

CHM 101 LECTURE NOTE

COURSE TITLE: INTRODUCTORY PHYSICAL CHEMISTRY

CREDIT UNIT: 03

PART TITLE: CHEMICAL EQUILIBRIUM

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COURSE SYNOPSIS

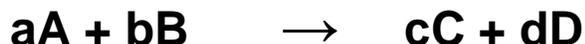
- **The concept of equilibrium**
- **Equilibrium Law (Law of Mass action)**
- **Relationship between K_p and K_c**
- **Relationship between ΔG and K**
- **Effect of temperature on the equilibrium constant.**
- **Homogenous chemical equilibria**
- **Heterogeneous equilibria system**
- **Factors affecting equilibrium constants**
- **Chemical equilibrium in solution**
 - **water dissociation constant**
 - **hydrolysis and hydrolysis constant**
- **Solubility equilibria**
- **Common-ion effects**

RECOMMENDED TEXTBOOKS/ **REFERENCES**

- 1. Principle of physical chemistry by J.M. Gross**
- 2. Physical chemistry by Atkins**
- 3. Essentials of physical chemistry by Bahl and Bahl**
- 4. Chemistry: The central science by Brown, Lemay,
Bursten and Murphy.**
- 5. Physical chemistry by K.K. Sharma and L.K.
Sharma**

Concept of Equilibrium

Consider this direct reaction,



The reaction stops when the reactants are used up.

However, for a reversible reaction like this



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 coefficient (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, $R_f \propto [A]^a [B]^b$

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

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

$$\Rightarrow R_b = K_b [C]^c [D]^d$$

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,

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

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



the equilibrium constant in term of pressure is expressed as

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

the partial pressure of various gaseous species at equilibrium.

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

For an ideal gases,

$$PV = nRT$$

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

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

$$\therefore P = CRT$$

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

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

Recall that

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

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

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

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

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

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

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

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T \times_1 T_2} \right]$$

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°), the equation becomes

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

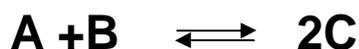
HOMOGENOUS CHEMICAL EQUILIBRUM

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

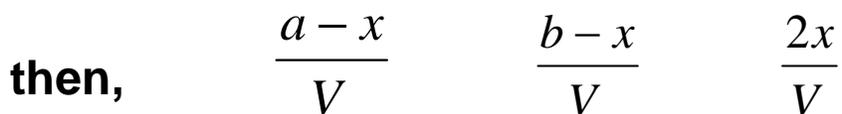
-Homogenous gaseous equilibria

Case I: The Hydrogen-iodide system

Consider a reaction



if V (in dm^3) is the total volume of the reaction mixture



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

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

K_c is independent of the

volume

In term of partial pressure,

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

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

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

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

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

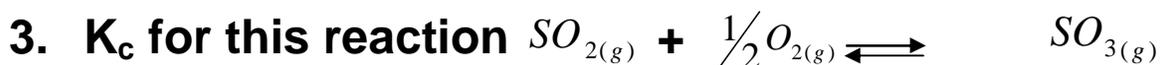
Examples:

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



Given that the partial pressures of the following substances at 45°C are $P_{H_2} = 0.065\text{atm}$, $P_{I_2} = 0.45\text{atm}$. and $P_{HI} = 0.245\text{atm}$. Calculate (a) the equilibrium constant K_p for the reaction at 45°C (b) the equilibrium constant K_p for the backward reaction

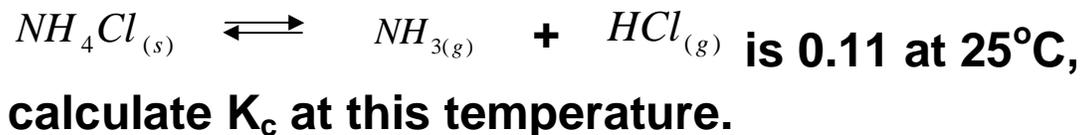


at 727°C is 16.7, calculate K_p for this reaction at 727°C .

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

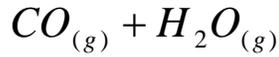
Exercises:

1. The K_p for this equilibrium reaction:



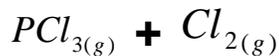
2. The following results were obtained during

analysis of a reaction $\text{CO}_{2(g)} + \text{H}_{2(g)}$



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

calculate the K_p for this reaction, $\text{PCl}_{5(g)}$



Case II: A \rightleftharpoons 2B

e.g. Decomposition of N_2O_4 , i.e. $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)}$$

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

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,

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

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

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

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

Examples:

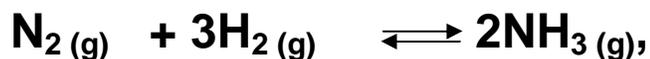
1. In an experiment, H₂ and N₂ in the mole ratio 3:1 produced 0.0735mole fraction of NH₃ at 350°C and total pressure of 1013KNm⁻². Calculate K_p for the forward and reverse reactions
2. The K_p for this equilibrium reaction

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 1.45×10^{-5}
 at 500°C. Calculate the partial pressure of NH₃ when the partial pressure of H₂ is 0.928atm and that of N₂ is 0.432atm.

Exercise:

1. The dissociation pressure of CaCO₃ 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.

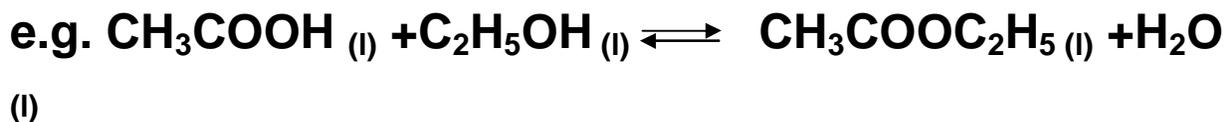
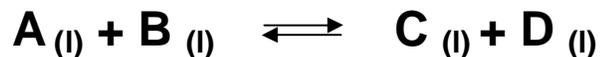
2. consider this reaction



The K_p is 1.64×10^{-4} at 400°C. calculate (i) the ΔG of the reaction (ii) ΔG when the partial pressure

of N₂, H₂ and NH₃ are 10atm, 30 atm and 3 atm respectively.

HOMOGENOUS (LIQUID) EQUILIBRIA



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

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

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

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.

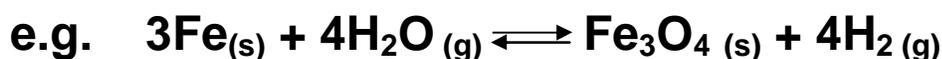
Example:

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.



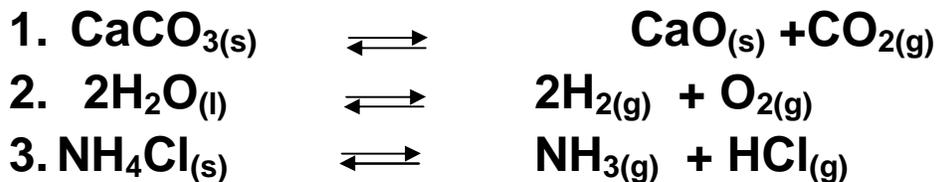
$$K_c = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4} = \frac{1 \times [\text{H}_2]^4}{1 \times [\text{H}_2\text{O}]^4} = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

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

In term of K_p ,

$$K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$

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



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.



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.

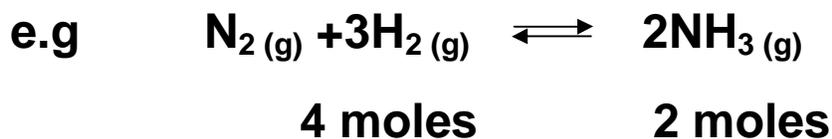
Reversible reactions where forward rxn is endothermic	When the temp. of equilibrium system	
	increases	decreases
$\text{N}_2\text{O}_{4(g)} \rightleftharpoons 2\text{NO}_{2(g)}$ $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$	Equilibrium position shifts to right, favouring forward rxn. K increases	Equilibrium position shifts to left, favouring backward rxn. K decreases
Forward rxn is exothermic	Equilibrium	Equilibrium

$2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$	position shifts to left, favouring backward rxn. K decreases	position shifts to right, favouring forward rxn. K increases
$2\text{H}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{H}_2\text{O}_{(g)}$		
$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$		

2. Effect of pressure changes on equilibrium mixture:

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.

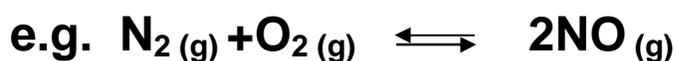


The forward reaction involves a decrease in the number of moles and hence, a decrease in the pressure of the system. Also, the backward reaction gives an increase in the number of moles, and hence an increase in the pressure of the system.

3.No change in volume		
$\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{2(g)}$ $3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(g)} \rightleftharpoons \text{Fe}_3\text{O}_{4(s)} + 2\text{H}_2(g)$	<hr/> <hr/>	<hr/> <hr/>

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

3. Effect of concentration 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.



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

Similarly, if the product formed is continually removed from 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 summarised in the table below

Reversible reactions	Addition of reactants or removal of products	removal of reactants or addition of products
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$	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. Effect of Catalyst: 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.

CHEMICAL EQUILIBRIUM IN SOLUTION

a. Dissociation of water:



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

But $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mol/dm}^3$ at 25°C and $[\text{H}_2\text{O}] = \text{constant}$

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

K_w is the water dissociation constant.

Examples

- 1. Calculate the $[\text{OH}^-]$ of the 0.01M HCL**
- 2. Calculate the $[\text{H}^+]$ of the 0.0001M NaCL**

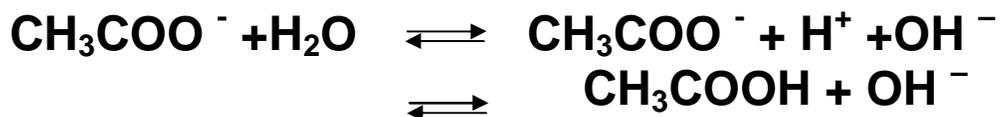
(b). Hydrolysis and hydrolysis constant

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

(CH₃COONa) react with water to give an alkaline solution.



As the CH₃COO⁻ consume the H⁺ from water to form ethanoic acid, more of the water molecules dissociate to produce more of their ions.

At equilibrium,

$$K_a = \frac{[\text{HEt}][\text{OH}^-]}{[\text{Et}^-][\text{H}_2\text{O}]}$$

But

$$\frac{[\text{HEt}][\text{OH}^-]}{[\text{Et}^-]} = [\text{H}_2\text{O}]K_a = K_h$$

K_h is the hydrolysis constant, but K_w = [H⁺][OH⁻]

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

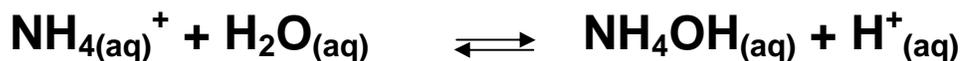
The hydrolysis constant K_h is related to the acid dissociation constant by the expression

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

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 NH_4Cl .



$$\therefore K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]}$$

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

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

c. Salt of weak acid-weak base, e.g $\text{CH}_3\text{COONH}_4$



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.



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

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

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°C . calculate K_{sp} value for CuBr.
3. The solubility of $\text{Mg}(\text{OH})_2$ at 25°C is 0.00764g/L. what is the value of K_{sp} for $\text{Mg}(\text{OH})_2$?

Exercises

1. Calculate the K_{sp} of AgCl whose solubility at 25°C is 1.05×10^{-5} mol/L.
2. The solubility of BaSO_4 at 18°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.



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 $K = 1.8 \times 10^{-5}$.