant. For a gas-phase reaction such as $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, K_{eq} represents K_p. If the value of K_c is given, we need to convert it to K_p before using the van't Hoff equation.

7.9.5 Effect of a Catalyst

A catalyst increases the rate of a chemical reaction by lowering the reaction's activation energy, i.e., by making available a new low energy pathway for the conversion of reactants to products.

As Figure 7.3 shows, a catalyst lowers the activation energy of the forward reaction to the same extent as it lowers that for the reverse reaction. This means that both the forward and reverse rates are affected to exactly the same degree. Therefore, we can conclude that the presence of a catalyst does not alter the equilibrium constant nor does it shift the position of an equilibrium system.

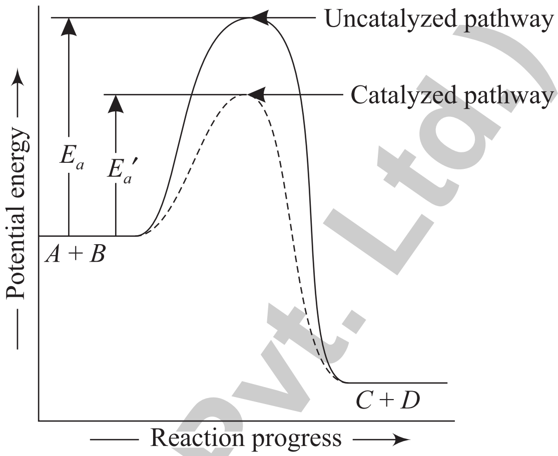


Figure 7.3 Effect of a catalyst

If we add a catalyst to a reaction mixture that is not at equilibrium, then the catalyst will speed up both the forward and backward reactions (to the same extent) and will help to achieve the equilibrium much faster. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait much longer for it to happen.

The same equilibrium mixture is achieved with or without the catalyst, but the equilibrium is established more quickly in the presence of a catalyst.

Let us consider the Haber process—the economically important industrial process by which atmospheric nitrogen, N_2 (very unreactive), is converted to ammonia, NH_3, a soluble reactive compound.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ \Delta_r H^\ominus = -92.6 \text{ kJ mol}^{-1}$$

$$K_c = \frac{C^2_{NH_3}}{C_{N_2}C^3_{H_2}} = 3.6 \times 10^8 \text{ (at 25°C)}$$

Innumerable dyes, plastics, explosives, fertilizes, and synthetic fibers are made from ammonia.

Very large value of K_c indicates that at equilibrium, virtually all of the N_2 and H_2 (mixture in a 1 : 3 mol ratio) would be converted into NH_3. However, at 25°C, the reaction occurs so slowly that no measurable amount of NH_3 is produced within a reasonable time.

The large equilibrium constant (a thermodynamic factor) indicates that the reaction proceeds toward the right almost completely but it tells us nothing about how fast the reaction occurs (a kinetic factor).

The reaction proceeds with decrease in the total number of moles formed as compared to the reactants (there are 4 mol of gas, 1 mol of N_2 + 3 mol of H_2, on the left side of the equation and only 2 mol of gas on the right). So, increasing the pressure favors the production of NH_3. Therefore, the Haber process is carried out at very high pressures, as high as the equipment will safely stand. Typically, the operating pressures are between 500 atm and 1000 atm.

The reaction is highly exothermic ($\Delta_r H^\ominus$ is negative). So increasing the temperature favors the decomposition of NH_3 (the reverse reaction) by decreasing the value of equilibrium constant. But the rates of both forward and reverse reactions increase as the temperature increases, i.e., high temperature gives satisfactory rate but poor yield. Moreover, high temperature operation is costly. Thus, for the maximum yield of NH_3, the reaction should be run at the lowest possible temperature. A low temperature operation (say, –53°C or 220 K) is desirable in other respects too. The boiling point of NH_3 is –33.5 °C. So, as it is formed, it would quickly condense to a liquid, which could be conveniently removed from the reacting system. (Both N_2 and H_2 are still gases at this temperature.) Consequently, the net reaction would shift from left to right, just as desired. But the rates of both forward and reverse reactions decrease as the temperature decreases, i.e., it takes long time to get higher yield of NH_3.

Commercially, a faster production of NH_3 is desirable even if it means a lower yield and a higher cost of operation. German chemist Fritz Haber discovered that the addition of a catalyst consisting of finely divided iron and small amounts of selected oxides speeds up both the forward and backward reactions and allows the equilibrium reaction to occur at a satisfactory rate at temperatures where the yield of NH_3 is reasonably high. Thus, the use of a catalyst allows NH_3 to be produced not only faster but at a relatively lower temperature, which increases the yield of NH_3 and extends the life of the equipment. Typically, the operation is usually carried between 450°C and 500°C. However, the reaction occurs so slowly even in the presence of a catalyst that it cannot be run economically at temperatures below 450°C.

Similarly, platinum or divanadium pentaoxide (V_2O_5) is used as a catalyst to increase the rate of reaction in the manufacture of sulphuric acid by the contact process:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\ K_c = 1.7 \times 10^{26}$$

Though the high value of K_c suggests that the reaction goes to completion, practically, the oxidation of SO_2 to SO_3 is very slow in the absence of a catalyst.

7.9.6 Summary of Factors that Affect the Equilibrium Position

Effect of concentration (or pressure of gaseous substance):

Reactant	Product	Direction of shift
Increases	Decreases	Forward
Decreases	Increases	Backward

Effect of total pressure (or total volume) of system:

Total pressure	Total volume	Direction of shift
Increases	Decreases	No shift if $\Delta n_g = 0$ Forward if Δn_g is –ve Backward if Δn_g is +ve
Decreases	Increases	No shift if $\Delta n_g = 0$ Backward if Δn_g is –ve Forward if Δn_g is +ve

Effect of adding an inert gas:

Δn_g	Direction of shift
Zero	No shift either at constant *P* or at constant *V*
Positive	No shift at constant *V* but forward shift at constant *P*
Negative	No shift at constant *V* but backward shift at constant *P*

Effect of temperature:

Temperature	Direction of shift
Increases	*Right* if forward reaction is endothermic and l*eft* if backward reaction is endothermic
Decreases	*Right* if forward reaction is exothermic and l*eft* if backward reaction is exothermic

Effect of adding a catalyst: There is no shift of equilibrium on adding of a catalyst. However, the same equilibrium state is attained quickly.

Follow-up Test 6

1. Le Chatelier's principle is applicable when
   (i) Fe(s) and S(s) react to from FeS(s)
   (ii) $PCl_5(g)$ decomposes to form $PCl_3(g)$ and $Cl_2(g)$
   (iii) $N_2(g)$ and $H_2(g)$ react to form $NH_3(g)$
   (iv) $H_2(g)$ and $I_2(g)$ react to form HI(g)
   (1) (i), (ii), (iii), (iv) (2) (i), (ii), (iii)
   (3) (ii), (iii), (iv) (4) (i), (iii), (iv)
2. Iron (III) thiocyanate [$Fe(SCN)_3$] dissolves readily in water to give a red solution. The red color of the solution deepens when _________ is added.
   (i) oxalic acid ($H_2C_2O_4$)
   (ii) sodium thiocyanate (NaSCN)
   (iii) iron (III) nitrate [$Fe(NO_3)_3$]
   (iv) mercuric chloride ($HgCl_2$)
   (1) (i), (ii), (iii) (2) (i), (iv)
   (3) (i), (iii), (iv) (4) (i), (ii), (iii), (iv)
3. For a physical equilibrium
   $H_2O(s) \rightleftharpoons H_2O(l)$
   which of the following is true?
   (1) At low pressure, the nature of equilibrium changes to
   $H_2O(s) \rightleftharpoons H_2(g) + 1/2O_2(g)$
   (2) More of liquid freezes if the pressure on the system is increased.
   (3) The pressure change does not affect the equilibrium.
   (4) More of ice melts if the pressure on the system is increased.
4. Which of the following equilibria remains unaffected by a change in pressure (or volume)?
   (1) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
   (2) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

(3) $2PbS(s) + 3O_2(g) \rightleftharpoons 2PbO(s) + 2SO_2(g)$
(4) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

5. Which of the following equilibrium is favored by a temperature increase?
   (1) C (graphite) $\rightleftharpoons$ C (diamond)
   (2) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$
   (3) $2O_3 \rightleftharpoons 3O_2$
   (4) $2SO_2 + O_2 \rightleftharpoons 2SO_3$
6. Consider the following equilibrium system:
   $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
   Some inert gas is added to the above system at constant volume. Predict which of the following is true?
   (1) More of SO_3 is produced.
   (2) Less SO_2 is produced.
   (3) Addition of inert gas does not affect equilibrium.
   (4) System moves to new equilibrium position which cannot be predicted theoretically.
7. Which of the following is not true for the equilibrium reaction
   $N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \Delta H = 180 \text{ kJ mol}^{-1}$
   (1) The formation of NO is increased at higher temperature.
   (2) The volume change at constant pressure does not affect the equilibrium.
   (3) The pressure change at constant volume does not affect the equilibrium.
   (4) The formation of NO is decreased at higher temperature.
8. When $NaNO_3$ is heated in a closed vessel, O_2 is liberated and $NaNO_2$ is left behind. At equilibrium,
   (1) increased temperature favors forward reaction
   (2) addition of $NaNO_2$ favors reverse reaction
   (3) increased pressure favors forward reaction
   (4) adding of $NaNO_2$ favors forward reaction
9. Adding a catalyst to a reaction at equilibrium
   (1) changes Q
   (2) changes K_{eq}
   (3) changes both Q and K_{eq}
   (4) changes neither Q nor K_{eq}
10. Consider the following equilibrium system:
   $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$
   set up in a cylinder fitted with a piston. Some inert gas is added and the piston is moved outwards to keep the total gaseous pressure constant. Predict which of the following is true?
   (1) Addition of inert gas does not affect the equilibrium.
   (2) Less $SO_3(g)$ is produced.
   (3) More $SO_3(g)$ is produced.
   (4) The system moves to new equilibrium position which cannot be predicted theoretically.

7.10 IONIC EQUILIBRIUM IN SOLUTION

Any type of equilibrium involving ions in aqueous solution is called *ionic equilibrium*. We have already come across equilibrium involving ions under the effect of change of concentration on the direction of equilibrium:

$$\text{Fe SCN}^{2+}(aq.) \rightleftharpoons Fe^{3+}(aq.) + SCN^{-}(aq.)$$

There are numerous equilibria that involve ions in aqueous solutions. In aqueous solutions, the solute initially is a gas, a liquid, or a solid and the solvent is water. Aqueous solutions are very important. Nearly three-fourths of the earth's surface is covered with water. Enormous numbers of chemical reactions occur in the oceans and smaller bodies of water. Body fluids of plants and animals are mostly water. Life processes (chemical reactions) of all plants and animals (including human beings) occur in aqueous solutions or in contact with water. Before we were born, all of us developed in sacs filled with aqueous solutions, which protected and nurtured us until we had developed to the point that we could live in the atmosphere.

It is a well known fact that the aqueous solution of sugar does not conduct electricity. On the other hand, when sodium chloride (common salt) is added to water, the resulting aqueous solution conducts electricity. Moreover, the conductance of electricity increases with an increase in the concentration of common salt.

Michael Faraday classified the solutes in aqueous solution into two categories based on their ability to conduct electricity: electrolytes and nonelectrolytes. *An electrolyte is a compound whose aqueous solution conducts electricity. A nonelectrolyte is a compound that when dissolved in water results in a solution that does not conduct electricity*. This happens because an electrolyte produces ions in solution, while a nonelectrolyte does not. When solid NaCl dissolves in water, it breaks up into Na^+ and Cl^- ions. The movement of Na^+ ions toward the negative electrode and Cl^- ions toward the positive electrode is equivalent to the flow of electrons along a metal wire. In this way, a solution containing an electrolyte is able to conduct electricity. Thus, we say that NaCl is an electrolyte. On the other hand, when solid sugar ($C_{12}H_{22}O_{11}$) dissolves in water, it does not break up into ions. Its aqueous solution consists of neutral molecules and, thus, does not conduct electricity. Note that pure water is a very poor conductor of electricity because there are very few ions present in pure water. Hence, it cannot conduct electricity.

Faraday further classified electrolytes into strong and weak electrolytes. A comparison of the brightness of the light bulb for the same molar amounts of different dissolved substances helps us distinguish between strong and weak electrolytes. Thus, *strong electrolytes* are electrolytes that conduct electricity well in dilute aqueous solution (the bulb glows brightly) while *weak electrolytes* are electrolytes that conduct electricity poorly in dilute aqueous solution (the bulb glows dimly). This happens because a solution of a strong electrolyte contains a high concentration of ions while a solution of a waek electrolyte contains a low concentration of ions.

Strong electrolytes on dissolution in water are ionized or dissociated completely or very nearly completely. On the other hand, weak electrolytes are only partially dissociated or ionized (i.e., their dissociation or ionization takes place to a limited extent).

Dissociation refers to the process in which a solid ionic compound, such as NaCl, separates into its ions in solution.

Thus, we can represent the dissolving of sodium chloride in water as

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq.) + Cl^-(aq.)$$

Since sodium chloride is a strong electrolyte, the above equation says that all the sodium chloride that enters the solution ends up as Na^+ and Cl^- ions. There are no undissociated NaCl units in solution.

Molecular covalent compounds (such as pure HCl) exist as discrete molecules and do not contain ions (charged particles). However, polar covalent compounds (such as HCl) form ions in solution. *Ionization refers to the process in which a polar covalent compound reacts with water to form ions in solution*:

$$HCl(g) \xrightarrow{H_2O} H^+(aq.) + Cl^-(aq.)$$

Thus, when hydrogen chloride gas dissolves in water, it forms hydrated H^+ and Cl^- ions. Since HCl is a strong electrolyte (it ionizes almost completely), the above equation tells us that all the dissolved HCl molecules give hydrated H^+ and Cl^- ions in solution. Thus, when we write HCl(aq.), it is understood that it is a solution of only H^+(aq.) and Cl^-(aq.) ions, and there are no hydrated HCl molecules present.

The term "dissociation" is used for ionic compounds while the term "ionization" is used for polar covalent compounds.

We represent the dissociation or ionization of weak electrolytes (such as acetic acid) as

$$CH_3COOH(aq.) \rightleftharpoons CH_3COO^-(aq.) + H^+(aq.)$$

where CH_3COO^- is called the acetate ion. Since acetic acid is a weak electrolyte (i.e., it ionizes to a limited extent, less than 5%), the above equation says that aqueous acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and protons.

The double arrow $\rightleftharpoons$ means that the reaction of acetic acid with water is reversible, i.e., the reaction can occur in both directions. Initially, a number of CH_3COOH molecules ionize (break up) to yield CH_3COO^- and H^+ ions. As time goes on, some of the CH_3COO^- and H^+ ions recombine to give CH_3COOH molecules. Eventually, a state is reached in which the acid molecules break up as fast as their ions recombine. *Such a chemical state (involving ions) in which no net change can be observed (although continuous activity is taking place at the molecular level) is called ionic equilibrium*.

Acids, bases, and salts come under the category of electrolytes and may act as either strong or weak electrolytes. Thus, three major classes of strong electrolytes which are completely or nearly completely ionized (or dissociated) in dilute aqueous solutions are (i) strong acids, (ii) "strong bases, and (iii) strong salts (most soluble salts). Similarly, there are three major classes of weak electrolytes which ionize to a limited extent: (i) weak acids, (ii) weak bases, and (iii) weak salts.

Strong acids	**Weak acids**
HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_4$, $HClO_3$	CH_3CO_2H, H_2CO_3, H_3BO_3, H_3PO_4, $(COOH)_2$, H_2SO_3, HNO_2, HCN, HF
Strong bases	**Weak bases**
LIOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$	NH_3(aq.), aniline, methyl amine, hydrazine, hydroxylamine
Strong salts	**Weak salts**
NaCl, KNO_3	$HgCl_2$, $CdBr_2$, $Pb(CH_3COO)_2$

To describe the limited extent of ionization (or dissociation) of any weak electrolyte, the term *degree of ionization* (or *dissociation*) is used. *It is represented by the symbol alpha* (α)*, and is defined as the fraction of one mole of electrolyte that ionizes* (*or dissociates*):

$$\alpha = \frac{\text{Moles of electrolyte ionized (or dissociated)}}{\text{Moles of electrolyte dissolved in water}}$$

There is another classification of electrolytes: true electrolyte and pseudoelectrolyte. A true electrolyte always consists of ions while a pseudoelectrolyte always consists of polar covalent molecules. Thus, a true electrolyte (an ionic compound) can conduct electricity in its molten state while a pseudoelectrolyte (a molecular compound) cannot conduct electricity in its molten state.

Follow-up Test 7

1. Which of the following is an electrolyte?
   (1) $C_6H_{12}O_6$ (2) $C_{12}H_{22}O_{11}$
   (3) H_2O (4) K_2CrO_4
2. Which of the following is a nonelectrolyte?
   (1) Urea (2) Methanol
   (3) Ethanol (4) All of these
3. Which of the following is a weak electrolyte?
   (1) HF (2) HCl
   (3) HBr (4) HI
4. Which of the following is not a strong electrolyte?
   (1) $Ba(OH)_2$ (2) $SrOH)_2$
   (3) $Ca(OH)_2$ (4) $Mg(OH)_2$
5. Which of the following gives the maximum number of ions per mole when dissolved in water?
   (1) K_2MgI_4 (2) $CuSO_4$
   (3) $FeCl_3$ (4) KI_3
6. Which of the following is the best conductor of electricity?
   (1) 1 M H_3PO_4 (2) 1 M H_2SO_4
   (3) 1 M H_2CO_3 (4) 1 M HCl

7.11 ACIDS, BASES, AND SALTS

In technological societies, acids, bases, and salts are indispensable compounds. Many acids, bases, and salts occur in nature and serve a wide variety of purposes. For example, our "digestive juice" contains approximately 0.10 mol of hydrochloric acid per day. Human blood and the aqueous components of most cells are mildly acidic. The liquid in our car battery is approximately 40% H_2SO_4 by mass. Many organic acids (carboxylic acids) and their derivatives occur in nature. Acetic acid is present in vinegar, and the sting of an ant bite is due to formic acid. Amino acids are the building blocks of proteins, which are important structural materials in the bodies of animals, including humans. Amino acids are carboxylic acids that also contain basic groups derived from ammonia. The pleasant odors and flavors of ripe fruits are mainly due to the presence of esters, which are formed from the acids in unripe fruits.

Baking soda is a salt of carbonic acid. Sodium hydroxide, a base, is used in the manufacture of soaps, paper, and many other chemicals. Sodium chloride is used to season food and as a food preservative. Calcium chloride is used to melt ice on highways and in the emergency treatment of cardiac arrest. Several ammonium salts are usesd as fertilizers. Drano (a drain cleaner) is solid NaOH that contains some Al chips.

Many common household liquids are acidic, including soft drinks, vinegar, and fruit juices. Most cleaning materials are basic.

Before scientists developed theories to understand the behavior of acids and bases, the properties of acids and bases in aqueous solutions were well known.

7.11.1 General Properties of Aqueous Solutions of Acids

1. They have a sour taste. For example, vinegar owes its taste to acetic acid, and lemon and other citrus fruits contain citric acid, which is responsible for their characteristic sour taste. Pickles are usually preserved in vinegar, a 5% solution of acetic acid. Many pickled condiments contain large amounts of sugar so that the taste of acetic acid is partially masked by the sweet taste of sugar. The word "acid" has been derived from a latin word "acidus" meaning sour.
2. They change the colors of many indicators (highly colored plant and artificial dyes). For example, they turn blue litmus red and cause bromothymol blue to change from blue to yellow.
3. Nonoxidizing acids (such as hydrochloric acid) react with metals (Zn, Mg, and Fe) above hydrogen in the activity series to liberate hydrogen gas, H_2. A typical reaction is that between hydrochloric acid and magnesium:
$$2HCl(aq.) + Mg(s) \longrightarrow MgCl_2(aq.) + H_2(g)$$
HNO_3, a common oxidizing acid, reacts with metals to produce nitrogen oxides, not H_2.
4. They react with (neutralize) metal oxides and metal hydroxides to form salts and water:
$$2HCl(aq.) + MgO(s) \longrightarrow MgCl_2(aq.) + H_2O(l)$$
$$HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O(l)$$
5. They react with salts of weaker or more volatile acids to form a weaker or more volatile acid and a new salt. For example, mineral acids react with carbonates and bicarbonates such as Na_2CO_3, $CaCO_3$, and $NaHCO_3$ to form carbonic acid which decomposes to produce carbon dioxide gas:
$$2HCl(aq.) + CaCO_3(s) \longrightarrow CaCl_2(aq.) + H_2O(1) + CO_2(g)$$
$$HCl(aq.) + NaHCO_3(s) \longrightarrow NaCl(aq.) + H_2O(1) + CO_2(g)$$
6. Aqueous solutions of acids conduct an electric current because they are totally or partially ionized.

7.11.2 General Properties of Aqueous Solution of Bases

1. They have a bitter taste.
2. They have a slippery feeling. Soaps, which are mildly basic, exhibit this property, i.e., they feel slippery. A solution of household bleach feels very slippery because it is quite basic.
3. They cause color changes in plant dyes. For example, they change the color of litmus from red to blue and the color of bromothymol blue from yellow to blue.
4. They react with (neutralize) acids to form salts and in most cases, water.
$$NaOH(aq.) + HNO_3(aq.) \longrightarrow NaNO_3(aq.) + H_2O(1)$$
5. Their aqueous solutions conduct electric current because they are ionized (or dissociated) partly or completely.

7.11.3 Operational Definitions of Acids and Bases

Acids	Bases
Have a sour taste	Have a bitter taste
Turn blue litmus red	Turn red litmus blue
React with active metals to liberate hydrogen gas	Have no such property
Have no soapy touch	Have a soapy touch
Conduct electricty	Conduct electricity.
Lose their acidic properties on addition of a base	Lose their properties on addition of an acid.

As discussed above, when acids and bases are mixed, they react with each other to produce salts. Some commonly known examples of salts are sodium chloride, sodium nitrate, and barium sulphate. Sodium chloride (common salt), an important component of our diet, is formed by the reaction between hydrochloric acid and sodium hydroxide:
$$HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O(1)$$

In the solid state, NaCl exists as a crystal of positively charged sodium ions (Na^+) and negatively charged chloride ions (Cl^-) which are held together by strong electrostatic interactions between oppositely charged ions. The electrostatic force between two opposite charges is inversely proportional to the dielectric constant of the solvent in which the salt is to be dissolved.

Water (a universal solvent) is a very effective solvent for ionic compounds such as salts, because it possesses a very high dielectric constant of 80. Thus, when sodium chloride is added to water, the electrostatic interactions between Na^+ and Cl^- ions are reduced by a factor of 80. This facilitates the ions to move freely. Moreover, in the solution, the ions are well separated due to hydration with water molecules:

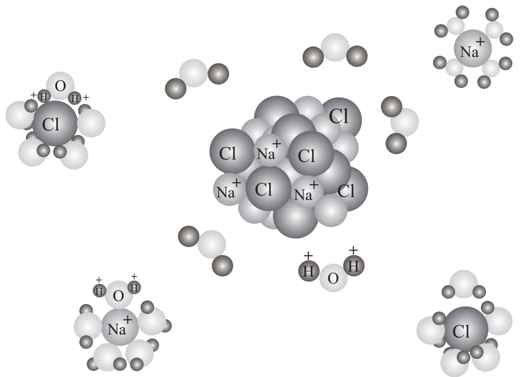


Figure 7.4 Dissolution of sodium chloride in water. Na^+ and Cl^- ions are stabilized by their hydration with polar water molecules.

Although water is an electrically neutral molecule, it has a positive end (the H atoms) and a negative and (the O atom), or positive and negative poles. For this reason, water is often referred to as a polar solvent. When an ionic compound (such as sodium chloride) is added to water, it dissolves because the three-dimensional network of the ions in the crystal is destroyed, and the Na^+ and Cl^- ions are separated from each other. In the resulting aqueous solution, each Na^+ ion is surrounded by a number of H_2O molecules oriented with their negative ends toward the cation. Similarly, each Cl^- ion is surrounded by a number of water molecules with their positive ends oriented toward the anion (Figure 7.4). *The process in which an ion (cation or anion) is surrounded by water molecules arranged in a specific manner is called hydration*. The process of hydration helps to stabilize ions in solution and prevent cations from combining with anions.

Follow-up Test 8

1. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of ______ L day^{-1}.
   (1) 1.2–1.5 (2) 0.5–1.0
   (3) 1.5–2.0 (4) 1.0–2.0
2. Which of the following acids is known to be the main component of vinegar?
   (1) Hydrocyanic acid (2) Formic acid
   (3) Butyric acid (4) Acetic acid
3. Lemon and orange juices contain
   (1) citric acid (2) ascorbic acid
   (3) tartaric acid (4) both (1) and (2)
4. Which of the following acids is not completely ionized in aqueous solution?
   (1) Hydrochloric acid (2) Sulphuric acid
   (3) Acetic acid (4) Nitric acid
5. Which of the following salts is a base and is used for washing purposes?
   (1) $NaHCO_3$ (2) Na_2CO_3
   (3) Na_2SO_4 (4) NaCl

7.11.4 Arrhenius Concept of Acids and Bases

In 1680, Robert Boyle noted that acids (i) dissolve many substances, (ii) change the colors of some natural dyes (indicators), and (iii) lose their characteristic properties when mixed with alkalis (bases). By 1814, Gay–Lussac concluded that acids neutralize bases and that the two classes of substances should be defined in terms of their reactions with each other.

In 1884, Svante Arrhenius presented his theory of electrolytic dissociation, which resulted in the Arrhenius theory of acid–base reactions. *According to the Arrhenius theory, an acid can be described as a substance that contains at least one H atom per molecule and yields hydrogen ions* (H^+) *when dissolved in water. A base is a substance that contains at least one hydroxyl group* (OH) *per molecule and produces hydroxide ions* (OH^-) *when dissolved in water.* Typical examples of Arrhenius acids are hydrochloric acid (HCl), nitric acid (HNO_3), sulphuric acid (H_2SO_4), carbonic acid (H_2CO_3), phosphoric acid (H_3PO_4), hydrocyanic acid (HCN), hydrosulphuric acid (H_2S), and acetic acid (CH_3COOH).

Typical examples of Arrhenius bases are sodium hydroxide (NaOH), potassium hydroxide (KOH), and barium hydroxide $Ba(OH)_2$.

Formulas for inorganic acids contain one or more H atoms as well as an anionic group. Anions whose names end in "-ide" have associated acids with a "hydro-" prefix and an "-ic" ending:

$$\underset{\text{(Chloride)}}{Cl^-} \longrightarrow \underset{\text{(Hydrochloric acid)}}{HCl}$$

$$\underset{\text{(Cyanide)}}{CN^-} \longrightarrow \underset{\text{(Hydrocyanic acid)}}{HCN}$$

We may have noticed that in some cases, two different names are assigned to the same chemical formula:

HCl (hydrogen chloride), H_2S (hydrogen sulphide)
HCl (hydrochloric acid), H_2S (hydrosulphuric acid)

The name given to the compound depends on its physical state. When HCl exists in the pure (gaseous, liquid, or solid) state, it is a molecular covalent compound and we call it hydrogen chloride. When HCl is dissolved in water, the molecules ionize into H^+ and Cl^- ions. In aqueous solution, the substance is called hydrochloric acid. Similarly, we can understand the case of H_2S.

Acids that contain hydrogen, oxygen, and another element (the central element) are called oxoacids. They are also called ternary acids because a ternary compound consists of three elements. The formulas of oxoacids are usually written with the H first, followed by the central element (usually a nonmetal), and then O, as illustrated by the following series of oxoacids: H_2CO_3, HNO_3, H_2SO_4, and $HClO_3$.

Often, nonmetals that exhibit more than one oxidation state form more than one ternary acid. These ternary acids differ in the number of oxygen atoms they contain. Starting with the oxoacid whose name ends with "-ic", we use the following rules to name other oxoacids:

1. **Addition of one O atom to the "-ic" acid:**
   The acid is called "per ... ic" acid.

$$\underset{\text{Chloric acid}}{HClO_3} \xrightarrow{+O} \underset{\text{Perchloric acid}}{HClO_4}$$

2. **Removal of one O atom from the "-ic" acid:**
   The acid is called "-ous" acid.

$$\underset{\text{Chloric acid}}{HClO_3} \xrightarrow{-O} \underset{\text{Chlorus acid}}{HClO_2}$$

$$\underset{\text{Nitric acid}}{HNO_3} \xrightarrow{-O} \underset{\text{Nitrous acid}}{HNO_2}$$

3. **Removal of two O atoms from the "-ic" acid:**
   The acid is called "hypo ... ous" acid.

$$\underset{\text{Chloric acid}}{HClO_3} \xrightarrow{-2O} \underset{\text{Hypochlorus acid}}{HClO}$$

The rules for naming the anions of oxoacids, called oxoanions, are as follows:

1. When one or more of the H atoms are removed as H^+ ions from the "-ic" acid, the anion's name ends with "-ate."

$$\underset{\text{Perchloric acid}}{HClO_4} \xrightarrow{-H^+} \underset{\text{Perchlorate}}{ClO_4^-}$$

$$\underset{\text{Chloric acid}}{HClO_3} \xrightarrow{-H^+} \underset{\text{Chlorate}}{ClO_3^-}$$

$$\underset{\text{Carbonic acid}}{H_2CO_3} \xrightarrow{-2H^+} \underset{\text{Carbonate}}{CO_3^{2-}}$$

2. When one or more of the H atoms are removed as H^+ ions from the "-ous" acid, the anion's name ends with "-ite."

$$\underset{\text{Chlorus acid}}{HClO_2} \xrightarrow{-H^+} \underset{\text{Chlorite}}{ClO_2^-}$$

$$\underset{\text{Hypochlorus acid}}{HClO} \xrightarrow{-H^+} \underset{\text{Hypochlorite}}{ClO^-}$$

3. The names of anions in which one or more but not all the H atoms have been removed as H^+ ions must indicate the number of H atoms present:

$$\underset{\text{Phosphoric acid}}{H_3PO_4} \xrightarrow{-H^+} \underset{\text{Dihydrogen phosphate}}{H_2PO_4^-}$$

$$\underset{\text{Phosphoric acid}}{H_3PO_4} \xrightarrow{-2H^+} \underset{\text{Hydrogen phosphate}}{HPO_4^{2-}}$$

Note that we usually omit the prefix "mono-" when there is only one H in the anion.

The Arrhenius acids ionize in water to give aqueous solutions that conduct electric current. The ionization of an acid HZ(aq.) can be described by the following equation:

$$HZ(aq.) \longrightarrow H^+(aq.) + Z^-(aq.)$$

For example, hydrogen chloride gas dissolves in water. The resulting aqueous solution is called hydrochloric acid because dissolved HCl ionizes as follows:

$$HCl(aq.) \longrightarrow H^+(aq.) + Cl^-(aq.)$$

According to Arrhenius, the properties of aqueous solutions of most protonic acids (those containing acidic H atoms) are actually the properties of hydrogen ions in aqueous solution.

The Arrhenius bases ionize in water to give aqueous solutions that conduct electric current. The ionization of a base MOH(aq.) can be described by the following equation:

$$MOH(aq.) \longrightarrow M^+(aq.) + OH^-(aq.)$$

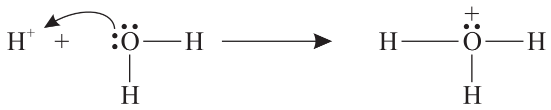
For example, NaOH(s) is called an Arrhenius base because it dissolves in water and dissociates as follows:

$$NaOH(aq.) \longrightarrow Na^+(aq.) + OH^-(aq.)$$

According to Arrhenius, the properties of aqueous solutions of most bases are due to the hydroxide ions present in the aqueous solution of bases.

Although Arrhenius described H^+ ions in water as bare ions (protons), we now know that they are hydrated in aqueous solution and exist as $H^+ (H_2O)_n$, in which n is some small integer. This is due to the attraction of the H^+ ions (or protons) for the oxygen-end (δ–) of water molecules. Although we do not know the extent of hydration of H^+ ions in most solutions, we usually represent the hydrated hydrogen ion as the hydrated hydronium ion, H_3O^+(aq.), or H^+(aq.). Whether we use the designation H^+(aq.) or H_3O^+(aq.), we always mean the hydrated hydrogen ion. *Then the species that gives the aqueous solution of acids their characteristic acidic properties is the hydrated hydrogen ion.* Similarly, the hydroxide ion in water exists as hydrated hydroxide ion, OH^-(aq.). In fact, all ions are hydrated in aqueous solution.

The most common isotope of hydrogen ^1_1H has no neutrons. Thus, $^1_1H^+$ is a bare proton. On account of very small size (~ 10^{-15} m radius) and intense electric field, H^+ ion (bare proton) is very reactive. Thus, it binds itself through coordinate covalent bond to one of the two lone pairs of electrons on the O atom to give trigonal pyramidal hydronium ion, H_3O^+ or $H^+(H_2O)$:



Hydronium ion has been detected in many compounds (such as $H_3O^+ Cl^-$) in the solid state. In aqueous solution, the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$. Similarly, the hydroxide ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$, $H_7O_4^-$, etc.

The neutralization of protonic acids with metal hydroxides (hydroxy bases) is, thus, defined as the combination of hydrated H^+ ions with hydrated OH^- ions to form H_2O molecules:

$$H^+(aq.) + OH^-(aq.) \longrightarrow H_2O(l) \text{ (Neutralization)}$$

7.11.5 Limitations of Arrhenius theory

1. The Arrhenius concept of acid and base suffers from the limitation of being applicable only to aqueous solutions. It fails to explain the neutralization in the absence of water.
   $$\underset{\text{Base}}{NH_3(g)} + \underset{\text{Acid}}{HCl(g)} \longrightarrow \underset{\text{Salt}}{NH_4^+Cl^-(s)}$$
2. It does not account for the acidity of substances like CO_2, SO_2, SO_3, etc., which do not possess an H atom. When carbon dioxide dissolves in water, dissolved CO_2 reacts partially with water to yield H^+(aq.) ions:
   $$CO_2(aq.) + H_2O(l) \rightleftharpoons H_2CO_3(aq.) \rightleftharpoons 2H^+(aq.) + CO_3^{2-}(aq.)$$
3. It does not account for the basicity of substances like NH_3, Na_2CO_3, CaO, etc, which do not possess a hydroxyl (OH) group. Ammonia (NH_3), a molecular compound in the pure state, is classified as a common base. When ammonia dissolves in water, dissolved NH_3 react partially with water to yield NH_4^+ and OH^- ions:
   $$NH_3(aq.) + H_2O(l) \longrightarrow NH_4^+(aq.) + OH^-(aq.)$$
4. Bare H^+ and OH^- ions cannot exist in aqueous solution.

7.11.6 Brönsted–Lowry Acids and Bases

The Arrhenius model of acids and bases, although limited in scope, led to the development of more general theories of acid–base behavior. In 1923, J. N. Brönsted and T. M. Lowry independently presented logical extensions of the Arrhenius theory. Brönsted's contribution was more thorough than Lowry's and the result is known as the Brönsted theory or the Brönsted–Lowry theory. *According to this theory, an acid is a substance that is capable of donating a hydrogen ion (H^+) while a base is a substance capable of accepting a hydrogen ion (H^+). In short, an acid is defined as a proton donor while a base is defined as a proton acceptor.*

Substances that behave according to this definition are called *Brönsted acids* and *Brönsted bases***.** These definitions are sufficiently broad that any hydrogen-containing molecule or ion capable of releasing a proton (H^+) is an acid, whereas any molecule or ion that can accept a proton is a base. (Note that in the Arrhenius theory of acids and bases, only substances that contain the OH^- group would be called bases.)

Arrhenius' definitions of acids and bases are limited in that they apply only to aqueous solutions. The Brönsted definitions (unlike the Arrhenius definitions) do not restrict acid and base behavior to water solutions.

According to the Brönsted theory, an acid–base reaction is the transfer of a proton from an acid to a base. Thus, the complete ionization of hydrogen chloride (HCl), a strong acid, in water is an acid–base reaction in which water acts as a base (or proton acceptor):

Step 1: $HCl(aq.) \longrightarrow H^+(aq.) + Cl^-(aq.)$(Arrhenius description)

Step 2: $H_2O(l) + H^+(aq.) \longrightarrow H_3O^+(aq.)$

$$\text{Overall: } \underset{\text{base}_1}{H_2O(l)} + \underset{\text{acid}_2}{HCl(aq.)} \longrightarrow \underset{\text{acid}_1}{H_3O^+(aq.)} + \underset{\text{base}_2}{Cl^-(aq.)}$$

Brönsted description

The ionization of hydrogen fluoride (a weak acid) is similar, but it occurs to only a slight extent. Thus, we use a double arrow to indicate that it is reversible.

$$\underset{\text{acid}_1}{HF(aq.)} + \underset{\text{base}_2}{H_2O(l)} \rightleftharpoons \underset{\text{base}_1}{F^-(aq.)} + \underset{\text{acid}_2}{H_3O^+(aq.)}$$

Various measurements (electrical conductivity, freezing point, depression, etc.) indicate that HF is only slightly ionized in water.

The double arrow is used to indicate that the reaction occurs in both the forward and reverse directions. In the forward reaction, the HF molecule acts as proton donor and the H_2O molecule acts as proton acceptor, and these are, thus, called Brönsted acid and base, respectively. In the reverse reaction, H^+ is transported from H_3O^+ to F^-. Thus, H_3O^+ acts a Brönsted acid while F^- act as a Brönsted base.

An extension of the Brönsted definition of acids and bases is the concept of the conjugate acid–base pair—the two species that differ by a proton. It can also be defined as an acid and its conjugate base or a base and its conjugate acid. The conjugate base of a Brönsted acid is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brönsted base. *In short, a base formed from an acid after the loss of a proton is called the conjugate base of the acid while an acid formed from a base after the acceptance of a proton is called the conjugate acid of the base*.

The acid–base pair that differs only by one proton is called a conjugate acid–base pair. Conjugate means "joined together."

Every Brönsted acid has a conjugate base, and every Brönsted base has a conjugate acid. Therefore, in the preceding equation, the fluoride ion (F^-) is the conjugate base formed from the acid HF and HF is the conjugate acid of the base F^-. Similarly, H_3O^+ is the conjugate acid of the base H_2O and H_2O is the conjugate base of the acid H_3O^+. The subscripts 1 and 2 designate the two conjugate acid–base pairs. Therefore, HF (acid$_1$) and F^- (base$_1$) are one conjugate acid–base pair, and H_2O (base$_2$) and H_3O^+ (acid$_2$) are the other pair. The members of each conjugate pair are designated by the same numerical subscript. It makes no difference which conjugate acid–base pair (HF and F^- or H_3O^+ and H_2O) is assigned the subscripts 1 and 2.

$$\text{Conjugate acid (CA)} \xrightleftharpoons[\text{Add H}^+\text{, increase charge by 1}]{\text{Remove H}^+\text{, decrease charge by 1}} \text{Conjugate base (CB)} + H^+$$

$$\begin{tikzcd} \text{HF (CA)} \arrow[r, bend left, "-H^+"] & \text{F}^- \text{ CB} \arrow[l, bend left, "+H^+"] \end{tikzcd}$$

$$\begin{tikzcd} H_3O^+ \text{ CA} \arrow[r, bend left, "-H^+"] & H_2O \text{ CB} \arrow[l, bend left, "+H^+"] \end{tikzcd}$$

The formula of a conjugate base always has one fewer H atom and one more negative charge (or one fewer positive charge) than the formula of the corresponding acid.

When the weak acid, HF, dissolves in water, the HF molecules give up some H^+ ions that can be accepted by either of the two bases, F^- or H_2O. The fact that HF is only slightly ionized tell us that F^- is a stronger base than H_2O. On the other hand, when the strong acid, HCl, dissolves in water, the HCl molecules give up H^+ ions that can be accepted by either of two bases, Cl^- or H_2O. The fact that HCl is completely ionized in dilute aqueous solution tell us that Cl^- is a weaker base than H_2O. Thus, the weaker acid, HF, has the stronger conjugate base, F^-. The stronger acid, HCl, has the weaker conjugate base, Cl^-. We can generalize: *The stronger the acid, the weaker is its conjugate base and the weaker the acid, the stronger is its conjugate base*. Thus, an acid–base reaction is always favored in that direction which leads to the formation of weaker conjugate acid and weaker conjugate base. "Strong" and "weak," like many other adjectives, are used in a relative sense. We do not mean to imply that the fluoride ion, F^-, is a strong base compared with species such as the hydroxide ion, OH^-. We mean that relative to the anions of strong acids, which are very weak bases, F^- is a much stronger base.

F^- is a stronger base than H_2O. H_2O is a stronger base than Cl^-. Therefore, F^- is a stronger base than Cl^-.

The concept of the conjugate acid–base pair clearly shows that the presence of a base is must for an acid to show its acidic behavior. Similarly, the presence of an acid is must for a base to show its basic behavior.

The Brönsted definition allows us to classify ammonia as a base because of its ability to accept a proton. In the ionization of aqueous ammonia (NH_3 dissolved in water), ammonia acts as a weak Brönsted base and water acts as an acid:

$$\underset{\text{base}_1}{NH_3(aq.)} + \underset{\text{acid}_2}{H_2O(l)} \rightleftharpoons \underset{\text{acid}_1}{NH_4^+(aq.)} + \underset{\text{base}_2}{OH^-(aq.)}$$

Ammonia is a weak electrolyte (and therefore, a weak base) because only a small fraction of dissolved NH_3 molecules reacts with water to form NH_4^+ and OH^- ions. The resulting solution is basic due to the presence of hydroxide ions. In the forward reaction, H_2O molecule acts as proton donor while NH_3 molecule acts as proton acceptor, and they are, thus, called the Brönsted acid and base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH^-. Thus, NH_4^+ (proton donor) acts as a Brönsted acid while OH^- (proton acceptor) acts as a Brönsted base. In this case, NH_4^+ (ammonia ion) is the conjugate acid of the base NH_3 (ammonia) and OH^- (hydroxide ion) is the conjugate base of the acid H_2O (water).

Be careful to avoid confusing solubility in water and extent of ionization. They are not essentially related. Ammonia is very soluble in water (≈ 15 mol L^{-1} at 25°C). In 0.10 M solution, NH_3 is only 1.3% ionized and 98.7% nonionized. Aqueous ammonia is sometimes erroneously called ammonium hydroxide. There is no evidence that the species NH_4OH actually exists.

Strictly speaking, NaOH is not a Brönsted base because it cannot accept a proton. However, NaOH is a strong electrolyte that ionizes completely in solution. The hydroxide ion (OH^-) formed by that ionization is a Brönsted base because it can accept a proton:

$$H_3O^+(aq.) + \overline{O}H(aq.) \rightleftharpoons 2H_2O(l)$$

Thus, when we call NaOH or any other metal hydroxide a base, we are actually refering to the OH^- species derived from the hydroxide.

It is interesting to observe the dual role of water as an acid and as a base. Water acts as an acid (H^+ donor) in its reaction with NH_3, whereas it acts as a base (H^+ acceptor) in its reaction with HCl and with HF. Thus, whether water acts as an acid or as a base depends on the other species present.

Finally, we note that protons (hydrogen ions) are hydrated in solution and it is equally acceptable to represent the hydrated proton in aqueous solution as $H^+(aq.)$ or $H_3O^+(aq.)$. The formula $H^+(aq.)$ is for convenience as it is less cumbersome in calculations involving hydrogen-ion concentrations and in calculations involving equilibrium constants. The $H_3O^+(aq.)$ notation is closer to reality and is more useful when discussing the Brönsted acid–base properties.

Example 7.10 Write the conjugate bases for the following Brönsted acids: HF, H_2SO_4, and HCO_3^-.

Strategy: The conjugate bases should have one proton less in each case.

Solution:

$$HF(aq.) \longrightarrow H^+(aq.) + \underset{\text{Conjugate base}}{F^-(aq.)}$$

$$H_2SO_4(aq.) \longrightarrow H^+(aq.) + \underset{\text{Conjugate base}}{HSO_4^-(aq.)}$$

$$HCO_3^-(aq.) \longrightarrow H^+(aq.) + \underset{\text{Conjugate base}}{CO_3^{2-}(aq.)}$$

Each conjugate base has one less proton because base is formed when acid loses one proton.

Example 7.11 Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3, and $HCOO^-$.

Strategy: The conjugate acid should have one extra proton in each case.

Solution:

$$NH_2^-(aq.) + H^+(aq.) \longrightarrow \underset{\text{Conjugate acid}}{NH_3(aq.)}$$

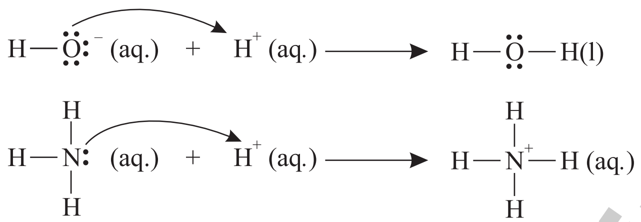
$$NH_3(aq.) + H^+(aq.) \longrightarrow \underset{\text{Conjugate acid}}{NH_4^+(aq.)}$$

$$HCOO^- + H^+ \longrightarrow \underset{\text{Conjugate acid}}{HCOOH}$$

Each conjugate acid has one extra proton because an acid is formed when a base accepts one proton.

7.11.7 Lewis Acids and Bases

To behave as a Brönsted base, a substance (molecule or ion) must be able to accept protons. By this definition, both the hydroxide ion and ammonia are bases:



$$H-\ddot{O}:^- (aq.) + H^+(aq.) \longrightarrow H-\ddot{O}-H(l)$$

$$NH_3(aq.) + H^+(aq.) \longrightarrow NH_4^+(aq.)$$

In each case, the atom to which the proton becomes attached possesses at least one unshared pair of electrons. This characteristic property of the OH^- ion, of NH_3, and of other Brönsted bases suggests a more general definition of acids and bases.

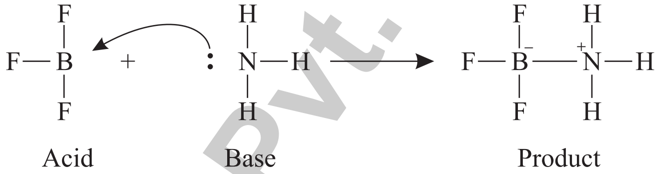
In 1923, Professor G.N. Lewis formulated such a definition and presented the most comprehensive of the classical acid–base theories. *According to the Lewis theory, an acid, is a substance that can accept a pair of electrons, and a base is a substance that can donate a pair of electrons*.

For example, in the protonation of ammonia, NH_3 acts as a Lewis base because it donates a pair of electrons to the proton H^+, which acts as a Lewis acid by accepting the pair of electrons. Note that these definitions do not specify that an electron pair must be transferred from one atom to another (i.e., there is no loss and gain of electrons). It only specifies that an electron pair, residing originally on one atom, must be shared between two atoms. Therefore, a Lewis acid–base reaction (neutralization) is defined as *coordinate covalent bond formation*, i.e., it involves the donation of a pair of electrons from one species to another. This results in a covalent bond in which both electrons are furnished by one atom or ion. Such a reaction does not produce a salt and water.

As far as bases are concerned, there is no difference between the Brönsted and the Lewis concepts because in both the cases, the base provides a lone pair. However, in the Lewis concept, many acids do not have proton to donate. Thus, the significance of the Lewis concept is that it is much more general than the other definitions as it includes many acid–base reactions that do not involve the Brönsted acids.

All Brönsted bases are Lewis bases.

For example, consider the reaction between boron trifluoride (BF_3) and ammonia (NH_3):

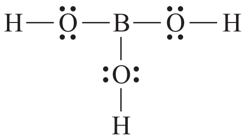


The B atom in BF_3 is sp^2-hybridized. The vacant, unhybridized $2p$ orbital accepts the pair of electrons from NH_3. Thus, BF_3 functions as an acid according to the Lewis definition, even though it does not contain an ionizable proton. Note that a coordinate covalent bond is formed between the B and N atoms as illustrated by the formal charges.

A coordinate covalent bond is always formed in a Lewis acid–base reaction.

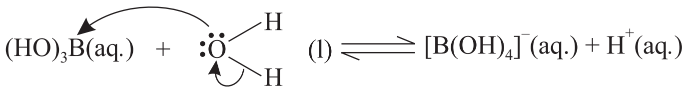
Theoretically, any species that contains an unshared electron pair can act as a base. In fact, most ions and molecules that contain unshared electron pairs undergo some reactions by sharing their electron pairs. Conversely, many Lewis acids contain only six electrons in the highest occupied energy level of the central element. They react by accepting a share in an additional pair of electrons. These species are said to have on open sextet. Many compounds of group 13 elements are Lewis acids, as illustrated by the reaction of BF_3 with NH_3.

Another Lewis acid containing B is boric acid. Boric acid, H_3BO_3 (a weak acid used in eyewash), is an oxoacid with the following structure:



Boric acid

However, unlike the other oxoacids (such as H_2SO_4), boric acid does not ionize in water to produce an H^+ ion. Instead, it undergoes Lewis acid–base reaction with water, in which boric acid accepts a pair of electrons from the hydroxide ion that is derived from the H_2O molecule:



$$(HO)_3B(aq.) + H_2O(l) \rightleftharpoons [B(OH)_4]^-(aq.) + H^+(aq.)$$

Anhydrous aluminium chloride ($AlCl_3$) is a common Lewis acid that is used to catalyze many organic reactions such as the

Friedel–Crafts alkylation and acylation. $AlCl_3$ acts as a Lewis acid when it dissolves in hydrochloric acid (HCl) to give a solution that contains $AlCl_4^-$ ions:

$$\underset{\text{Acid}}{AlCl_3(s)} + \underset{\text{Base}}{Cl^-(aq.)} \longrightarrow AlCl_4^-(aq.)$$

Other ions and molecules behave as Lewis acids by the expansion of valence shell of the central element. Anhydrous tin (IV) chloride is a colorless liquid that is frequently used as a Lewis acid catalyst. The tin atom (group 14) can expand its valence shell by utilizing vacant *d*-orbitals. It can accept shares in two additional electron pairs, as its reaction with hydrochloric acid illustrates:

$$\underset{\text{Acid}}{SnCl_4(l)} + \underset{\text{Base}}{2Cl^-(aq.)} \longrightarrow SnCl_6^{2-}$$

Other examples of the Lewis acid–base reactions are as follows:

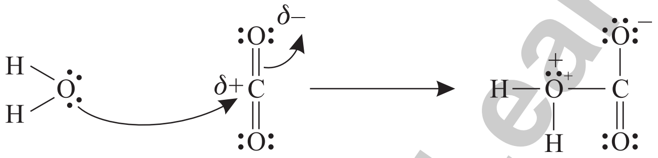
$$Ni(s) + 4\,CO(g) \rightleftharpoons Ni(CO)_4(g)$$
$$Cd^{2+}(aq.) + 4I^-(aq.) \rightleftharpoons CdI_4^{2-}(aq.)$$
$$Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.)$$

It is important to note that the hydration of metal ions in aqueous solution is in itself a Lewis acid–base reaction. Thus, when copper (II) sulphate ($CuSO_4$) dissolves in water, each Cu^{2+} ion gets associated with water molecules as $[Cu(H_2O)_6]^{2+}$. In this case, the Cu^{2+} ion acts as the acid while the H_2O molecules act as the base.

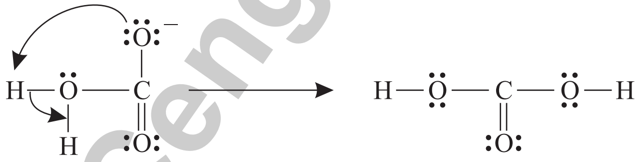
The hydration of carbon dioxide to produce carbonic acid

$$CO_2(g) + H_2O(1) \rightleftharpoons H_2CO_3(aq.)$$

can be understood in the Lewis framework as follows: The first step involves the donation of a lone pair on the O atom in H_2O to the C atom in CO_2.



Carbon is a second-period element. It cannot expand its valence shell and can accommodate only eight valence electrons. Thus, an orbital is vacated on the C atom to accommodate the lone pair by the removal of the electron pair in the C–O pi bond. These shifts of electrons are indicated by the curved arrows as shown in the above reaction. Therefore, H_2O is a Lewis base and CO_2 is a Lewis acid. Next, a proton is transferred onto the O atom bearing a negative charge to form H_2CO_3:



Thus, a species (molecule or ion) can act as a Lewis base if it carries an atom capable of donating a lone pair of electrons (e.g., NH_3). On the other hand, a species (molecule or ion) can act as a Lewis acid if it carries an atom which (i) has an incomplete octet, e.g., B in BF_3 or (ii) has an electron deficient atom (with complete octet) π-bonded to a more electronegative atom (e.g., C in CO_2) or (iii) has an electron deficient atom (with expanded octet) π bonded to a more electronegative atom (e.g., S in SO_3) or (iv) is capable of expanding its valence shell (e.g., Sn in $SnCl_4$). Many organic and biological reactions, which are acid–base reactions, do not fit within the Arrhenius or Brönsted theories. Experienced chemists find the Lewis theory to be very useful because so many other chemical reactions are covered by it. The less experienced sometimes find the theory less useful, but as their knowledge expands, so does its utility.

Which acid–base theory should be used?

Remember the following:

1. Arrhenius acids and bases are also Brönsted acids and bases but the reverse is not true.
2. Brönsted acids and bases are also Lewis acids and bases but the reverse is not true.
3. We usually prefer the Arrhenius or the Brönsted theory when water or another protonic solvent is present.
4. Although the Lewis theory can be used to explain the acidic or basic property of some species in protonic solvents, the most important use of the Lewis theory is for acid–base reactions in many nonaqueous solvents.

Although the Lewis definition of acids and bases is of greater significance because of its generality, we normally speak of an acid and a base in terms of the Brönsted definition. The term Lewis acid is usually reserved for substances that can accept a pair of electrons but do not contain ionizable H atoms.

Example 7.12 Classify the following species into Lewis acids and bases and show how these act as such:

(i) BCl_3 (ii) H^+ (iii) F^- (iv) HO^-

Strategy: A Lewis acid is any species that can accept a share in an electron pair while a Lewis base is any species that can make available or donate a share in an electron pair.

Solution:

(i) BCl_3 acts as a Lewis acid because the central B atom has incomplete octet and, therefore, can accept a lone pair of electrons from species like ammonia or amine molecules.

(ii) A proton is a Lewis acid as it can form an H atom by accepting a lone pair of electrons from species like hydroxide ion and fluoride ion.

(iii) Fluoride ion acts as a Lewis base as it can donate any one of its four lone pairs of electrons.

(iv) Hydroxide ion is a Lewis base as it can donate any one of its three lone pairs of electrons.

Follow-up Test 9

1. Which of the following is not a typical Arrhenius acid?

(1) CO_2	(2) SO_2
(3) SO_3	(4) All of these

2. Which of the following is not a typical Arrhenius base?
   (1) NH_3 (2) Na_2CO_3
   (3) CaO (4) All of these
3. Which of the following is a Brönsted acid?
   (i) HCN (ii) $H_2PO_4^-$
   (iii) NH_4^+ (iv) HCl
   (1) (i), (iii) (2) (i), (ii), (iii), (iv)
   (3) (ii), (iii) (4) (i), (iii), (iv)
4. Which of the following is a Brönsted base?
   (i) NH_3 (iii) CH_3NH_2
   (iii) HCO_3^- (iv) SO_4^{2-}
   (1) (i), (ii), (iii), (iv) (2) (i), (ii)
   (3) (i), (ii), (iv) (4) (ii), (iii), (iv)
5. The conjugate base of hydroxide ion is
   (1) H_2O (2) H_3O^+
   (3) O^{2-} (4) O_2
6. The conjugate acid of amide ion (NH_2^-) is
   (1) N_2H_4 (2) NH_2OH
   (3) NH_4^+ (4) NH_3
7. Which of the following can act both as a Brönsted acid as well as a Brönsted base?
   (1) H_2SO_4 (2) HCO_3^-
   (3) O^{2-} (4) NH_4^+
8. Which of the following acid–base reactions cannot be explained by the Brönsted theory?
   (1) $CO_2 + CaO \longrightarrow CaCO_3$
   (2) $BF_3 + NH_3 \longrightarrow \bar{B}F_3\overset{+}{N}H_3$
   (3) $Ni + 4CO \longrightarrow Ni(CO)_4$
   (4) All of these
9. Which of the following Brönsted acids has the weakest conjugate base?
   (1) H_2O (2) HCN
   (3) HCOOH (4) HF
10. Which of the following is a Lewis acid?
   (1) BF_3 (2) $SnCl_4$
   (3) CO_2 (4) All of these
11. Which of the following is not a Lewis base?
   (1) CH_4 (2) CN^-
   (3) ROH (4) NH_3
12. Which of the following is correct according to the Lewis acid–base concept?
   (1) All positively charged ions are bases.
   (2) All negatively charged ions are acids.
   (3) A molecule in which the central atom has vacant *d*-orbitals available acts as an acid.
   (4) Species in which the central atom has complete octet cannot act as an acid.
13. Which of the following ions can act as Lewis acids?
   (1) Alkali metal ions
   (2) Transition metal ions
   (3) Alkaline earth metal ions
   (4) All metal ions
14. Which of the following is correct regarding the Lewis concept of acids and bases?
   (1) It cannot explain the cases when a species is donating as well as accepting electron pairs.
   (2) It cannot explain the acidic character of protonic acids.
   (3) It cannot explain quantitatively the strength of acids as well as bases.
   (4) All of these

7.12 IONIZATION OF ACIDS AND BASES

Since most of the reactions in chemical and biological systems occur in aqueous medium, the Arrhenius concept of acids and bases is the most common and frequently used concept in case of ionization (or dissociation) of acids and bases.

Acids like hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3), perchloric acid ($HClO_4$), and sulphuric acid are strong electrolytes because they are nearly completely ionized into their constituent ions in an aqueous medium. According to the Arrhenius concept, they are strong acids as they produce high concentration of hydrogen ions (or hydronium ions) through complete ionization:

$$HCl(aq.) \longrightarrow H^+(aq.) + Cl^-(aq.)$$
$$HNO_3(aq.) \longrightarrow H^+(aq.) + NO_3^-(aq.)$$
$$HClO_4(aq.) \longrightarrow H^+(aq.) + ClO_4^-(aq.)$$

Bases like barium hydroxide [$Ba(OH)_2$], strontium hydroxide [$Sr(OH)_2$], caesium hydroxide [Cs(OH)], potassium hydroxide (KOH), sodium hydroxide (NaOH), and lithium hydroxide (LiOH) are also strong electrolytes as they are completely dissociated into their constituent ions in an aqueous medium. According to the Arrhenius concept, they are strong bases as they produce high concentration of hydroxide ions through complete dissociation:

$$Ba(OH)_2(aq.) \longrightarrow Ba^{2+}(aq.) + 2OH^-(aq.)$$
$$KOH(aq.) \longrightarrow K^+(aq.) + OH^-(aq.)$$
$$NaOH(aq.) \longrightarrow Na^+(aq.) + OH^-(aq.)$$

Most acids ionize to a limited extent in water. Such acids are classified as weak acids. Ammonia is a weak base as it ionizes only to a small extent in water.

We can also gauge the strength of an acid or a base in terms of the Brönsted theory of acids and bases. According to this theory, a strong acid implies a good proton donor while a strong base implies a good proton acceptor. Let us consider the acid–base ionization equilibrium of a weak acid HB.

$$\underset{\text{acid}_1}{HB(aq.)} + \underset{\text{base}_2}{H_2O(l)} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+(aq.)} + \underset{\text{base}_1}{B^-(aq.)}$$

Recall that acid–base ionization equilibrium is dynamic in nature as it involves the transfer of proton in forward as well as in reverse directions. We need to compare the relative strengths of the two acids (or bases) involved in the dissociation equilibrium in order to decide which direction of equilibrium is favored and what is the driving force behind it.

There are two acids, HB (forward direction) and H_3O^+ (reverse direction), present in the above-mentioned acid-dissociation equilibrium. We need to find which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other is termed as the stronger acid, and the equilibrium will shift in the direction of the weaker acid.

For example, if HB is a stronger acid than H_3O^+, then HB will mainly donate protons and not H_3O^+. Thus, the resulting aqueous solution mainly contains B^-(aq.) and H_3O^+(aq.) ions. The stronger the acid HB, the greater is the concentration of its conjugate base B^- in aqueous solution.

The acid–base equilibrium always moves in the direction of formation of weaker acid and weaker base because the stronger acid prefers to donate a proton to the stronger base.

It further follows that as a strong acid ionizes completely in water, the resulting conjugate base formed will be very weak on account of its very small tendency to accept a proton in the reverse direction. *Thus, strong acids yield very weak conjugate bases*.

According to the Brönsted theory, strong acids like sulphuric acid (H_2SO_4), nitric acid HNO_3, hydroiodic acid (HI), hydrobromic acid (HBr), hydrochloric acid (HCl), and perchloric acid ($HClO_4$) yield conjugate base ions HSO_4^-, NO_3^-, I^-, Br^-Cl^-, and ClO_4^-, which are much weaker bases than H_2O. Similarly, a very strong base (NaOH) will give a very weak conjugate acid (Na^+). On the other hand, a weak acid such as acetic acid (CH_3CO_2H) ionizes only to a limited extent in water. Thus, at equilibrium, its aqueous solution mainly contains unionized CH_3COOH molecules along with H_3O^+ ions and the conjugate base CH_3COO^-. Nitrous acid (HNO_2), hydrofluoric acid (HF), and ammonium ion (NH_4^+) are other examples of weak acids. Note that weak acids yield relatively strong conjugate bases. For example, NH_2^-, O^{2-}, and H^- are very good proton acceptors (and hence) much stronger bases than H_2O.

Suppose we have two aqueous solutions containing the Brönsted acids HA and HB at the same concentration and temperature:

$$HA(aq.) + H_2O(l) \rightleftharpoons H_3O^+(aq.) + A^-(aq.)$$
$$HB(aq.) + H_2O(l) \rightleftharpoons H_3O^+(aq.) + B^-(aq.)$$

Suppose HA ionizes to a greater extent than HB, i.e., HA transfers a proton to water (which acts as a Brönsted base in this case) more readily than HB. At equilibrium, the solution containing HA has a higher concentration of H_3O^+ ions. Therefore, HA is a stronger acid than HB.

Table 7.2 lists some important conjugate acid–base pairs in order of their relative strengths. By examining this table, we can make several conclusions.

Table 7.2

Strongest	Acid	Conjugate base	Weakest
↓	$HClO_4$	ClO_4^-	↑
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	H_2SO_4	HSO_4^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	HF	F^-	
	HNO_2	NO_2^-	
	HCOOH	$HCOO^-$	
	CH_3COOH	CH_3COO^-	
	HCN	CN^-	
	H_2O	OH^-	
Weakest	NH_3	NH_2^-	Strongest

Strongest	Base	Conjugate acid	Weakest
↓	CH_3NH_2	$CH_3NH_3^+$	↑
	NH_3	NH_4^+	
	N_2H_4	$N_2H_5^+$	
	NH_2OH	$NH_2OH_2^+$	
Weakest	H_2O	H_3O^+	Strongest

1. If an acid is strong, its conjugate base has no measurable strength. Within a series of weak acids, the stronger the acid, the weaker is its conjugate base, and vice versa. For example, both HNO_2 and CH_3COOH are weak acids, but HNO_2 is a stronger acid than CH_3COOH. Therefore, NO_2^- is a weaker base than CH_3COO^-.
2. H_3O^+ is the strongest acid that can exist in aqueous solution. Acids stronger than H_3O^+ react with water to produce H_3O^+ and their conjugate bases. Thus HCl, which is a stronger acid than H_3O^+, reacts with water completely to form H_3O^+ and Cl^-:
$$HCl(aq.) + H_2O(l) \longrightarrow H_3O^+(aq.) + Cl^-(aq.)$$
Acids weaker than H_3O^+ react with water to a much smaller extent producing low concentration of H_3O^+ and their conjugate bases. For example, the following equilibrium lies mainly to the left:
$$HF(aq.) + H_2O(l) \rightleftharpoons H_3O^+(aq.) + F^-(aq.)$$
3. The OH^- ion is the strongest base that can exist in aqueous solution. Bases stronger than OH^- react with water to produce OH^- and their conjugate acids. For example, the amide ion (NH_2^-) is a stronger base than OH^-. So, it reacts with water completely as follows:
$$NH_2^-(aq.) + H_2O(l) \longrightarrow NH_3(aq.) + OH^-(aq.)$$
For this reason, the amide ion does not exist in aqueous solutions. However, the amide ion does exist in liquid ammonia.

7.12.1 Ionization Constant of Water and its Ionic Product

We all know that water is a unique solvent. One of its special properties is its ability to act both as an acid and as a base. In reactions with substances which are stronger acids than water, e.g., HCl, CH_3COOH, etc., water functions as a **base** and accepts a proton:

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

On the other hand, in reactions with substances which are stronger bases than water, e.g., NH_3, water functions as an acid and donates a proton:

$$NH_3(aq.) + H_2O(l) \rightleftharpoons NH_4^+(aq.) + OH^-(aq.)$$

A substance like H_2O which can act both as an acid as well as a base is called *amphoteric. Thus, amphoteric substances chemically react as acidic to strong bases and as basic towards strong acids*. A substance like water capable both of accepting and of yielding protons in solution is called *amphiprotic*. *Thus, amphiprotic substances can both donate as well as accept protons*. Thus, water is both amphoteric and amphiprotic.

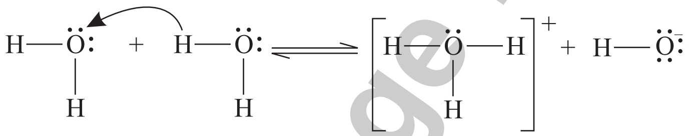
> The prefix "amphi" means "of both kinds." Amphiprotism refers to amphoterism by accepting and donating a proton in different reactions.

Careful experiments on its electrical conductivity have shown that pure water ionizes to a very slight extent. In simplified notation, we represent the ionization of water as

$$H_2O(l) \rightleftharpoons H^+(aq.) + OH^-(aq.)$$

Therefore, pure water is a very weak electrolyte and a poor conductor of electricity. Tap water and water from underground sources conduct electricity because they contain many dissolved ions. The reaction describing the ionization of water is sometimes called *autoionization* of water.

According to the Brönsted theory, this autoionization (self-ionization) of water is basically an acid–base reaction:



or $$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq.) + OH^-(aq.) \qquad (7.27)$$

$$\text{base}_1 \quad \text{acid}_2 \quad \text{acid}_1 \quad \text{base}_2$$

One H_2O molecule (the acid) donates a proton to another H_2O molecule (the base). The water molecule that donates a proton becomes an OH^- ion, the conjugate base of water. The H_2O molecule that accepts a proton becomes an H_3O^+ ion, the conjugate acid of water. The acid–base conjugate pairs are

1. H_2O (acid) and OH^- (base) and
2. H_3O^+ (acid) and H_2O (base).

Examination of the reverse reaction (right to left) shows that H_3O^+ (an acid) donates a proton to OH^- (a base) to form two H_2O molecules.

> One H_2O molecule behaves as an acid and the other acts as a base in the autoionization of water.

Recall that H_3O^+ and OH^- ions combine to form nonionized water molecules when strong acids and strong soluble bases react to form soluble salts and water. The reverse reaction, the autoionization of water, occurs only slightly, as expected.

Applying the law of chemical equilibrium to Eq. (7.27), we can write the ionization constant (K_I) of water as

$$K_I = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad (7.28)$$

Since H_2O is a pure liquid, its active mass is constant. Thus, $[H_2O]^2$ is omitted from the denominator and is incorporated within the ionization constant to give a new equilibrium constant, K_w, which is known as the *ion product for water*:

$$K_I\,[H_2O]^2 = [H_3O^+]\,[OH^-]$$
$$K_w = [H_3O^+]\,[OH^-] \qquad (7.29)$$

In the study of acid–base reactions in aqueous solutions, the important quantity is the hydrogen ion (H^+) concentration. Numerically, $[H^+] = [H_3O^+]$ as for every one H^+ exchanged between two water molecules, there is the formation of one H_3O^+. Expressing the proton as H^+ rather than H_3O^+, we can write the ionic product of water as

$$K_w = [H^+]\,[OH^-] \qquad (7.30)$$
$$= C_{H^+} \cdot C_{OH^-}$$

Thus, ionic product of water (K_w) is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.

The formation of an H_3O^+ ion by the ionization of water is always accompanied by the formation of an OH^- ion. Thus, in pure water, the concentration of H_3O^+ ion is always equal to the concentration of OH^-. Consequently, pure water at every temperature is neutral. Careful measurements show that in pure water at 25°C

$$C_{H^+} = C_{OH^-} = 1.0 \times 10^{-7} \text{ mol L}^{-1}$$

Substituting these concentrations into the K_w expression gives

$$K_w = C_{H^+} \cdot C_{OH^-} = (1.0 \times 10^{-7})\,(1.0 \times 10^{-7})$$
$$= 1.0 \times 10^{-14} \text{ (at 25°C)} \qquad (7.31)$$

Although the expression $K_w = C_{H^+}C_{OH^-} = 1.0 \times 10^{-14}$ was obtained for pure water, it is equally valid for aqueous solutions of dissolved species at 25°C. This is one of the most useful relationships chemists have discovered. It gives a simple relationship between C_{H^+} and C_{OH^-} in all aqueous solutions.

Because K_w is an equilibrium constant, its value is temperature dependent, i.e., the value of K_w is different at different temperatures. But the relationship $K_w = C_{H^+}C_{OH^-}$ is still valid for pure water as well as for any aqueous solution. Since the autoionization of water is an endothermic reaction, the value of K_w increases with rise of temperature but at very high temperature, $C_{H^+} = C_{OH^-}$ for pure water.

We can distinguish acidic, neutral, and basic aqueous solutions by the relative values of the H^+ and OH^- concentrations. Whenever $C_{H^+} = C_{OH^-}$, the aqueous solution is said to be *neutral*. When an acidic substance such as nitric acid is added to pure water, large number of H^+ ions are produced. The large increase in C_{H^+} shifts the water equilibrium

$$H_2O(l) \rightleftharpoons H^+(aq.) + OH^-(aq.)$$

far to the left (Le Chatelier's principle) and C_{OH^-} decreases. Thus, in acidic solution, there is an excess of H^+ ions and the H^+ concentration is always greater than the OH^- concentration, i.e., $C_{H^+} > C_{OH^-}$. We should not conclude that acidic solutions contain no OH^-. Rather, the C_{OH^-} is always less than 1.0×10^{-7} M in such solutions at 25°C. The reverse is true for basic solutions, in which there is an excess of hydroxide ions. So, $C_{H^+} < C_{OH^-}$, i.e., in basic solutions, C_{OH^-} is always greater than 1.0×10^{-7} M.

> Neutral aqueous solutions at 25°C are solutions in which $C_{H_3O^+} = C_{OH^-} = 1.0 \times 10^{-7}$ M.

In practice, we can change the concentration of either H^+ or OH^- ions in solutions, but we cannot vary both of them independently. If we adjust the solution so that $C_{OH^-} = 1.0 \times 10^{-8}$ M, then C_{H^+} must change to

$$C_{H^+} = \frac{K_w}{C_{OH^-}} = \frac{1.0\times10^{-14}}{1.0\times10^{-8}} = 1.0 \times 10^{-6}\ \text{M}$$

Solution	General condition
Acidic	$C_{H^+} > C_{OH^-}$
Neutral	$C_{H^+} = C_{OH^-}$
Basic	$C_{H^+} < C_{OH^-}$

Example 7.13 Calculate the degree of ionization of pure water at 25°C.

Strategy: The degree of ionization of pure water (α) is the ratio of ionized water to that of unionized water.

Solution: The density of pure water is 1 g mL^{-1} or 1000 g L^{-1}. The molar mass of water is 18 g mol^{-1}. Thus, the molarity of pure water can be given as

$$C_{H_2O} = \frac{d_{H_2O}}{\text{Molar mass}_{H_2O}} = \frac{1000\ \text{g L}^{-1}}{18\ \text{g mol}^{-1}}$$

$$= 55.5\ \text{mol L}^{-1}$$

Now, we can calculate the degree of ionization of pure water as

$$\alpha = \frac{C_{H^+}}{C_{H_2O}} \quad \text{or} \quad \frac{C_{OH^-}}{C_{H_2O}} = \frac{1.0\times10^{-7}}{55.5}$$

$$= 1.8 \times 10^{-9}$$

> Water equilibrium lies mainly towards undissociated water.

pH Scale

Because the concentrations of H^+ and OH^- ions in aqueous solutions are frequently very small numbers and, therefore, inconvenient to work with, Soren Sorensen in 1909 proposed a more practical measure called pH (potenz de hydrogen ion-power of H^+ ion). In pure water at 25°C,

$$C_{H^+} = 10^{-7}\ \text{M}$$

In terms of pH, we can write

$$C_{H^+} = 10^{-\text{pH}}\ \text{M}$$

Comparing the two expressions, we conclude that

$$\text{pH} = 7 \quad \text{(for pure water at 25°C).}$$

> Sorensen (Danish biochemist) originally wrote the symbol as P_H and called "P" the hydrogen ion exponent. It is the initial letter of *potenz* (German), *puissance* (French), and power (English). It is now customary to write the symbol as pH.

The pH of a solution is defined as the negative logarithm (to the base 10) of the activity (a_{H^+}) of the hydrogen ion. The solutions in which the concentration of solute is less than about 1 mol L^{-1} are usually called dilute solutions. In dilute solutions, the activity of hydrogen ion is numerically equal to the molarity of hydrogen ion (C_{H^+}). Thus, activity, which has no units, is given as

$$a_{H^+} = \frac{C_{H^+}}{\text{mol L}^{-1}} \tag{7.33}$$

From the definition of pH, we can write

$$\text{pH} = -\log a_{H^+} = -\log \frac{C_{H^+}}{\text{mol L}^{-1}} \tag{7.34}$$

Note that Eq. (7.33) is simply a definition designed to give us convenient numbers to work with. The negative logarithm gives us a positive number for pH, which otherwise would be negative due to the very small value of C_{H^+}. Furthermore, the term a_{H^+} in Eq. (7.33) pertains only to the numerical part of the expression for hydrogen ion concentration, because we cannot take the logarithm of physical quantities as they are associated with units. Thus, like equilibrium constant, the pH of a solution is a dimensionless quantity.

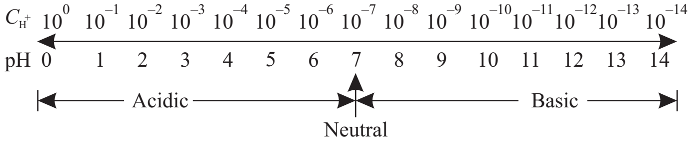
At 25°C, pure water has a concentration of hydrogen ions (C_{H^+}) = 10^{-7} M. Thus, the pH of pure water (neutral substance) is given as

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

At 25°C, acidic solutions possess $C_{H^+} > 10^{-7}$ M while basic solutions possess $C_{H^+} < 10^{-7}$ M. Since pH is simply a way to express C_{H^+}, acidic and basic solutions at 25°C can be identified by their pH values as follows:

Acidic solutions: pH < 7
Basic solutions: pH > 7
Neutral solutions: pH = 7

Note that pH increases as C_{H^+} decreases. The above information can be expressed on the pH scale which runs from 0 to 14:



On the pH scale or the Sorensen scale, the pH values range from 0 to 14. However, the pH values can be less than 1 and greater than 14. For example, for $C_{H^+} > 1.0$ M, pH becomes negative.

Note that we use pH rather than pH_3O because at the time the pH concept was developed, H_3O^+ was represented as H^+.

A pOH scale analogous to the pH scale can be devised by using the negative logarithm of the activity (a_{OH^-}) of hydroxide ion. Thus, we define pOH as

$$\text{pOH} = -\log a_{OH^-} = -\log \frac{C_{OH^-}}{\text{mol L}^{-1}} \qquad (7.35)$$

or $$C_{OH^-} = 10^{-\text{pOH}} \text{ mol L}^{-1}$$

Various “p” terms are used. In general, a lower-case “p” before a symbol means the “negative logarithm of the symbol.” Thus, pH is the negative logarithm of the H^+ concentration (or H_3O^+ concentration), pOH is the negative logarithm of the OH^- concentration, and pK_{eq} refers to the negative logarithm of equilibrium constant. It is convenient to describe the autoionization of water in terms of pK_w:

$$pK_w = -\log K_w$$

A convenient relationship between pH and pOH in all aqueous solutions at 25°C can be easily derived. Consider again Eq. (7.31) at 25°C (298 K):

$$K_w = a_{H^+} a_{OH^-} = 1.0 \times 10^{-14}$$

Taking logarithm of both sides of this equation gives

$$\log K_w = \log a_{H^+} + \log a_{OH^-} = \log (1.0 \times 10^{-14})$$

Multiplying both sides of this equation by –1 gives

$$-\log K_w = (-\log a_{H^+}) + (-\log a_{OH^-}) = -\log (1.0 \times 10^{-14})$$

or $$pK_w = \text{pH} + \text{pOH} = 14.00 \qquad (7.36)$$

Note that this relationship is valid only at 25°C. At any other temperature, pK_w = pH + pOH.

Equation (7.36) provides us with another way to express the relationship between the H^+ ion concentration and the OH^- ion concentration. From this relationship, we see that both pH and pOH can be positive only if both are less than 14. If either pH or pOH is greater than 14, the other is obviously negative.

Please study carefully the following summary. It will be helpful.

Solution	General condition
Acidic	$C_{H^+} > C_{OH^-}$
	pH < pOH
Neutral	$C_{H^+} = C_{OH^-}$
	pH = pOH
Basic	$C_{H^+} < C_{OH^-}$
	pH > pOH

Although K_w may change with temperature, the variations in pH with temperature are so small that we often ignore it.

> pK_w is a very important quantity for aqueous solutions. It controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. Note that as the pH scale is logarithmic, a change in pH by just one unit means a change in C_{H^+} by a factor of 10. Similarly, when the hydrogen ion concentration (C_{H^+}) changes by a factor of 100, the value of pH changes by just two units. That is why the change in pH with temperature is often ignored.

Consider again the relationship between pK_w, pH, and pOH:

$$pK_w = \text{pH} + \text{pOH}$$

For pure water and for any neutral aqueous solution, we have

$$\text{pH} = \text{pOH}$$

Therefore, we can write

$$pK_w = 2\text{pH} \quad \text{or} \quad 2\text{ pOH}$$

or $$\text{pH} = \frac{pK_w}{2} = \text{pOH} \qquad (7.37)$$

The measurement of pH of a solution is very essential as its value should be known while dealing with biological and cosmetic applications. The pH of a solution can be determined by using a pH meter or by the indicator method. A pH meter gives the pH of the solution directly. When the electrode is dipped into a solution, the meter displays the pH. Acid–base indicators are intensely colored complex organic compounds that have different colors in solutions of different pH. Many are weak acids or weak bases that are useful over rather narrow ranges of pH values. *Universal indicators* are mixtures of several indicators; they show several color changes over a wide range of pH values.

In the indicator method, we prepare a series of solutions of known pH (standard solutions). We add a universal indicator to each; solutions with different pH have different colors. We then add the same universal indicator to the unknown solution and compare its color to those of the standard solutions. Solutions with the same pH have the same color.

Universal indicator papers can also be used to determine pH. A drop of solution is placed in a piece of paper or a piece of paper is dipped into a solution. The color of the paper is then compared with a color chart to establish the pH of the solution.

Material	pH	Material	pH
Gastric juice	1.4	Rain water	6.5
Lemon juice	2.1	Pure water	7.1
Vinegar	2.9	Human saliva	7.0
Soft drinks	3.0	Blood plasma	7.4
Sauerkraut	3.5	Tears	7.4
Beer	4.5	Egg	7.8
Black coffee	5.0	Household Ammonia	11.9
Cow’s milk	6.5		

Follow-up Test 10

1. The concentration of OH^- ions in a 0.050 M HNO_3 solution is
   (1) 2.0×10^{-13} (2) 1.0×10^{-13}
   (3) 0.5×10^{-13} (4) 1.5×10^{-13}
2. The pH of a 0.005 M H_2SO_4 solution is
   (1) 3.3 (2) 5.0
   (3) 2.0 (4) 4.0

3. Which of the following has the minimum pH?
   (1) Blood (2) Gastric juice
   (3) Saliva (4) Milk
4. The pH of a solution is 1.30. The number of significant figures is
   (1) three (2) one
   (3) zero (4) two
5. The pH of an aqueous solution containing 0.1 M HCl will be
   (1) smaller than 0.1 M H_2SO_4
   (2) smaller than 0.1 M acetic acid solution
   (3) greater than 0.1 M acetic acid solution
   (4) equal to 0.1 M acetic acid solution.
6. Which of the following solvents will undergo self-ionization?
   (1) H_2O (2) NH_3
   (3) HF (4) All of these
7. If pure water has pK_w = 13.36 at 50°C, the pH of pure water will be
   (1) 6.63 (2) 7.0
   (3) 7.13 (4) 6.0
8. How many H^+ ions are present in 1 ml of a solution whose pH is 13?
   (1) 10^{-16} (2) 6.022×10^{13}
   (3) 6.022×10^{7} (2) 6.022×10^{23}
9. What will be the change in the pH of water if 10^{-3} mol of NaOH is added to 1.0 L of water?
   (1) Decreased by 4 (2) Increased by 4
   (3) Increased by 3 (2) Decreased by 4
10. The pH of solutions *A*, *B*, *C*, and *D* are 9.5, 2.5, 3.5, and 5.5, respectively. The most acidic solution is
    (1) *D* (2) *C*
    (3) *A* (4) *B*
11. On dilution, the pH of a basic solution
    (1) increases
    (2) remains the same
    (3) decreases
    (4) may increase or decrease depending upon the nature of the solution
12. Given pK_w (H_2O) = 6.77 at 40°C, predict the nature of the solution having pH = 7 at 40°C?
    (1) Basic (2) Acidic
    (3) Neutral (4) Cannot be predicted
13. With decrease of temperature, ionic product of water
    (1) increases (2) decreases
    (3) remains the same (4) may increase or decrease
14. 10^{-5} M HCl solution at 25°C is diluted 1000 times. The pH of the diluted solution will
    (1) be equal to 8
    (2) remain unchanged
    (3) lie between 5 and 6
    (4) lie between 6 and 7
15. pH of a 100 cc solution is 2. It will not change if
    (1) 100 cc of 0.1 M HCl is added to it
    (2) 100 cc of water is added to it
    (3) 100 cc of 0.01 N HCl is added to it
    (4) 1 cc of 0.1 M HCl is added to it

7.12.2 Ionization of Weak Acids

The classification of acids as strong or weak is based on the extent to which they ionize in aqueous solution. There are relatively few strong acids; weak acids are much more numerous than strong acids.

We are familiar with several weak acids. Vinegar is a 5% solution of acetic acid, CH_3COOH. Carbonated beverages are saturated solutions of carbon dioxide in water, which produce carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Citrus fruits contain citric acid, $C_3H_5O(COOH)_3$. Some ointments and powders used for medicinal purposes contain boric acid, H_3BO_3. These everyday uses of weak acids suggest that there is a significant difference between strong and weak acids. *The difference is that strong acids ionize completely in dilute aqueous solution, whereas weak acids ionize only slightly*.

Let us consider the reaction that occurs when a weak acid, such as acetic acid, is dissolved in water. The equation for the ionization of acetic acid is

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

Applying the law of chemical equilibrium, the equilibrium constant for this reaction can be represented as

$$K_{eq} = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]\,[H_2O]}$$

Recall that the thermodynamic definition of K_{eq} is in terms of activities. In dilute solutions, the activity of (nearly) pure H_2O is essentially constant and is incorporated into the value of the equilibrium constant to give a new constant K_a which is called the ionization constant of a weak acid.

$$K_{eq}\,[H_2O] = K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Note that K_a does not include a term for the active mass of water. The active mass (or activity) of each dissolved species is numerically equal to its molar concentration. Thus,

$$K_a = \frac{C_{H_3O^+}C_{CH_3COOO^-}}{C_{CH_3COOH}}$$

We often use HA as a general representation for weak monoprotic acid A^- for its conjugate base. The equation for the partial ionization in water can be written as

$$HA(aq.) + H_2O(l) \rightleftharpoons H_3O(aq.) + A^-(aq.)$$

or simply $HA(aq.) \rightleftharpoons H^+(aq.) + A^-(aq.)$

Let us assume that C is the initial concentration of the unionized acid (i.e., C_{HX} at time $t = 0$) and α is the degree of ionization of weak acid (i.e., extent up to which HX is ionized into ions). In terms of molar concentrations, the reaction summary is

$$
\begin{array}{lccc}
 & \text{HX(aq.)} & \rightleftharpoons \text{H}^+(\text{aq.}) & + \text{A}^-(\text{aq.}) \\
\text{Initial} & C & 0 & 0 \\
\text{Change due to reaction} & -C\alpha & +C\alpha & +C\alpha \\
\hline
\text{equilibrium} & C - C\alpha & C\alpha & C\alpha
\end{array}
$$

The equilibrium constant for weak acid ionization, which we call the acid ionization constant (or simply ionization constant), K_a, is given by

$$K_a = \frac{C_{\text{H}^+} C_{\text{A}^+}}{C_{\text{HA}}} \tag{7.38}$$

All concentrations in this equation are equilibrium concentrations. At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of K_a, because its value is directly related to C_{H}+. Thus, the larger the K_a, the stronger the acid—that is, the greater the concentration of H^+ ions at equilibrium due to its ionization. Because the ionization of weak acids is never complete, all species (the nonionized acid, the H^+ ions, and the A^- ions) are present at equilibrium. The predominant species in solution (other than the solvent) is the nonionized acid.

Substituting the equilibrium concentrations into Eq. (7.38), we get

$$K_a = \frac{(C\alpha)(C\alpha)}{C - C\alpha} = \frac{C^2\alpha^2}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha}$$

Since α is very small for weak acids, it can be neglected in comparison to 1. Hence, the expression for K_a is simplified to the form

$$K_a = C\alpha^2$$

or
$$\alpha = \sqrt{\frac{K_a}{C}} \tag{7.39}$$

The reciprocal of molar concentration (C) is called dilution. It is defined as the volume of solution containing 1 mol of solute. It is represented by the symbol V. Thus, in terms of dilution, we can rewrite Eq. (7.39) as

$$\alpha = \sqrt{K_a V} \tag{7.40}$$

Equation (7.40) is the mathematical expression of Ostwald's dilution law which states that for any weak electrolyte (acid, base, or salt) of the type HA (i.e., 1 : 1 electrolyte), the degree of ionization is directly proportional to the square root of dilution.

HELP Approximations can be used only for sums and differences, and never for products or quotients. Approximation may be valid when the error introduced is less than 5%, i.e., if α is more than 5%, it cannot be neglected relative to 1.

In practice, acidity constant (K_a) is used to define the strength of only those acids which are weaker than H_3O^+ such as acetic acid (CH_3COOH) and formic acid (HCOOH). If two different weak acids (HA_1 and HA_2) of equal concentrations are compared for their relative strengths, then according to Eq. (7.39), we have

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Since the degree of ionization measures the acidic strength of a weak acid, we can write

$$\frac{\text{Acidic strength of HA}_1}{\text{Acidic strength of HA}_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \tag{7.40}$$

i.e., the relative strengths of two different weak acids of equal concentration can be compared by taking the square root of the ratio of their respective ionization constants.

We can also measure the strength of the weak acid (HA) in terms of pK_a which is defined as

$$pK_a = -\log K_a = \log \frac{1}{K_a} \tag{7.41}$$

Thus, the smaller the value of pK_a, the stronger is the acid.

Ionization constants for weak acids (and weak bases) must be calculated from experimentally determined data. Measurement of pH, conductivity, or depression of freezing point provide data form which these constants can be calculated.

We can calculate K_a from the initial concentration of the acid and the pH of the solution. Using K_a and the initial concentration of the acid, we can calculate the equilibrium concentrations of all the species, pH of the solution, and the degree of ionization of the acid. For this purpose, we follow essentially the same step-wise approach outlined in Section 7.7. The systems are different, but the calculations are based on the same principle: the law of mass action.

A general step-wise approach is as follows:

Step 1: Identify the species (present before ionization) as Brönsted acids and bases.

Step 2: Write balanced equations for all possible ionization reactions.

Step 3: Identify the reaction with the higher K_a as the primary reaction and treat the others as subsidiary reactions.

Step 4: Express the equilibrium concentrations of all species (of primary reaction) in terms of the initial concentrations and a single unknown x, which represents the change in concentration.

Step 5: Write the acid ionization constant in terms of the equilibrium concentrations. Knowing the value of K_a, we can solve for x.

Step 6: Having solved for x, calculate the equilibrium concentrations of all species, the degree of ionization of the acid, and the pH of the solution.

Unless otherwise stated, we will assume that the temperature is 25°C for all such calculations.

Example 7.14 The ionization constant of HF is 3.2×10^{-4}. Calculate the degree of ionization of HF in its 0.02 M solution. Calculate the concentration of all species present in the solution and its pH.

Strategy: Identify the primary reaction and write the reaction summary in terms of unknown x. Solve for x, knowing the value of K_a.

Solution:

Steps 1–2: The following ionization reactions are possible:

$$HF(aq.) \rightleftharpoons H^+(aq.) + F^-(aq.)$$
$$K_a = 3.2 \times 10^{-4}$$
$$H_2O(l) \rightleftharpoons H^+(aq.) + OH^-(aq.)$$
$$K_w = 1.0 \times 10^{-14}$$

Step 3: As $K_w << K_a$, the first reaction is the primary reaction.

Step 4: Let x be the equilibrium concentration of H^+ and F^- ions in mol L^{-1}. Then the equilibrium concentration of HF must be $(0.02 - x)$ mol L^{-1}. We can write the reaction summary as follows:

		$HF(aq.) \rightleftharpoons$	$H^+(aq.)$	$+ F^-(aq.)$
Initial	(M)	0.02	0	0
Change	(M)	$-x$	$+x$	$+x$
Equilibrium	(M)	$(0.02 - x)$	x	x

Step 5:

$$K_a = \frac{C_{H^+}C_{F^-}}{C_{HF}}$$

$$3.2 \times 10^{-4} = \frac{(x)\,(x)}{0.02 - x} = \frac{x^2}{0.02 - x}$$

This equation can be rewritten as

$$x^2 + 3.2 \times 10^{-4}\, x - 6.4 \times 10^{-6} = 0$$

which fits the quadratic equation $ax^2 + bx + c = 0$. Using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

we get

$$x = 2.4 \times 10^{-3}\text{ M or } -2.4 \times 10^{-3}\text{ M}$$

The second solution is physically impossible since the concentration of ions produced as a result of ionization cannot be negative. Thus,

$$x = 2.4 \times 10^{-3}\text{ M}$$

Step 6: Thus, at equilibrium,

$$C_{H^+} = 2.4 \times 10^{-3}\text{ M}$$
$$C_{F^-} = 2.4 \times 10^{-3}\text{ M}$$
$$C_{HF} = (0.02 - 2.4 \times 10^{-3})\text{ M}$$
$$= 1.76 \times 10^{-2}\text{ M}$$

$$\alpha = \frac{C_{H^+}}{C_{HF}} = \frac{2.4 \times 10^{-3}}{0.02} = 0.12$$

$$\text{pH} = -\log \frac{C_{H^+}}{\text{mol L}^{-1}} = -\log(2.4 \times 10^{-3})$$
$$= 2.62$$

Do not neglect x with respect to 0.02 as x is more than 5% at the original concentration:

$$\frac{2.4 \times 10^{-3}}{0.02} \times 100\% = 12\%$$

7.12.3 Percent Ionization

We have just seen that the magnitude of acidity constant (K_a) measures the strength of an acid. Another way to describe (quantitatively) the strength of an acid is to measure its *percent ionization* which is defined as

Percent ionization =

$$\frac{\text{Ionized acid concentration at equilibrium}}{\text{Initial concentration of acid}} \times 100\% \tag{7.42}$$

The greater the percent ionization, the stronger is the acid. For a weak monoprotic acid such as HA, the concentration of the acid that undergoes ionization is equal to the concentration of the H^+ ions and the concentration of the conjugate base (A^-) at equilibrium. Therefore, we can write its percent ionization as

$$\text{Percent ionization} = \frac{C_{H^+}}{C_{HA}} \times 100\% \tag{7.43}$$

where $C_H{}^+$ is the concentration of H^+ ions at equilibrium and C_{HA} is the initial concentration of weak acid HA.

We can compare the strengths of acids in terms of their percent ionization only if the acids are at the same concentration.

Example 7.15 Calculate the percent ionization of 0.10 M acetic acid ($K_a = 1.8 \times 10^{-5}$).

Strategy: Write the ionization equation and the expression for K_a. Next, follow the procedure used in Example 7.14 to find the concentration of acid that is ionized. Then substitute the concentration of acid that ionized into the expression for percent ionization.

Solution:

Step 1: Let x be the concentration of H^+ and CH_3COO^- ions at equilibrium in mol L^{-1}. Reaction summary can now be written as:

	$CH_3COOH(aq.) \rightleftharpoons$	$H^+(aq.)$	$+ F^-(aq.)$
Initial (M)	0.10	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.10 - x)$	x	x

Step 2: $K_a = \dfrac{C_{H^+}C_{CH_3COO^-}}{C_{CH_3COOH}}$

$$1.8 \times 10^{-5} = \frac{(x)\,(x)}{(0.10 - x)}$$

Making the simplifying assumption that $(0.10 - x) \approx 0.10$, we have

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5}$$
$$x^2 = 1.8 \times 10^{-6}$$
$$x = 1.3 \times 10^{-3}$$

Step 3: This gives $[C_{CH_3COOH}]_{\text{ionized}} = x = 1.3 \times 10^{-3}$. Now, we can calculate the percent ionization for 0.10 M_{CH_3COOH} solution

$$\%\text{ Ionization} = \frac{[C_{CH_3COOH}]_{\text{ionized}}}{[C_{CH_3COOH}]_{\text{initial}}} \times 100\%$$

$$= \frac{1.3 \times 10^{-3}\text{ M}}{0.10\text{ M}} \times 100\% = 1.3\%$$

Our assumption that $(0.10 - x) \approx 0.10$ is reasonable because $(0.10 - x) = (0.10 - 0.0013)$. This is only about 1% different than 0.10.

7.12.4 Ionization of Weak Bases

All alkali metal hydroxides are soluble in water. Of the alkaline earth metal hydroxides, $Be(OH)_2$ and Mg $(OH)_2$ are insoluble, $Ca(OH)_2$ and $Sr(OH)_2$ are slightly soluble, and $Ba(OH)_2$ is soluble. Strong bases such as the hydroxides of alkali metals and of the alkaline earth metals other than Be and Mg are completely ionized in water:

$$NaOH(aq.) \longrightarrow Na^+(aq.) + OH^-(aq.)$$

$$Ba(OH)_2(aq.) \longrightarrow Ba^{2+}(aq.) + 2OH^-(aq.)$$

Very few common weak bases are soluble in water. Aqueous ammonia is the most frequently encountered example. Weak bases are treated like weak acids. There is one unshared pair of electrons on the N atom in NH_3. When ammonia dissolves in water, it accepts H^+ from a water molecule in a reversible reaction:

$$NH_3(aq.) + H_2O(l) \rightleftharpoons NH_4^+(aq.) + OH^-(aq.)$$

We say that NH_3 ionizes slightly when it undergoes this reaction. Aqueous solutions of NH_3 are basic because OH^- ions are produced. (Note that NH_3 does not ionize like an acid because it does not split up to form ions the way HCl does.) At 25°C, in this solution, $C_{OH^-} > C_{H^+}$, and therefore, pH > 7. Applying the law of chemical equilibrium, we have

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3][H_2O]}$$

$$[H_2O]\,K_{eq} = K_b = \frac{[NH_4^+][OH]}{[NH_3]}$$

Expressing the active masses of dissolved species in molar concentration allows us to write

$$K_b = \frac{C_{NH_4^+}C_{OH^-}}{C_{NH_3}}$$

where K_b, the equilibrium constant for base ionization, is called the base ionization constant or basicity constant. Many scientists prefer to use pK_b values rather than K_b values for weak bases. Recall that, in general, "p" terms refer to negative logarithms. Thus, pK_b value for a weak acid is just the negative logarithm of its K_b value:

$$pK_b = -\log K_b = \log\frac{1}{K_b} \qquad (7.44)$$

We use K_b's for weak bases in the same way we used K_a's for weak acids and pK_b values for weak bases in the same way we used pK_a values for weak acids. *Thus, the larger the value of K_b, the smallar is the value of pK_b and the stronger is the base.*

We often use BOH as a general representation for weak monoacidic basic and B^+ for its conjugate acid. If C is the initial concentration of the unionized base and α is the degree of ionization of weak base, then the reaction summary is as follows:

	$BOH(aq.) \rightleftharpoons$	$B^+(aq.)$ +	$OH^-(aq.)$
Initial (M)	C	0	0
Change (M)	$-C\alpha$	$+C\alpha$	$+C\alpha$
Equilibrium (M)	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_b = \frac{C_{B^+}\,C_{OH^-}}{C_{BOH}}$$

$$= \frac{(C\alpha)\,(C\alpha)}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha}$$

Neglecting α relative to 1 ($\alpha << 1$), we have

$$K_b = c\alpha^2$$

or $$\alpha = \sqrt{\frac{K_b}{C}} \qquad (7.45)$$

In terms of dilution "V", we can write

$$\alpha = \sqrt{K_b V} \qquad (7.46)$$

In practice, K_b is used to define the strength of only those bases that are weaker than OH^-.

According to Eq. (7.45), the relative strengths of any two weak bases at the same concentration are given by the ratio of the square roots of their dissociation constants:

$$\frac{\text{Basic strength of }(BOH)_1}{\text{Basic strength of }(BOH)_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} \qquad (7.47)$$

Many organic bases such as amines are weak bases. Amines are the derivatives of NH_3 in which one or more H atoms have been replaced by organic groups. Typical examples are methylamine, caffeine, pyridine, urea, codeine, quinine, and nicotine. All behave as weak bases due to their small K_b. The basicity of all these compounds is attributable to the lone pair of electrons on the N atom, which makes these substances Brönsted bases and Lewis bases.

Example 7.16 The pH of 0.004 M hydrazine solution is 9.7. Calculate its ionization constant K_b and pK_b.

Strategy: From the pH, calculate the hydrogen ion concentration. Knowing the H^+ ion concentration and the ionic product of water, calculate the concentration of hydroxyl ions. Using the concentration of OH^- ions, calculate K_b and pK_b.

Solution:

$$pH = -\log a_{H^+}$$

$$9.7 = -\log a_{H^+}$$

Taking the antilog of both sides, we get

$$C_{H^+} = 1.67 \times 10^{-10}$$

The ionic product of water is given as

$$K_w = C_{H^+}\,C_{OH^-}$$

$$\therefore \quad C_{OH^-} = \frac{K_w}{C_{H^+}} = \frac{1\times10^{-14}}{1.67\times10^{-10}}$$

$$= 5.98 \times 10^{-5}$$

Write the reaction summary:

	$NH_2NH_2(aq.)$ +	$H_2O(l) \rightleftharpoons$	$NH_2\overset{+}{N}H_3(aq.)$ +	OH^-
Initial (M)	0.004		0.000	0.000
Change (M)	-5.98×10^{-5}		$+5.98 \times 10^{-5}$	$+5.98 \times 10^{-5}$
Equilibrium (M)	$(0.004 - 5.98 \times 10^{-5})$		5.98×10^{-5}	5.98×10^{-5}

Note that the concentration of the hydrazinium ion is also the same as that of the hydroxide ion. Since the concentration of both these ions is very small, the concentration of the unionized base can be taken (approximately) equal to 0.004 M.

Writing the basicity constant

$$K_b = \frac{[NH_2\overset{+}{N}H_3][OH^-]}{[NH_2NH_2]}$$

$$= \frac{(5.98\times10^{-5})\,(5.98\times10^{-5})}{(0.004)}$$

$$= 8.94 \times 10^{-7}$$

$$pK_b = -\log K_b = -\log (8.96 \times 10^{-7})$$

$$= 6.1$$

7.12.5 Relation between K_a and K_b

We have seen that the magnitudes of K_a and K_b measure the strength of an acid and a base, respectively. An important but simple relationship between the K_a of a weak acid and the K_b of its conjugate base exists. Thus, if one is known, the other can be deduced. The relationship can be derived as follows, using hydrofluoric acid as an example:

$$HF(aq.) \rightleftharpoons H^+(aq.) + F^-(aq.)$$

We can write the acid ionization constant as

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

The conjugate base, F^- reacts with water according to the equation

$$F^-(aq.) + H_2O(l) \rightleftharpoons HF(aq.) + OH^-(aq.)$$

The base ionization constant can be written as

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

The product of these two ionization constants is given by

$$K_aK_b = \frac{[H^+][F^-]}{[HF]} \times \frac{[HF][OH^-]}{[F^-]}$$

$$= [H^+]\,[OH^-]$$

$$= K_w$$

This result (which may seem strange at first) can be understood by realizing that the sum of reactions (a) and (b) below is simply the autoionization of water:

(a) $HF(aq.) \rightleftharpoons H^+(aq.) + F^-(aq.)\ K_a$

(b) $F^-(aq.) + H_2O(l) \rightleftharpoons HF(aq.) + OH^-(aq.)\ K_b$

(c) $H_2O(l) \rightleftharpoons H^+(aq.) + OH^-(aq.)\ K_w$

This example illustrates one of the general rules we learned about chemical equilibria: The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions:

$$K_{net} = K_1 \times K_2 \times K_3 \times \cdots$$

Thus, for any conjugate acid–base pair, it is always true that

$$K_aK_b = K_w \tag{7.48}$$

Expressing Eq. (7.48) as

$$K_a = \frac{K_w}{K_b} \quad \text{or} \quad K_b = \frac{K_w}{K_a}$$

enables us to draw an important conclusion: The stronger the acid (the larger the K_a), the weaker is its conjugate base (the smaller is the K_b), and vice versa.

We can use Eq. (7.48) to calculate one ionization constant through the knowledge of the other.

Taking negative logarithm of both sides of Eq. (7.48) gives the relation between the p*K* values of the conjugate acid and base pair:

$$pK_a + pK_b = pK_w \tag{7.49}$$

$$= 14 \text{ (at 298 K)}$$

7.12.6 Di- and Polybasic Acids and Di- and Polyacidic Bases

Among the acids commonly used in the laboratory are hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), hydrosulphuric acid (H_2S), oxalic acid ($H_2C_2O_4$), sulphuric acid (H_2SC_4), and phosphoric acid (H_3PO_4). *The first three acids are monoprotic (or monobasic) acids. Such acids can furnish only one hydrogen ion (or hydronium ion) per molecule.*

$$HCl(aq.) \longrightarrow H^+(aq.) + Cl^-(aq.)$$

$$HNO_3(aq.) \longrightarrow H^+(aq.) + NO_3^-(aq.)$$

$$CH_3COOH(aq.) \longrightarrow H^+(aq.) + CH_3COO^-(aq.)$$

Each unit of the acid yields one hydrogen ion only.

Other acids have more than one ionizable proton per molecule of the acid. *Such acids that can furnish two or more hydrogen ions (or hydronium ions) per molecule are called polyprotic (or polybasic) acids.*

Sulphuric acid, oxalic acid, and hydrosulphuric acid are the examples of diprotic acid because each unit of the acid yields two H^+ ions. There are relatively few triprotic acids—acids that yield three H^+ ions per unit. The best known example of a triprotic acid is phosphoric acid.

The treatment of diprotic and polyprotic acids is more involved than that of monoprotic acids because these substances may yield more than one hydrogen ion per molecule. The ionizations of polyprotic acids occur stepwise, that is, one proton at a time. An ionization constant expression can be written for each ionization stage. Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution.

Consider carbonic acid (H_2CO_3) as a typical diprotic acid. It contains two acidic H atoms and ionizes in two steps:

$$H_2CO_3(aq.) \rightleftharpoons H^+(aq.) + HCO_3^-(aq.)\ K_{a_1} = \frac{C_{H^+}C_{HCO_3^-}}{C_{H_2CO_3}}$$

$$= 4.7 \times 10^{-7}$$

$$HCO_3^-(aq.) \rightleftharpoons H^+(aq.) + CO_3^{2-}(aq.)\ K_{a_2} = \frac{C_{H^+}C_{CO_3^-}}{C_{HCO_3^-}}$$

$$= 4.8 \times 10^{-11}$$

Note that the conjugate base in the first stage (HCO_3^-) becomes the acid in the second ionization stage. Here, K_{a_1} and K_{a_2} are called the first and the second ionization constants, respectively, of the carbonic acid. We can see that K_{a_1} is much greater than K_{a_2}. *This is* *generally true for polyprotic acids, that is, for a given polyprotic acid, the first ionization constant is much larger than the second ionization constant, and so on*. This trend is reasonable because it is easier to remove an H^+ ion from a neutral molecule (H_2CO_3) than to remove another H^+ ion from a negatively charged ion (HCO_3^-) derived from the molecule.

In case of a diprotic acid (H_2A), the aqueous solution contains a mixture of H_2A, HA^-, and A^{2-} (along with H^+ and OH^-). Since H_2A is a relatively strong acid, the primary reaction involves the ionization of H_2A, i.e., H^+ ion in the solution comes mainly from the first ionization step.

For diprotic acids, if $K_{a_1} >> K_{a_2}$, then the concentration of the H^+ ions at equilibrium may be assumed to result only from the first stage of ionization. Moreover, the concentration of the conjugate base for the second-stage ionization is numerically equal to K_{a_2}.

Phosphoric acid (H_3PO_4), largely responsible for much of the "tangy" flavor of popular cola drinks, is an important example of a triprotic acid. It contains three ionizable (or acidic) H atoms and ionizes in three steps:

$$H_3PO_4(aq.) \rightleftharpoons H^+(aq.) + H_2PO_4^-(aq.)\ K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq.) \rightleftharpoons H^+(aq.) + HPO_4^{2-}(aq.)\ K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq.) \rightleftharpoons H^+(aq.) + PO_4^{3-}(aq.)\ K_{a_8} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 3.6 \times 10^{-13}$$

Note that all three species (H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-}) are weak acids, and we use double arrows to represent each ionization step. Anions such as $H_2PO_4^-$ and HPO_4^{2-} are generated when compounds such as NaH_2PO_4 and Na_2HPO_4 dissolve in water. Since H_3PO_4 is a weak polyprotic acid and its ionization constants decrease markedly for the second and third stages, we can predict that in a solution containing phosphoric acid, the concentration of the nonionized acid is the highest and the only other species present in significant concentrations are H^+ and $H_2PO_4^-$ ions.

Example 7.17 Calculate the concentrations of all species present in 0.010 M H_2SO_4 solution. ($K_{a_2} = 1.3 \times 10^{-2}$)

Strategy: Sulphuric acid (H_2SO_4) is an example of a diprotic acid because each unit of the acid yields two H^+ ions, in two separate steps:

$$H_2SO_4(aq.) \longrightarrow H^+(aq.) + HSO_4^-(aq.)$$
$$HSO_4^-(aq.) \rightleftharpoons H^+(aq.) + SO_4^{2-}(aq.)$$

H_2SO_4 is a strong electrolyte (or strong acid) as the first step of ionization is complete, but HSO_4^- is a weak acid; we need a double arrow to represent its incomplete ionization.

Because the first ionization step of H_2SO_4 is complete, we read the concentration for the first step from the balanced equation. The second ionization step is not complete. Thus, we write the ionization equation, the K_{a_2} expression, and the algebraic representations of equilibrium concentrations. Then we substitute into K_{a_2} for H_2SO_4.

Solution: Summarize the changes in the first stage of ionization which is complete:

	$H_2SO_4(aq.)$ $\xrightarrow{100\%}$	$H^+(aq.)$ +	$HSO_4^-(aq.)$
Initial (M)	0.010	0.00	0.00
Change (M)	– 0.010	+ 0.010	+ 0.010
Final (M)	0.00	0.010	0.010

For the second stage of ionization (which is not complete), we proceed as for a weak monoprotic acid.

Step 1: Let $x = C_{HSO_4^-}$ that ionizes (or the concentration in mol L^{-1} of H^+ and SO_4^{2-} produced by the ionization of HSO_4^-). The total concentration of H^+ ions at equilibrium must be the sum of the H^+ ion concentration produced in the first and second steps. So we represent the equilibrium concentrations as

	$HSO_4^-(aq.)$ $\rightleftharpoons$	$H^+(aq.)$ +	$SO_4^{2-}(aq.)$
Initial (M)	0.10	0.010	0.00
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.010 - x)$	$(0.010 + x)$	x

Step 2: Substitution into the ionization constant expression for K_{a_2} gives

$$K_{a_2} = \frac{C_{H^+} C_{SO_4^{2-}}}{C_{HSO_4^-}}$$

$$1.3 \times 10^{-2} = \frac{(0.010 + x)(x)}{(0.010 - x)}$$

Since the K_{a_2} of H_2SO_4 is quite large, x cannot be neglected. We must solve the quadratic equation, which simplifies to

$$x^2 + 0.023x - 1.3 \times 10^{-4} = 0$$

Applying the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

we have

$$x = \frac{-0.023 \pm \sqrt{(0.023)^2 - 4(1)(-1.3\times10^{-4})}}{2(1)}$$
$$= 4.7 \times 10^{-3}\ M$$

$$\therefore \quad (C_{H^+})_{2nd} = C_{SO_4^{2-}} = 4.7 \times 10^{-3}\ M$$

The concentrations of different species in 0.010 M H_2SO_4 are

$$C_{H_2SO_4} \approx 0\ M;\ C_{HSO_4^-} = (0.010 - x) = (0.010 - 4.7 \times 10^{-3}) = 5.3 \times 10^{-3}$$

$$C_{H^+} = (0.010 + x) = (0.010 + 4.7 \times 10^{-3}) = 0.015$$

$$C_{SO_4^{2-}} = 4.7 \times 10^{-3}$$

$$C_{OH^-} = \frac{K_w}{C_{H^+}} = \frac{1.0\times10^{-14}}{0.015} = 6.7\times10^{-13}$$

7.12.7 Factors Affecting Acid Strength

The ease of ionization of an acid (i.e., the strength of an acid) depends on a number of factors, such as

1. the properties of the solvent,
(2. the temperature, and
3. the molecular structure of the acid.

By considering the ionization of acids in the same solvent and at the same temperature, we can focus on the structures of the acids.

In general, the factors that determine the strength of the acid HA are the polarity and the bond strength of the H–A bond. The more polar the bond, the more readily the acid ionizes into H^+ and A^- ions. Thus, as the electronegativity difference between the atoms H and A increases, the H–A bond becomes more polar and there is a marked charge separation. Consequently, the cleavage of the bond to generate charged particles (H^+ and A^-) becomes easier and the acid strength increases. On the other hand, strong bonds (that is, bonds with high bond energies) are less easily ionized than weaker ones. Thus, when the strength of the H–A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid.

Binary acids are those acids that contain only two different elements. Thus, all the binary Brönsted acids contain hydrogen plus another element. While comparing elements in the same group of the periodic table, H–A bond strength is a more predominating factor in determining the acidic strength than its polarity. As we move down the group, the size of A increases. Consequently, H–A bond strength decreases and the acid strength increases.

The halogens form a particularly important series of binary protonic acids called *hydrohalic acids*. The strength of the hydrohalic acids increases in the following order:

$$HF \ll HCl < HBr < HI$$

The $\ll$ sign means "much less than." Hydrogen fluoride ionizes only slightly in dilute aqueous solution. However, HCl, HBr, and HI ionize completely or nearly completely in dilute aqueous solution. The order of bond strengths for hydrogen halides is

$$HF > > HCl > HBr > HI$$

HF has the highest bond dissociation enthalpy (568.2 kJ mol^{-1}) of the four hydrogen halides. Since more energy is required to break the H–F bond, HF is a weak acid. The strength of the HF bond is largely due to the very small size of the F atom. At the other extreme in the series, HI has the lowest bond enthalpy. So HI is the strongest acid of the group. Notice that the maximum decrease of bond enthalpy is from HF to HCl. In this series of acids, the polarity of the bond actually decreases from HF to HI because F is the most electronegative of the halogens. This property should enhance the acidity of HF relative to the other hydrohalic acids, but its magnitude is not great enough to break the trend in bond dissociation enthalpies.

A weak acid may be very reactive. For example, HF dissolves sand and glass. The equation for its reaction with sand is

$$SiO_2(s) + 4HF(g) \longrightarrow SiF_4(g) + 2H_2O(l)$$

The reaction with glass and other silicates is similar. These reactions are not related to acid strength as none of the three strong hydrohalic acids (HCl, HBr, and HI) undergoes such a reaction.

Another factor controlling the acidic strength is the stability of the resulting ions in solution. The small highly charged F^- ion formed when HF ionizes causes increased ordering of the water molecules. This increase is unfavorable to the process of ionization.

Acid strengths for other vertical series of binary acids vary in the same way as those of group 17 elements. The order of bond strengths for the group 16 hydrides is

$$H_2O > > H_2S > H_2Se > H_2Te$$

H–O bonds are much stronger than the bonds in the other group 16 hydrides. As we might expect, the order of acid strengths for these hydrides is just the reverse of the order of bond strengths:

$$H_2O < < H_2S < H_2Se < H_2Te$$

The relative importance of bond enthalpy versus bond polarity in determining the acid strength is reversed for binary compounds in a particular period of the periodic table. *Thus, when we discuss elements in the same row of the periodic table, the H–A bond polarity becomes the deciding factor for determining acid strength*. As the electronegativity of A increases, the polarity of the H–A bond increases and, hence, the strength of the acid increases.

Let us consider the binary hydrides of the second period elements: CH_4, NH_3, H_2O, and HF. Methane (CH_4) has no measurable acidic properties whatsoever, whereas hydrofluoric acid (HF) is an acid of measurable strength in water. The strengths of the compounds as acids increase as follows:

$$CH_4 < NH_3 < H_2O < HF$$

This trend is the reverse of what we would expect on the basis of bond enthalpy consideration. (HF molecule has the highest bond enthalpy of the four molecules: $HF > H_2O > NH_3 > CH_4$). We can explain the trend by considering the increase in electronegativity as we move from C to F. As the electonegativity increases, the H–A bond becomes more polar (A denotes the C, N, O, or F atom), and thus, the compound has a greater tendency to ionize into H^+ and the corresponding anion.

Any molecule containing an H atom is potentially a Brönsted acid.

Follow-up Test 11

1. Calculate the concentration of the formate ion present in 0.100 M formic acid (HCOOH) solution at equilibrium (K_a = 1.7×10^{-4}).

(1) 4.1×10^{-3} M (2) 3.1×10^{-3} M
(3) 2.1×10^{-3} M (4) 5.1×10^{-3} M

2. Which of the following is the weakest acid?
   (1) Phenol ($K_a = 1.3 \times 10^{-10}$)
   (2) Hydrocyanic acid ($K_a = 4.9 \times 10^{-10}$)
   (3) Acetic acid ($K_a = 1.8 \times 10^{-5}$)
   (4) Benzoic acid ($K_a = 6.5 \times 10^{-5}$)
3. The correct expression for Ostwald's dilution law is
   (1) $K_a = \alpha^2 V$ (2) $K_a = \dfrac{\alpha^2}{V}$
   (3) $K_a = \dfrac{\alpha^2}{(1-\alpha)V}$ (4) $K_a = \dfrac{\alpha^2}{(1-\alpha)C}$
4. The pH of 0.1 M monobasic acid is 4.50. The acidity constant (K_a) of the monobasic acid is
   (1) 1.0×10^{-7} (2) 1.0×10^{-5}
   (3) 1.0×10^{-4} (4) 1.0×10^{-8}
5. If the concentration of the weak monoprotic acid HA is C mol L^{-1} and its ionization constant is K_a, then
   (1) $C_{H^+} = C/2$ (2) $C_{H^+} = \sqrt{C}$
   (3) $C_{H^+} = \sqrt{K_a C}$ (4) $C_{H^+} = C/C_a$
6. Which of the following is the strongest base?
   (1) $C_6H_5NH_2$ (pK_b = 9.42)
   (2) $C_6H_5NHCH_3$ (pK_b = 9.15)
   (3) $C_6H_5N(CH_3)_2$ (pK_b = 8.94)
   (4) $C_6H_5NHC_2H_5$ (pK_b = 8.89)
7. The pK_b of NH_3 is 4.75. Calculate the concentration of H^+ ions in solution formed by mixing 0.2 M NH_4Cl and 0.1 M NH_3.
   (1) 0.88×10^{-5} (2) 1.12×10^{-9}
   (3) 1.12×10^{-5} (4) 0.88×10^{-9}
8. K_a for a weak monobasic acid is 1.0×10^{-6}. The pK_b of its conjugate base is
   (1) 8.0 (2) 1.0×10^{-8}
   (3) 1.0×10^{-6} (4) 6.0
9. If the dissociation constants of two weak acids HA_1 and HA_2 are K_1 and K_2, then the relative strengths of HA_1 and HA_2 are given by
   (1) $\sqrt{K_2/K_1}$ (2) $\sqrt{K_1/K_2}$
   (3) K_2/K_1 (4) K_1/K_2
10. Which of the following is arranged in the order of increasing ionization constants of H_3PO_4?
   (1) $K_3 < K_1 < K_2$ (2) $K_1 < K_2 < K_3$
   (3) $K_2 < K_1 < K_3$ (4) $K_3 < K_2 < K_1$
11. Oxoacids are __________ acids.
   (1) binary (2) ternary
   (3) quaternary (4) secondary
12. Which of the following is correct for a compound of the type ZOH?
   (1) It is a hydroxide.
   (2) It is an oxoacid.
   (3) It is either a hydroxide or an oxoacid.
   (4) It is neither a hydroxide nor an oxoacid.
13. Which of the following oxoacids is the strongest acid?
   (1) HClO (2) HBrO
   (3) HIO (4) All are equally strong
14. Which of the following oxoacids is the weakest acid?
   (1) $HClO_4$ (2) $HClO_3$
   (3) $HClO_2$ (4) HClO
15. Which of the following order of acidic strengths is incorrect?
   (1) $H_3PO_4 < HNO_3$ (2) $H_2SeO_3 < H_2SO_3$
   (3) $H_3PO_3 < HNO_2$ (4) $H_2SO_3 < H_2SO_4$
16. Which of the following is the strongest acid?
   (1) H_3PO_4 2 H_3PO_3
   (3) H_3PO_2 (4) All are equally strong

7.12.8 Common Ion Effect in the Ionization of Acids and Bases

Equilibrium achieved through the ionization of acetic acid is represented as:

$$CH_3\,COOH(aq.) \rightleftharpoons H^+(aq.) + CH_3COO^-(aq.)$$

or

$$HAc(aq.) \rightleftharpoons H^+(aq.) + Ac^-(aq.)$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]}$$

The addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions (H^+) by shifting the equilibrium to the left. Similarly, if H^+ ions are added from an external source (such as hydrochloric acid), then again the equilibrium moves to the left, i.e., in the direction of unionized acetic acid. This again reduces the concentration of H^+ ions from acetic acid.

In this section, we will consider the acid–base properties of a solution containing two dissolved solutes that contain the same ion (cation or anion), called the *common ion*. As mentioned above, the presence of a common ion suppresses the ionization of a weak electrolyte such as a weak acid or a weak base.

Consider a solution that contains acetic acid and sodium acetate, a soluble ionic salt of CH_3COOH. If both sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH_3COO^- ions:

$$NaCH_3COO(s) \xrightarrow{H_2O} Na^+(aq.) + CH_3COO^-(aq.)$$

$$CH_3COOH(aq.) \rightleftharpoons H^+(aq.) + CH_3COO^-(aq.)$$

$NaCH_3COO$ is a strong electrolyte. So it dissociates completely in solution into its constituent ions, but CH_3COOH, a weak acid, ionizes slightly. Both acetic acid and sodium acetate are sources of CH_3COO^- ions, but the completely dissociated $NaCH_3COO$ provides a high concentration of acetate ions. According to Le Chatelier's principle, the addition of CH_3COO^- ions from sodium acetate to a solution of acetic acid will shift the ionization equilibrium of CH_3COOH far to the left as CH_3COO^- ions combine with H^+ ions to from nonionized CH_3COOH. This will suppress the ionization of CH_3COOH, thereby causing a drastic decrease in the hydrogen ion concentration in the solution. Thus, a solution containing both CH_3COOH and $NaCH_3COO$ will be less acidic than a solution containing only CH_3CHOOH at the same concentration. The shift in equilibrium of the acetic acid ionization is caused by the additional acetate ions from the salt. The CH_3COO^- ion is called the common ion because it is supplied by both CH_3COOH and CH_3COONa.

Solutions that contain a weak acid plus a salt of the weak acid are always less acidic than solutions that contain the same concentration of the weak acid alone.

When a solution of a weak electrolyte is altered by adding one of its ions from another source, the ionization of the weak electrolyte is suppressed. This behavior is termed as the *common ion effect*. The common ion effect plays an important role in determining the pH of a solution and the solubility of a slightly soluble salt. We will deal with the latter in the section of solubility product. Here we will study the common ion effect as it relates to the pH of a solution. Keep in mind that despite its common name, the common ion effect is simply a special case of Le Chatelier's principle.

Example 7.18 Calculate the concentration of H_3O^+ of a mixture (solution) that is 0.010 M in CH_3COOH and 0.20 M in $NaCH_3COO$. ($K_a = 1.8 \times 10^{-5}$)

Strategy: Write the suitable equations for both $NaCH_3COO$ and CH_3COOH and the ionization constant expression for CH_3COOH. Then, represent the equilibrium concentrations algebraically and substitute into the K_a expression and solve for the unknown.

Solution:

The suitable equations and the ionization constant expression are

$$Na^+CH_3COO^- \longrightarrow Na^+ + CH_3COO^- \text{ (to completion)}$$

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \text{ (reversible)}$$

$$K_a = \frac{[H_3O^+][H_3COO^-]}{[CH_3COOH]} = 1.8\times10^{-5}$$

This expression of K_a is valid for all solutions that contain CH_3COOH. In solutions that contain both CH_3COOH and $NaCH_3COO$, acetate ions (CH_3COO^-) come from two sources. The ionization constant is satisfied by the total CH_3COO^- concentration.

Because $NaCH_3COO$ is completely dissociated, the $[CH_3COO^-]$ from $NaCH_3COO$ will be 0.20 mol L^{-1}:

$NaCH_3COO(aq.) \longrightarrow$	$Na^+(aq.)$ +	$CH_3COO^-(aq.)$
0.20 M	0.0	0.0
0.0	0.20 M	0.20 M

Let $x = [CH_3COOH]$ that ionizes. Then x is also equal to $[H_3O^+]$ and $[CH_3COO^-]$ from CH_3COOH. The total concentration of CH_3COO^- is $(0.20 + x)$ M and the concentration of unionized CH_3COOH is $(0.10 - x)$ M.

	$CH_3COOH(aq.) + H_2O(l) \rightleftharpoons$	$H_3O^+(aq.)$ +	$CH_3COO^-(aq.)$
Initial (M)	0.10	0	0.20
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$(0.10 - x)$	x	$(0.20 + x)$

The substitution of equilibrium concentrations into the ionization constant expression for acetic acid gives

$$K_a = \frac{C_{H_3O^+}C_{CH_3COO^-}}{C_{CH_3COOH}}$$

$$1.8 \times 10^{-5} = \frac{(x)\,(0.20 + x)}{(0.10 - x)}$$

The small value of K_a suggests that x is very small. This leads to two assumptions:

(i) $x << 0.10$. So $(0.10 - x) \approx 0.10$. This implies that very little CH_3COOH ionizes.

(ii) $x << 0.20$. So $(0.20 + x) \approx 0.20$. This implies that most of the CH_3COO^- comes from $NaCH_3COO$ and very little CH_3COO^- comes from the ionization of CH_3COOH.

It is reasonable to assume that x (from the ionization of CH_3COOH) is small, because CH_3COOH is a weak acid, and its ionization is further suppressed by the high concentration of CH_3COO^- formed by the soluble salt, $NaCH_3COO$.

Applying these assumptions gives

$$\frac{0.20\,x}{0.10} = 1.8\times10^{-5}$$

$$x = 9.0 \times 10^{-6}$$

$$\therefore \quad C_{H_3O^+} = x = 9.0 \times 10^{-6}$$

The calculation of the pH of a solution containing significant amounts of both a weak acid HA and a soluble salt of the weak acid, such as NaA, may be carried out as follows:

$$NaA \xrightarrow{H_2O} Na^+(aq.) + A^-(aq.) \text{ (to completion)}$$

$$HA(aq.) + H_2O(l) \rightleftharpoons H_3O^+(aq.) + A^-(aq.) \text{ (reversible)}$$

or simply $HA(aq.) \rightleftharpoons H^+(aq.) + A^-(aq.)$

The ionization constant K_a is given by

$$K_a = \frac{C_{H^+}C_{A^-}}{C_{HA}}$$

Note that HA and A^- represent the weak acid and its conjugate base, respectively. Rearranging ionization constant expression gives

$$C_{H^+} = K_a \times \frac{C_{HA}}{C_{A^-}}$$

Consider a solution in which the concentration of both the weak acid and its anion (from an added salt) are some reasonable values, such as greater than 0.050 M. Under these conditions, the concentration of the anion (C_{A^-}) in the solution can be assumed to be entirely due to the dissolved salt, i.e.,

$$C_{A^-} \approx C_{salt}$$

Similarly, the concentration of unionized weak acid (C_{HA}) in the solution can be assumed to be the total acid concentration taken initially, i.e.,

$$C_{HA} \approx C_{acid}$$

With these approximations, the preceding expression becomes

$$C_{H^+} = K_a \times \frac{C_{acid}}{C_{salt}}$$

Taking the negative logarithm of both sides, we obtain

$$-\log C_{H^+} = -\log K_a - \log \frac{C_{acid}}{C_{salt}}$$

$$= -\log K_a + \log \frac{C_{salt}}{C_{acid}}$$

Recalling that in the previous section we defined –log C_{H^+}(mol L^{-1}) as pH and –log K_a as pK_a, the preceding equation becomes

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{C_{\mathrm{salt}}}{C_{\mathrm{acid}}} \tag{7.50}$$

Equation (7.50) is called the *Henderson–Hasselbalch equation*. It is used to calculate the pH of a solution containing a weak acid such as acetic acid and its soluble salt with a strong base such as sodium acetate.

> HELP The relationship called the Henderson–Hasselbalch equation is valid only for solutions that contain a weak monoprotic acid and a soluble, ionic salt of the weak acid with a univalent cation, both in reasonable concentrations.

Workers in biological sciences use Eq. (7.50) frequently. In a more general form, it can be expressed as

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{C_{\text{conjugate base}}}{C_{\mathrm{acid}}} \tag{7.51}$$

In our discussion, HA is the acid and A^- is the conjugate base. Thus, if we know K_a and the concentration of the acid and of the salt of the acid, we can calculate the pH of the solution.

It is significant to note that the Henderson–Hasselbalch equation is derived from the equilibrium constant expression. It is valid regardless of the source of the conjugate base (that is, whether it comes from the acid alone or is supplied by both the acid and its salt).

In solving problems that involve the common ion effect, we are usually given the starting concentrations of a weak acid (HA) and of its salt, such as NaA. As long as the concentrations of these species are reasonably high (≥ 0.1 M), we can neglect the ionization of the acid and the hydrolysis of the salt. Thus, we can use the starting concentrations as the equilibrium concentrations in Eq. (7.51).

The common ion effect, i.e., the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance, also operates in a solution containing a weak base and a soluble salt of the base. A solution that contains aqueous NH_3 and ammonium chloride, NH_4Cl (a soluble ionic salt of NH_3), is a typical example of this kind. The NH_4Cl is completely dissociated, but aqueous NH_3 is only slightly ionized.

$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq.) + Cl^-(aq.) \text{ (to completion)}$$

$$NH_3(aq.) + H_2O(l) \rightleftharpoons NH_4^+(aq.) + OH^-(aq.) \text{ (reversible)}$$

Both NH_4Cl and aqueous NH_3 are sources of NH_4^+ ions. The completely dissociated NH_4Cl provides a high $[NH_4^+]$. This shifts the ionization equilibrium of aqueous NH_3 far to the left as NH_4^+ ions combine with OH^- ions to form unionized NH_3 and H_2O. The result is that $[OH^-]$ is decreased significantly.

> Solutions that contain a weak base plus a salt of the weak base are always less basic than solutions that contain the same concentration of the weak base alone.

We can derive a relationship to calculate $[OH^-]$ in a solution that contains a weak base B plus a salt that contains the cation, BH^+, of the weak base, just as we did for weak acid and salt of weak acid. The equilibrium equation for the ionization of a monoprotic weak base is

$$B(aq.) + H_2O(l) \rightleftharpoons BH^+(aq.) + OH^-(aq.)$$

The ionization constant K_b is given by

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Rearranging the above equation, we obtain

$$[OH^-] = K_b \times \frac{[B]}{[BH^+]}$$

Taking the logarithm of both sides of the equation gives

$$\log [OH^-] = \log K_b + \log \frac{[B]}{[BH^+]}$$

Multiplying by –1 gives

$$-\log [OH^-] = -\log K_b - \log \frac{[B]}{[BH^+]}$$

$$= -\log K_b + \log \frac{[BH^+]}{[B]}$$

or $$\mathrm{pOH} = \mathrm{p}K_b + \log \frac{[\mathrm{Salt}]}{[\mathrm{Base}]} \tag{7.52}$$

Equation (7.52) is another form of the Henderson–Hasselbalch equation for solutions containing a weak base plus a salt of the weak base. Note that Eq. (7.52) is valid for solutions of weak bases plus salts of weak bases with univalent anions in reasonable concentrations. In general terms, we can also write the equation as

$$\mathrm{pOH} = \mathrm{p}K_b + \log \frac{[\text{Conjugate acid}]}{[\mathrm{Base}]} \tag{7.53}$$

7.12.9 Hydrolysis of Salts and the pH of their Solutions

Solvolysis is the reaction of a substance with the solvent in which it is dissolved. The solvolysis reactions that occur in aqueous solutions are called *hydrolysis reactions*. Thus, hydrolysis is the reaction of a substance with water. Some hydrolysis reactions involve reaction with H_3O^+ or OH^- ions.

A *salt* is an ionic compound made up of a cation other than H^+ and an anion other than OH^- or O^{2-}. It is formed by the reaction between an acid and a base. All salts are strong electrolytes that completely dissociate in water and in some cases react with water. *The term salt hydrolysis* describes *the reaction of an anion or a cation of a salt or both with water*. Salt hydrolysis usually affects the pH of a solution. Thus, a salt is said to be *hydrolyzed* if the resulting aqueous solution is either acidic or basic. If the resulting aqueous solution is neutral, either there is no hydrolysis or no net hydrolysis.

> The word hydrolysis is derived from the Greek words hydro meaning water and lysis meaning to split apart.

Based on the classification of acids and bases, we can identify four different kinds of salts:

1. Salts of strong bases and strong acids
2. Salts of strong bases and weak acids

3. Salts of weak bases and strong acids
4. Salts of weak bases and weak acids

Salts of strong bases and strong acids do not undergo hydrolysis. Thus, such salts produce neutral aqueous solutions. Halides, nitrates, and sulphates of alkali metals and alkaline earth metals (except Be) are examples of such salts.

We can also describe these as salts that contain the cation of a strong base and the anion of a strong acid. Salts derived from strong bases and strong acids give neutral solutions because neither the cation nor the anion reacts appreciably with water. Consider NaCl, which is the salt of the strong base NaOH and the strong acid HCl. Sodium chloride is ionic even in the solid state. When NaCl (formed by the reaction between NaOH and HCl) dissolves in water, it dissociates completely into hydrated ions in H_2O as follows:

$$\mathrm{NaCl(aq.)} \xrightarrow{100\%} \mathrm{Na^+(aq.) + Cl^-(aq.)}$$

Water ionizes slightly to produce equal concentrations of H^+ and OH^- ions:

$$\mathrm{H_2O(l)} \leftrightarrows \mathrm{H^+(aq.) + OH^-(aq.)}$$

We can see that the aqueous solution of NaCl contains four ions: Na^+, Cl^-, H^+, and OH^-. The interaction of Na^+ and OH^- ions gives a strong base NaOH which is dissociated completely. Thus, the concentration of OH^- ions remains unaffected. Similarly, the concentration of H^+ remains unaffected as the interaction of H^+ and Cl^- ions gives a strong acid HCl which is completely ionized. Moreover, the cation of the salt (Na^+) is such a weak acid that it does not react appreciably with water to produce H^+ ions. Similarly, the anion of the salt (Cl^-) is such a weak base that it does not react appreciably with water to produce OH^- ions. Consequently, a solution containing Na^+ and Cl^- ions is neutral, with a pH of 7 at 25°C.

The solutions of salts of strong bases and strong acids are neutral because neither ion of such a salt reacts to upset the H^+/OH^- balance in water.

Salts of strong bases and weak acids undergo anionic hydrolysis to produce basic solutions. Na and K salts other than halides, nitrates, and sulphates are of this type: sodium acetate ($NaCH_3COO$), sodium carbonate (Na_2CO_3), sodium cyanide (NaCN), sodium phosphate (Na_3PO_4), sodium hydrogen phosphate (Na_2HPO_4), borax ($Na_2B_4O_7{\cdot}10H_2O$), etc.

When salts derived from strong bases and weak acids are dissolved in water, the resulting solutions are always basic because the anions of weak acids react with water to form hydroxide ions. Consider sodium acetate, $NaCH_3COO$, which is the salt of the strong base NaOH and the weak acid CH_3COOH. It is soluble in water and dissociates completely in it.

$$\mathrm{NaCH_3COO(s)} \xrightarrow[100\%]{\mathrm{H_2O}} \mathrm{Na^+(aq.) + CH_3COO^-(aq.)}$$

H_2O ionizes slightly to produce equal concentrations of H^+ and OH^- ions:

$$\mathrm{H_2O(l)} \rightleftharpoons \mathrm{H^+(aq.) + OH^-(aq.)}$$

The interaction of Na^+ with OH^- does not disturb the water equilibrium because NaOH is a strong base. However, the interaction of CH_3COO^- with H^+ yields CH_3COOH, a weak acid. The ionization of CH_3COOH does not reproduce equal number of H^+ ions. As H^+ is removed from the solution, the water equilibrium is disturbed and shifts to the right. This causes more H_2O to ionize and an excess of OH^- builds up. So the solution becomes basic.

There is another view of hydrolysis. The hydrated Na^+ has no acidic or basic properties because it neither donates nor accepts H^+ ions. However, the acetate ion CH_3COO^- is the conjugate base of a weak acid, CH_3COOH. Thus, it is a stronger base (but it is still weak), having an affinity for H^+ ions. Consequently, it reacts with water to yield OH^- ions as illustrated by the following hydrolysis reaction:

$$\mathrm{CH_3COO^-(aq.) + H_2O(l)} \rightleftharpoons \mathrm{CH_3COOH(aq.) + OH^-(aq.)}$$

	CH_3COO^-	CH_3COOH	OH^-
Initial (M)	C	0	0
Change (M)	$C - Ch$	Ch	Ch
Equilibrium (M)	$C(1-h)$	Ch	Ch

where the initial concentration of the salt in the solution is C mol L^{-1} and h is the degree of hydrolysis of salt (i.e., the fraction of 1 mol of salt that is hydrolyzed) at this concentration.

Because this reaction produces OH^- ions, the sodium acetate solution will be basic. The equilibrium constant for this hydrolysis reaction is called the hydrolysis constant (K_h) for the salt or the base ionization constant (K_b) for the acetate ion:

$$K_h = \frac{C_{CH_3COOH}C_{OH^-}}{C_{CH_3COO^-}} \tag{7.54}$$

We can evaluate this equilibrium constant from other known expressions. Multiplying Eq. (7.54) by C_{H^+}/C_{H^+}, we get

$$K_h = \frac{C_{CH_3COOH}\ C_{OH^-}}{C_{CH_3COO^-}} \times \frac{C_{H^+}}{C_{H^+}} = \frac{C_{CH_3COOH}}{C_{CH_3COO^-}\ C_{H^+}} \times \frac{C_{H^+}\ C_{OH^-}}{1}$$

We recognize that

$$K_h = \frac{1}{K_a\ (CH_3COOH)} \times \frac{K_w}{1} = \frac{K_w}{K_a\ (CH_3COOH)}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

which gives

$$K_h = \frac{C_{CH_3COOH}C_{OH^-}}{C_{CH_3COO^-}} = 5.6 \times 10^{-10}$$

We have calculated K_h, the hydrolysis constant for sodium acetate, or K_b, the base ionization constant for the acetate ion, CH_3COO^-.

In general, for a salt of strong base and weak acid, we can write

$$K_h = \frac{K_w}{K_a} \tag{7.55}$$

where K_a refers to the ionization constant for the weak monoprotic acid from which the anion is derived.

Since K_h for any salt of strong base and weak acid is the K_b for the anion of weak monoprotic acid, the above relation is nothing but the relationship between conjugate acid–base ionization constant, i.e., $K_a K_b = K_w$. Substituting the equilibrium concentrations into Eq. (7.54), we get

$$K_h = \frac{(Ch)\,(Ch)}{C\,(1-h)} = \frac{Ch^2}{1-h}$$

Since $h << 1$, $1 - h \approx 1$, we can write

$$K_h = Ch^2$$

or
$$h = \sqrt{\frac{K_h}{C}} \qquad (7.56)$$

Substituting K_h from Eq. (7.55) gives

$$h = \sqrt{\frac{K_w}{K_a \cdot C}} \qquad (7.57)$$

The equilibrium concentration of OH^- ions is given as

$$C_{OH^-} = Ch$$

Substituting the value of h from Eq. (7.57), we get

$$C_{OH^-} = C\sqrt{\frac{K_w}{K_a C}} = \sqrt{\frac{K_w C}{K_a}} \qquad (7.58)$$

The ionic product of water is given as

$$K_w = C_{H^+} C_{OH^-}$$

$$C_{H^+} = \frac{K_w}{C_{OH^-}}$$

Substituting C_{OH^-} from Eq. (7.58), we get

$$C_{H^+} = \frac{K_w}{\sqrt{\frac{K_w C}{K_a}}} = \sqrt{\frac{K_w K_a}{C}}$$

Taking the logarithm of both sides, we obtain

$$\log C_{H^+} = \log\left(\frac{K_w K_a}{C}\right)^{1/2}$$

$$= \frac{1}{2}(\log K_w + \log K_a - \log \mathrm{C})$$

Multiplying by –1 gives

$$-\log C_{H^+} = \frac{1}{2}(-\log K_w - \log K_a + \log \mathrm{C})$$

or
$$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K_w + \mathrm{p}K_a + \log C) \qquad (7.59)$$

At 298 K, $\mathrm{p}K_w = 14$. Thus,

$$\mathrm{pH} = 7 + \frac{1}{2}(\mathrm{p}K_a + \log C) \qquad (7.60)$$

Hence, knowing the dissociation constant (K_a) of the weak monoprotic acid and the molar concentration (C) of the salt solution, the pH of the salt solution can be calculated.

Salts of weak bases and strong acids undergo cationic hydrolysis to produce acidic solutions. Halides, sulphates, and nitrates of all metals except alkali metals and alkaline earth metals (except Be) are of this type: $FeCl_3$, NH_4Cl, $CuSO_4$, $AlCl_3$, etc.

When a salt derived from a weak base and a strong acid dissolves in water, the resulting aqueous solution is always acidic because the cation of weak base reacts with water to form unionized molecules of the weak base and H^+ ions. This upsets the H^+/OH^- balance in water, giving an excess of H^+ and making such solution acidic. Consider ammonium chloride (NH_4Cl), an ionic salt that is soluble in water. It is the salt of weak base (NH_3) and strong acid (HCl).

$$NH_4Cl(s) \xrightarrow[100\%]{H_2O} NH_4^+(aq.) + Cl^-(aq.)$$

$$H_2O(l) \rightleftharpoons H^+(aq.) + OH^-(aq.)$$

The interaction of Cl^- with H^+ does not disturbs the equilibrium of water because HCl is a strong acid and, thus, releases back the same concentration of H^+ ions. On the other hand, the interaction of NH_4^+ with OH^- yields NH_4OH (or aq. NH_3), a weak base. The ionization of weak base (NH_3) does not reproduce the same number of OH^- ions as were consumed to form NH_3. As OH^- is removed (by the reaction of NH_4^+ with OH^-) from the aqueous solution, the water equilibrium is disturbed and shifts to the right. This causes more H_2O molecules to ionize to produce an excess of H^+ ions. So the resulting solution becomes acidic.

Let us look at the other viewpoint. The Cl^- ion has no affinity for H^+. The hydrated NH_4^+ ion is the conjugate acid of a weak base, NH_3. Thus, it is a stronger acid (but it is still weak), having an affinity for OH^- ions. Consequently, it reacts with water to yield H^+ ions as illustrated by the following hydrolysis reaction:

$$NH_4^+(aq.) + H_2O(l) \rightleftharpoons NH_3(aq.) + H_3O^+(aq.)$$

or simply $NH_4^+(aq.) \rightleftharpoons NH_3(aq.) + H^+(aq.)$

Initial (M)	C	0	0
Change (M)	$C - Ch$	Ch	Ch
Equilibrium (M)	$C(1-h)$	Ch	Ch

where the initial concentration of the salt (NH_4Cl) in the solution is C mol L^{-1} and h is the degree of hydrolysis of the salt (i.e., the fraction of one mole of salt that is hydrolyzed) at this concentration.

Since this reaction produces H^+ ions, the pH of the solution decreases. As we can see, the hydrolysis of the NH_4^+ ion is the same as the ionization of the NH_4^+ acid. The equilibrium constant for this hydrolysis reaction is given by

$$K_h = \frac{[NH_3][H^+]}{[NH_4^+]} \qquad (7.61)$$

Multiplying Eq. (7.61) by $[OH^-]/[OH^-]$, we get

$$K_h = \frac{[NH_3][H^+]}{[NH_4^+]} \times \frac{[OH^-]}{[OH^-]} = \frac{[NH_3]}{[NH_4^+][OH^-]} \times \frac{[H^+][OH^-]}{1}$$

We recognize that

$$K_h = \frac{1}{K_b\,(NH_3)} \times \frac{K_w}{1} = \frac{K_w}{K_b\,(NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

which gives

$$K_h = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.6 \times 10^{-10}$$

In general, for a salt of weak base and strong acid, we can write

$$K_h = \frac{K_w}{K_b}$$

where K_b refers to the ionization constant for the weak monoacidic base from which the cation is derived. Since K_h is the same as the ionization constant (K_a) of the NH_4^+ acid, the above relation is actually the relationship between conjugate acid–base ionization constants, i.e., $K_a K_b = K_w$.

Substituting the equilibrium concentrations into Eq. (7.61), we get

$$K_h = \frac{(Ch)(Ch)}{C(1-h)} = \frac{Ch^2}{1-h}$$

Since $h << 1$, $1 - h \approx 1$, we can write

$$K_h = Ch^2 \tag{7.63}$$

or $$h = \sqrt{\frac{K_h}{C}}$$

Substituting K_h from Eq. (7.62) gives

$$h = \sqrt{\frac{K_w}{K_b C}} \tag{7.64}$$

The equilibrium concentration of H^+ ions is given as

$$C_{H^+} = Ch$$

Substituting the value of h from Eq. (7.64), we get

$$C_{H^+} = C\sqrt{\frac{K_w}{K_b C}} = \sqrt{\frac{K_w C}{K_b}} = \left(\frac{K_w C}{K_b}\right)^{1/2}$$

Taking the logarithm of both sides, we obtain

$$\log C_{H^+} = \log\left(\frac{K_w C}{K_b}\right)^{1/2}$$

$$= \frac{1}{2}(\log K_w + \log \mathrm{C} - \log K_b)$$

Multiplying by –1 gives

$$-\log C_{H^+} = \frac{1}{2}(-\log K_w - \log \mathrm{C} + \log K_b)$$

or $$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K_w - \mathrm{p}K_b - \log \mathrm{C}) \tag{7.65}$$

At 298 K, $\mathrm{p}K_w = 14$. Thus,

$$\mathrm{pH} = 7 - \frac{1}{2}(\mathrm{p}K_b + \log C) \tag{7.66}$$

This expression clearly indicates that the pH of an aqueous solution of salt of weak base and strong acid is always less than 7 at 25°C.

Salts of weak bases and weak acids undergo anionic as well as cationic hydrolysis to produce an aqueous solution which may be neutral, acidic, or basic depending upon the relative strengths of weak acid and weak base. Such a salt cannot be an Na or a K salt; it cannot be a halide, nitrate, or sulphate; but it can be ammonium acetate (NH_3OOCCH_3), ammonium phosphate $(NH_3)_3PO_4$, calcium phosphate $[Ca_3(PO_4)_2]$, anilinium acetate ($C_6H_5\overset{+}{N}H_3CH_3CO\bar{O}$), ammonium carbonate $[(NH_3)_2CO_3]$, aluminium phosphate ($AlPO_4$), etc.

The salts of weak bases and weak acids are the fourth class of salts. Most are soluble. So far we have considered salts in which only one ion undergoes hydrolysis. Salts of weak bases and weak acids contain cations that would give acidic solutions and anions that would give basic solutions. Since the aqueous solutions of such salts may be neutral, basic, or acidic depending on the relative strengths of the weak molecular acid and weak molecular base (from which each salt is derived), the salts of this class may be divided into three types:

Salts of weak bases and weak acids for which $K_b = K_a$: Ammonium acetate (NH_4CH_3COO) is the common example of a salt of this type. It is the salt of weak base (NH_3) and weak acid (CH_3COOH). The ionization constants for both aqueous NH_3 and CH_3COOH are 1.8×10^{-5}. We have seen that ammonium ions (NH_4^+) react with water to produce H_3O^+(aq.):

$$NH_4^+(aq.) + H_2O(l) \rightleftharpoons NH_3(aq.) + H_3O^+(aq.)$$

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.6 \times 10^{-10}$$

We can recall that acetate ions (CH_3COO^-) react with water to produce OH^-(aq.):

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

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.6 \times 10^{-10}$$

Since these K_h values are equal, the NH_4^+ produces just as many H_3O^+ ions as the CH_3COO^- produces OH^- ions. Thus, the aqueous solutions of ammonium acetate are found to be neutral as predicted. There are very few salts that have cations and anions with equal K_h values.

> Cation hydrolyzes to yield H^+(aq.) ions while anion hydrolyzes to yield OH^-(aq.) ions. If both ions are produced in equal amounts, the resulting aqueous solution of the salt is neutral.

Salts of weak bases and weak acids for which $K_b > K_a$: Ammonium cyanide (NH_4CN) is the common example of a salt of this type. It is the salt of weak base (NH_3) and weak acid (HCN). The salts of weak bases and weak acids for which K_b is greater than K_a are always basic because the anion of the weaker acid hydrolyzes to a greater extent than the cation of the stronger base.

K_a for HCN (4.0×10^{-10}) is much smaller than K_b for NH_3 (1.8×10^{-5}). So K_h (or K_b) for CN^- (2.5×10^{-5}) is much larger than K_h (or K_a) for NH_4^+ (5.6×10^{-10}). This implies that the CN^- ions hydrolyze to a much greater extent than NH_4^+ ions:

$$NH_4^+(aq.) + H_2O(l) \rightleftharpoons NH_3(aq.) + H_3O^+(aq.)$$

$$CN^-(aq.) + H_2O(l) \rightleftharpoons HCN(aq.) + OH^-(aq.)$$

Since the second reaction occurs to a greater extent, the aqueous solution of ammonium cyanide is distinctly basic. Stated differently, CN^- is much stronger as a base than NH_4^+ is as an acid.

> If K_b for the anion (of the salt) is greater than K_a for the cation (of the salt), then the solution must be basic because the anion (yielding OH^-) will hydrolyze to a greater extent than the cation (yielding H^+).

Salts of weak bases and weak acids for which $K_b < K_a$: Ammonium fluoride (NH_4F) is the common example of a salt of this type. It is the salt of weak base (NH_3) and weak acid (HF). Salts of weak bases and weak acids for which K_b is less than K_a are always acidic because the cation of the weaker base hydrolyzes to a greater extent than the anion of the stronger acid.

K_b for NH_3 (1.8×10^{-5}) is slightly smaller than K_a for HF (7.2×10^{-4}). So K_h (or K_a) for NH_4^+ (5.6×10^{-10}) is slightly larger than the K_h (or K_b) for F^- (1.4×10^{-11}). This implies that NH_4^+ ions hydrolyze to a slightly greater extent than F^- ions:

$$NH_4^+(aq.) + H_2O(l) \rightleftharpoons NH_3(aq.) + H_3O^+(aq.)$$

$$F^-(aq.) + H_2O(l) \rightleftharpoons HF(aq.) + OH^-(aq.)$$

Since the first reaction occurs slightly to a greater extent, the aqueous solution of ammonium fluoride is slightly acidic. Stated differently, NH_4^+ is slightly stronger as an acid than F^- is as a base.

> If K_b of the anion (of the salt) is smaller than K_a of the cation (of the salt), the resulting aqueous solution will be acidic because cation hydrolysis yielding H^+ will be more extensive than anion hydrolysis (yielding OH^-).

Representing the salt of weak base and weak acid by BA, we have

$$\begin{array}{lcccc} & B^+(aq.) + & A^-(aq.) + H_2O & \rightleftharpoons BOH(aq.) + & HA(aq.) \\ \text{Initial} & C & C & 0 & 0 \\ \text{Change} & C(1-h) & C(1-h) & Ch & Ch \end{array}$$

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} \tag{7.67}$$

Multiplying Eq. (7.67) by $\dfrac{[H^+][OH^-]}{[H^+][OH^-]}$, we get

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} \times \frac{[H^+][OH^-]}{[H^+][OH^-]}$$

$$= \frac{[BOH]}{[B^+][OH^-]} \times \frac{[HA]}{[H^+][A^-]} \times \frac{[H^+][OH^-]}{1}$$

$$= \frac{1}{K_b} \times \frac{1}{K_a} \times \frac{K_w}{1}$$

$$\therefore \quad K_h = \frac{K_w}{K_a K_b} \tag{7.68}$$

Substituting the equilibrium concentrations into Eq. (7.67), we get

$$K_h = \frac{(Ch)(Ch)}{[C(1-h)][C(1-h)]} = \frac{h^2}{1-h^2}$$

Since $h << 1$, $1 - h^2 \approx 1$, we can write

$$K_h = h^2$$

or $$h = \sqrt{K_h} \tag{7.69}$$

Since the relationship between h and K_h does not involve C, it can be said that the degree of hydrolysis of the salt of weak base and weak acid (for which $K_b = K_c$) is independent of the concentration of the salt solution.

Substituting K_h from Eq. (7.68) gives

$$h = \sqrt{\frac{K_w}{K_a K_b}} \tag{7.70}$$

Considering the ionization of the weak acid, HA, we have

$$HA(aq.) \rightleftharpoons H^+(aq.) + A^-(aq.)$$

The ionization constant is given as

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

or $$[H^+] = K_a \frac{[HA]}{[A^-]} = K_a \frac{Ch}{C(1-h)} = K_a \frac{h}{1-h}$$

Now, $1 - h \approx 1$. Thus,

$$[H^+] = K_a h$$

Substituting h from Eq. (7.70) gives

$$[H^+] = K_a \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{K_w K_a}{K_b}} = \left(\frac{K_w K_a}{K_b}\right)^{1/2}$$

$$\log [H^+] = \frac{1}{2}(\log K_w + \log K_a - \log K_b)$$

$$-\log [H^+] = \frac{1}{2}(-\log K_w - \log K_a + \log K_b)$$

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

At 298 K, $pK_w = 14$. Thus,

$$pH = 7 + \frac{1}{2}(pK_a - pK_b) \tag{7.71}$$

This expression clearly indicates that at 298 K,

1. the pH of the solution will be equal to 7 (neutral solution) if $pK_a = pK_b$,
2. the pH of the solution will be greater than 7 (basic) if $pK_a > pK_b$, and
3. the pH of the solution will be less than 7 (acidic) if $pK_a < pK_b$.

Follow-up Test 12

1. The pH of a solution containing 0.20 M CH_3COOH and 0.30 M CH_3COONa is
   (1) 2.89 (2) 4.92
   (3) 5.04 (4) 3.89
2. When sodium acetate ($NaCH_3COO$) is added to aqueous solution of acetic acid (CH_3COOH), the
   (1) pH value becomes zero
   (2) pH value remains unchanged
   (3) pH value decreases
   (4) pH value increases
3. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be
   (1) completely ionized in the small intestine and in the stomach
   (2) ionized in the small intestine and almost unionized in the stomach
   (3) ionized in the stomach and almost unionized in the small intestine
   (4) unionized in the small intestine and in the stomach
4. 50.0 mL of 0.10 M ammonia solution is treated with 25.0 mL of 0.10 M HCl. If $K_b(NH_3) = 1.77 \times 10^{-5}$, the pH of the resulting solution will be
   (1) 11.12 (2) 8.75
   (3) 10.34 (4) 9.24
5. Which of the following cations is not hydrolyzed in aqueous solution?
   (i) Ba^{2+} (ii) Ca^{2+}
   (iii) Na^+ (iv) K^+

(1) (i), (ii) (2) (iii), (iv)
(3) (i), (ii), (iii), (iv) (4) (i), (ii), (iii)

6. Which of the anions is not hydrolyzed in aqueous solution?
 (i) Cl^- (ii) NO_3^-
 (iii) Br^- (iv) ClO_4^-
 (1) (i), (ii), (iii), (iv) (2) (ii), (iii), (iv)
 (3) (i), (ii), (iii) (4) (ii), (iv)
7. Which of the following salts does not undergo hydrolysis?
 (1) KCN (2) KCl
 (3) NH_4NO_3 (4) $FeCl_3 \cdot 6H_2O$
8. Which of the following salts undergoes anionic hydrolysis?
 (1) $AlCl_3$ (2) $CuSO_4$
 (3) Na_2CO_3 (4) NH_4Cl
9. The aqueous solution of aluminium chloride is acidic due to the
 (1) formation of $Al(OH)_3$
 (2) hydrolysis of cation and anion
 (3) hydrolysis of anion
 (4) hydrolysis of cation
10. Which of the following relations is correct during the hydrolysis of salts of weak acid and strong bases?
 (1) $K_h = \frac{K_w}{K_a}$ (2) $K_h = \frac{K_w}{K_a K_b}$
 (3) $K_h = \frac{K_w}{K_b}$ (4) $K_h = \frac{K_a}{K_w}$
11. For the aqueous solution of a salt of a weak acid and a weak base,
 (1) $K_h = \sqrt{\frac{h}{1-h}}$ (2) $\sqrt{K_h} = \frac{h^2}{1-h}$
 (3) $\sqrt{K_h} = \frac{h}{1-h}$ (4) $K_h = \frac{h}{1-h}$
12. For cationic hydrolysis, pH is given by
 (1) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$
 (2) $pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C$
 (3) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b$
 (4) $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_b + \frac{1}{2}\log C$
13. Which of the following salts is neutral in water?
 (1) NH_4CH_3COO (2) NH_4NO_3
 (3) NH_4CN (4) NH_4F

7.13 BUFFER SOLUTION

In laboratory reactions, industrial processes, and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids or bases. The oxygen-carrying capacity of the hemoglobin in our blood and the activity of the enzymes in our cells are very sensitive to the pH of our body fluids. Our bodies use a combination of compounds known as a buffer solution to keep the pH within a narrow range.

Buffer solutions, or just called buffers, resist changes in pH.

A buffer solution is a solution which has a detinite pH which changes insignificantly on the addition of a limited amount of any strong acid or strong base. A buffer solution always contains two components: a weak acid and a weak base, which can be provided either by a single substance (e.g., NH_4CH_3COO or by a mixture, e.g., $CH_3COOH/NaCH_3COO$ or NH_3/NH_4CI). The solution has the ability to resist the changes in pH upon the addition of a small amount of either acid or base. Buffer maintains its pH by converting a strong acid into a weak acid and a strong base into a weak base.

A buffer solution must contain a relatively large concentration of weak acid to react with any OH^- ions that may be added and must contain a similar concentration of weak base to react with any added H^+ ions. Furthermore, the acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are nicely satisfied by a conjugate acid–base pair (a weak acid and its conjugate base or a weak base and its conjugate acid) with both acid and base in reasonable concentrations. The acidic component reacts with added strong bases while the basic component reacts with added strong acids.

Many types of solutions exhibit this behavior. Two of the most frequently encountered kinds are as follows:

1. A solution of a weak acid (e.g., CH_3COOH) plus a soluble ionic salt of the weak acid with a strong base (e.g., $Na^+CH_3COO^-$). Such a buffer is called an *acid buffer* because its range (at 298 K) is below 7.
2. A solution of a weak base (e.g., NH_3) plus a soluble ionic salt of the weak base with a strong acid (e.g., NH_4 CI). Such a buffer is called a *basic buffer* because its range (at 298 K) is above 7.

A buffer solution is able to react with either H^+ or OH^- ions, whichever is added.

7.13.1 Preparation of Acid Buffer

A solution containing acetic acid (CH_3COOH) and sodium acetate ($NaCH_3COO$) is an example of this kind of buffer solution. The acidic component is CH_3COOH while the basic component is $NaCH_3COO$ because acetate ion (CH_3COO^-) is the conjugate base of acetic acid. The solution has a definite pH which we can calculate by means of the Henderson–Hasselbalch equation:

$$pH = pK_a + \log \frac{[\text{salt, } CH_3COO^-]}{[\text{acid, } CH_3COOH]}$$

The operation of this buffer (buffering action) depends on the following equilibrium:

$$\underset{\text{High conc.}}{CH_3COOH(aq.)} + H_2O(l) \rightleftharpoons H_3O^+(aq.) + \underset{\substack{\text{High conc.}\\\text{(from salt)}}}{CH_3COO^-(aq.)}$$

If we add a strong acid such as HCI to this solution, it produces large concentration of $H_3O^+(aq.)$. As a result of the added H_3O^+, the equilibrium should shift to the left, to use up most of the added H_3O^+ and reestablish equilibrium. However, the shift in equilibrium is insignificant (i.e., the decrease in pH is very very small) because the added H_3O^+ ions are nullified by the $CH_3\ COO^-$ ions present in the buffer in high concentration:

$$H_3O^+(aq.) + CH_3COO^-(aq.) \xrightarrow{\approx 100\%} CH_3COOH(aq.) + H_2O$$

This reaction goes nearly to completion because CH_3COOH is a weak acid. Thus, the effect of addition of a strong acid (HCl) is nullified by the buffer by converting it into a weak acid (CH_3COOH) by means of the base CH_3COO^- (called reserved base).

During this process, the concentration of CH_3COO^- (salt) decreases while the concentration of CH_3COOH (acid) increases but the ratio [salt]/[acid] remains practically unchanged. Thus, according to the Henderson equation, the pH of the buffer solution remains practically unchanged.

The net effect is to neutralize most of the H_3O^+ from HCl by forming nonionized CH_3CHOOH molecules. This slightly decreases the ratio $[CH_3COO^-]$ $[CH_3COOH]$, which governs the pH of the solution.

When a strong base, such as NaOH, is added to the CH_3COOH–$NaCH_3COO$ buffer solution, it produces OH^- ions. As a result of the added OH^- ions (which tend to nullify H_3O^+ions), the buffer equilibrium should shift to the right, to consume most of the added OH^- ions and reestablish equilibrium. However, the shift in equilibrium is insignificant (i.e., the increase in pH value is very very small) because the added OH^- ions are nullified by the CH_3COOH present in the buffer. Because the CH_3COOH is present in high concentration, this can occur to a great extent:

$$\underset{\substack{\text{Added}\\\text{strong}\\\text{base}}}{OH^-(aq.)} + \underset{\substack{\text{Reserved}\\\text{acid}}}{CH_3COOH(aq.)} \xrightarrow{\sim 100\%} \underset{\substack{\text{Weaker}\\\text{base}}}{CH_3COO^-(aq.)} + H_2O(l)$$

This reaction goes nearly to completion because CH_3COO^- is a weak base. Thus, the effect of addition of a strong base (NaOH) is nullified as the buffer converts it into a weak base (CH_3COO^-) by means of the acid CH_3COOH (called reserved acid). During this process, the concentration of CH_3COOH (acid) decreases while the concentration of CH_3COO^- (salt) increases but the ratio [salt]/[acid] which governs the pH of the buffer remains practically unchanged.

TThe net effect is to neutralize most of the OH^- from NaOH by forming a weaker base (CH_3COO^-). This slightly increases the ratio $[CH_3COO^-]/[CH_3COOH]$, which governs the pH of the solution.

The best acidic buffer should be the one which is able to neutralize both the added acid and the added base to the same extent, i.e., it is equally effective against acid as well as base.

Since H^+ (from added HCl) is neutralized by CH_3COO^- ions (from salt) while OH^- (from added NaOH) is neutralized by CH_3COOH, the best buffer should have salt and acid in equal concentration (or equal moles):

$$[\text{salt}] = [\text{acid}]$$

Substituting this result in the Henderson–Hasselbalsch equation, we get

$$pH = pK_a + \log 1$$

or $$pH = pK_a \tag{7.72}$$

Thus, the best acidic buffer is the one whose pH is equal to pK_a. This can be prepared by mixing the salt (conjugate base) and the weak acid in equal moles in a given volume.

Through experiments it has been found that a mixture of the weak acid (HA) and its conjugate base (A^-) will act as a buffer only when the ratio of the weak acid to its conjugate base is neither very large nor very small, that is, when the pH of the solution does not differ greatly from the pK_a of the acid. This is found to be possible when the ratio [salt]/[acid] is between 0.1 and 10. Substituting this result into the Henderson equation, we get

$$pH = pK_a + \log 0.1 = pK_a - 1$$
$$= pK_a + \log 10 = pK_a + 1$$

Combining this result with Eq. (7.72), we get the range of pH in which the mixture HA/A^- exhibits its buffer properties:

$$pH = pK_a \pm 1 \tag{7.73}$$

For example, for CH_3COONa/CH_3COOH system, $pK_a = 4.74$. Thus, its buffer range will be 4.74 ± 1, i.e., 3.74 to 5.74. This implies that this system will act as a buffer only when its pH lies in this range, i.e., it wil not act as a buffer if its pH is below 3.74 or above 5.74, and it will act as the best buffer at pH = 4.74. Since this range lies below 7 (at 298 K), it is called an acidic buffer.

7.12.2 Preparation of Basic Buffer

An example of this type of buffer solution is one that contains the weak base ammonia (NH_3) and its soluble ionic salt with a strong acid, ammonium chloride (NH_4Cl). The solution has a definite pOH and, hence, a definite pH which can be calculated by means of the Handerson–Hasselbalch equation:

$$pOH = pK_b + \log\frac{[\text{salt}, NH_4^+]}{[\text{base}, NH_3]}$$

The operation of this buffer (buffering action) depends on the following equilibrium.

$$\underset{\text{High conc.}}{NH_3(aq.)} + H_2O(l) \rightleftharpoons \underset{\substack{\text{High conc.}\\\text{from salt}}}{NH_4^+(aq.)} + OH^-(aq.)$$

NH_3 is the reserved base of buffer which neutralizes the added H_3O^+ ions from a strong acid like HCl:

$$\underset{\substack{\text{Added}\\\text{strong acid}}}{H_3O^+(aq.)} + \underset{\substack{\text{Reserved}\\\text{base}}}{NH_3(aq.)} \xrightarrow{\sim 100\%} \underset{\substack{\text{Weaker}\\\text{acid}}}{NH_4^+(aq.)} + \underset{\text{Water}}{H_2O(l)}$$

NH_4^+ is the reserved acid of buffer which neutralizes the added OH^- ions from a strong base like NaOH:

$$\underset{\text{Added base}}{OH^-(aq.)} + NH_4^+(aq.) \xrightarrow{\sim 100\%} \underset{\text{Weak base}}{NH_3} + H_2O$$

> Changes in pH are minimized in the buffer solution because the basic component can react with H_3O^+ ions and the acidic component can react with OH^- ions.

pH of the buffer solution can be calculated by using the equation

$$pH + pOH = pK_w$$

We know that $pK_a + pK_b = pK_w$. On putting these values in the Henderson equation, we get

$$pK_w - pH = pK_w - pK_a + \log\frac{[\text{salt}]}{[\text{base}]}$$

or

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{salt}]} \qquad (7.74)$$

The best basic buffer can be prepared by taking base (NH_3) and salt (NH_4Cl) in equal concentration. In this situation, the pH of the buffer solution will be the same as pK_a for the base (when [base] = [salt], log [base]/[salt] = 0, and pH = pK_a).

As we discussed in the case of acidic buffer, the pH range of the basic buffer is given as

$$pH = pK_a \pm 1 \qquad (7.75)$$

For NH_3/ NH_4^+ system, pK_a is 9.25. Thus, the buffer range of this buffer solution will be 8.25 to 10.25. Since this range lies above 7 (at 298 K), NH_3/NH_4^+ system in called a basic buffer.

Follow-up Test 13

1. A buffer solution is one which has
   (1) reserved acid
   (2) reserved base
   (3) reserved acid and reserved base
   (4) pH equal to 7
2. Which of the following solutions cannot act as a buffer system?
   (1) KH_2PO_4/H_3PO_4 (2) $NaClO_4/HClO_4$
   (3) C_5H_5N/C_5H_5NHHCl (4) $Na_2CO_3/NaHCO_3$
3. An acidic buffer solution can be prepared by mixing equimolar amounts of
   (1) $B(OH)_3$ and $Na_2B_4O_7\cdot 10H_2O$
   (2) NH_3 and NH_4Cl
   (3) HCl and NaCl
   (4) CH_3COOH and CH_3COONa
4. Which of the following salt solution will act as a buffer?
   (1) NH_4CH_3COO(aq.) (2) NH_4Cl(aq.)
   (3) Na CH_3COO(aq.) (4) NaCl(aq.)
5. Which of the following expressions represents the Henderson equation for an acidic buffer ?
   (1) $pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$
   (2) $pH = pK_a - \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$
   (3) $pH = pK_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$
   (4) $pH = pK_a$
6. A buffer solution contains 0.1 mol each of $NaCH_3COO$ and CH_3COOH. On diluting the solution to double its volume, the pH of the solution
   (1) will become half (2) will remain unchanged
   (3) will be doubled (4) cannot be predicted
7. Which of the following combinations will make a buffer solution?
   (i) CH_3COONa (2 mol) + HCl (1 mol)
   (ii) CH_3COOH (2 mol) + NaOH (1 mol)
   (iii) CH_3COOH (1 mol) + CH_3COONa (1 mol)
   (1) (iii) (2) (i), (ii)
   (3) (ii), (iii) (4) (i), (ii), (iii)
8. Which of the following conditions will make the buffer most efficient?
   (1) $pH = pK_a$ (2) $pH = pK_a \pm 1$
   (3) $pH = pK_a + 1$ (4) $pH = pK_a - 1$
9. The range of pH for acidic and basic buffers is
   (1) from $pH = pK_a \pm 2$ to $pH = pK_b \pm 2$
   (2) from $pH = pK_a + 1$ to $pH = pK_b + 1$
   (3) from $pH = pK_a \pm 1$ to $pH = pK_b \pm 1$
   (4) from $pH = pK_a + 1$ to $pH = pK_b - 1$
   where K_a and K_b are the acid and base dissociation constants, respectively.
10. The pH of blood circulating in a human body is maintained around 7.4 by the action of the buffer system
    (1) CH_3COOH/CH_3COONa
    (2) NH_4Cl/NH_3
    (3) $H_2PO_4^-/HPO_4^{2-}$
    (4) CO_2/HCO_3^-

7.14 SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

The acid–base equilibria discussed in the previous sections are homogeneous equilibria, that is, the equilibria of reactions that occur in a single phase. Another important type of solution equilibrium involves the dissolution and precipitation of slightly soluble substances. These processes are examples of heterogeneous equilibria, that is, they pertain to reactions that occur in more than one phase.

Precipitation reactions are characterized by the formation of an insoluble product called precipitate. A precipitate is an insoluble solid that separates from the solution. For example, when an aqueous solution of lead nitrate [$Pb(NO_3)_2$] is added to sodium iodide (NaI), a yellow precipitate, lead iodide (PbI_2), is formed:

$$Pb(NO_3)_2(aq.) + 2NaI(aq.) \longrightarrow PbI_2(s) + 2NaNO_3(aq.)$$

In order to predict whether a precipitate will be formed when two solutions are mixed or when a compound is added to a solution, we need to know the *solubility*, that is, the maximum amount of solute that can be dissolved in a given quantity of solvent at a specific temperature.

All ionic compounds are strong electrolytes, but they are not equally soluble. We classify ionic compounds (on the basis of their solubility) as (i) soluble, (ii) slightly soluble, and (iii) sparingly soluble or insoluble:

Category	**Solubility**
Soluble	> 0.1 M
Slightly soluble	> 0.01 M but < 0.1 M
Sparingly soluble	< 0.01 M

The solubility of ionic solids in water varies a great deal. Some of these such as $CaCl_2$ (calcium chloride) are so soluble that they are *hygroscopic* in nature, that is, tend to absorb moisture (water vapor) even from the atmosphere. Others like LiF (lithium fluoride) have so little solubility that they are commonly termed as insoluble.

The solubility of salt (an ionic compound) depends on a number of factors but the most important ones are (i) the lattice enthalpy of salt and (ii) the solution enthalpy of ions of salt. For the dissolution of a salt in a given solvent, the strong attractive forces between the ions (lattice enthalpy) of salt must be overcome by the ion–solvent interactions (solution enthalpy). Since energy is released in the process of solution, the salt will dissolve if the solution enthalpy of the ions is greater than the lattice enthalpy of the salt.

The amount of solvation enthalpy depends on the nature of the solvent. In case of a nonpolar (covalent) solvent, the solvation enthalpy of ions is very small and, hence, not sufficient to overcome the lattice enthalpy of the salt. Consequently, the salt does not dissolve in nonpolar solvent.

For a salt to be able to dissolve in a particular solvent, its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by the former.

Precipitation reactions are important in industry, medicine, and everyday life. For example, the preparation of many essential industrial chemicals such as Na_2CO_3 (sodium carbonate) makes use of precipitation reactions (Solvay process). The dissolving of tooth enamel, which is mainly made of hydroxyapatite $[Ca_5(PO_4)_3OH]$, in an acidic medium, leads to tooth decay. Barium sulphate ($BaSO_4$), an insoluble compound that is opaque to X rays, is used to diagnose the ailments of the digestive tract. Stalactites and stalagmites, which consist of calcium carbonate ($CaCO_3$), are produced by a precipitation reaction, and so are many foods such as fudge.

7.14.1 Solubility Product Constant

Suppose we add 1g of solid barium sulphate ($BaSO_4$) to 1.0 L of water at 25°C and stir until the solution is saturated. Careful measurements of conductivity show that 1 L of a saturated solution of barium sulphate contains only 0.0025 g of $BaSO_4$, no matter how much more $BaSO_4$ is added.

Let us consider a saturated aqueous solution of barium sulphate that is in contact with insoluble solid barium sulphate. The solubility equilibrium between the undissolved solid and the ions in a saturated solution can be represented by the equation:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq.) + SO_4^{2-}(aq.)$$

Because salts such as $BaSO_4$ are treated as strong electrolytes, all the $BaSO_4$ that dissolves in water is assumed to be completely dissociated into its constituent ions. Applying the law of mass action, we can write down the equilibrium constant expression as

$$K_{eq} = \frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]}$$

The active mass of the pure solid $BaSO_4$ is constant. Hence, its value is incorporated in the equilibrium constant to give a new equilibrium constant called solubility product constant:

$$K_{eq}[BaSO_4] = K_{sp} = [Ba^{2+}][SO_4^{2-}] \tag{7.76}$$

where K_{sp} is called the *solubility product constant* or simply the solubility product. Note that the active mass of the solid is not included in the modified equilibrium constant expression.

TIn equilibria that involve slightly soluble compounds in water, the equilibrium constant is called the solubility product constant, K_{sp}.

In aqueous solution, the active mass of solute is numerically equal to its molar concentration. Thus, we can write the Eq. (7.76) as

$$K_{sp} = C_{Ba^{2+}} C_{SO_4^{2-}} \tag{7.77}$$

The right-hand side expression of Eq. (7.77) is called *ionic product* (the product of the concentrations of constituent ions) of the dissolved salt. Thus, we can say that the solubility product of $BaSO_4$ is the product of the concentrations of its constituent ions (ionic product) in a saturated solution.

In general, the solubility product of a compound (such as a salt) is the product of the molar concentrations of its constituent ions (in saturated solution), each raised to the power that corresponds to the number of ions in one formula unit of the compound.

Being an equilibrium constant, the value of solubility product (K_{sp}) is constant at constant temperature for a saturated solution of the compound. This statement is the *solubility product principle*.

Because each $BaSO_4$ unit contains only one Ba^{2+} ion and one SO_4^{2-} ion, its solubility product expression is particularly simple to write. A salt may on dissociation give two or more than two cations and anions carrying different charges. The following cases are relatively more complex:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq.) + 2F^-(aq.)$$

$$K_{sp} = C_{Ca^{2+}} C_{F^-}^2$$

$$(Zn)_3(PO_4)_2(s) \rightleftharpoons 3Zn^{2+}(aq.) + 2PO_4^{3-}(aq.)$$

$$K_{sp} = C_{Zn^{2+}}^3 C_{PO_4^{3-}}^2$$

One of the applications of the knowledge of solubility product expression is to calculate molar solubility as well as the solubility of the salt. The value of K_{sp} indicates how soluble an ionic compound is in water. For compounds having similar formulas, the larger the K_{sp}, the more soluble the compound.

The molar solubility of a compound is the number of moles of compound in one liter of a saturated solution (mol L^{-1}) while solubility is the number of grams of compound in one liter of a saturated solution (g L^{-1}). Note that K_{sp}, molar solubility, and solubility all refer to the concentration of saturated solutions at some given temperature (usually 25°C).

Let us assume that the molar solubility of $BaSO_4$ is S (mol L^{-1}). Then according to the solubility expression, the equilibrium concentrations of the two constituent ions will be equal to the molar solubility of the barium sulphate.

$$BaSO_4(s) \rightleftharpoons \underset{S}{Ba^{2+}(aq.)} + \underset{S}{SO_4^{2-}(aq.)}$$

$$\begin{aligned} K_{sp} &= C_{Ba^{2+}}C_{SO_4^{2-}} \\ &= (S)\,(S) \\ &= S^2 \end{aligned}$$

or $$S = \sqrt{K_{sp}}$$

This relationship between molar solubility and solubility product is equally valid for any 1:1 compound (that is, a compound furnishing one cation and one anion). If we compare K_{sp} value for two 1:1 compounds, for example, AgCl and $BaSO_4$, the compound with the larger K_{sp} value has higer molar solubility. The same is true for any two compounds that have the same ion ratio.

Consider a salt like zirconium sulphate of formula $(Zr^{4+})_3(PO_4^{3-})_4$. It dissociates into 3 zirconium cations of charge 4+ and 4 phosphate anions of charge 3–. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that

$$C_{Zr^{4+}} = 3S \text{ and } C_{PO_4^{3-}} = 4S$$

The solubility equilibrium can be represented as

$$(Zr^{4+})_3(PO_4^{3-})_4(s) \rightleftharpoons \underset{3S}{3Zr^{4+}(aq.)} + \underset{4S}{4PO_4^{3-}(aq.)}$$

$$\begin{aligned} K_{sp} &= C^3_{Zr^{4+}}C^4_{PO_4^{3-}} \\ &= (3S)^3(4S)^4 \\ &= 3^3 4^4 S^{3+4} \\ &= (27)(256)S^7 \\ &= 6912S^7 \end{aligned}$$

or $$S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$$

A sparingly soluble solid salt of the general formula M_yX_z in equilibrium with its saturated aqueous solution may be represented as

$$M_yX_z(s) \rightleftharpoons yM^{z+}(aq.) + zX^{y-}(aq.)$$

where $y(z^+) = z(y^-)$

The solubility product expression is given as

$$K_{sp} = C^y_{M^{z+}}C^z_{X^{y-}}$$

Assuming S to be the molar solubility of the salt, we can write

$$\begin{aligned} K_{sp} &= (yS)^y\,(zS)^z \\ &= y^y \cdot z^z \cdot S^{(y+z)} \qquad (7.78) \end{aligned}$$

or $$S^{(y+z)} = K_{sp}/y^y \cdot z^z$$

$$S = (K_{sp}/y^y \cdot z^z)^{1/y+z} \qquad (7.79)$$

Equations (7.78) and (7.79) clearly show that solubility product and solubility are related to each other. If we know one, we can calculate the other, but each quantity provides different information.

> We should be able to derive the relationships. Do not memorize them.

Following the procedure in Section 7.6, we use Q, called the ionic product, to represent the product of the molar concentration of the ions raised to the power of their stoichiometric coefficients. Thus, for an aqueous solution containing Ba^{2+} and SO_4^{2-} ions at 25°C,

$$Q = [Ba^{2+}]_0[SO_4^{2-}]_0$$

The subscript 0 reminds us that these are initial concentrations and do not necessarily correspond to those at equilibrium.

For an ionic compound in aqueous solution, any one of the following conditions may exist: (i) the solution is unsaturated, (ii) the solution is saturated, or (iii) the solution is supersaturated. These conditions may be described in terms of the three possible relationships between ionic product (Q) and solubility product (K_{sp}):

1. If $Q < K_{sp}$, the solution is unsaturated. Forward process, i.e., the process of dissolution is favored. No precipitation occurs. If solid is present, more solid can dissolve.
2. If $Q = K_{sp}$, the solution is just saturated. Solid and solution are in dynamic equilibrium. Neither forward nor reverse process is favored.
3. If $Q > K_{sp}$, the solution is supersaturated. Reverse process, i.e., the process of precipitation is favored. Solid will precipitate out until the product of the ionic concentrations is equal to K_{sp}.

> A precipitation reaction takes place whenever the ionic product just exceeds the solubility product.

7.14.2 Common Ion Effect on Solubility of Ionic Salts

The common ion effect applies to solubility equilibria just as it does to other ionic equilibria. The solubility of a compound is less in a solution that contains an ion common to the compound than it is in pure water (as long as no other reaction is caused by the presence of the common ion).

The solubility product is basically an equilibrium constant. The precipitation of an ionic compound from solution occurs whenever the ionic product (Q) just exceeds K_{sp} for that substance. Let us consider a saturated solution of silver chloride. The ionic product $C_{Ag^+}C_{Cl^-}$ is equal to K_{sp}. Furthermore, $C_{Ag^+} = C_{Cl^-}$, in accordance with the simple stoichiometry:

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

But this equality does not hold in all situations.

If solid $AgNO_3$ is added to a saturated AgCl solution, in addition to the dissociation of AgCl, the following process also contributes to the total concentration of the common silver ions in solution:

$$AgNO_3(s) \xrightarrow{H_2O} Ag^+(aq.) + NO_3^-(aq.)$$

The increase in C_{Ag^+} will make the ionic product greater than the solubility product:

$$Q > K_{sp}$$

To reestablish equilibrium, a net reaction happens in the backward direction and some solid AgCl precipitates out as predicted by Le Chatelier's principle. Precipitation continues until the ionic product is once again equal to K_{sp}. Thus, the effect of adding a common ion is a decrease in the solubility of the salt (AgCl) in solution. Note that in this case, C_{Ag^+} is no longer equal to C_{Cl^-} at equilibrium, rather $C_{Ag^+} > C_{Cl^-}$.

> As expected from Le Chatelier's principle, when we increase the concentration of any one of the ions, it combines with the ion of opposite charge and some of the salt gets precipitated till once again $Q = K_{sp}$.

This is equally applicable to saturated aqueous solution of soluble salts such as NaCl (which have very large K_{sp}) except that due to large concentrations of the constituent ions (Na^+ and Cl^-), we need to use active masses (or activities) instead of molarities in the expression for K_{sp}.

Let us consider a saturated aqueous solution of NaCl:

$$NaCl(s) \rightleftharpoons Na^+(aq.) + Cl^-(aq.)$$

$$K_{sp} = [Na^+][Cl^-] = Q$$

When we pass HCl gas through it, hydrochloric acid [HCl(aq.)] is formed which ionizes completely to furnish Cl^- ions. This increases the concentration (activity) of chloride ions. As a result, Q (ionic product) increases but K_{sp} (which depends only on temperature) remains unchanged:

$$Q > K_{sp}$$

Thus, the equilibrium shifts to the left (to consume some of the added Cl^- ions) and some solid NaCl is precipitated until the ionic product is once again equal to K_{sp}. Sodium chloride so obtained is of very high purity. This technique called *salting out* is used to get rid of impurities like sodium and magnesium sulphates from a sample of impure NaCl.

A precipitate dissolves when the concentration of one of the constituent ions in solution is decreased, that is, when $Q < K_{sp}$. The precipitate (insoluble salt) continues to dissolve until $Q = K_{sp}$. For example, a precipitate of AgCl dissolves in liquid NH_3 (or aqueous NH_3). The NH_3 (a Lewis base) combines with Ag^+ ions (Lewis acid) in the saturated solution of AgCl. This results in the formation of a complex ion $[Ag(NH_3)_2]^+$ and a decrease in the concentration of Ag^+ ion. This results in $Q < K_{sp}$, hence, the equilibrium shifts to the right and the precipitate of AgCl(s) dissolves:

$$\begin{array}{ll} & AgCl(s) \rightleftharpoons Ag^+(aq.) + Cl^-(aq.) \\ & \underline{Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons [Ag(NH_3)_2]^+(aq.)} \\ \text{Overall reaction} & AgCl(s) + 2NH_3(aq.) \rightleftharpoons [Ag(NH_3)_2]^+(aq.) \end{array}$$

The solubilities of many compounds also depend on the pH of the solution. Consider the solubility equilibrium of magnesium hydroxide:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq.) + 2OH^-(aq.)$$

Increasing the pH (by adding OH^- ions) shifts the equilibrium from right to left, thereby decreasing the solubility of $Mg(OH)_2$—another example of the common ion effect. On the other hand, decreasing the pH (by adding H^+ ions) shifts the equilibrium from left to right (as H^+ ions react with OH^- ions to from the weak electrolyte H_2O). This increases the solubility of $Mg(OH)_2$. Thus, insoluble bases tend to dissolve in acidic solutions. Similarly, we can understand why insoluble acids dissolve in basic solutions.

The pH also influences the solubility of salts that contain a basic anion. For example, the solubility of salts of weak acids such as fluorides and phosphates increases with the decrease of pH (adding H^+ ions). This is because in adding H^+ ions (decreasing the pH), the concentration of the anion decreases due to the formation of weak acid. This makes $Q < K_{sp}$ and the equilibrium shifts to the right causing an increase in the solubility of the salt. Finally, $Q = K_{sp}$. For example, the solubility equilibrium for BaF_2 is

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq.) + 2F^-(aq.)$$

and $K_{sp} = [Ba^{2+}][F^-]^2$

In an acidic medium, the high $[H^+]$ shifts the following equilibrium (HF is a weak acid) from left to right:

$$H^+(aq.) + F^-(aq.) \rightleftharpoons HF(aq.)$$

As $[F^-]$ decreases, $[Ba^{2+}]$ must increase to maintain equilibrium condition. Thus, more BaF_2 dissolves. Note that the solubilities of salts containing anions that do not hydrolyze (for example, Cl^-, Br^-, and I^-) are unaffected by pH. Let us reconsider the above case. Two equilibria are involved:

$$MX(s) \rightleftharpoons M^+(aq.) + X^-(aq.)$$

$$K_{sp} = [M^+]\,[X^-]$$

$$HX(aq.) \rightleftharpoons H^+(aq.) + X^-(aq.)$$

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

Rearranging,

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

Taking the inverse of both sides and adding, we get

$$\frac{[HX]}{[X^-]} + 1 = \frac{[H^+]}{K_a} + 1$$

or

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

Again taking the inverse, we get

$$\frac{[X^-]}{[HX] + [X^-]} = F = \frac{K_a}{[H^+] + K_a}$$

We can see that F decreases as the pH decreases (by adding $[H^+]$). If S is the molar solubility of the salt at a given pH, then

$$K_{sp} = [S]\,[FS]$$

$$= S^2 f$$

$$= S^2\left(\frac{K_a}{[H^+] + K_a}\right)$$

or $$S = \left[K_{sp}\left(\frac{[H^+] + K_a}{K_a}\right)\right]^{1/2} \qquad (7.80)$$

Thus, solubility S increases with decrease in pH (by adding H^+ ions).

Follow-up Test 14

1. Which of the following is the correct representation of the solubility product expression for mercurous iodide (Hg_2I_2)?
   (1) $[Hg_2^{2+}][I^-]^2$
   (2) $[Hg^+]^2\,[I^-]^2$
   (3) $[Hg^+]\,[I^-]$
   (4) $[Hg^{2+}]\,[I^-]^2$
2. The units of solubility product of silver chromate ($AgCrO_4$) will be
   (1) $mol^2\ L^{-2}$
   (2) $mol^3\ L^{-3}$
   (3) $mol\ L^{-1}$
   (3) $mol^{-1}\ L$
3. Which of the following quantities refers to a saturated solution?
   (1) Molar solubility
   (2) Solubility
   (3) Solubility product
   (4) All of these
4. At a certain temperature, the solubility of the salt A_xB_y is S moles per liter. The general expression for the solubility product will be
   (1) $K_{sp} = X^yY^xS^{x+y}$
   (2) $K_{sp} = (XY)^{x+y}S^{x+y}$
   (3) $K_{sp} = (X^xY^y)S^{x+y}$
   (4) $K_{sp} = X^yY^xS^{xy}$
5. The molar solubility of silver sulphate is 1.5×10^{-2} mol L^{-1}. The solubility product of the salt will be
   (1) 2.25×10^{-4}
   (2) 1.4×10^{-5}
   (3) 1.7×10^{-6}
   (4) 3.0×10^{-3}
6. Which of the following metal sulphide solutions will have the maximum concentration of cation?
   (1) MnS ($K_{sp} = 6.0 \times 10^{-16}$)
   (2) FeS ($K_{sp} = 1.1 \times 10^{-19}$)
   (3) ZnS ($K_{sp} = 1.2 \times 10^{-21}$)
   (4) CdS ($K_{sp} = 3.5 \times 10^{-29}$)
7. The ionic product of an ionic solid
   (1) can be equal to or less than K_{sp}
   (2) is always equal to K_{sp}
   (3) is always less than K_{sp}
   (4) can be less than, equal to, or greater than K_{sp}
8. The pH of an aqueous solution of $Ba(OH)_2$ is 10.0. If the K_{sp} of $Ba(OH)_2$ is 1.0×10^{-9}, the concentration of Ba^{2+} ions in the solution is
   (1) 1.0×10^{-5} M
   (2) 1.0×10^{-1} M
   (3) 1.0×10^{-4} M
   (4) 1.0×10^{-2} M
9. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed:
   (1) 10^{-3} M Ca^{2+} + 10^{-5} M F^-
   (2) 10^{-5} M Ca^{2+} + 10^{-3} M F^-
   (3) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
   (4) 10^{-4} M Ca^{2+} + 10^{-4} M F^-
10. If S_0, S_1, S_2, and S_3 are the solubilities of AgCl in water, 0.01 M $CaCl_2$, 0.01 M NaCl, and 0.5 M $AgNO_3$ solutions, respectively, then which of the following is true?
    (1) $S_0 > S_2 > S_1 > S_3$
    (2) $S_0 = S_2 = S_1 = S_3$
    (3) $S_3 > S_1 > S_2 > S_0$
    (4) $S_0 > S_2 > S_3 > S_1$
11. The solubility of calcium sulphate is 0.67 g L^{-1}. The value of K_{sp} for calcium sulphate will be
    (1) 1.7×10^{-6}
    (2) 3.5×10^{-4}
    (3) 2.4×10^{-5}
    (4) 9.3×10^{-8}
12. Given K_{sp}(AgI) = 8.5×10^{-17}. The solubility of AgI in 0.1M KI solution is
    (1) 0.1 M
    (2) 8.5×10^{-16} M
    (3) 8.5×10^{-17} M
    (4) 8.5×10^{-18} M

QUESTION BANK
(BUILDING THE KNOWLEDGE)

Level – I

1. For the reaction
   $$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$$
   if we write $K_p = K_c(RT)^x$, then x becomes
   (1) –1/2
   (2) –1
   (3) 1/2
   (4) 1
2. At 90°C, pure water has $[H_3O^+]$ as 10^{-6} mol L^{-1}. What is the value of K_w at 90°C?
   (1) 10^{-14}
   (2) 10^{-6}
   (3) 10^{-12}
   (4) 10^{-8}
3. In which of the following equilibrium, does the change in the volume of the system not alter the number of moles?
   (1) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$
   (2) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (3) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
   (4) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
4. What is the equilibrium expression for the reaction
   $$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$$
   (1) $K_{eq} = [O_2]^5$
   (2) $K_{eq} = \frac{1}{5}\frac{[P_4O_{10}]}{[P_4][O_2]}$
   (3) $K_{eq} = \frac{1}{[O_2]^5}$
   (4) $K_{eq} = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$

Level – II

5. Which of following reactions carried out in closed vessels are reversible?
   (i) $2KClO_3 \longrightarrow 2KCl + O_2$
   (ii) $N_2 + O_2 \longrightarrow 2NO$
   (iii) $PCl_5 \longrightarrow PCl_3 + Cl_2$
   (iv) $Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$

(1) (i), (ii), (iii), (iv) (2) (ii), (iii), (iv)
(3) (i), (ii), (iii) (4) (i), (iii), (iv)

6. Which of the following is not the characteristic of chemical equilibrium?
   (1) At equilibrium, the concentration of each of the reactants and the products becomes constant.
   (2) At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction, and hence, the equilibrium is dynamic in nature.
   (3) A chemical equilibrium can be established only if none of the products is allowed to escape out or separate out as a solid.
   (4) Chemical equilibrium for the reversible reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ can be attained from forward direction only.

7. How many liters of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?
   (1) 0.9 L (2) 2.0 L
   (3) 9.0 L (4) 0.1 L

8. The K_{sp} of $AgCrO_4$ is 1.1×10^{-12} at 298 K. The solubility (in mol L^{-1}) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is
   (1) 1.1×10^{-10} (2) 1.1×10^{-11}
   (3) 1.1×10^{-12} (4) 1.1×10^{-9}

9. Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$)
   (1) 8.1×10^{-7} M (2) 8.1×10^{-5} M
   (3) 5.1×10^{-5} M (4) 4.1×10^{-5} M

10. In the case of gaseous homogeneous reaction, the active mass of the reactant is obtained by the expression
   (1) $\frac{n}{v}RT$ (2) $\frac{P}{RT}$
   (3) $\frac{RT}{P}$ (4) $\frac{PV}{RT}$

11. For the following three reactions, (A), (B) and (C), equilibrium constants are given:
   (A) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$
   (B) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$
   (C) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$
   Which of the following relations is correct?
   (1) $K_2K_3 = K_1$ (2) $K_1\sqrt{K_2} = K_3$
   (3) $K_3 = K_1K_2$ (4) $K_2K_3 = K_1$

12. Phosphorous pentachloride dissociates as follows (in a closed reaction vessel):
   $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
   If the total pressure at equilibrium of the reaction mixture is P and the degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be
   (1) $\left(\frac{x}{x+1}\right)P$ (2) $\left(\frac{x}{1-x}\right)P$
   (3) $\left(\frac{2x}{1-x}\right)P$ (4) $\left(\frac{x}{x-1}\right)P$

13. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is
   (1) 10 (2) 8
   (3) 9 (4) 7

14. For the reaction
   $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
   K_p/K_c is equal to
   (1) 1.0 (2) RT
   (3) $\sqrt{RT}$ (4) $1/RT$

15. Which of the following acids has the smallest dissociation constant?
   (1) $BrCH_2CH_2COOH$ (2) $CH_3CHBrCOOH$
   (3) FCH_2CH_2COOH (4) $CH_3CHFCOOH$

16. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25°C) is
   (1) $Ba(OH)_2$ (2) $Mg(OH)_2$
   (3) $Be(OH)_2$ (4) $Ca(OH)_2$

Level – III

17. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1 M) is 1/100th of that of a strong acid (HX, 1 M) at 25°C. The K_a of HA is
   (1) 1×10^{-3} (2) 1×10^{-4}
   (3) 1×10^{-5} (4) 1×10^{-6}

18. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions
   $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
   For this equilibrium, the correct statements are
   (i) K is dependent on the pressure of CO_2 at a given T.
   (ii) ΔH is dependent on T.
   (iii) ΔH is independent of the catalyst, if any.
   (iv) K is independent of the initial amount of $CaCO_3$.
   (1) (i), (ii), (iii), (iv) (2) (i), (ii), (iii)
   (3) (ii), (iii), (iv) (4) (i), (ii), (iv)

19. Which of the following will decrease the pH of a 50 ml solution of 0.01 M HCl?
   (1) Addition of Mg
   (2) Addition of 50 ml 0.002 M HCl
   (3) Addition of 50 ml 0.01 M HCl
   (4) Addition of 5 ml 1 M HCl

20. The pK_a of weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is
   (1) 4.5 (2) 7.0
   (3) 9.5 (4) 2.5

21. The pH of 0.1 M solution of the following salts increases in the order
   (1) HCl < NaCl < NaCN < NH_4Cl
   (2) NaCN < NH_4Cl < NaCl < NaCN
   (3) HCl < NH_4Cl < NaCl < NaCN
   (4) NaCl < NH_4Cl < NaCN < HCl

Level – IV

22. Chemical equilibrium for the reaction
   $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
   can be achieved in ________ different ways.
   (1) two (2) three
   (3) four (4) just one

23. A solution of $CoCl_2 \cdot 6H_2O$ in isopropyl alcohol and water is purple. The color changes to blue when we add
    (1) concentrated HCl (2) $AgNO_3$(aq.)
    (3) both (1) and (2) (4) none of these

24. 2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)
    (1) 2.7×10^{-2} M (2) 3.2×10^{-2} M
    (3) 3.2×10^{-7} M (4) 2.7×10^{-13} M

25. Solubility product constants (K_{sp}) of salts of types MX, MX_2, and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14}, and 2.7×10^{-15}, respectively. The solubility (mol dm^{-3}) of the salts of temperature T is in the order
    (1) $MX_2 > M_3X > MX$ (2) $M_3X > MX_2 > MX$
    (3) $MX > M_3X > MX_2$ (4) $MX > MX_2 > M_3X$

26. 0.1 mol of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mol of HCl and diluted to one liter. What will be the H^+ concentration in the solution?
    (1) 8×10^{-11} M (2) 8×10^{-2} M
    (3) 1.6×10^{-11} M (4) 8×10^{-5} M

ARCHIVES

1. Identify the correct order of solubility in aqueous medium: **(NEET–UG 2013)**
    (1) $ZnS > Na_2S > CuS$ (2) $Na_2S > CuS > ZnS$
    (3) $Na_2S > ZnS > CuS$ (4) $CuS > ZnS > Na_2S$

2. Which of these is the least likely to act as a Lewis base? **(NEET–UG 2013)**
    (1) F^- (2) BF_3
    (3) PF_3 (4) CO

3. Which is the strongest acid in the following? **(NEET–UG 2013)**
    (1) $HClO_3$ (2) $HClO_4$
    (3) H_2SO_3 (4) H_2SO_4

4. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10}, respectively. The equilibrium constant for the following equilibrium is
    $CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ **(AIPMT 2009)**
    (1) 3.0×10^{-5} (2) 3.0×10^{-4}
    (3) 3.0×10^{4} (4) 3.0×10^{5}

5. What is the $[OH^-]$ in the final solution prepared by mixing 20.0 ml of 0.050 M HCl with 30.0 ml of 0.10 M $Ba(OH)_2$? **(AIPMT 2009)**
    (1) 0.40 M (2) 0.050 M
    (3) 0.12 M (4) 0.10 M

6. The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. The hydrolysis constant of ammonium chloride is
    (1) 6.50×10^{-12} (2) 5.65×10^{-13}
    (3) 5.65×10^{-12} (4) 5.65×10^{-10}

7. Which of the following molecules acts as a Lewis acid? **(AIPMT 2009)**
    (1) $(CH_3)_2O$ (2) $(CH_3)_3P$
    (3) $(CH_3)_3N$ (4) $(CH_3)_3B$

8. Equimolar concentrations of H_2 and I_2 are heated to equilibrium in a 2 L flask. At equilibrium, the forward and backward rate constants are found to be equal. What percentage of initial concentration of H_2 has reached at equilibrium? **(Kerala PMT 2008)**
    (1) 33% (2) 66%
    (3) 50% (4) 40%
    (5) 20%

9. The number of H^+ ions present in 250 ml of lemon juice of pH = 3 is **(Kerala PMT 2008)**
    (1) 1.506×10^{22} (2) 1.506×10^{23}
    (3) 1.506×10^{20} (4) 3.012×10^{21}
    (5) 2.008×10^{23}

10. The values of K_{P_1} and K_{P_2} for the reactions
    $X \rightleftharpoons Y + Z$ (a)
    and $A \rightleftharpoons 2B$ (b)
    are in the ratio of 9 : 1. If the degree of dissociation of X and A is equal, then the total pressure at equilibriums (a) and (b) is in the ratio **(AIPMT 2008)**
    (1) 3 : 1 (2) 1 : 9
    (3) 36 : 1 (4) 1 : 1

11. The dissociation equilibrium of a gas AB_2 can be represented as
    $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$
    The degree of dissociation is 'x' and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_P and total pressure P is **(AIPMT 2008)**
    (1) $(2K_P/P)$ (2) $(2K_P/P)^{1/3}$
    (3) $(2K_P/P)^{1/2}$ (4) (K_P/P)

12. If the concentration of OH^- ions in the reaction
    $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq.) + 3OH^-(aq.)$
    is decreased by 1/4 times, then the equilibrium concentration of Fe^{3+} will increase by **(AIPMT 2008)**
    (1) 8 times (2) 16 times
    (3) 64 times (4) 4 times

13. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH? **(AIPMT 2008)**
    (1) $SrCl_2$ (2) $BaCl_2$
    (3) $MgCl_2$ (4) $CaCl_2$

14. Equal volumes of three acid solutions of pH 3, 4, and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture? **(AIPMT 2008)**

(1) 1.11×10^{-4} M (2) 3.7×10^{-4} M
(3) 3.7×10^{-3} M (4) 1.11×10^{-3} M

15. The equilibrium constant (K_p) for the decomposition of gaseous H_2O

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$$

is related to the degree of dissociation α at a total pressure P by **(Kerala PMT 2007)**

(1) $K_p = \dfrac{\alpha^3 P^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$

(2) $K_p = \dfrac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(3) $K_p = \dfrac{\alpha^{3/2} P^{2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(4) $K_p = \dfrac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(5) $K_p = \dfrac{\alpha^2 P}{\sqrt{2}}$

16. The aqueous solutions of HCOONa, $C_6H_5NH_3Cl$, and KCN are, respectively, **(Kerala PMT 2007)**
(1) acidic, acidic, basic
(2) acidic, basic, neutral
(3) basic, neutral, neutral
(4) basic, acidic, basic
(5) basic, neutral, basic

17. Which one of the following ionic species has the greatest proton affinity to form stable compound? **(AIPMT 2007)**
(1) I^- (2) HS^-
(3) NH_2^- (4) F^-

18. A weak acid, HA, has a K_a of 1.00×10^{-5}. If 0.100 mol of the acid is dissolved in 1 L of water, the percentage of the acid dissociated at equilibrium is the closest to **(AIPMT 2007)**
(1) 0.100% (2) 99.0%
(3) 1.00% (4) 99.9%

19. Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, i.e., H_3O^+. **(AIPMT 2007)**
(1) 1.000 (2) 7.000
(3) 4.000 (4) 9.000

20. When hydrogen molecules decompose into its atoms, which conditions give the maximum yield of hydrogen atoms? **(UP CPMT 2006)**
(1) High temperature and low pressure
(2) Low temperature and high pressure
(3) High temperature and high pressure
(4) Low temperature and low pressure

21. For the reaction

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$$
$$\Delta_r H = -170.8 \text{ kJ mol}^{-1}$$

Which of the following statements is not true? **(AIPMT 2006)**
(1) Addition of $CH_4(g)$ or $O_2(g)$ at equilibrium will cause a shift to the right.
(2) The reaction is exothermic.
(3) At equilibrium, the concentrations of $CO_2(g)$ and H_2O are not equal.
(4) The equilibrium constant for the reaction is given by $K_p = \dfrac{[CO_2]}{[CH_4][O_2]}$

22. Choose the correct order arranged in decreasing order of basicity: **(AMU MED. 2006)**
(1) $CH \equiv C^- > CH_3O^- > OH^-$
(2) $OH^- > CH_3O^- > CH \equiv C^-$
(3) $CH_3O^- > OH^- > CH \equiv C^-$
(4) $CH_3O^- > CH \equiv C^- > OH^-$

23. If at a given temperature, $pK_w = 13.68$, then pH is **(AMU MED. 2006)**
(1) 6.84 (2) 7
(3) 6.79 (4) none of these

24. Which of the following is not a Lewis acid? **(UP CPMT 2006)**
(1) $AlCl_3 \cdot 6H_2O$ (2) $AlCl_3$
(3) $SnCl_4$ (4) $FeCl_3$

25. The degree of dissociation of 0.1 N CH_3COOH is ($K_a = 1 \times 10^{-5}$) **(UP CPMT 2006)**
(1) 10^{-5} (2) 10^{-4}
(3) 10^{-3} (4) 10^{-2}

26. 40 ml of 0.1 M ammonia is mixed with 20 ml of 0.1 M HCl. What is the pH of the mixture? (pK_b of ammonia solution is 4.74.) **(AIIMS 2006)**
(1) 4.74 (2) 2.26
(3) 9.26 (4) 5.00

27. Which of the following pairs constitutes a buffer? **(AIPMT 2006)**
(1) HNO_3 and NH_4NO_3 (2) HCl and KCl
(3) HNO_2 and $NaNO_2$ (4) NaOH and NaCl

28. The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 K ($K_w = 10^{-14}$) is **(AIPMT 2006)**
(1) 9.525×10^{-8} M (2) 1.0×10^{-8} M
(3) 1.0×10^{-6} M (4) 1.0525×10^{-7} M

29. $NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
If equilibrium pressure is 3 atm for the above reaction, then K_P for the reaction is **(DPMT 2005)**
(1) 4 (2) 27
(3) 4/27 (4) 1/27

30. $A + B \rightleftharpoons C + D$
If initially the concentrations of A and B are equal but at equilibrium the concentration of D is twice that of A, then what will be the equilibrium constant of the reaction? **(BHU 2005)**

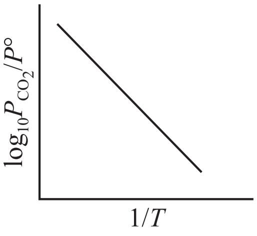
(1) 4/9 (2) 9/4
(3) 1/9 (4) 4

31. For the chemical equilibrium

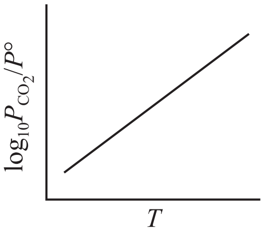
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

ΔH^o_r can be determined from which of the following plots? **(AIIMS 2005)**

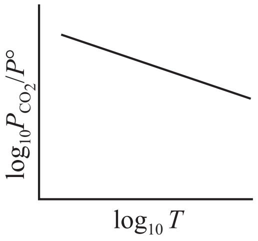
(1)



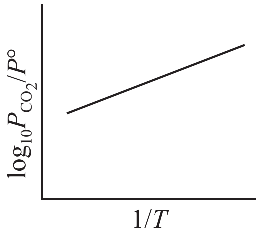
(2)



(3)



(4)



32. The equilibrium constants K_1 and K_2 for the following equilibria **(AIPMT 2005)**

$$NO(g) + \frac{1}{2}O_2(g) \xrightleftharpoons{K_1} NO_2(g)$$

$$2NO_2(g) \xrightleftharpoons{K_2} 2NO(g) + O_2(g)$$

are related as

(1) $K_2 = 1/K_1$ (2) $K_2 = K_1/2$
(3) $K_2 = 1/K_1^2$ (4) $K_2 = K_1^2$

33. Which of the following anions is the weakest base? **(Manipal PMT 2005)**

(1) $C_2H_5O^-$ (2) CN^-
(3) CH_3COO^- (4) NO_3^-

34. A solution has pH = 5. It is diluted 100 times. It will become **(AFMC 2005)**

(1) neutral (2) basic
(3) unaffected (4) more acidic

35. The K_{sp} of $Mg(OH)_2$ is 1×10^{-12}. 0.01 M Mg^{2+} will precipitate at the limiting pH of **(DPMT 2005)**

1. 3 (2) 9
3. 5 (4) 8

36. At 25°C, the dissociation constant of a base. BOH is 1.0×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be **(AIPMT 2005)**

(1) 1.0×10^{-6} mol L^{-1} (2) 1.0×10^{-7} mol L^{-1}
(3) 2.0×10^{-6} mol L^{-1} (4) 1.0×10^{-5} mol L^{-1}

37. When 10 ml of 0.1 M acetic acid ($pK_a = 5.0$) is titrated against 10 ml of 0.1 M ammonia solution ($pK_b = 5.0$), the equivalence point occurs at **(AIIMS 2005)**

(1) 5.0 (2) 6.0
(3) 7.0 (4) 9.0

38. H_2S gas when passed through a solution of cations containing HCl precipitates the cations of the second group of qualitative analysis but not those belonging to the fourth group. It is because the **(AIPMT 2005)**

(1) presence of HCl decreases the sulphide ion concentration
(2) sulphides of group IV are unstable in HCl
(3) solubility product of group II sulphides is more than that of group IV sulphides
(4) presence of HCl increases the sulphide ion concentration

39. The correct order of acid strength is **(AIPMT 2005)**

(1) $HClO_4 < HClO_3 < HClO_2 < HClO$
(2) $HClO_2 < HClO_3 < HClO_4 < HClO$
(3) $HClO_4 < HClO < HClO_2 < HClO_3$
(4) $HClO < HClO_2 < HClO_3 < HClO_4$

40. What is the correct relationship between the pH of isomolar solutions of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3), and sodium telluride (pH_4)? **(AIPMT 2005)**

(1) $pH_1 < pH_2 < pH_3 < pH_4$
(2) $pH_1 > pH_2 > pH_3 > pH_4$
(3) $pH_1 < pH_2 < pH_3 \approx pH_4$
(4) $pH_1 > pH_2 \approx pH_3 > pH_4$

41. 2 mol of N_2 is mixed with 6 mol of H_2 in a closed vessel of 1 L capacity. If 50% of N_2 is converted into NH_3 at equilibrium, the value of K_C for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is **(Kerala PMT 2004)**

(1) 4/27 (2) 27/4
(3) 1/27 (4) 27
(5) 9

42. Ammonium carbonate when heated to 200°C gives a mixture of NH_3 and CO_2 vapors with a density of 13.0. What is the degree of dissociation of ammonium carbonate? **(Kerala PMT 2004)**

(1) 3/2 (2) 1/2
(3) 2 (4) 1
(5) 5/2

43. A mixture of NO_2 and N_2O_4 has a vapor density of 38.3 at 300 K. What is the number of moles of NO_2 in 100 g of the mixture? **(Kerala PMT 2004)**

(1) 0.043 (2) 4.4
(3) 3.4 (4) 3.86
(5) 0.437

44. Of the following, which change will shift the reaction towards the product?

$I_2(g) \rightleftharpoons 2I(g)$; ΔH^o_r (298 K) = +150 J **(AIIMS 2004)**

(1) Increase in concentration of I
(2) Decrease in concentration of I_2
(3) Increase in temperature
(4) Increase in total pressure

45. What will be the pH of 0.05 M barium hydroxide solution? **(UP CPMT 2004)**

(1) 8 (2) 9
(3) 7 (4) 13

46. The only cations present in a slightly acidic solution are Fe^{3+}, Zn^{2+}, and Cu^{2+}. The reagent that when added in excess to this solution would identify and separate Fe^{3+} ions in one step is **(UP CPMT 2004)**

(1) 2 M HCl (2) 6 M NH_3
(3) 6 M NaOH (4) H_2S gas

47. The principal buffer present in human blood is **(Kerala PMT 2004)**

(1) $NaH_2PO_4 + Na_2HPO_4$
(2) $H_3PO_4 + NaH_2PO_4$
(3) $CH_3COOH + CH_3COONa$
4 $Na_2HPO_4 + Na_3PO_4$
(5) $H_2CO_3 + HCO_3^-$

48. 40 mg of pure sodium hydroxide is dissolved in 10 L of distilled water. The pH of the solution is **(Kerala PMT 2004)**

(1) 9.0 (2) 10
(3) 11 (4) 12
(5) 8

49. The rapid change of pH near the stoichiometric point of an acid–base titration is the basis of indicator detection. pH of the solution is related to the ratio of concentration of conjugate acid (HIn) to the concentration of base (In^-) forms of the indicator by the expression **(AIPMT 2004)**

(1) $\log \dfrac{[In^-]}{[HIn]} = pK_{In} - pH$

(2) $\log \dfrac{[HIn]}{[In^-]} = pK_{In} - pH$

(3) $\log \dfrac{[HIn]}{[In^-]} = pH - pK_{In}$

(4) $\log \dfrac{[In^-]}{[HIn]} = pH - pK_{In}$

50. What is the pH of 0.01 M glycine solution? For glycine, $K_{a_1} = 4.5 \times 10^{-3}$ and $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K. **(AIIMS 2004)**

(1) 3.0 (2) 10.0
(3) 6.1 (4) 7.2

51. In the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

the equilibrium concentrations of PCl_5 and PCl_3 are 0.4 and 0.2 mol^{-1}, respectively. If the value of K_c is 0.5, what is the concentration of Cl_2 in moles per liter? **(EAMCET 2003)**

(1) 2.0 (2) 1.5
(3) 1.0 (4) 0.5

52. The following equilibrium constants are given:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3; K_1$$
$$N_2 + O_2 \rightleftharpoons 2NO; K_2$$
$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O; K_3$$

The equilibrium constant for the oxidation of NH_3 by oxygen to give NO is **(AIPMT 2007, 2003)**

(1) K_1K_2/K_3 (2) $K_2K_3^3/K_1$
(3) $K_2K_3^2/K_1$ (4) $K_2^2K_3/K_1$

53. The reaction quotient (Q) for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is given by

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

The reaction will proceed from right to left if **(AIPMT 2003)**

(1) $Q = K_C$ (2) $Q < K_C$
(3) $Q > K_C$ (4) $Q = 0$

where K_C is the equilibrium constant.

54. 1 mol of N_2 and 2 mol of H_2 are allowed to react in a 1 dm^3 vessel. At equilibrium, 0.8 mol of NH_3 is formed. The concentration of H_2 in the vessel is **(Manipal 2002)**

(1) 0.6 mol (2) 0.8 mol
(3) 0.2 mol (4) 0.4 mol

55. 1 mol of hydrogen and 2 mol of iodine are taken initially in a 2 L vessel. The number of moles of hydrogen at equilibrium is 0.2. Then the number of moles of iodine and hydrogen iodide at equilibrium are **(UPCPMT 2002)**

(1) 1.2, 1.6 (2) 1.8, 1.0
(3) 0.4, 2.4 (4) 0.8, 2.0

56. The solubility of PbI_2 is 0.0013 M. Then the solubility product of PbI_2 is **(DPMT 2003)**

(1) 2.2×10^{-9} (2) 8.8×10^{-9}
(3) 6.8×10^{-6} (4) 8.8×10^{-6}

57. The solubility product of AgI at 25°C is 1.0×10^{-16} mol^2 L^{-2}. The solubility of AgI in 10^{-4} N solution of KI at 25°C is approximately (in mol L^{-1}) **(AIPMT 2003)**

(1) 1.0×10^{-16} (2) 1.0×10^{-12}
(3) 1.0×10^{-10} (4) 1.0×10^{-8}

58. At 18°C, the solubility product of AgCl is 1.8×10^{-10}. In the solution, the value of Ag^+ is 4×10^{-3} mol L^{-1}. The value of $[Cl^-]$ to precipitate AgCl from this solution should be greater than **(BHU 2003, CPMT 1991)**

(1) 4.5×10^{-8} mol L^{-1} (2) 7.2×10^{-12} mol L^{-1}
(3) 4.0×10^{-3} mol L^{-1} (4) 4.5×10^{-7} mol L^{-1}

59. The number of moles of $Ca(OH)_2$ required to prepare 250 ml of solution with pH 14 (assuming complete ionization) is **(DPMT 2003)**

(1) 0.25 (2) 1.0
(3) 0.125 (4) 10.0

60. The least soluble compound (salt) of the following is **(BHU 2003)**

(1) CsCl ($K_{sp} = 10^{-12}$)
(2) HgS ($K_{sp} = 1 \times 10^{-52}$)
(3) $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$)
(4) ZnS ($K_{sp} = 1.2 \times 10^{-23}$)

61. In which of the following acid–base titration, the pH is greater than 8 at the equivalence point? **(AIIMS 2003)**
(1) Acetic acid versus ammonia
(2) Acetic acid versus sodium hydroxide
(3) Hydrochloric acid versus ammonia
(4) Hydrochloric acid versus sodium hydroxide.

62. Which one of the following is not a buffer solution? **(AIIMS 2003)**
(1) 0.8 M H_2S + 0.8 M KHS
(2) 2 M $C_6H_5NH_2$ + 2 M $C_6H_5\overset{+}{N}H_3Br^-$
(3) 3 M H_2CO_3 + 3 M $KHCO_3$
(4) 0.05 M $KClO_4$ + 0.05 M $HClO_4$

63. A certain buffer solution contains equal concentration of X^- and HX. The K_a for HX is 10^{-8}. The pH of the buffer is **(Manipal PMT 2002)**
(1) 3 (2) 8
(3) 11 (4) 14

64. Solution of 0.1 N NH_4OH and 0.1 N NH_4Cl has pH 9.25. Then pK_b of NH_4OH is **(AIPMT 2002)**
(1) 9.25 (2) 4.75
(3) 3.75 (4) 8.25

65. The concentration of water molecules in pure water at 298 K is **(Manipal PMT 2002)**
(1) 10^{-7} M (2) 55.5 M
(2) 5.55 M (4) 7.26 M

66. A solution of an acid has pH = 4.70. Find out the concentration of OH^- ions ($pK_w = 14$). **(Rajasthan PMT 2002)**
(1) 5×10^{-10} M (2) 4×10^{-10} M
(3) 2×10^{-5} M (4) 9×10^{-10} M

67. Among the following, the weakest base is **(MP PMT 2002)**
(1) H^- (2) CH_3^-
(3) CH_3O^- (4) Cl^-

68. Which has the highest pH? **(AIPMT 2002)**
(1) CH_3COOK (2) Na_2CO_3
(3) NH_4Cl (4) $NaNO_3$

69. What is the value of K_{sp} for $PbCl_2$? **(Manipal PMT 2001)**
(1) $[Pb^{2+}]\,[2Cl^-]$ (2) $[Pb^{2+}2Cl^-]^2$
(3) $[Pb^{2+}]\,[Cl^-]^2$ (4) $[Pb^{2+}Cl^-]^2s$

ANSWER KEY

Follow-up Test 1

1. (3) 2. (4) 3. (1) 4. (4) 5. (4) 6. (2) 7. (1) 8. (2) 9. (3) 10. (1)

Follow-up Test 2

1. (3) 2. (4) 3. (3) 4. (4) 5. (2) 6. (4) 7. (1)

Follow-up Test 3

1. (4) 2. (4) 3. (3) 4. (1) 5. (2) 6. (3) 7. (3) 8. (2) 9. (3) 10. (1)
11. (3) 12. (1) 13. (4)

Follow-up Test 4

1. (2) 2. (1) 3. (4) 4. (3) 5. (2) 6. (4) 7. (1): 8. (3): 9. (4): 10. (1)

Follow-up Test 5

1. (4) 2. (4) 3. (4)

Follow-up Test 6

1. (3) 2. (1) 3. (4) 4. (2) 5. (1) 6. (3) 7. (4) 8. (1) 9. (4) 10. (2)

Follow-up Test 7

1. (4) 2. (4) 3. (1) 4. (4) 5. (3) 6. (2)

Follow-up Test 8

1. (1) 2. (4) 3. (4) 4. (3) 5. (2)

Follow-up Test 9

1. (4) 2. (4) 3. (2) 4. (1) 5. (3) 6. (4) 7. (2) 8. (4) 9. (4) 10. (4)
11. (1) 12. (3) 13. (2) 14. (*)

Follow-up Test 10

1. (1) 2. (3) 3. (2) 4. (4) 5. (2) 6. (4) 7. (1) 8. (3) 9. (2) 10. (4)
11. (3) 12. (1) 13. (2) 14. (4) 15. (3)

Follow-up Test 11

1. (1) 2. (1) 3. (2) 4. (4) 5. (3) 6. (4) 7. (2) 8. (1) 9. (2) 10. (4)
11. (2) 12. (3) 13. (1) 14. (4) 15. (3) 16. (3)

Follow-up Test 12

1. (2) 2. (4) 3. (2) 4. (4) 5. (3) 6. (1 7. (2) 8. (3) 9. (4) 10. (1)
11. (3) 12. (2) 13. (1)

Follow-up Test 13

1. (3) 2. (2) 3. (4) 4. (1) 5. (3) 6. (2) 7. (4) 8. (1) 9. (3) 10. (4)

Follow-up Test 14

1. (1) 2. (2) 3. (4) 4. (3) 5. (2) 6. (1) 7. (4) 8. (2) 9. (3) 10. (1)
11. (3) 12. (2)

Question Bank (Building the Knowledge)

1. (1) 2. (3) 3. (4) 4. (3) 5. (2) 6. (4) 7. (3) 8. (1) 9. (3) 10. (2)
11. (3) 12. (1) 13. (2) 14. (4) 15. (1) 16. (3) 17. (2) 18. (3) 19. (4) 20. (3)
21. (3) 22. (2) 23. (1) 24. (1) 25. (3) 26. (1)

Archives

1. (3) 2. (2) 3. (2) 4. (3) 5. (4) 6. (4) 7. (4) 8. (2) 9. (3): 10. (3)
11. (2) 12. (*) 13. (2) 14. (*) 15. (4) 16. (4) 17. (*) 18. (3) 19. (3) 20. (1)
21. (4) 22. (1) 23. (1) 24. (1) 25. (4) 26. (3) 27. (3) 28. (4) 29. (1) 30. (4)
31. (1) 32. (3) 33. (4) 34. (1) 35. (2) 36. (*) 37. (3) 38. (1) 39. (4) 40. (2)
41. (1) 42. (4) 43. (5) 44. (3) 45. (*) 46. (2) 47. (5) 48. (2) 49. (4) 50. (3)
51. (3) 52. (2) 53. (3) 54. (2) 55. (1) 56. (2) 57. (2) 58. (1) 59. (*) 60. (2)
61. (*) 62. (4) 63. (2) 64. (2) 65. (2) 66. (1) 67. (4) 68. (*) 69. (3)