

FEDERAL UNIVERSITY OF TECHNOLOGY MINNA
SCHOOL OF PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY

CHM 111 GENERAL CHEMISTRY I. 2021/2022 SESSION

PART 1 (Released on 12/10/2021)

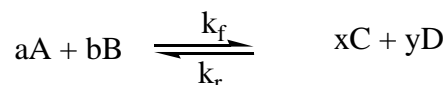
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1.0 CHEMICAL EQUILIBRIUM.

Most chemical reactions do not go to completion. That is, when reactants are mixed in stoichiometric quantities, they are not completely converted to products. Reactions that do not go to completion or that can occur in either direction (depending on the prevailing conditions of temperature and pressure) are called reversible reactions.

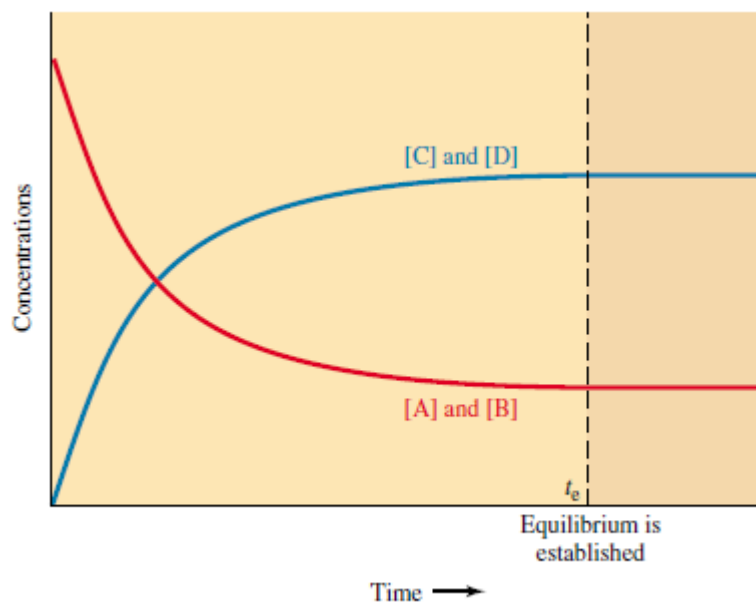
Reactions takes place due to the collision of the reactant particles and immediately, products are formed. As soon as some product molecules are formed, the reversible process, that is, the formation of the reactant molecules begins to take place. At this point, equilibrium is said to be reached because the reactants and products concentrations stop changing as the forward and reverse reactions become equal. In other words, Chemical equilibrium exists when two opposing reactions occur simultaneously at the same rate. This state of equilibrium is dynamic, that is, the reaction is proceeding normally, although ordinarily it may seem to have stopped.

Consider the reaction;



Where k_f and k_r are the rate constants for the forward and reverse reactions respectively.

As the concentrations of C and D builds up, A and B begins to re-form. If the reaction begins with only species C and D, the rate of the backward reaction decreases with time and the rate of the forward reaction increases with time until the two rates are equal.



From the rate law;

$$\text{Rate of forward reaction} = k_f [A]^a [B]^b$$

$$\text{Rate of reverse reaction} = k_r [C]^x [D]^y$$

At equilibrium, the two rates are equal. Thus; $k_f [A]^a [B]^b = k_r [C]^x [D]^y$

$$\frac{k_f}{k_r} = \frac{[C]^x [D]^y}{[A]^a [B]^b} = K_c$$

Where K_c is the equilibrium constant. The subscript 'C' indicates that the equilibrium constant is expressed in concentration units.

Equilibrium constant K is equal to a particular ratio of equilibrium product and reactant terms at a particular temperature. Although the concentration of the reactants and products are constant in a system at equilibrium, this does not mean that the system contains 50% reactants and 50% products. It is the opposing rates that are equal at equilibrium, not necessarily the concentrations. Generally, K is large for reactions that reach equilibrium with high concentration of products and small for reactions that reach equilibrium with low concentration of products.

For gaseous reactions, the partial pressures of the reacting species are used. Thus;

$$\frac{k_f}{k_r} = \frac{P_C^x \cdot P_D^y}{P_A^a \cdot P_B^b} = K_p$$

Where P^a , P^b , P^x and P^y are the partial pressures of the species A, B, C and D respectively.

1.1 The mass action expression and equilibrium constant

The particular ratio of terms written for a given reaction is called the mass action expression, Q , (or reaction quotient). The law of mass action states that at a given temperature, a chemical system reaches a state in which a particular ratio of reactant and products concentration terms has a constant value.

The reaction quotient for the general reaction above can be expressed as

$$Q = \frac{[C]^x [D]^y}{[A]^a [B]^b}, \text{ where } Q \text{ is the reaction quotient.}$$

The reaction quotient has the same form as the equilibrium constant, but it involves specific values that are not necessarily equilibrium concentrations. If they are equilibrium concentrations, then $Q = K_c$. The concept of the reaction quotient is very useful. It can be used to compare the magnitude of Q with that of K_c for a reaction under given condition to decide whether the forward or the reverse reaction must occur to a greater extent to establish equilibrium.

The reaction quotient, Q , can be thought of as a measure of the progress of the reaction. When the mixture contains only reactants, the concentrations in the numerator are zero, so $Q = 0$. 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 reactants have been consumed and only products remain. The value of K_c is a particular value of Q that represents equilibrium mixtures for the reaction.

If at any time $Q < K_c$, the forward reaction must occur to a greater extent than the reverse reaction for equilibrium to be established. This is because when $Q < K_c$, the numerator of Q is too small and the denominator is too large. To increase the numerator and to reduce the denominator, A and B must react to produce C and D. Conversely, if $Q > K_c$, the reverse reaction must occur to a greater extent than the forward reaction for equilibrium to be reached. When the value of Q reaches the value of K_c , the system is at equilibrium, so no further net reaction occurs.

Therefore when;

$Q < K_c$, forward reaction predominates until equilibrium is established.

$Q = K_c$, system is at equilibrium.

$Q > K_c$, reverse reaction predominates until equilibrium is established.

1.2 Equilibrium constant expressions.

Equilibrium conditions in which all the reacting species are in the same phase are known as homogeneous equilibrium.

Examples;



In terms of pressure, K_p is given as;

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

In terms of concentration, K_c is given as;

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$



$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

Here, water is not used in the K_c expression because the concentration of water is constant.

Note:

K_p and K_c can be used to express equilibrium constants for gases depending on whether the concentrations are expressed in terms of their partial pressures or in mol dm^{-3} .

In heterogeneous equilibria, the reactants and products are in different phases.

Example;



$$K_c = [\text{CO}_2] \text{ or } K_p = P_{\text{CO}_2}$$

Also note that the concentration of the solid reactants or products is not used because their concentration is considered to be constant throughout the reaction.

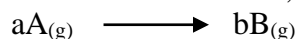
The equilibrium constant K_c , is defined as the product of the equilibrium concentrations (moles per liter) of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the equilibrium concentrations of reactants, each raised to the power that corresponds to its coefficient in the balanced equation. Similarly, The equilibrium constant K_p , is defined as the product of the equilibrium partial pressures (in atmospheres) of the products, each raised to the power that corresponds to its coefficient in the

balanced equation, divided by the product of the equilibrium partial pressures of reactants, each raised to the power that corresponds to its coefficient in the balanced equation.

1.3 Relationship between K_c and K_p

Generally, K_c is not equal to K_p , since the partial pressures of reactants and products are not equal to their concentration expressed in moles per dm^{-3} .

Consider the reaction;



where a and b are the stoichiometric coefficients. The equilibrium constant K_c is

$$K_c = \frac{[B]^b}{[A]^a} \dots\dots\dots (1)$$

And

$$K_p = \frac{P_B^b}{P_A^a} \dots\dots\dots (2)$$

Where P_A and P_B are the partial pressures of species A and B.

Assuming ideal gas behaviour,

$$P_A V = n_A RT \dots\dots\dots (3)$$

$$P_A = \frac{n_A RT}{V} \dots\dots\dots (4)$$

Where V is the volume of the container in dm^{-3}

Similarly,

$$P_B V = n_B RT \dots\dots\dots (5)$$

$$P_B = \frac{n_B RT}{V} \dots\dots\dots (6)$$

Substituting equation (4) and (6) in equation (2)

We have

$$K_p = \frac{\left(\frac{n_B RT}{V}\right)^b}{\left(\frac{n_A RT}{V}\right)^a} = \frac{\left(\frac{n_B}{V}\right)^b}{\left(\frac{n_A}{V}\right)^a} (RT)^{b-a} \dots\dots\dots (7)$$

Now, both $\frac{n_A}{V}$ and $\frac{n_B}{V}$ have the units of moles per dm^{-3} and can be replaced by [A] and [B], so that

$$K_p = \frac{[B]^b}{[A]^a} (RT)^{\Delta n} \dots\dots\dots (8)$$

$$\therefore K_p = K_c (RT)^{\Delta n} \dots\dots\dots (9)$$

Where $\Delta n = b - a$, that is, moles of gaseous products minus moles of gaseous reactants. Since pressure is usually expressed in atmosphere, the gas constant, R, is given by $0.0821 \text{ L.atmK}^{-1}$, we can write the relationship between K_p and K_c as

$$K_p = K_c (0.0821 T)^{\Delta n} \dots\dots\dots (10)$$

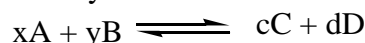
In general, $K_p \neq K_c$, except in the special case when $\Delta n = 0$. In that case, equation (10) can be written as;

$$K_p = K_c(0.0821 T)^0$$

$$\therefore K_p = K_c \dots\dots\dots (11)$$

1.4 Relationship between equilibrium constant and free energy.

For any reaction such as



The free energy change, ΔG , at any temperature, T , is given by;

$$\Delta G = \Delta G^0 + RT \ln \frac{a_c^c \cdot a_d^d}{a_A^x \cdot a_B^y}$$

Where ΔG is the free energy of the reaction. ΔG^0 is the free energy of the reaction when the reactants are in their standard states. a is the activity of the reacting species. But $\Delta G = 0$ at equilibrium, therefore, the above equation becomes

$$0 = \Delta G^0 + RT \ln \frac{a_c^c \cdot a_d^d}{a_A^x \cdot a_B^y}$$

$$\text{and } \Delta G^0 = -RT \ln \frac{a_c^c \cdot a_d^d}{a_A^x \cdot a_B^y}$$

since $\frac{a_c^c \cdot a_d^d}{a_A^x \cdot a_B^y} = K$, the equilibrium constant,

$$\Delta G^0 = -RT \ln K$$

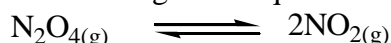
1.5 Le Chatelier's principle

This states that if one of the factors affecting the position of a system in equilibrium is changed, the system reacts in such a way as to nullify the effect of the change.

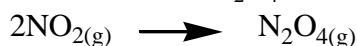
Factors affecting the equilibrium position.

1. Temperature

Consider the homogenous equilibrium reaction



The dissociation of N_2O_4 into NO_2 gives rise to a higher number of gaseous species in the enclosed system. This means an increase in the number of moles, n , of the mixture. From the general gas equation, $PV = nRT$. n can only increase if T increases, since PV/R will be constant. Thus, the dissociation of N_2O_4 is favoured by an endothermic reaction whereas, the reverse



is an exothermic process.

$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$$

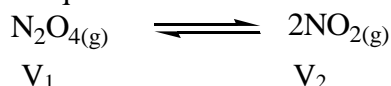
An example of a heterogeneous equilibrium is the dissociation of copper (ii) oxide into copper (i) oxide at elevated temperature.



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

2. Pressure

Using the equilibrium reaction



Note that V_1 is less than V_2 . To increase V_1 to V_2 , i.e for the forward reaction to occur, the pressure, P , of the system must be lowered.

Since

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

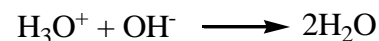
In the above expression, the term nRT is a constant. Increasing P drives the reaction to the left, leading to the formation of more N_2O_4 .

3. Concentration

Consider the dissociation of the acidic visual acid-base indicator, HX .



The indicator has different colours in acidic and basic media. Thus, if the concentration of H_3O^+ is increased by adding an acid to the mixture, the equilibrium will shift to the left and colour 1 becomes predominant. If on the other hand, a base (containing OH^- ions) is added to the system, the equilibrium will be in favour of the formation of the conjugate base, X^- ; the reaction will proceed in the forward direction since the reaction



removes H_3O^+ from the system, causing more HX to dissociate.

4. Catalyst

A catalyst influences both the forward and reverse reactions to the same extent and so has no effect on the equilibrium position of the reaction. It only helps the system to reach the state of equilibrium faster.

1.6 Equilibrium in acid-base media

1.6.1 The acid-base theory.

Arrhenius theory.

Acids and bases are substances that ionize in water to produce H^+ and OH^- ions respectively.

Brsted-Lowry theory;

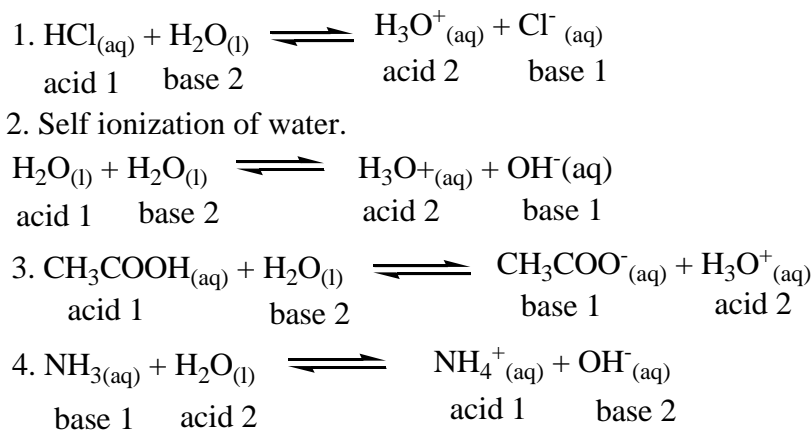
Acids and bases are species which donates and accepts protons respectively

Lewis theory classifies acids and bases as substances which can accept and donate a pair of electrons respectively.

1.6.2 Acid- base equilibria

The Lowry- Bronsted theory will be used in this section, since the concern here is the aqueous systems.

According to this theory, specie having a tendency to loose a proton is an acid and will give rise to a conjugate base for having a tendency to accept a proton. Therefore, the conjugate base of a Bronsted acid is the specie that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Bronsted base.

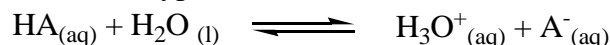


1.6.3 Strength of acids and bases

Strong acids and bases are completely dissociated in water while weak ones are weakly or partially ionised.

1.6.4 Dissociation constant

Consider a typical acid, HA,



Applying the equilibrium law, we obtain

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}, \text{ where } K_a \text{ is the dissociation constant of the acid.}$$

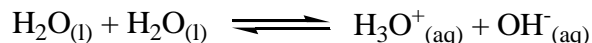
Water is weakly dissociated, so that essentially, the concentration is constant. We can therefore write; $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

For a typical base, B;



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}, \text{ } K_b \text{ is the dissociation constant of the base.}$$

1.6.5 Self ionization of water;



$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$, where K_w is the ionic product of water.

$K_w = 10^{-14}$ at 298K when concentration is expressed in mol dm^{-3} . For a neutral solution,

$[\text{H}_3\text{O}^+] = [\text{OH}^-]$ and since $[\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$

$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$.

1.6.6 The p^H scale

p^H is the negative logarithm of the hydrogen (or hydroxonium ion) concentration.

Thus,

$$p^H = -\log [\text{H}_3\text{O}^+]$$

In any solution, $[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$,

So that, $\log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] = \log K_w$,

$-\log [\text{H}_3\text{O}^+] - \log [\text{OH}^-] = -\log K_w$

$$p^{\text{H}} + p^{\text{OH}} = p^{K_w} = 14$$

In a neutral solution therefore, $p^{\text{H}} = p^{\text{OH}} = 7$.

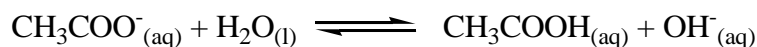
1.6.7 Relationship between acids - bases ionization constants

Consider the following reaction;



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

The conjugate base CH_3COO^- , reacts with water according to the equation



$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

Multiplying K_a by K_b gives,

$$K_a \cdot K_b = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

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

$$= K_w$$

Therefore,

$$K_a \cdot K_b = K_w$$

The above equation can be expressed as;

$$K_a = \frac{K_w}{K_b}, K_b = \frac{K_w}{K_a}$$

This means that the stronger the acid (larger K_a), the weaker its conjugate base (smaller K_b) and vice versa.

The equation can also be expressed in terms of the logarithms.

$$\log K_a + \log K_b = \log K_w$$

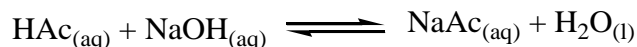
$$-\log K_a - \log K_b = -\log K_w$$

$$p^{K_a} + p^{K_b} = p^{K_w}$$

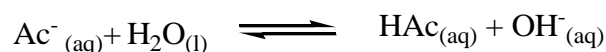
A large value of p^{K_a} (small K_a) indicates a weak acid. The neutralization reaction between a strong acid and a strong base gives rise to a stable product. On the other hand, if the reaction is between a strong acid and a weak base, or a weak acid and a strong base, or a weak acid and a weak base, the product reacts with the solvent.

1.6.8 Salt of a weak acid and a strong base, e.g NaAc.

In the reaction,



The product sodium ethanoate, NaAc reacts with water as follows;



$$K_h = \frac{[\text{HAc}][\text{OH}^-]}{[\text{Ac}^-]}, \text{ where } K_h \text{ is referred to as the hydrolysis constant.}$$

Multiplying both the numerator and denominator by $[H_3O^+]$, gives

$$K_h = \frac{[HAc][OH^-][H_3O^+]}{[Ac^-][H_3O^+]} \\ = K_w / K_a$$

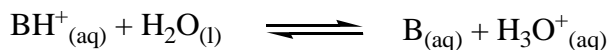
For a weak acid, K_a is small so that K_h will be large.

1.6.9 Salt of a strong acid and a weak base, e. g NH_4Cl .

Consider the reaction;



The product NH_4Cl may be written as BH^+ and reacts with water as follows:

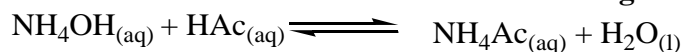


$$K_h = \frac{[B][H_3O^+]}{[BH^+]}$$

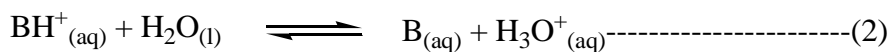
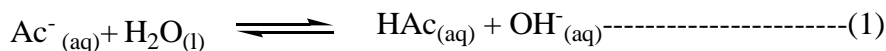
Multiplying the numerator and denominator by $[OH^-]$, gives

$$K_h = \frac{[B][H_3O^+][OH^-]}{[BH^+][OH^-]} \\ = K_w / K_b$$

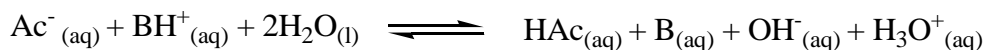
1.6.10 Salt of a weak acid and a weak base e. g NH_4Ac



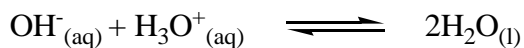
Writing NH_4Ac as BH^+Ac^- , we have the following reaction



Combining (1) and (2) gives



Now,



So that



$$\text{and } K_h = \frac{[HAc][B]}{[Ac^-][BH^+]}$$

Multiplying the numerator and denominator by $[H_3O^+][OH^-]$, gives

$$K_h = \frac{[HAc][B][H_3O^+][OH^-]}{[Ac^-][BH^+][H_3O^+][OH^-]} \\ = K_w / K_a \cdot K_b$$

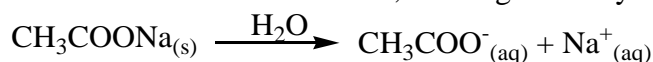
1.7 Buffer solutions

A buffer solution is a solution of a weak acid or a weak base and its salt with the ability to resist changes in p^H upon addition of small amounts of either acid or base.

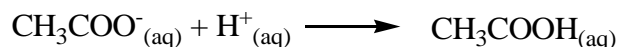
A buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that may be added to it and must contain similar concentration of base to react with any added H^+ ions. Furthermore, the acid and base components of buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair (a weak acid and its conjugate base or a weak base and its conjugate acid)

A simple buffer solution can be prepared by adding comparable amounts of ethanoic acid (CH_3COOH) and sodium ethanoate (CH_3COONa) to water. The equilibrium concentrations of both the acid and the conjugate base (from CH_3COONa) are assumed to be the same as the starting concentrations. This is so because; (1) CH_3COOH is a weak acid and the extent of hydrolysis of CH_3COO^- ion is very small and (2) the presence of CH_3COO^- ions suppresses the ionization of CH_3COOH , and the presence of CH_3COOH suppresses the hydrolysis of CH_3COO^- ions.

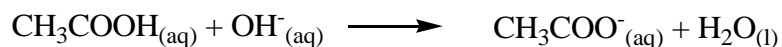
A solution containing these two substances has the ability to neutralize either added acid or added base. Sodium ethanoate, a strong electrolyte, dissociates completely in water;



If an acid is added, the H^+ ions will be consumed by the conjugate base in the buffer, CH_3COO^- , according to the equation;



If a base is added to the buffer system, the OH^- ions will be neutralized by the acid in the buffer;



The buffering capacity, that is the effectiveness of the buffer solution, depends on the amounts of acid and conjugate base from which the buffer is made. The larger the amount, the greater the buffering capacity.

In general, a buffer system can be represented as salt/acid or conjugate base/acid. Thus the sodium ethanoate-ethanoic acid buffer system can be written as

CH_3COONa/CH_3COOH or CH_3COO^-/CH_3COOH

1.7.1 Preparing a buffer solution with a specific P^H . (The Henderson-Hasselbalch equation)

Referring to the ethanoic acid-sodium ethanoate buffer system, we can write the equilibrium constant as;

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Rearranging the equation gives;

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Taking the negative logarithm of both sides, we obtain

$$-\log[H^+] = -\log K_a - \log \frac{[CH_3COOH]}{[CH_3COO^-]}$$

or

$$-\log[H^+] = -\log K_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

So that

$$p^H = p^{K_a} + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$p^H = p^{K_a} + \log \frac{[\text{salt}]}{[\text{acid}]}$$

This is called the Henderson-Hasselbalch equation.

Generally, it is written as

$$p^H = p^{K_a} + \log \frac{[\text{Conjugate base}]}{[\text{acid}]}$$

Similarly for a mixture of a weak base and its salt with a strong acid

$$p^{OH} = p^{K_b} + \log \frac{[\text{salt}]}{[\text{base}]}$$

If the molar concentrations of the acid and its conjugate base are approximately equal, that is, $[\text{acid}] \approx [\text{conjugate base}]$, then

$$\log \frac{[\text{Conjugate base}]}{[\text{acid}]} \approx 0$$

$$\text{Or } p^H \approx p^{K_a}$$

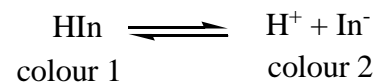
Thus, to prepare a buffer solution, we choose a weak acid whose p^{K_a} is close to the desired p^H .

This choice not only gives the correct p^H value of the buffer system, but also ensures that we have comparable amounts of the acid and its conjugate base present; both are prerequisites for the buffer system to function effectively.

1.8 Acid-Base Indicators

These are weak organic acids or bases used for visual end point location in the course of a titration involving neutralization. Acid-base indicators change colour over a definite pH range and have different colours in acid and basic media. The difference in colours is as a result of differences in the colours of the conjugate acid-base forms.

Consider a weak acid indicator HIn, It dissociates as follows;



$$K_{In} = \frac{[H^+][In^-]}{[HIn]}, \text{ where } K_{In} \text{ is the dissociation constant of the indicator HIn.}$$

Rearranging, we have;

$$[H^+] = K_{In} \cdot \frac{[HIn]}{[In^-]}$$

$$p^H = p^{K_{In}} - \log \frac{[\text{Acid form}]}{[\text{basic form}]}$$

For a weak base indicator, InOH,



$$K_{\text{In}} = \frac{[\text{In}^+][\text{OH}^-]}{[\text{InOH}]}$$

Rearranging, we have;

$$[\text{OH}^-] = K_{\text{In}} \cdot \frac{[\text{InOH}]}{[\text{In}^+]}$$

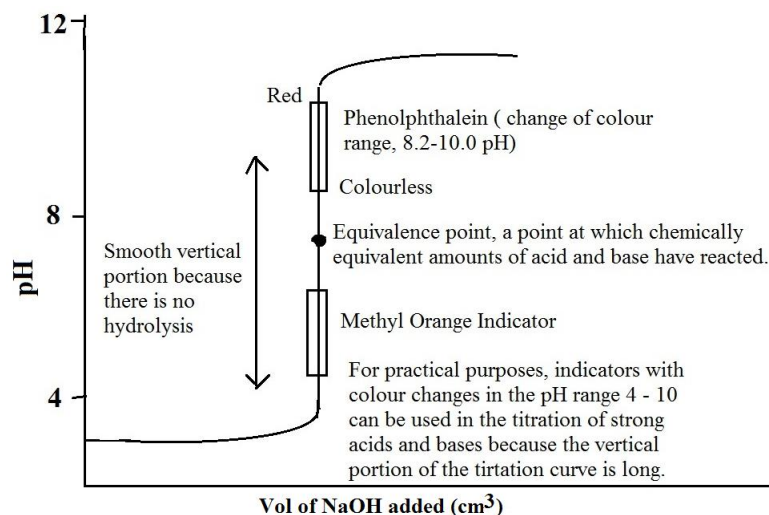
$$\therefore \text{p}^{\text{OH}} = \text{p}^{K_{\text{In}}} - \log \frac{[\text{Basic form}]}{[\text{Acid form}]}$$

Since indicators for acid-base titrations are weak organic acids and bases, and are added to the solution in very small amounts, the p^{H} or p^{OH} of the medium is essentially that of the solution. The colour changes depending on whether protons are removed or added to the solution.

1.9 Titration curves

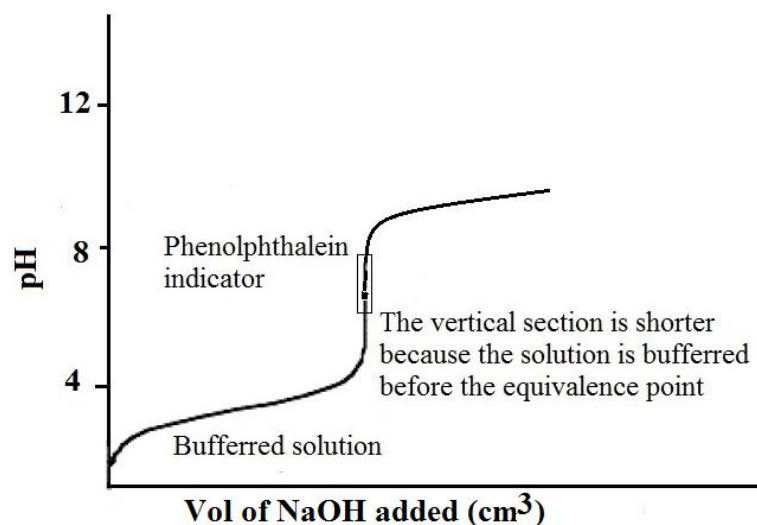
A titration curve is a plot of pH versus the amount (usually volume) of acid or base added. It displays graphically the change in pH as acid or base is added to a solution and shows how pH changes near the equivalence point. The point at which the color of an indicator changes in a titration is known as the end point. It is determined by the K_{in} value for the indicator. Typically, color changes occur over a range of 1.5 to 2.0 pH units. The equivalence point is the point at which chemically equivalent amounts of acid and base have reacted. Ideally, the end point and the equivalence point in a titration should coincide. In practice, an indicator is selected such that the range of color change includes the equivalence point.

1.9.1 Titration of a strong acid by a strong base (e.g HCl and NaOH)



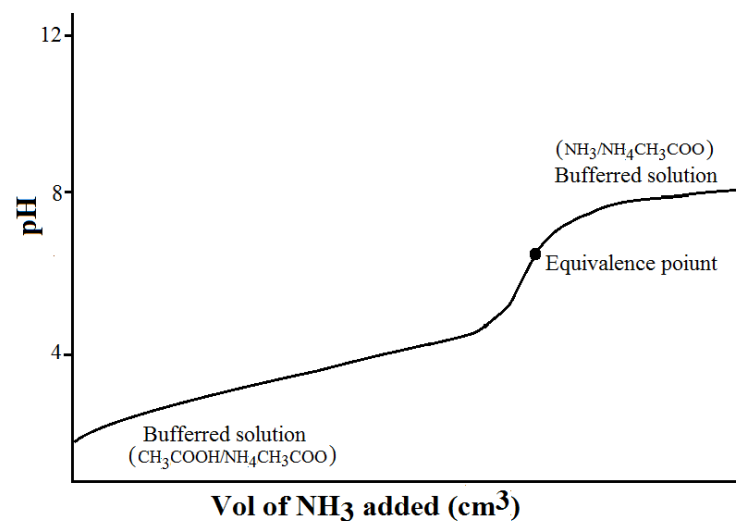
1. Before any strong base is added, the pH depends on the strong acid alone.
2. After some strong base has been, but before the equivalence point, the remaining (excess) strong acid determines the equivalent pH.
3. At the equivalence point, the solution is neutral.
4. Beyond the equivalence point, excess strong base determines the pH.

1.9.2 Titration of a weak acid by a strong base (e.g CH_3COOH and NaOH)



1. Before any base is added, the pH depends on the weak acid alone.
2. After some base has been added, but before the equivalence point, a series of weak acid/salt (e. g. $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$) buffer solutions determines the Ph.
3. At equivalence point, hydrolysis of the anions of the weak acid determines the pH.
4. Beyond the equivalence point, excess strong base determines the pH.

1.9.3 Titration of a weak acid by a weak base (e. g. CH_3COOH and NH_3)



In titration curves for weak acids and weak bases, pH changes near the equivalence point are too small for color indicators to be used. The solution is buffered both before and after the equivalence point.

1.10 Solubility product

Small amounts of sparingly soluble salts ionise in water. If a true equilibrium exists between the ions and the solid salt, an equilibrium constant expression can be written for the reaction. For example, silver chloride ionises as follows;



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

At constant temperature, the concentration of AgCl is unchanged since it does not dissolve in the water. This constant can therefore be combined with the equilibrium constant, thus,

$K[\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$ or $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$, where K_{sp} is known as the solubility product. It is the ionic product in a saturated aqueous solution at a given temperature. In an unsaturated solution, the ionic product is less than K_{sp} , therefore, any precipitate will dissolve until ionic product equals the value of K_{sp} . A super saturated solution contains more solute that can dissolve at a given temperature; the ionic product therefore, is greater than K_{sp} . Precipitation must take place in such a solution to make K_{sp} equal to the ionic product.

1.10.1 Application of solubility product

In both qualitative and quantitative chemical analysis, it may be necessary to remove one salt from a solution by using differences in solubilities of the salts. Consider the separation of Zn^{2+} and Fe^{2+} as their sulphides. Their solubility products are;

$[\text{Zn}^{2+}][\text{S}^{2-}] = 4.5 \times 10^{-24}$ and $[\text{Fe}^{2+}][\text{S}^{2-}] = 1 \times 10^{-19}$, the ZnS being less soluble.

Suppose the Zn^{2+} and Fe^{2+} concentration is 0.1 mol dm^{-3} . On adding S^{2-} ions to the solution, the precipitation of FeS occurs only when $[\text{Fe}^{2+}][\text{S}^{2-}] = K_{sp}$. That is, when

$$[\text{S}^{2-}] = \frac{K_{sp}}{[\text{Fe}^{2+}]} = \frac{1.0 \times 10^{-19}}{0.1} = 10^{-18} \text{ mol dm}^{-3}$$

While the precipitation of ZnS will occur when $[\text{S}^{2-}] = \frac{4.5 \times 10^{-24}}{0.1} = 4.5 \times 10^{-23}$

The $[\text{Zn}^{2+}]$ ion remaining in solution when FeS precipitates is

$$[\text{Zn}^{2+}] = \frac{K_{sp}}{[\text{S}^{2-}]} = \frac{4.5 \times 10^{-24}}{1 \times 10^{-18}} = 4.5 \times 10^{-6} \text{ mol dm}^{-3}.$$

This indicates that the precipitation of ZnS is essentially complete by the time FeS begins to precipitate and the two ions can be easily separated by precipitation method.

1.10.2 Common-Ion effect

Consider the equilibrium,

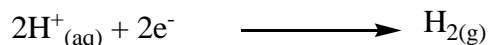
$\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$ in a solution of HX. This equilibrium is affected when more H^+ or X^- are added to the system from an external source. The system will not readily accept the added ions as it would if the same ions were not already present in the solution. This phenomenon is known as common ion effect. It affects the solubility of an electrolyte.

2.0 ELECTROCHEMISTRY

This branch of chemistry deals with the use of chemical reactions to produce electricity and the use of electricity to produce a chemical change. The process relies on redox reactions at the electrodes to produce ions in solution. These ions are responsible for maintaining electrolytic conduction; that is, the conduction of electric current by means of ions of electrolyte in solution or in molten state.

2.1 Electrode reactions

In an electrochemical cell, reduction occurs at the cathode and oxidation at the anode. Consider the electrolytic cell below; electrons enter the solution at the cathode, where H^+ or Na^+ ions react with them, leading to reduction of the cation



Electrons leave the solution at the anode by discharge of Cl^- or OH^- ions. The anions thus becomes oxidised.

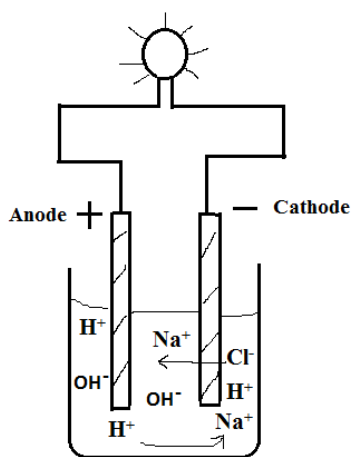


Figure 1. An electrolytic cell.

The electrode reactions indicate that oxidation is a process of electron loss and reduction is a process of electron gain. Both processes occur simultaneously in the cell, since every electron lost at the anode must be gained at the cathode to maintain electrical neutrality of the electrolyte solution.

2.2 Electrochemical cells

The experimental apparatus for generating electricity through the use of a redox reaction is called an electrochemical cell.

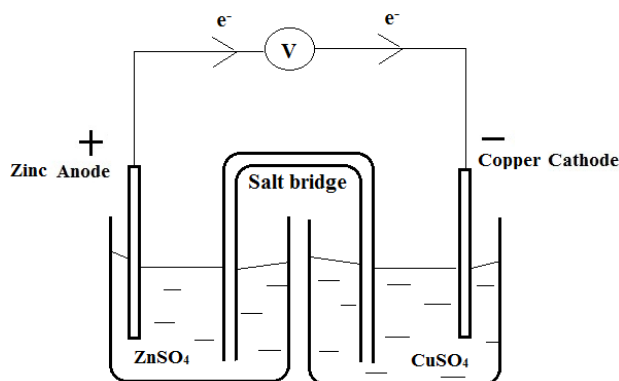
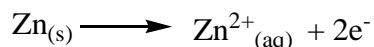


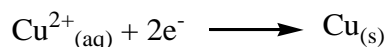
Fig 2. Daniel cell

A zinc bar is dipped into a ZnSO_4 solution and a bar of Cu is dipped into CuSO_4 solution. The galvanic cell operates on the principle that oxidation of Zn to Zn^{2+} and a reduction of Cu^{2+} to Cu can be made to take place simultaneously in separate locations with the transfer of electrons through the external wire. As the reaction progresses, it sets up a constant flow of electrons and hence, generates electricity. A salt bridge which is a glass tube connecting concentrated KCl or KNO_3 solution joins the two compartments together and serves to keep the two solutions electrically neutral. The origin of the current is through the half cell reactions at the electrodes.

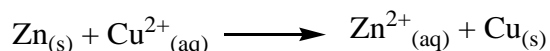
Anode;



Cathode;



Overall reaction;

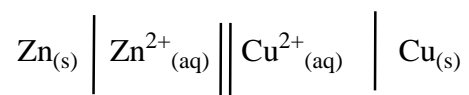


2.3 Electrode potential (E)

This is the tendency of an electrode to release to or attract electron from the surrounding electrolyte solution. The zinc plate in the example above has a negative electrode potential and thus, a great tendency to lose electrons to the surrounding solution. Another way of describing the phenomenon is to say that zinc in contact with a molar solution of its own ions has a greater electrolytic solution pressure than deposition pressure. Copper on the other hand has a positive electrode potential or greater deposition pressure.

2.4 Cell representation

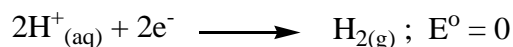
The arrangement of electrodes in a cell can be summarized by the notation such as that shown below for the Daniel cell.



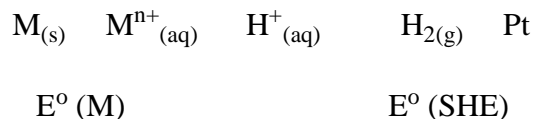
The cathode is shown on the right hand and the anode on the left. The double vertical bar separating the two compartments represents the salt bridge.

2.5 Standard electrode potential (E°)

This is the potential measured under standard conditions of temperature (298K), pressure (1 atmosphere) and concentration (1 mol dm^{-3}) of metal ion solution. It is measured against a reference standard. The hydrogen electrode has been adopted as the standard and it consists of H_2 gas at 1 atmosphere pressure, in contact with a molar solution of its ions at 298K. A platinum electrode coated with platinum black is incorporated to catalyse the attainment of equilibrium between H_2 gas and H^+ ions in the solution.



The hydrogen electrode under these conditions is assigned a value of zero by convention. The standard electrode potential of a given system $\text{M}^{n+}_{(\text{aq})}|\text{M}_{(\text{s})}$ is found by connecting it to a H_2 electrode via a salt bridge. By convention, the negative pole is assigned a negative potential and the positive pole, a positive potential.



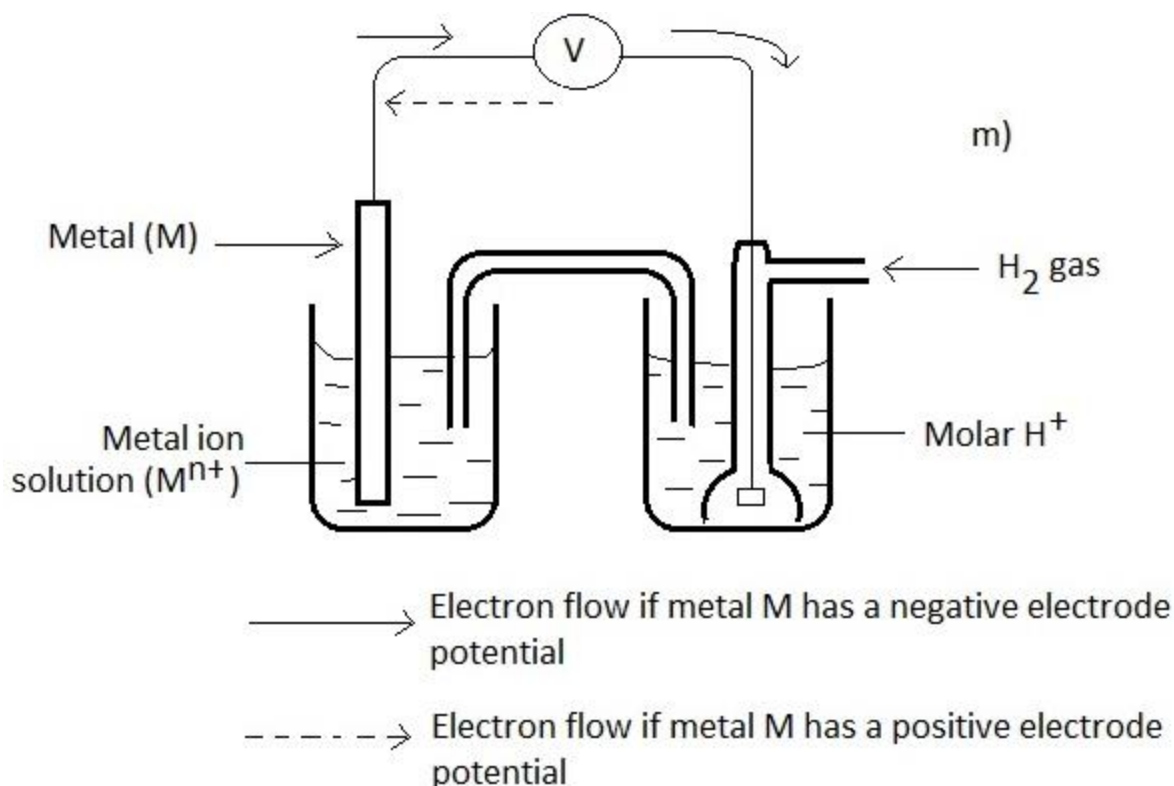


Figure 3. Set up for the standard hydrogen electrode

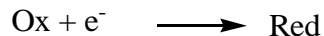
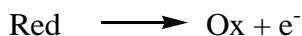
A table of standard hydrogen electrode potential is similar to the electrochemical series. Metals higher than hydrogen in the series (with alkaline metals lower down) have a positive electrode potential while those below have a negative electrode potential (also called redox potential). In other words, the lower the position of a couple in the table, the greater the reducing power of the reduced substance. It follows that when two couples form a cell, the couple lower down in the table forms the anode of the cell and the couple higher up forms the cathode. Thus, in the half-cell reaction, the lower couple can be written as the oxidation and the upper couple as a reduction.

Lower couple

upper couple

Anode compartment

Cathode compartment



2.6 Dependence of redox potentials on ionic concentration and temperature.

The value of the potential difference between a metal and a solution of its own ion is dependent upon the ionic concentration and the temperature. If the ionic concentration is decreased, the tendency for the metal ions to deposit on the metal will be reduced, that is, the electrode potential of the metal will become less positive. Similarly, if the metal ion concentration is increased, the electrode potential will be more positive. The dependence of electrode potential on metal ion concentration and temperature is expressed by the Nernst equation,

$$E = E^{\circ} + \frac{RT}{nF} \ln[M^{n+}]$$

Where E is the e.m.f of the cell and E° is the standard electrode potential, s.e.p, (for a molar solution of metal ions at 298K. R is the gas constant ($8.31 \text{ Jmol}^{-1} \text{ K}^{-1}$), T is the temperature in Kelvin, n is the number of electrons transferred and F is the Faraday.

Verification of the equation involves the measurement of electrode potential of a metal for different metal ion concentrations at a given temperature. A metal (metal ion hlf-cell) is connected via a salt bridge to a standard hydrogen electrode. The potential of various cells are recorded and a plot of E values against $\ln[M^{n+}]$ gives a straight line. A similar graph is obtained at various temperatures for fixed concentrations of M^{n+} .

2.7 Cell potential and reaction free energy

Cell potential, E, is proportional to the free energy of reaction.

$$\Delta G \propto -E$$

This is the case since a large negative value of ΔG indicates that the reaction has a tendency to occur spontaneously and drive electrons through the circuit. If ΔG is negative but small, we expect a small cell potential, while the value of $\Delta G = 0$ indicates that the cell reaction is at equilibrium and has no tendency to drive electrons through the circuit. Under this condition $E=0$ and no current flows in the circuit. The chemical energy released is equal to the decrease in free energy. If n moles of electrons are transferred per mole of chemical energy, the decrease in free energy is

$$-\Delta G = nFE \text{ or } \Delta G = -nFE$$

where F is the faraday (96500 Coulombs).

If the constituents of the cell are in their standard states, then we define the standard free energy of the half-cell reaction as

$$G^{\circ} = -nFE^{\circ}$$

where E° is the standard electrode potential and G° is the standard free energy of the reaction. This is a measure of the tendency of reactants in their standard states to yield products in their standard states.

2.8 Equilibrium constants of cell reactions

Since

$$\Delta G^{\circ} = -RT \ln K \text{ and } G^{\circ} = -nFE^{\circ}, \text{ then } \ln K = \frac{nFE^{\circ}}{RT}$$

The equilibrium constant for a cell reaction can thus be calculated from the above relationship.