COURSE CODE: CHM 101

COURSE TITLE: INTRODUCTORY PHYSICAL CHEMISTRY

NO OF UNITS: 03

COURSE DURATION: THREE HOURS PER WEEK

COURSE DETAILS:

PART TITLE: CHEMICAL EQUILIBRIUM

COURSE LECTURER: DR. S.A. AHMED

COURSE CONTENT:

The concept of equilibrium

- Equilibrium Law (Law of Mass action)

- Relationship between K_p and K_c

- Relationship between ΔG and K

- Effect of temperature on the equilibrium constant.

- Homogenous chemical equilibria

- Heterogeneous equilibria system

- Factors affecting equilibrium constants

- Chemical equilibrium in solution

  • water dissociation constant

  • hydrolysis and hydrolysis constant

- Solubility equilibria

- Common-ion effects

COURSE REQUIREMENTS:

Students are expected to have a minimum of 75% attendance in this course before they could be allowed to write the examination.

READING LIST:

1. Gross, J.M. and Wiseall, B. *Principle of physical chemistry*. MacDonald and Evans Handbook series, 1972

2. Atkins, P.W. *Physical chemistry*. Oxford University Press, sixth edition, 1999

3. Bahl, A and Bahl, B.S. *Essentials of physical chemistry*, S.Chand and Company Ltd. 2007

4. Brown, T.L., Lemay, H.E., Bursten, B.E and Murphy, C.J *Chemistry: The central science*. Pearson Education, 11th Edition 2009.

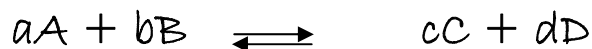5. Sharma, K.K. and Sharma, L.K. *Physical chemistry*

LECTURE NOTES

Lecture 1

Concept of Equilibrium

Consider this direct reaction,

$$aA + bB \longrightarrow cC + dD$$
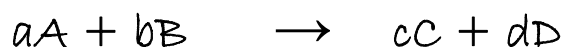
The reaction stops when the reactants are used up.

However, for a reversible reaction like this

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

the equilibrium is attained when the rate of forward reaction is equal to the rate of backward reaction.

Chemical equilibrium is the state of a reversible reaction when the two opposing reactions occur simultaneously.

At equilibrium, the concentrations of reactants and products do not change with time.

The Equilibrium Law (Law of Mass action)

The law states that "at constant temperature, the rate at which a substance reacts is directly proportional to the active masses of the reactant"

Active mass is a thermodynamic quantity and it is expressed $a=fc$, where a -active mass, f- activity co-efficient (fugacity), c- molar concentration.

For ideal gaseous and solution reaction, $f = 1$.

Therefore, the active mass is equal to molar concentration.

According to the law, $R_f \; \alpha \; [A]^a [B]^b$

$$\Rightarrow \quad R_f = K_f \; [A]^a [B]^b$$

Also, $R_b \; \alpha \;\; [C]^c [D]^d$

$\implies \quad R_b = K_b \;\; [C]^c [D]^d$

At equilibrium, $K_f \;\; [A]^a [B]^b = K_b \;\; [C]^c [D]^d$

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

K_c is the equilibrium constant in term of concentration,

In term of activities,

$$K_A = \left\{ \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} \right\},$$

The concept of activity addresses the deviation from ideal behaviour. Therefore, it can be defined as an idealized concentration. K_A is exact and does not depend on pressure.

In term of pressure,
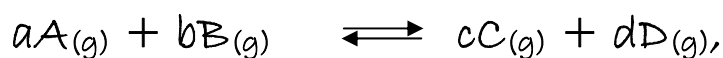
$$K_p = \frac{P_C^{\;c} P_D^{\;d}}{P_A^{\;a} P_B^{\;b}} \qquad \text{where } P_A^{\;a}, P_B^{\;b}, P_C^{\;c} \text{ and } P_D^{\;d} \text{ are the}$$

partial pressure of various gaseous species at equilibrium.

Relationship between K_p and K_c

In a gaseous reaction, the concentration of the gases at any given temp is expressed in term of their partial pressures.

Consider this gaseous reaction

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)},$$

the equilibrium constant in term of pressure is expressed as

$$K_p = \frac{P_C^{\,c}\, P_D^{\,d}}{P_A^{\,a}\, P_B^{\,b}}$$ where $P_A^{\,a}$, $P_B^{\,b}$, $P_C^{\,c}$ and $P_D^{\,d}$ are the

partial pressure of various gaseous species at equilibrium.

However, K_p and K_c are not numerically equal, the relationship can be derived as follow

For an ideal gases,

$$PV = nRT$$

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

But $\dfrac{n}{V} = C$

$\therefore \qquad P = CRT$

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

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

Recall that

$$K_c = \frac{C_C{}^c D_D{}^d}{A_A{}^a B_B{}^b}$$

$\therefore \qquad \boxed{K_p = K_c (RT)^{\Delta n}}$

Where $\Delta n = (c+d) - (a+b)$ i.e change in the amount of gaseous reagents

When Δn is positive, $\Rightarrow$ the number of molecules of products are larger than those of the reactants i.e $K_p > K_c$

When Δn is zero, $\Rightarrow$ the number of molecules of products = the number of molecules of the reactants i.e $K_p = K_c$

When Δn is negative, $\Rightarrow$ the number of molecules of products are smaller than those of the reactants i.e $K_p < K_c$

If the equilibrium constant is expressed in term of mole fractions, X it is related to K_p by

$$K_p = \frac{(X_C P)^c (X_C P)^d}{(X_A P)^a (X_B P)^b}$$

$$K_p = \left(\frac{(X_C)(X_D)}{(X_A)(X_B)} \right) \times P^{(c+d)-(a+b)}$$

$$\therefore \quad K_p = K_x P^{\Delta n}$$

where $\Delta n = (c+d) - (a+b)$

Relationship between ΔG and the equilibrium constant

The change in free energy of a reaction and the equilibrium constant K are related to each other by the expressions

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

Temperature dependence on the equilibrium constant

The value of equilibrium constant varies with temperature change. The relationship between the equilibrium constants at two different temperatures and the enthalpy change is given by

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^o}{2.303R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

Where K_{p_2} and K_{p_1} are the equilibrium constants at temperature T_2 and T_1 respectively.

In terms of change in internal energy (ΔE^o), the equation becomes

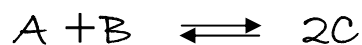$$\log\frac{K_{p_2}}{K_{p_1}} = \frac{\Delta E^o}{2.303R}\left[\frac{T_2 - T_1}{T \times_1 T_2}\right]$$
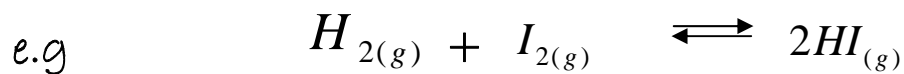
HOMOGENOUS CHEMICAL EQUILIBRUM

Homogenous equilibrium is an equilibrium in which the reactants and the products are in the same phase.

-Homogenous gaseous equilibria

<u>Case I:</u>   The Hydrogen-Iodide system

Consider a reaction

A + B $\rightleftharpoons$ 2C

e.g $\qquad H_{2(g)} \ + \ I_{2(g)} \ \rightleftharpoons \ 2HI_{(g)}$

t=0 $\qquad a \qquad\qquad b$

t=t $\qquad a\text{-}x \qquad b\text{-}x \qquad\qquad 2x$

if V (in dm³) is the total volume of the reaction mixture

then, $\qquad \dfrac{a-x}{V} \qquad\qquad \dfrac{b-x}{V} \qquad\qquad \dfrac{2x}{V}$

Hence, $\qquad K_c = \dfrac{[HI]^2}{[H_2][I_2]} \ = \dfrac{\left(\frac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-x}{V}\right)}$

$$K_c = \frac{4x^2}{(a-x)(a-b)}$$ K_c is independent of the volume

In term of partial pressure,

$$K_p = \frac{P_C^2}{P_A \times P_B}$$

But $\qquad P_A = \dfrac{n_A}{N} \times P, \qquad P_B = \dfrac{n_B}{N} \times P \quad$ and $\quad P_C = \dfrac{n_C}{N} \times P$

Where $\qquad N = n_A + n_B + n_C =$ total number of moles,

$P =$ total (external) pressures $P_A, P_B \,\&\, P_C$ are partial pressures of A, B and C respectively.

$$\therefore \quad K_p = \frac{\left(\dfrac{n_C}{N} \times P\right)^2}{\left(\dfrac{n_A}{N} \times P\right) \times \left(\dfrac{n_B}{N} \times P\right)} = \frac{n_C^2}{n_A + n_B}$$

Examples:

1. A mixture of 1 mole of H_2 and 1 mole of I_2 in a flask was heated until the equilibrium is reached. On analysis, the equilibrium mixture is found to contain 0.7mole of HI. Calculate the K_c

2. Consider this reaction $\quad H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ Given that the partial pressures of the following substances at 45°C are $P_{H_2} = 0.065$atm, $P_{I_2} = 0.45$ atm. and $P_{HI} = 0.245$ atm. Calculate (a) the equilibrium constant K_p for the reaction at 45°C (b) the equilibrium constant K_p for the backward reaction

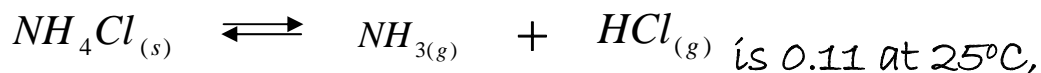3. K_c for this reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$
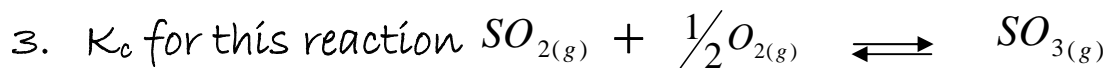
at 727°C is16.7, calculate K_p for this reaction at 727°C.

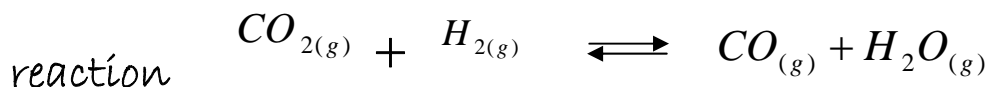N.B- Solutions to these examples shall be treated during the lecture hours

Exercises:

1. The K_p for this equilibrium reaction:

$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$ is 0.11 at 25°C,

calculate K_c at this temperature.

2. The following results were obtained during analysis of a

reaction $CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

3. At 25°C and 4 atm., PCl_5 is 10% dissociated, calculate

the K_p for this reaction, $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

Case II: $A \rightleftharpoons 2B$

e.g. Decomposition of N_2O_4,   i.e $N_2O_4 \rightleftharpoons 2NO_2$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(2x/V\right)^2}{\left(\dfrac{a-x}{V}\right)}$$

$$\therefore \quad K_c = \frac{4x^2}{(a-x)V}$$

In term of K_p,

$$K_p = \frac{[NO_2]^2}{[N_2O_4]} = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

Also, while considering the equation, if x represent the degree of dissociation, then $2x$ of NO_2 will be produced, then $1-x$ of N_2O_4 will be left. then, the total number of moles present at equilibrium = $(1-x) + 2x = 1+x$.

$$\therefore P_{N_2O_4} = \left(\frac{1-x}{1+x}\right)P \quad \& \quad P_{NO_2} = \left(\frac{2x}{1+x}\right)P$$

So,
$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{\left[\left(\dfrac{2x}{1+x}\right)P\right]^2}{\left(\dfrac{1-x}{1+x}\right)P}$$

$$\therefore \quad K_p = \frac{4x^2 P}{1-x^2}$$

Examples:

1. N_2O_4 at 1 atm and 25°C dissociated by 18.5%, calculate its K_p at this temperature. If the atmospheric temperature was reduced to half its original value at the same temperature, calculate the degree of dissociation of the gas.

2. N_2O_4 is 25% dissociated at 30°C and 1 atm., calculate
(a) The equilibrium constant for the decomposition

(b) The amount of NO_2 that would be attained if there had been 4 moles of N_2O_4 at the same temperature and pressure.

N.B- Solutions to these examples shall be treated during the lecture hours

Exercises:

1. N_2O_4 is 25% dissociated at 37°C and 1 atm., calculate
   (i)   The K_p and (ii) the % dissociation at 0.1 atm and 37°C
2. An equilibrium mixture at 27°C contains N_2O_4 and NO_2 having 0.28 atm. and 1.1 atm. pressures respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the gases.

Case III: A + 3B ⇌   2C

e.g. synthesis of Ammonia

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
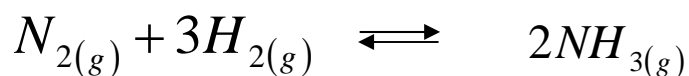
$$\frac{a-x}{V} \qquad \frac{b-x}{V} \qquad\qquad \frac{2x}{V}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(2x/V\right)^2}{\left(\dfrac{a-x}{V}\right) \times \left(\dfrac{b-x}{V}\right)^3}$$

$$\therefore \qquad K_c = \frac{4x^2V^2}{(a-x)(b-x)^3}$$

Also,

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

Examples:

1. In an experiment, H_2 and N_2 in the mole ratio 3:1 produced 0.0735mole fraction of NH_3 at 350°C and total pressure of 1013KNm⁻². Calculate Kp for the forward and reverse reactions

2. The K_p for this equilibrium reaction
$$N_2 {}_{(g)} + 3H_2 {}_{(g)} \rightleftharpoons 2NH_3 {}_{(g)}$$ is 1.45 x 10⁻⁵ at 500°C. Calculate the partial pressure of NH_3 when the partial pressure of H_2 is 0.928atm and that of N_2 is 0.432atm.

Exercise:

1. The dissociation pressure of $CaCO_3$ is 342mmHg at 840°C and at 860°C, the dissociation pressure is 420mmHg. Calculate the heat of dissociation of the carbonate. Given that R=8.314KJmol^{-1}.
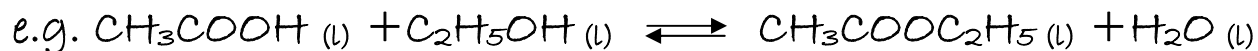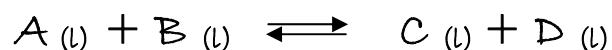
2. consider this reaction

N_2 (g) + $3H_2$ (g) ⇌ $2NH_3$ (g),
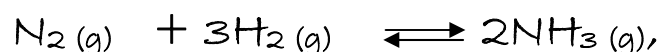
The K_p is 1.64x10^{-4} at 400°C. calculate (i) the ΔG of the reaction (ii) ΔG when the partial pressure of N_2, H_2 and NH_3 are 10atm, 30 atm and 3 atm respectively.

LECTURE 2

HOMOGENOUS (LIQUID) EQUILIBRIA

A (l) + B (l) ⇌ C (l) + D (l)

e.g. CH_3COOH (l) + C_2H_5OH (l) ⇌ $CH_3COOC_2H_5$ (l) + H_2O (l)

t=0	a	b	0	0
t=t	a-x	b-x	x	x

$$K_c = \frac{\left(\dfrac{x}{V}\right) \times \left(\dfrac{x}{V}\right)}{\left(\dfrac{a-x}{V}\right) \times \left(\dfrac{b-x}{V}\right)}$$

$$\therefore \qquad K_c = \frac{x^2}{(a-x)(b-x)}$$

The equation above is the general expression for the liquid equilibria. However, in the example above where water molecule is involved, the expression can be written as

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$\frac{K_c}{[H_2O]} = K_c^{'} = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

The above expression is written in term of $K_c^{'}$ because the concentration of water is taken to be constant, $K_c^{'}$ has the unit of $[Concn]^{-1}$ but K_c has no unit.

Example:

1. In an esterification process between 1 mole of ethanoic acid and 1 mole of ethanol at 25°C, 66.7% of the acid is esterified calculate the equilibrium constant and ΔG°.
2. When 1 mole of ethanoic acid and 1 mole of ethanol were heated together at a temperature of 25°C until the equilibrium is reached. Titration of the reaction mixture shows that 2/3 of the acid have been used up. Calculate the equilibrium constant.

HETEROGENEOUS EQUILIBRIA SYSTEM

Heterogeneous equilibrium is an equilibrium in which the reactants and the products are not in the same phase.
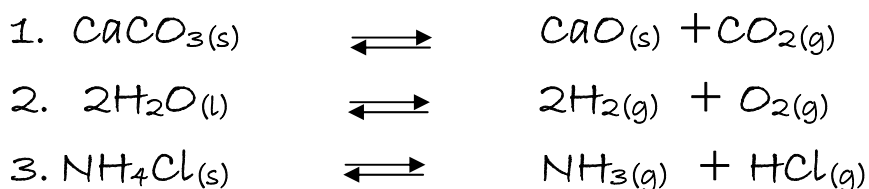
e.g. $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_4{}_{(s)} + 4H_2{}_{(g)}$
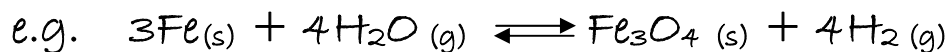
$$K_c = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4} = \frac{1 \times [H_2]^4}{1 \times [H_2O]^4} = \frac{[H_2]^4}{[H_2O]^4}$$

N.B: the concentration of substances in solid phase is
         taken to be unity.

In term of K_p,

$$K_p = \frac{P_{H_2}^4}{P_{H_2O}^4}$$

Exercises: Express the equilibrium constants K_p, for the
following reactions.

1. $CaCO_{3(s)}$ ⇌ $CaO_{(s)} + CO_{2(g)}$

2. $2H_2O_{(l)}$ ⇌ $2H_{2(g)} + O_{2(g)}$

3. $NH_4Cl_{(s)}$ ⇌ $NH_{3(g)} + HCl_{(g)}$

Le-Chatelier's Principle

It states that "if a chemical system is in equilibrium and one
of the factors involved in the equilibrium is altered, the
equilibrium will shift, so as to neutralize the effect of the
change".

FACTORS AFFECTING EQUILIBRIUM

The factors are: temperature, concentration and pressure of the reactants and products, catalyst.

N.B: catalyst does not change the position of equilibrium, but affects the reaction equally in both directions.

1. Effect of temperature changes on equilibrium mixture: If a chemical system is in equilibrium and the temperature is lowered, the equilibrium position according to Le-Chatelier's Principle will shift so as to neutralize the cooling effect by releasing more heat. Conversely, if the temperature is raised, the equilibrium position will shift so as to neutralize the heating effect by absorbing more heat.

e.g. $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ $\Delta H = +ve$
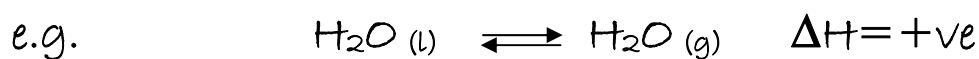
Since the forward reaction is an endothermic, if the temperature is raised, more steam will be produced and the equilibrium position will shift to the right. On the other hand, if the temperature is lowered, the equilibrium position shifts to the left and more water will be formed as the steam condenses.

The table below summarises the effect of temperature change on the equilibrium position.

Reversible reactions where	When the temp. of equilibrium system

forward rxn is endothermic	increases	decreases
$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$	Equilibrium position shifts to right, favouring forward rxn. K increases	Equilibrium position shifts to left, favouring backward rxn. K decreases
Forward rxn is exothermic $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$ $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$	Equilibrium position shifts to left, favouring backward rxn. K decreases	Equilibrium position shifts to right, favouring forward rxn. K increases

3. <u>Effect of temperature changes on equilibrium mixture:</u> This effect occurs in gaseous state reactions in which the total numbers of moles of gaseous molecules on the left hand side of the equation differ from that on the right hand side of the equation.

When the pressure of a system at equilibrium is increased, then the reaction that involves a reduction in pressure will be favoured. This is in line with the Le-Chatelier's principle. Conversely, if the pressure is lowered for a system at equilibrium, the reaction that will increase the pressure will be favoured.

e.g $\qquad$ $N_{2\ (g)} + 3H_{2\ (g)} \rightleftharpoons 2NH_{3\ (g)}$

$\qquad\qquad$ 4 moles $\qquad\qquad$ 2 moles
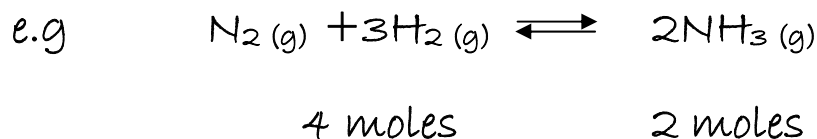
The forward reaction involves a decrease in the number of moles and hence, a decrease in the pressure of the system. Also, the backward reaction gives an increase in the number of moles, and hence an increase in the pressure of the system.

In the formation of ammonia, a high pressure will favour the forward reaction (where a reduction in volume occurs). This causes the equilibrium position to shift to the right. on the other hand, a low pressure will cause the equilibrium position to shift to the left, favouring the backward reaction.
The table below summarises the effect of a change in pressure on the equilibrium position.

Reversible reactions	Shift in equilibrium position when the pressure	
1.Forward rxns (decrease in vol)	Increases	decreases
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$	right right right	Left Left Left
2.Forward rxns (increase in vol)		
$N_2O_{4\ (g)} \rightleftharpoons 2NO_{2(g)}$	Left	right

3.No change in volume		
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{2\,(g)}$ $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4\,(s)}\ 2H_{2(g)}$	——— ———	——— ———

NB: the value of K remain constant irrespective of the shift in the equilibrium position.

Effect of temperature changes on equilibrium mixture: if the concentration of any of the substances present is changed without a change in any of the other conditions. According to Le-chatelier's principle, the equilibrium position will move to increase the concentration of the added substance.

e.g. $N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2NO_{(g)}$
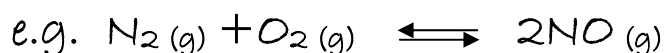
The addition of more reactants (either N_2 or O_2 or both)will upset the equilibrium. For the system to adjust, the equilibrium position will shift to the right thereby favourig

the forward reaction. This results in a proportional increase in the concentration of the product.

Similarly, if the product formed is continually removed fom the system, the equilibrium position will shift to the right to produce more of the product.

The effect of concentration change on equilibrium can be summarise in the table below

Reversible reactions	Addition of reactants or removal of products	removal of reactants or addition of products
$CaCO_{3(g)} \rightleftharpoons CaO_{2(g)} + CO_{2(g)}$ $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$	Equilibrium position shifts to the right	Equilibrium position shifts to the left

NB: the value of K remain constant irrespective of the shift in the equilibrium position.

4.<u>Effect of Catalyst</u>: Addition of catalyst has no effect on either the equilibrium constant or shift. It only speed up the rate at which the equilibrium is reached.

LECTURE III

CHEMICAL EQUILIBRIUM IN SOLUTION

  a. Dissociation of water:
$$H_2O_{(L)} \rightleftharpoons H^+ + OH^-$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

But $[H^+] = [OH^-] = 10^{-7}$ mol/dm³ at 25ºC and
$[H_2O] = $ constant

$$\therefore K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

K_w is the water dissociation constant.

Examples
  1. Calculate the $[OH^-]$ of the 0.01M HCL
 2. Calculate the $[H^+]$ of the 0.0001M NaCL

(b). Hydrolysis and hydrolysis constant

  when a salt of a strong acid and a strong base dissolved in water, the water remains neutral. However, when a salt

formed from a strong acid and a weak base or vice versa is dissolved in water, it either make the water acidic or basic.

e.g. (a) salt of strong base-weak acid like sodium ethanoate

(CH_3COONa) react with water to give an alkaline solution.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COO^- + H^+ + OH^-$$
$$\rightleftharpoons CH_3COOH + OH^-$$
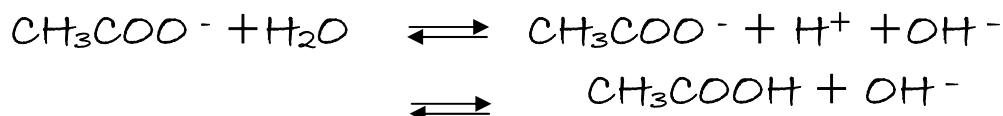
As the CH_3COO^- consume the H^+ from water to form ethanoic acid, more of the water molecules dissociate to produce more of their ions.

At equilibrium,

$$K_a = \frac{[HEt][OH^-]}{[Et^-][H_2O]}$$

But

$$\frac{[HEt][OH^-]}{[Et^-]} = [H_2O]K_a = K_h$$

K_h is the hydrolysis constant, but $K_w = [H^+][OH^-]$

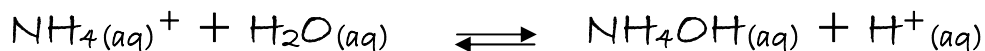$$\therefore \quad \left[OH^-\right] = \frac{K_w}{\left[H^+\right]} = \frac{K_w}{K_a}$$

The hydrolysis constant K_h is related to the aci dissociation constant by the expression

$$K_h = \frac{K_w}{K_a}$$

The degree of hydrolysis, **α**, is the fraction of the salt which has undergone hydrolysis when equilibrium is reached and it is given by

$$\alpha = \sqrt{\frac{K_w}{K_h \times C}}$$

(b). salt of weak base-strong acid, e.g NH₄Cl.
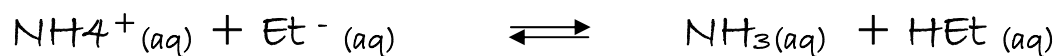
$$NH_{4(aq)}^+ + H_2O_{(aq)} \rightleftharpoons NH_4OH_{(aq)} + H^+_{(aq)}$$

$$\therefore \quad K_h = \frac{\left[NH_4OH\right]\left[H^+\right]}{\left[NH_4^+\right]}$$

but $\left[H^+\right] = \frac{K_w}{\left[OH^-\right]}$

$$\therefore \quad K_h = \frac{K_w}{K_b}$$

c. Salt of weak acid-weak base, e.g CH_3COONH_4

$$NH4^+_{(aq)} + Et^-_{(aq)} \rightleftharpoons NH_{3(aq)} + HEt_{(aq)}$$

The hydrolysis constant is given by

$$K_h = \frac{K_w}{K_a \times K_b}$$

and the degree of hydrolysis is given by

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Solubility Product

When a sparingly soluble salt e.g AgCl dissolves in water at a given temperature, a stage will be reached when it will not dissolve further and both the solid and and solution will co-exist in equilibrium.

$$AgCl_{(aq)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

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

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

Examples
1. Calculate the hydrolysis of a base whose dissociation constant is 1.75×10^{-5}.
2. The solubility of CuBr is found to be 2.0×10^{-4} mol/L at $25^{\circ}C$. calculate K_{sp} value for CuBr.
3. The solubility of Mg(OH)$_2$ at $25^{\circ}C$ is 0.00764g/L. what is the value of K_{sp} for Mg(OH)$_2$?

Exercises
1. Calculate the K_{sp} of AgCl whose solubility at $25^{\circ}C$ is 1.05×10^{-5} mol/L.
2. The solubility of BaSO$_4$ at $18^{\circ}C$ is 0.00233g/L. what is the value of K_{sp} for BaSO$_4$?

Common-ion Effect

When a soluble salt (say, A^+C^-) is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB will be suppressed.

$$AB \rightleftharpoons A^+ + B^-$$
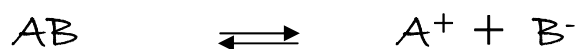
By the addition of the salt (AC), the concentration of A^+ increases. In line with the Le-chatelier's principle, the equilibrium will shift to the left, thereby decreasing the concentration of A^+ (i.e the degree of dissociation of AB will be reduced).

==Thus, the reduction of the degree of dissociation of a salt by the addition of a common-ion is called the common-ion effect.==

Examples
1. Calculate the $[H^+]$ when 0.1 mol acetic acid was treated with 0.2 mol acetate ion. The equilibrium constant is 1.8×10^{-5}.
2. Calculate the $[H^+]$ when 1 mol of sodium formate was added to 0.5 mol formic acid. Given that $K = 1.8 \times 10^{-5}$.