

9 ACIDS AND BASES

The chemistry of acids and bases has remained the core of chemistry from ancient times to the modern era, and indeed, most of chemistry that was performed in laboratories in olden times was the acid-base chemistry.

When chemistry began to strengthen its theoretical side at the end of the 19th century, the first topic attacked by theoretical chemists was the acid-base chemistry. As a result of this theoretical thrust, chemistry became remarkably quantified. Hence, this chapter is very quantitative in comparison with other chapters.

In this chapter, such important concepts as hydrogen ion concentration, the ionization constant, hydrolysis, titration curves, buffer solutions, and indicators, will be discussed. These concepts are essentially the fundamentals of chemistry, and it is impossible for you to learn about chemistry and yet avoid the study of them.

9.1 Formation of the concept of acids and bases

Acids and bases are most common chemicals. It was rather recent, however, that chemists could store and use freely a variety of acid-base in the shelves of their laboratories.

The only acid known to the alchemists of the ancient age was impure acetic acid, and the bases they could use were such as crude potassium carbonate obtained from ashes of plants. In the middle age, Arabian alchemists developed methods to produce mineral acids such as hydrochloric acid or nitric acid and used these. Much the same was the case with bases. In fact, the word “alkali”, a common name of strong bases, is Arabic in origin.

In the modern age, the increase of population and the rise of living standard became gradually remarkable, and demands for various materials were increased. For instance, soap, once luxurious and expensive, became widely used. Consequently, demand for sodium carbonate, the raw material for soap, rapidly increased. Demand for clothes also increased, which caused the increase of demand for a variety of chemicals for breathing and dyeing. To satisfy these demands, it became a serious problem to supply sufficient acids and bases, especially strong acids and bases in quantity. This was the origin of chemical industry.

In the middle of the 17th century, the German chemist Johann Rudolf Glauber (1604-1670), who was based in the Netherlands, produced and sold not only a variety of acids and bases, but also many chemical apparatus. In this regard he might be called the first chemical engineer. He sold sodium sulfate as a miracle medicine and obtained a big profit.

Basic studies on acid-base started at the same time. Boyle, a contemporary of Glauber, established the method of using dyes obtained from some plants such as *Roccella* as the indicator of acid-base reaction.^{a)} In these days, it was already understood that acids and bases had opposite properties which were cancelled each other. Before the advent of modern chemistry, acids were defined as something sour, and alkalis were something which could cancel, or rather, neutralize, the effect of acids.

There had been some confusion about the nature of acids. Oxygen had been regarded as the essential constituent of acids. In fact, the word “oxygen” is Greek in origin, meaning “to make something sour”. In the middle of the 19th century, Davy found that hydrogen chloride (its aqueous solution is hydrochloric acid) did not contain any oxygen, and thus denied the theory that oxygen was essential constituent of acids. He proposed alternatively that hydrogen was the essential constituent of acids.

The nature of acid was first quantitatively understood at the end of the 19th century. In 1884, the Swedish chemist Svante August Arrhenius (1859-1927) proposed the **theory of electrolytic dissociation** which stated that **electrolytes** such as acids, bases and salts dissociated into their component ions in aqueous solution. He further stated that some electrolytes dissociated nearly

^{a)} You must remember that we owe the litmus paper to Boyle.

completely (**strong electrolytes**) but some dissociated only partly (**weak electrolytes**). The theory of acid-base developed rapidly based on this theory.

9.2 Theory of acid-base

(a) Chemical equilibrium

When substances A, B and C change into substances X, Y and Z and simultaneously substances X, Y and Z change into substances A, B and C, the combined processes are called **reversible reactions** and are expressed by the following equation with a double arrows.



where the substances in the left side are called **reactants**, and substances in the right side are called **products**.

In the initial stage of the reaction, the concentrations of products are low, and consequently the rate of the reverse reaction is slow. As the reaction proceeds, the rate of the reverse reaction will increase, and to the contrary, the rate of the forward reaction will decrease. When finally the rate of two reactions will be equal, no reaction seems to take place in appearance. Such a state is called the **chemical equilibrium**. At equilibrium, the concentrations of components vary depending on the temperature.

The concentration (usually in mol dm⁻³) of each component, *e.g.*, that of the component A, is designated as [A]. Then the equilibrium constant *K* is defined as below.

$$K = ([X][Y][Z] \cdot \cdot \cdot) / ([A][B][C] \cdot \cdot \cdot) \quad (9.2)$$

(b) Electrolytic dissociation equilibrium

A dissociation reaction in which an electrolyte AB dissolves in water and dissociates into its component ions A⁻ and B⁺ is called **electrolytic dissociation** or **ionization**. This reaction is also a reversible reaction.



Dissociation equilibrium of an electrolyte is called electrolytic dissociation equilibrium. The equilibrium constant of this type of equilibrium is called **electrolytic dissociation constant**. It is defined as below.

$$K = [A^-][B^+] / [AB] \quad (9.4)$$

Where [AB], [A⁻] and [B⁺] are the concentration at equilibrium of electrolyte AB, anion A⁻ and cation B⁺, respectively.

Water dissociates to a small extent. The electrolytic dissociation constant of water is defined as below:



The **ion-product constant** *K_w* of water is defined as:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ (298.15 K)} \quad (9.6)$$

This equation is applicable not only to pure water but also to aqueous solutions in general. Hence, in acidic solutions, [H⁺] is larger and [OH⁻] is smaller.

Hydrogen ion concentration [H⁺] of 1 molar hydrochloric acid is [H⁺] = 1.0 mol dm⁻³ (a strong

electrolyte) and that of 1 molar aqueous sodium hydroxide is $[H^+] = 10^{-14}/[OH^-] = 10^{-14} \text{ mol dm}^{-3}$. This indicates that $[H^+]$ of solutions varies in the order of 10^{14} as they change from acidic to basic. Moreover, $[H^+]$ of an aqueous solution is typically quite small. Thus, it is convenient to use the **hydrogen ion exponent, pH scale**, which is a log scale based on 10 where

$$\text{pH} = -\log [H^+] \quad (9.7)$$

(c) Arrhenius's theory of electrolytic dissociation

In 1886, Arrhenius proposed the theory of electrolytic dissociation in which he defined acids and bases as below:

Arrhenius' theory of acids and bases

acid: substances which dissolve and ionize in water to yield protons (H^+)

base: substances which dissolve and ionize in water to yield hydroxide ions (OH^-)

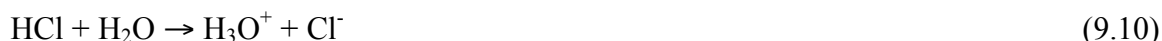
Accordingly, the acidity of hydrochloric acid and the basicity of aqueous sodium hydroxide are explained by the following equations:



where (aq) indicates an aqueous solution.

Though Arrhenius' theory was novel and persuasive, it failed to explain the fact that such compounds like gaseous ammonia, which do not have a hydroxy group and hence cannot give a hydroxide ion, exhibited basicity.

A proton H^+ is the nucleus of a hydrogen atom and does not have any electron. Hence it is expected that a proton is much smaller than other atoms, ions or molecules. Since H_2O has high polarity, a proton is surrounded and attracted by many water molecules, *i.e.*, **hydrated** (this state is called **hydration**). In other words, a proton is not free in water. If a proton is bonded with one molecule of H_2O to form a **hydronium ion** H_3O^+ , the equation for the electrolytic dissociation of hydrochloric acid will be as follows:



Since it is accepted that the real structure of a hydronium ion is a little more complicated, a proton is designated as H^+ rather than H_3O^+ .

(d) The theory of Brønsted and Lowry

In 1923, the Danish chemist Johannes Nicolaus Brønsted (1879-1947) and the English chemist Thomas Martin Lowry (1874-1936) independently proposed a novel theory of acids and bases, which turned out more general.

The theory of Brønsted and Lowry

acid: substances which can yield and donate protons (H^+) to other substances

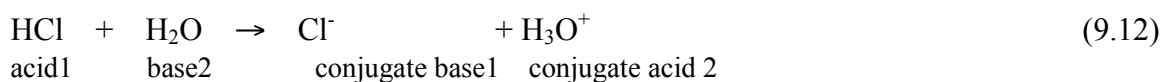
base: substances which can accept and receive protons (H^+) from other substances.

According to this theory, the reaction between gaseous hydrogen chloride and gaseous ammonia can be explained as an acid-base reaction. Thus,



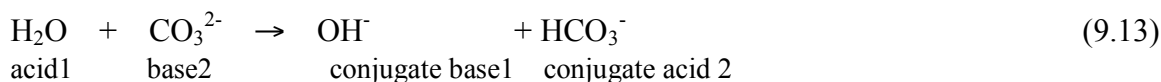
where the symbols (g) and (s) indicate that the relevant substance is a gas or a solid, respectively. Hydrogen chloride donated a proton to ammonia to act as an acid.

According to the theory of Brønsted and Lowry, a substance can behave either as an acid or as a base. If a substance in question can more readily emit a proton, it will act as an acid and the counterpart will act as a base. To the contrary, if the substance can more readily accept a proton, it will act as a base. In an aqueous solution of acid, water behaves as a base.

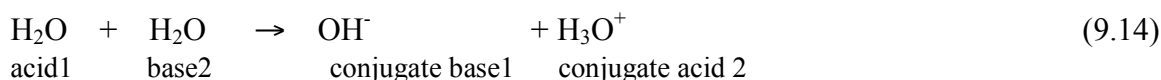


Among the chemical species in the above reaction, the difference between HCl and Cl⁻ is whether there is a proton or not, and the interconversion between them is reversible. This type of relation is called a **conjugate relation**, and the pair HCl and Cl⁻ is called **conjugate acid-base pair**.

An aqueous carbonate ion CO₃²⁻ is basic. In the reaction between CO₃²⁻ and H₂O, the former behaves as a base and the latter as an acid and they form a conjugate acid-base pair.



A substance is said to be **amphoteric** if it can behave either as an acid or as a base. Water is a typical **amphoteric substance**. The reaction between two molecules of water to give a hydronium ion and a hydroxide ion is a typical reaction of amphoteric substances.



Sample exercise 9.1 Conjugate acid-base pair

Point out the conjugate acid-base pair in the following reaction.



Answer

HCO₂H and HCO₂⁻ form one pair, and PO₄³⁻ and HPO₄²⁻ form another pair.

(e) Dissociation of acids and bases

The interaction which forms crystals of sodium chloride is ionic which are very strong as can be inferred from its high melting point (>1400°C). It means that a substantial energy should be required to dissociate crystals into ions. Sodium chloride dissolves, however, into water. This means that the stabilization obtained by hydration of ions, *i.e.*, interaction between ions and polar water molecules.



The system emits a substantial amount of energy (**hydration energy**) and obtains stabilization. In addition, by dissociation, the randomness (strictly speaking, entropy) of the system increases. The combined effects, hydration and the increase of randomness, are large enough for the crystals completely dissociate. Without such stabilization, dissolution of sodium chloride into water is a difficult process like its vaporization.

The electrolytic dissociation of strong acids and strong bases are similar processes. By

stabilization of dissociated ions by hydration, these essentially completely dissociate. In the following equations, (aq) is omitted though in fact hydration takes place.



Such is the case with strong bases.



Sample exercise 9.2 Concentration of protons in strong acids and strong bases

Calculate $[\text{H}^+]$ and pH of $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous sodium hydroxide, assuming a complete dissociation.

Answer

$$[\text{OH}^-] = 10^{-3}, \quad \therefore [\text{H}^+] = 10^{-14}/10^{-3} = 10^{-11}$$

$$\text{pH} = -\log 10^{-11} = 11$$

Weak acids and weak bases behave in a different manner. In aqueous solution, electrolytic dissociation is not complete, and a part or almost all of these remain as neutral species. Thus, in the case of acetic acid,



The equilibrium constant for this dissociation, K_a , is called **electric dissociation constant** or **acid dissociation constant**. In analogy with pH, $\text{p}K_a$, **electric dissociation exponent**, is defined as below:

$$\text{p}K_a = -\log K_a \quad (9.22)$$

$$K_a = ([\text{H}^+][\text{CH}_3\text{COO}^-])/[\text{CH}_3\text{COOH}] = 1.75 \times 10^{-5} \text{ mol dm}^{-3}, \text{p}K_a = 4.56 \text{ (25}^\circ\text{C)} \quad (9.23)$$

By using $\text{p}K_a$, extremely small values of K_a are converted to values easy to handle. Thus, the effect of using $\text{p}K_a$ is the same as that of using pH.

The strength of acids is defined by electric dissociation constants or electric dissociation exponents. The larger electric dissociation constants or the smaller electric dissociation exponents, the stronger the acid. In Table 9.1, electric dissociation constants and electric dissociation exponents of some of the representative weak acids are given.

Table 9.1 electric dissociation constants and electric dissociation exponents of some weak acids

acid	dissociation constants	dissociation exponents ($\text{p}K_a$)
formic acid HCOOH	1.77×10^{-4}	3.55
acetic acid CH_3COOH	1.75×10^{-5}	4.56
chloroacetic acid ClCH_2COOH	1.40×10^{-3}	2.68
benzoic acid $\text{C}_6\text{H}_5\text{COOH}$	6.30×10^{-5}	4.20
carbonic acid H_2CO_3	$K_1 4.3 \times 10^{-7}$	6.35

	K_2	5.6×10^{-11}	10.33
hydrogen sulfide H_2S	K_1	5.7×10^{-8}	7.02
	K_2	1.2×10^{-15}	13.9
phosphoric acid H_3PO_4	K_1	7.5×10^{-6}	2.15
	K_2	6.2×10^{-8}	7.20
	K_3	4.8×10^{-13}	12.35

Sample exercise 9.3 Hydrogen ion concentration of weak acids

K_a of butanoic acid (butyric acid) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ is $1.51 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the pH of a $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ solution of this acid.

Answer

$$K_a = [\text{H}^+][\text{C}_3\text{H}_7\text{COO}^-]/[\text{C}_3\text{H}_7\text{COOH}] = 1.51 \times 10^{-5} \text{ mol dm}^{-3} \text{ and } [\text{H}^+] = [\text{C}_3\text{H}_7\text{COO}^-].$$

$[\text{C}_3\text{H}_7\text{COOH}]$ can be approximated by the initial concentration of butanoic acid (the extent of ionization is small). Then $([\text{H}^+])^2 = 1.51 \times 10^{-5} \times 1.00 \times 10^{-2}$. Hence,

$$[\text{H}^+] = 3.89 \times 10^{-4} \text{ mol dm}^{-3}. \quad \text{pH} = 3.42$$

Ammonia is a weak base, and when it dissolves in water, a part of it reacts with water to give hydroxide ion OH^- .



In this reaction water acts as a solvent and at the same time as a reagent. The equilibrium constant of this equilibrium reaction is defined by the equation below:

$$K = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3][\text{H}_2\text{O}] \quad (9.25)$$

The concentration of water, $[\text{H}_2\text{O}]$, may be regarded almost constant (55.5 mol dm^{-3}) at ambient temperature and pressure, and the base dissociation constant is defined as below.

$$K_b = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3] = 1.76 \times 10^{-5} \text{ mol dm}^{-3} \quad (9.26)$$

In aqueous solutions, K_b can be converted to K_a with the aid of ion product K_w . Thus,

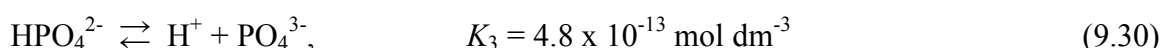
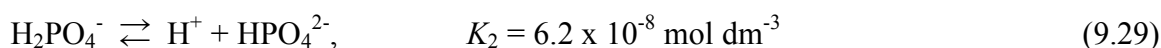
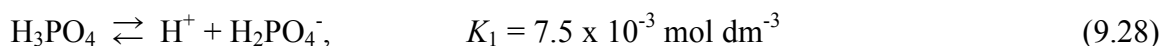
$$K_b = K_a/K_w \quad (9.27)$$

This is equal to express the strength of a base by the strength (in fact the weakness) of its conjugate acid. With this procedure, acids and bases are compared with a common standard.

Polyprotic acids

Sulfuric acid H_2SO_4 is a diprotic acid since it can release two protons in two steps. For polyprotic acids, more than one dissociation constants are defined. The dissociation constant for the 1st step is designated as K_1 , and that for the 2nd step is K_2 .

As compared with the first ionization step in which the first proton is released, the 2nd ionization, that is, the release of proton from HSO_4^- , is less extensive. This tendency is more significant for phosphoric acid, which is considerably weaker than sulfuric acid. Phosphoric acid is a trivalent acid and dissociates in three steps as shown below.



These data indicate that the acid involved in each step of the dissociation is successively weaker.

Similarly, calcium hydroxide $\text{Ca}(\text{OH})_2$ is a divalent base since it can release two hydroxide ions.

(f) The Lewis acid-base theory

In the year (1923) when Brønsted and Lowry proposed their acid-base theory, Lewis also proposed a new acid-base theory. Lewis, who proposed the octet theory, accepted the acid-base theory as a fundamental problem to be solved based on the atomic structure, rather than something which can be explained by experimental results.

The Lewis acid-base theory

acid: substances which can accept electron pairs.

base: substances which can donate electron pairs.

All substances defined as acids by the Arrhenius theory are also acids in the framework of the Lewis theory since a proton is an acceptor of an electron pairs. In neutralization reactions, a proton forms a coordinate bond with a hydroxide ion.



The situation is the same with the gas-phase reaction which was first accepted as an acid-base reaction in the framework of the Brønsted and Lowry theory.



In this reaction, proton from HCl makes a coordinate bond with the lone pair of the nitrogen atom.

The great advantage of the Lewis acid-base theory lies in the fact that several reactions which were not regarded as acid-base reactions in the framework of both the Arrhenius theory and the Brønsted and Lowry theory proved acid-base reactions in the light of the Lewis theory. An example is the reaction between boron trifluoride BF_3 and fluoride ion F^- .



This reaction includes the coordination of boron trifluoride to the lone pair of fluoride ion. According to the Lewis acid-base theory, BF_3 is an acid. In order to differentiate such acids as BF_3 from protic acids (which release protons, in other words, acids in the framework of the Arrhenius and the Brønsted and Lowry theories) are called **Lewis acids**. Boron forms compounds that are not obeyed the octet rule, and thus one of the representative elements which produces Lewis acids.

Since all Brønsted and Lowry bases donate their lone pairs to protons, they are also Lewis acids. All Lewis acids are, however, not necessarily Brønsted and Lowry acids as indicated by the above example.

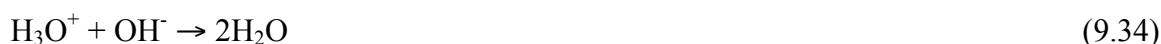
Of the three definitions of the acid-base, the definition of the Arrhenius theory is most limiting. The Lewis theory includes the widest range of compounds as acid-base. As far as the reactions in aqueous solutions are discussed, the Brønsted and Lowry theory is most convenient, but the Lewis theory is most appropriate when the acid-base type reactions of compounds without proton are involved.

9.3 Neutralization

The most fundamental and practical concept in acid-base chemistry is no doubt **neutralization**. The fact that acids and bases cancel each other has been well known as the fundamental property of them before the advent of modern chemistry,

(a) Neutralization

Neutralization can be defined as the reaction between proton (or hydronium ion) and hydroxide ion with concomitant formation of water. In this chapter we discuss only neutralization in aqueous solution.



where the mols of the acid (*i.e.*, proton) should be equal to that of the base (hydroxide ion).

Stoichiometry of neutralization

$$\begin{array}{ccc} n_A M_A V_A & = & n_B M_B V_B \\ \text{mols of proton} & & \text{mols of hydroxide ion} \end{array}$$

where subscripts *A* and *B* indicate acid and base, respectively, *n* the valence, *M* the mols of acid or base, and *V* the volume of acid or base.

where subscripts *A* and *B* indicate acid and base, respectively, *n* the valence, *M* the mols of acid or base, and *V* the volume of acid or base.

With the aid of the above equation, it is possible to determine the concentration of a solution of a base (or an acid) whose concentration is unknown by the neutralization with a solution of an acid (or a base) whose concentration is known. This procedure is called the **neutralization titration**.

Sample exercise 9.5 Neutralization titration

0.500 g of impure ammonium chloride NH_4Cl was heated with excess sodium hydroxide, and the generated ammonia NH_3 was absorbed in 25.0 cm^3 of $0.200 \text{ mol dm}^{-3}$ sulfuric acid. 5.64 cm^3 of $0.200 \text{ mol dm}^{-3}$ sodium hydroxide was required to neutralize excess sulfuric acid. Calculate the purity of ammonium chloride.

Answer

Remember sulfuric acid is diprotic. Assuming that the mole of generated ammonia is *x* m mol, the sum of moles of ammonia and sodium hydroxide is twice as large as that of sulfuric acid. Thus,

$$\begin{aligned} x \text{ (m mol)} + 0.200 \text{ (mol dm}^{-3}) \times 5.64 \times 10^{-3} \text{ (dm}^3) \\ = 2 \times 0.200 \text{ (mol dm}^{-3}) \times 25.0 \times 10^{-3} \text{ (dm}^3) \\ x + 1.128 = 10.0 \quad \therefore x = 8.872 \text{ (m mol)} \end{aligned}$$

Since molar mass of ammonium chloride is 52.5, 8.872 m mol is equivalent to 0.466 g of it. Then the purity is $(0.466 \text{ G}/0.500 \text{ g}) \times 100 = 93 \text{ (\%)}$

(b) Salts

Each acid or salt has its own counterion, and acid-base reactions involve all these ions. In a typical neutralization reaction such as the one between HCl and NaOH ,



NaCl is formed in addition to water from chloride ion, the counterion of proton, and sodium ion, the counterion of the base. Such substances formed during neutralization are called **salts**. As far as the reaction proceeds in water, both sodium ion and chloride ion exist independently as ions, not as a salt NaCl. If water is evaporated, sodium chloride remains as such. One tends to believe that salts are neutral since they are formed during neutralization. In fact aqueous sodium chloride is completely neutral. However, aqueous solutions of some of the salts are sometimes acidic or basic. For instance, sodium acetate, CH_3COONa , a salt generated from the reaction between acetic acid and sodium hydroxide, is weakly basic.

On the other hand, ammonium chloride NH_4Cl , a salt of a strong acid, hydrochloric acid, and a weak base, ammonia, is acidic. This phenomenon is called **hydrolysis** (of salts).

A schematic diagram of hydrolysis is shown in Fig. 9.1. In aqueous solutions, the salt AB is in equilibrium with small amounts of H^+ and OH^- generated from electrolysis of water to yield an acid HA and a base BOH (equilibrium in vertical direction). Since HA is a weak acid, the equilibrium is shifted to the acid side, and consequently $[\text{H}^+]$ decreases. On the other hand, BOH is a strong base, and dissociates nearly completely, and hence there is no decrease of the concentration of OH^- . By dissociation of water, an equal amount of H^+ and OH^- is formed.

Of the vertical equilibrium of Fig. 9.1, the acid equilibrium is downward, and the base equilibrium is upward. Consequently $[\text{OH}^-]$ of the aqueous solution increases to make the solution basic. This explanation is applicable to all salts of a weak acid and a strong base.

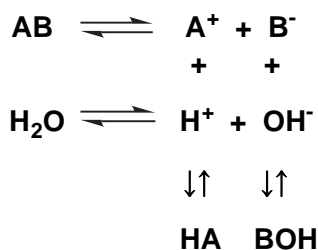


Fig. 9.1 Hydrolysis (of salts)

To summarize, in hydrolysis of a salt from a weak acid and a strong base, a part of the anion of the salt reacted with water to give hydroxide ion.



By treating this reaction as an equilibrium, hydrolysis of a salt can be expressed in a quantitative manner.



where h is the degree of hydrolysis to represent the ratio of hydrolyzed salt at equilibrium. The equilibrium constant K_h for this equilibrium

$$K_h = [\text{HA}][\text{OH}^-]/[\text{A}^-] = (c_s h)^2 / c_s (1 - h) = c_s h^2 / (1 - h) \quad (9.38)$$

is called **hydrolysis constant** where c_s is the initial concentration of the salt. A^- is the conjugate base of the weak acid HA and K_h corresponds to its base dissociation constant. Accordingly the following relation holds if the acid dissociation constant of HA is K_a : thus,

$$K_a K_h = K_w \quad (9.39)$$

When $h \ll 1$, $K_a \doteq c_s h$; $h \doteq \sqrt{K_h/c_s}$. Then the concentration of $[\text{OH}^-]$ and $[\text{H}^+]$ is given by the following equations.

$$[\text{OH}^-] = c_s h \doteq \sqrt{(c_s K_w / K_a)} \quad (9.40)$$

$$[\text{H}^+] = K_w / [\text{OH}^-] \doteq \sqrt{(K_w K_a / c_s)} \quad (9.41)$$

Since a weak acid is involved,

$$K_a / c_s < 1, \therefore [\text{H}^+] < \sqrt{K_w} = 10^{-7} \quad (9.42)$$

Thus, a salt of a weak acid is basic.

In a similar manner, $[\text{H}^+]$ of a salt of a weak base and a strong acid is given below.

$$[\text{H}^+] = c_s h \doteq \sqrt{(c_s K_w / K_b)} \quad (9.43)$$

Since a weak base is involved,

$$c_s / K_b > 1, \therefore [\text{H}^+] > \sqrt{K_w} = 10^{-7} \quad (9.44)$$

Thus, a salt of a weak base is acidic.

(c) Titration curve

During neutralization of an acid with a base, or, neutralization of a base with an acid, how hydrogen ion concentration, $[\text{H}^+]$, or pH, of the solution varies? The calculation of $[\text{H}^+]$ during the titration of a strong acid with a strong base, or reversibly, or the titration of a strong base with a strong acid is not difficult at all. It can be obtained by dividing the mol of remaining acid (or base) by the volume of the solution.

The treatment is more complicated when the combination of a weak acid and a strong base, or that of a strong acid and a weak base is involved. $[\text{H}^+]$ will depend not only the remaining acid or base, but also the hydrolysis of the salt formed.

The plot of $[\text{H}^+]$ or pH vs. the amount of acid or base added is called the **titration curve** (Fig. 9.2).

Let us draw titration curves where the initial volume of acid is V_A , the concentration of it is M_A , and the volume of added base is v_B and its concentration is M_B .

(1) Titration of a strong acid with a strong base.

[1] Before the equivalent point:

Since the dissociation of water can be neglected, the mole of H^+ is equal to the mole of the remaining acid. Thus,

$$[\text{H}^+] = (M_A V_A - M_B v_B) / (V_A + v_B) \quad (9.45)$$

[2] At the equivalent point:

Dissociation of water cannot be neglected here.

$$[\text{H}^+] = \sqrt{K_w} = 10^{-7} \quad (9.46)$$

[3] After the equivalent point:

The mole of excess base is equal to the mole of hydroxide ion. The $[\text{OH}^-]$ can be obtained by dividing the mole by the volume of the solution. The obtained $[\text{OH}^-]$ can be converted into $[\text{H}^+]$.

$$[\text{OH}^-] = (M_B v_B - M_A V_A) / (V_A + v_B) \quad (9.47)$$

$$[\text{H}^+] = K_w / [\text{OH}^-] = (V_A + v_B) K_w / (M_B v_B - M_A V_A) \quad (9.48)$$

The curve is symmetric near the equivalent point since $v_B \doteq V_A$.

The titration of $10 \times 10^{-3} \text{ dm}^3$ of a strong acid such as 0.1 mol dm^{-3} hydrochloric acid with a strong base such as 0.1 mol dm^{-3} aqueous sodium hydroxide gives a characteristic titration curve as shown in Fig. 9.2(a). At the initial stage, the change of pH is slow. The change of pH is very rapid near the equivalent point ($v_B = 10 \times 10^{-3} \text{ dm}^3$). Near the equivalent point, pH changes for a few units with one drop of the base.

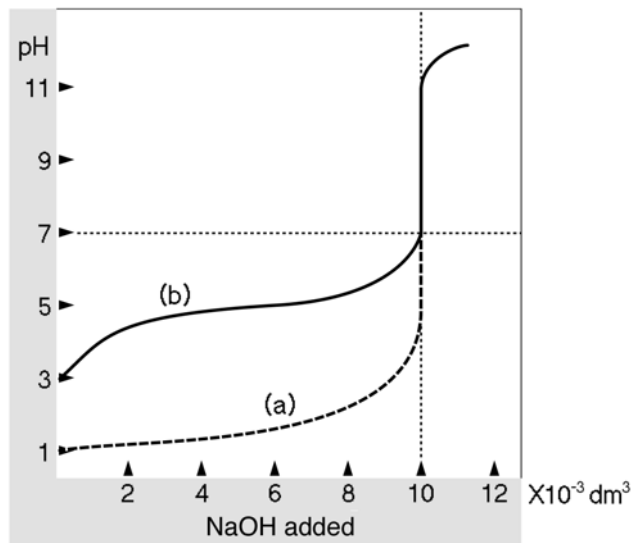


Fig 9.2 Titration curve: (a) Titration of HCl with NaOH. A rapid change of pH at the equivalent point is characteristic. (b) Titration curve: titration of CH_3COOH with NaOH. The change of pH at the equivalent point is not so rapid.

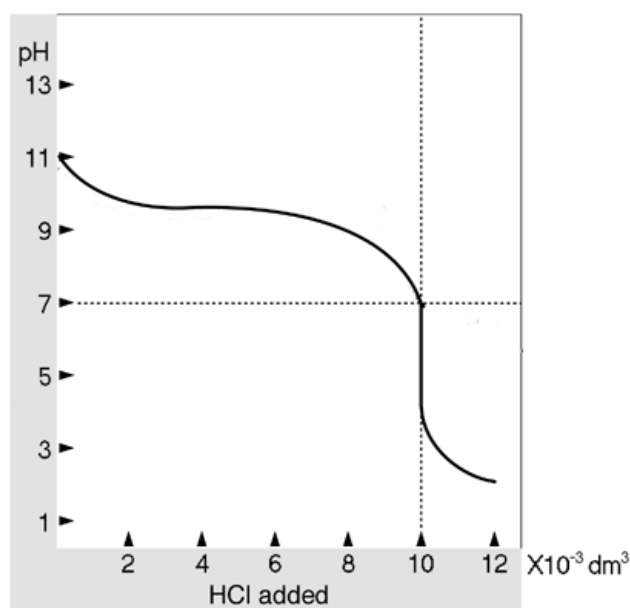


Fig 9.3 Titration curve: titration of NH_3 with HCl.

(2) Titration of a weak acid with a strong base

The result is different when a weak acid is titrated with a strong base. The titration of $10 \times 10^{-3} \text{ dm}^3$ of a 0.1 mol dm^{-3} acetic acid with 0.1 mol dm^{-3} aqueous sodium hydroxide will be an example (Fig. 9.2(b)).

[1] Starting point: $v_B = 0$. The pH at the initial stage is larger than the previous case.

$$[\text{H}^+] = M_A \alpha \quad (9.49)$$

where α is the dissociation constant of acetic acid.

[2] Before the equivalent point: Until the equivalent point, the change of pH is rather slow.

[3] At the equivalent point ($v_B = 10 \times 10^{-3} \text{ dm}^3$): At this point only sodium acetate CH_3COONa exists. $[\text{H}^+]$ can be obtained in a manner similar to the one for hydrolysis of salts.

[4] After the equivalent point: $[\text{H}^+]$ of the solution is determined by the concentration of NaOH rather than that of CH_3COONa .

The slow change of pH value before the equivalent point is due to the buffer action (Ch. 9.3 (d)). Before the equivalent point, there exist in the solution sodium acetate (a salt of a weak acid and a strong base) and acetic acid (a weak acid). Because of the presence of sodium acetate, the dissociation equilibrium of sodium acetate



shifts to the left side, and $[\text{H}^+]$ decreases. Approximately $[\text{CH}_3\text{COO}^-] = c_s$, $[\text{HA}] \doteq c_0$, where c_s is the concentration of the salt, then

$$[\text{H}^+]c_s/c_0 = K_a, \quad [\text{H}^+] = (c_0/c_s)K_a \quad (9.51)$$

If an acid is added to this solution, the equilibrium shifts to the left since there is plenty acetate ion so that the added acid is neutralized.



To the contrary, if a base is added, acetic acid in solution is going to neutralize it. Thus,



Hence $[\text{H}^+]$ does not scarcely change

(3) Titration of a weak base with a strong acid

The titration of $10 \times 10^{-3} \text{ dm}^3$ of a weak base such as a 0.1 mol dm^{-3} aqueous ammonia with a strong acid such as a 0.1 mol dm^{-3} hydrochloric acid will be considered (Fig. 9.3). In this case, pH value at the equilibrium point is slightly smaller than that of the titration of a strong acid and a strong base. The curve is steep, however, and its change is rapid near the equilibrium point. Accordingly titration is possible if a proper indicator with a narrow indicator range.

(3) Titration of a weak base (a weak acid) with a weak acid (a weak base).

In this type of titration, the titration curve fails to be steep at the equilibrium point, and the change of pH is slow. Hence no indicator can exhibit a clear color change. This means that such types of titration are not possible.

(d) Buffer action

The **buffer action** is defined as an action to the effect that the pH of a solution scarcely changes

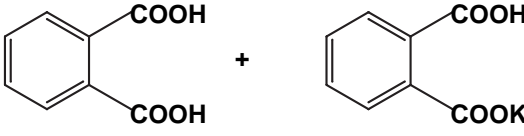
upon addition of an acid or of a base. A solution that has the buffer action is called the **buffer solution**. Most of buffer solutions are composed of a combination of a salt of a weak acid and a strong base, and a weak acid. The body fluid of living organism is a buffer solution, which will suppress a rapid change of pH, which is harmful for living organism.

The pH values of a buffer solution made of a weak acid and its salt can be calculated by the following equation.

$$\text{pH} = \text{p}K_a + \log([\text{salt}]/[\text{acid}]) \quad (9.54)$$

Table 9.2 gives some buffer solutions.

Table 9.2 Some buffer solutions

components	range of pH
	2.2--3.8
$\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$	3.7--5.6
$\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$	5.8--8.0
$\text{H}_3\text{BO}_3 + \text{Na}_2\text{B}_4\text{O}_7$	6.8--9.2

Sample exercise 9.5 pH of buffer solutions

Three solutions (a), (b) and (c) contain a 0.10 mol dm^{-3} propanoic acid (propionic acid; $\text{p}K_a = 1.80 \times 10^{-5} \text{ mol dm}^{-3}$) and (a) a 0.10 mol dm^{-3} , (b) a 0.20 mol dm^{-3} and (c) a 0.50 mol dm^{-3} sodium propanoate, respectively. Calculate pH of three solutions.

Answer

Substitute appropriate figures into the equation (9.54)

- (a) $\text{pH} = \text{p}K_a + \log([\text{salt}]/[\text{acid}]) = \text{p}K_a + \log([0.1]/[0.1]) = \text{p}K_a + \log 1 = 4.75$
 (b) $\text{pH} = \text{p}K_a + \log([0.2]/[0.1]) = \text{p}K_a + \log 2 = 5.05$
 (c) $\text{pH} = \text{p}K_a + \log([0.5]/[0.1]) = \text{p}K_a + \log 5 = 5.45$

Note that the $([\text{salt}]/[\text{acid}])$ value changes from 1 to 5, but the change of pH is only 0.7.

(e) Indicators

Such pigments as phenolphthalein and methyl orange used as an indicator for titration are themselves weak acids (hereafter designated as HIn) and their colors are determined by $[\text{H}^+]$ of the solution. Thus,



The concentration ratio of the indicator and its conjugate base which determines the color of the solution is given below:

$$K_I = [\text{H}^+][\text{In}^-]/[\text{HIn}], \quad \therefore [\text{In}^-]/[\text{HIn}] = K_I/[\text{H}^+] \quad (9.56)$$

where K_I is the dissociation constant of the indicator.

The range of pH in which a remarkable change of the color of the indicator is called the **transition interval**. The reason why there are so many indicators available is due to the fact that pH

values at the equivalent point vary depending on the combination of an acid and a base. The key point of selecting an indicator should depend on whether a remarkable change of color will take place near the equivalent point. In Table 9.3, some important indicators are listed.

Table 9.3 Representative indicators and their transition interval.

Indicator	transition interval(pH)	color change (acidic→basic)
thymol blue	1.2-2.8	red → yellow
methyl orange	3.1-4.4	red → yellow
methyl red	4.2-6.3	red → yellow
bromothymol blue	6.0-7.6	yellow → blue
cresol red	7.2-8.8	yellow → red
phenolphthalein	8.3-10.0	colorless → red
alizarin yellow	10.2-12.0	yellow → red

Sample exercise 9.6 Neutralization titration of a mixture; how to use indicators

A 25 dm³ solution containing sodium hydroxide NaOH and sodium carbonate Na₂CO₃ was titrated with a 0.100 mol dm⁻³ hydrochloric acid with phenolphthalein as an indicator. The color of the indicator disappeared when 30.0 dm³ of hydrochloric acid was added. Methyl orange was added and the titration was continued. 12.5 dm³ of hydrochloric acid was necessary before the color of methyl orange changed. Calculate the concentration of NaOH and Na₂CO₃ in the solution.

Answer

Carbonic acid is a diprotic acid, and neutralization is a two-stage reaction.



The 1st stage of neutralization of the NaOH-Na₂CO₃ mixture reaches to the endpoint when the color of phenolphthalein disappears. The change of color of methyl orange indicates the end of the 2nd stage neutralization of sodium carbonate.

Hence, the combined amounts of NaOH-Na₂CO₃ is 0.100 mol dm⁻³ x 30.0 x 10⁻³ dm³ = 3.0 x 10⁻³ mol as indicated by the 1st stage neutralization. The amount of Na₂CO₃ is 0.100 mol dm⁻³ x 12.5 x 10⁻³ dm³ = 1.25 x 10⁻³ mol as indicated by the 2nd stage neutralization. The amount of NaOH is the difference between the two figures, 1.75 x 10⁻³ mol. This amount is contained in the solution of 25 dm³. Thus,

$$[\text{Na}_2\text{CO}_3] = 1.25 \times 10^{-3} \text{ mol} / 25.0 \times 10^{-3} \text{ dm}^3 = 0.050 \text{ mol dm}^{-3}$$

$$[\text{NaOH}] = 1.75 \times 10^{-3} \text{ mol} / 25.0 \times 10^{-3} \text{ dm}^3 = 0.070 \text{ mol dm}^{-3}$$

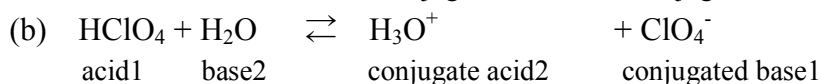
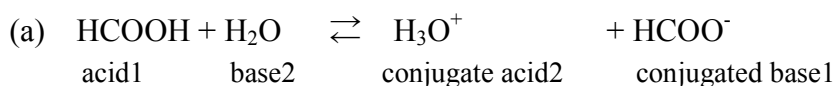
Exercises

9.1 Conjugate acid-base

Draw the equations of electrolytic dissociation, including water, of following compounds and point out the conjugate acid-base pair.

(a) formic acid HCOOH, (b) perchloric acid HClO₄

9.1 Answer



9.2 Conjugate acid-base

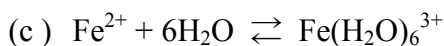
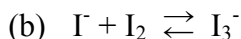
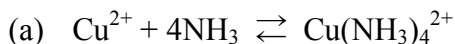
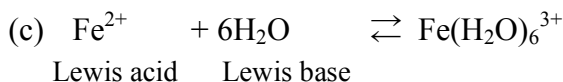
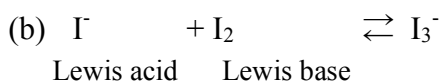
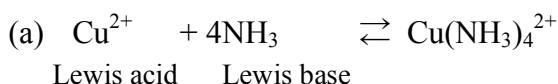
The dissociation constants of a pair of conjugate acid-base are K_a and K_b , respectively. Prove the relation $K_a \times K_b = K_w$ where K_w is the ion product of water.

9.2 Answer

See the relevant page of the text.

9.3 Lewis acids and Lewis bases

Point out Lewis acids and Lewis bases in the following reactions.

**9.3 Answer****9.4 Hydrogen ion concentration and pH of strong acids**

Perchloric acid is a strong acid, and its dissociation can be assumed complete. Calculate hydrogen ion concentration $[\text{H}^+]$ and pH of a 5.0 mol dm^{-3} perchloric acid.

9.4 Answer

$$[\text{H}^+] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}; \text{pH} = -\log[\text{H}^+] = 2.30$$

9.5 Hydrogen ion concentration and pH of weak acids

Calculate hydrogen ion concentrations and pH of a $0.001 \text{ mol dm}^{-3}$, a 0.01 mol dm^{-3} and a 0.1 mol dm^{-3} acetic acid. The dissociation constant K_a of acetic acid at 25°C is $1.75 \times 10^{-5} \text{ mol dm}^{-3}$.

9.5 Answer

Approximately $[\text{H}^+] = \sqrt{c_s K_a}$. Then $[\text{H}^+]$ and pH are given as below.

A $0.001 \text{ mol dm}^{-3}$ acetic acid; $[\text{H}^+] = 1.32 \times 10^{-4} \text{ mol dm}^{-3}$, pH = 3.91.

A 0.01 mol dm^{-3} acetic acid; $[\text{H}^+] = 4.18 \times 10^{-4} \text{ mol dm}^{-3}$, pH = 3.39.

A 0.1 mol dm^{-3} acetic acid; $[\text{H}^+] = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$, pH = 2.88.

9.6 Calculation of dissociation constants

In a 0.5 mol dm^{-3} solution, the dissociation of uric acid $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ is 1.6 %. Calculate K_a of uric acid.

9.6 Answer

$1.6 \times 10^{-2} = [\text{C}_5\text{H}_3\text{N}_4\text{O}_3^-]/0.5 \text{ mol dm}^{-3}$, $[\text{C}_5\text{H}_3\text{N}_4\text{O}_3^-] = [\text{H}^+] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$. Hence,
 $K_a = (8.0 \times 10^{-3})^2/0.50 = 1.28 \times 10^{-4} \text{ mol dm}^{-3}$.

9.7 Neutralization titration

A detergent for domestic use contains some ammonia. 25.37 g of this detergent is dissolved in water to prepare a 250 cm^3 solution. 37.3 cm^3 of a $0.360 \text{ mol dm}^{-3}$ sulfuric acid was required when 25.0 cm^3 portion of this solution was titrated. Calculate the mass percent of ammonia in the detergent.

9.7 Answer

18.0 %.

9.8 Buffer solution

- (1) Calculate pH of a buffer solution in which the concentration of formic acid HCOOH ($K_a = 1.8 \times 10^{-4} \text{ mol dm}^{-3}$) is $0.250 \text{ mol dm}^{-3}$, and that of sodium formate HCOONa is $0.100 \text{ mol dm}^{-3}$.
- (2) Suppose 10 cm^3 of $6.00 \times 10^{-3} \text{ mol dm}^{-3}$ NaOH is added to 500 cm^3 of this buffer solution. Calculate the pH of the solution after NaOH is added.

9.8 Answer

- (1) $[\text{H}^+] = 4.5 \times 10^{-4} \text{ mol dm}^{-3}$, $\text{pH} = 3.35$.
- (2) The mols of HCOOH , OH^- and HCOO^- before and after NaOH is added are shown in the table below.

m mol	HCOOH	OH^-	HCOO^-
before	125	60	50
after	65	0	110

Notice that the volume of the solution is now 510 cm^3 .

$$1.8 \times 10^{-4} \text{ mol dm}^{-3} = ([\text{H}^+] \times 0.216)/(0.128), [\text{H}^+] = 1.06 \times 10^{-4} \text{ mol dm}^{-3}, \text{pH} = 3.97$$

The change of pH is rather small although a substantial amount a strong base is added.