

CHAPTER 7

CHEMICAL EQUILIBRIUM

CHEMICAL EQUILIBRIUM

Chemical Equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of the reactants and products do not change with time.

Forward reaction starts with maximum speed and gradually slows down, whereas the reverse reaction starts at zero speed and gradually increases its speed.

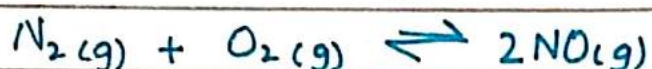
Eventually a time comes when both reactions proceed at the same speed. The reaction at this stage is said to be in chemical equilibrium. The concentration of reactants and products become constant.

Since the concentration of reactants and products become constant it may appear that the reaction has stopped. But this is not true. On the microscopic level there is excited activity. Individual molecules of reactants continue to combine. But the rate of one process is exactly balanced by rate of another. Therefore this is dynamic equilibrium. The system is dynamic bcz individual molecules react continuously, but the rate of forward and reverse reactions are equal. It is at equilibrium bcz no net change occurs.

TYPES OF CHEMICAL EQUILIBRIUM

1. HOMOGENOUS EQUILIBRIA

In homogeneous equilibria all the components occur only in one phase. e.g

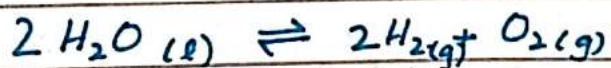


2 HETEROGENEOUS EQUILIBRIA

A heterogeneous equilibrium is one which involves more than one phases. e.g



→ If pure solids or pure liquids are involved in an equilibrium system, their concentrations are not included in the equilibrium constant expression. This is bcz the change in concentration of any pure solid or liquid has no effect on equilibrium system. e.g



$$K_c = [\text{H}_2]^2 [\text{O}_2]$$

LAW OF MASS ACTION

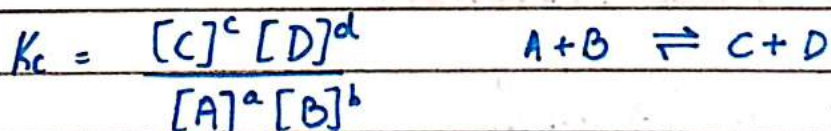
"The rate at which a substance reacts is proportional to its active mass and the rate of chemical reaction is proportional to the product of the active masses of the reacting substances"

ACTIVE MASS:

The term active mass mean the molar concentration or number of moles per dm^3 in a dilute solution.

K_c

K_c is defined as the ratio of the product of the molar concentration of the products to that of reactants.



K_c DEPENDS ON TEMPERATURE:

- Greater the temperature, greater will be K_c value for endothermic reactions and vice versa.
- Greater the temperature, lesser will be K_c value for exothermic reactions and vice versa.

K_c INDEPENDENT OF:

- Initial conc. of reactants
- Pressure or volume
- Direction of reaction
- Catalyst

UNIT OF K_c :

- When no. of moles of reactant = no. of moles of product, then K_c has no unit.
- When no. of moles of reactants \neq no. of moles of products, then K_c has some units and can be calculated by using formula:

$$K_c = (\text{mol} \cdot \text{dm}^{-3})^{\Delta n}$$

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

IN TERMS OF PARTIAL PRESSURES:

$$K_p = \frac{P_c^c \times P_d^d}{P_A^a \times P_B^b}$$

IN TERMS OF MOLE FRACTION

$$K_x = \frac{(X_c)^c \times (X_d)^d}{(X_A)^a \times (X_B)^b}$$

$$X = \frac{\text{Mole of that component}}{\text{Total No. of mole components}}$$

$$X_A = \frac{n_A}{n_A + n_B + n_C + n_D}$$

RELATION BETWEEN K_p AND K_c

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

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

When $\Delta n = 0$, $K_p = K_c$

$\Delta n > 0$, $K_p > K_c$

$\Delta n < 0$, $K_p < K_c$

RELATION BETWEEN K_p AND K_x

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

RELATION BETWEEN K_p AND K_n

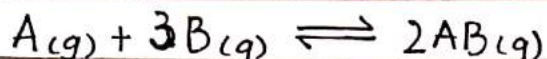
$$K_p = K_n (P/N)^{\Delta n}$$

IF $\Delta n = 0$

then $K_p = K_c = K_x = K_n$

CALCULATIONS

1. The following equilibrium concentrations were observed for the reaction at 500°C



$$[\text{A}] = 0.399\text{M}, [\text{B}] = 1.197\text{M}, [\text{AB}] = 0.203\text{M}$$

Calculate K_c

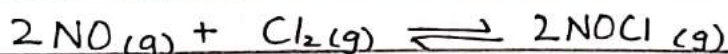
Sol:

$$K_c = \frac{[\text{AB}]^2}{[\text{A}][\text{B}]^3}$$

$$= \frac{(0.203 \text{ mol dm}^{-3})^2}{(0.399 \text{ mol dm}^{-3})(1.197 \text{ mol dm}^{-3})^3}$$

$$K_c = 6 \times 10^{-2} \text{ dm}^6 \text{ mol}^{-2}$$

2. Following reaction was studied at 25°C . Calculate its K_p and K_c



The partial pressures at equilibrium were found to be

$$P_{\text{NOCl}} = 1.2 \text{ atm}$$

$$P_{\text{NO}} = 5.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{Cl}_2} = 3.0 \times 10^{-1} \text{ atm}$$

Sol:

$$K_p = \frac{(P_{\text{NOCl}})^2}{(P_{\text{NO}})^2 (P_{\text{Cl}_2})}$$

$$K_p = \frac{(1.2)^2}{(5 \times 10^{-2})^2 (3 \times 10^{-1})}$$

$$K_p = 1.9 \times 10^3$$

Now

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

$$\Delta n = 2 - (2+1) = -1$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$T = 25^\circ\text{C} + 273 = 298 \text{ K}$$

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

$$1.9 \times 10^3 = K_c (0.0821 \times 298)^{-1}$$

$$1.9 \times 10^3 = \frac{K_c}{0.0821 \times 298}$$

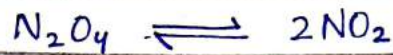
$$0.0821 \times 298$$

$$K_c = (1.9 \times 10^3)(0.0821 \times 298)$$

$$K_c = 4.65 \times 10^4$$

3. At 100°C , 0.1 mole of N_2O_4 is heated in a one dm^3 flask. At equilibrium concentration of NO_2 was found to be 0.12 moles. Calculate K_c .

Sol:



$$[\text{NO}_2] = 0.12 \text{ mol}$$

Since 1 mol of N_2O_4 gives 2 mol of NO_2

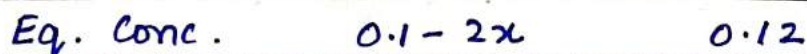
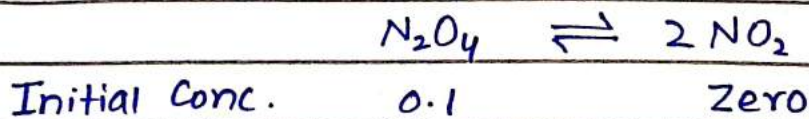
$$\begin{array}{l} 1 \text{ mol of } \text{N}_2\text{O}_4 = 2 \text{ mol of } \text{NO}_2 \\ x \text{ mol of } \text{N}_2\text{O}_4 = 0.1 \text{ mol of } \text{NO}_2 \end{array}$$

$$2x = 0.12$$

$$x = \frac{0.12}{2}$$

$$x = 0.06$$

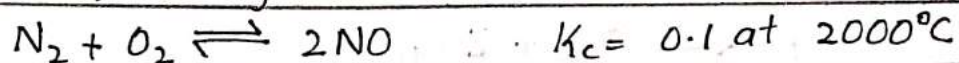
$$\begin{aligned} [\text{N}_2\text{O}_4] &= 0.1 - 0.06 \\ &= 0.04 \end{aligned}$$



$$\begin{aligned} K_c &= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \\ &= \frac{(0.12)^2}{(0.04)} \end{aligned}$$

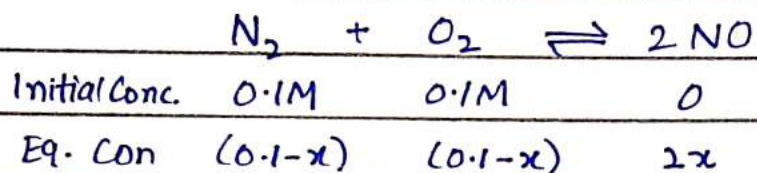
$$K_c = 0.36$$

4. Consider the following reaction



If original concentrations of N_2 and O_2 are 0.1M each. Calculate the concentrations of NO at equilibrium

Sol:



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

$$0.1 = \frac{(2x)^2}{(0.1-x)(0.1-x)}$$

Taking $\sqrt{\quad}$ on b. sides

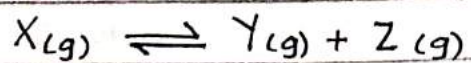
$$0.32 = \frac{2x}{0.1-x}$$

$$x = 0.014\text{M}$$

$$\begin{aligned}[\text{N}_2] &= [\text{O}_2] = 0.1 - x \\ &= 0.1 - 0.014 \\ &= 0.086\text{M each}\end{aligned}$$

$$\begin{aligned}[\text{NO}] &= 2x \\ &= 2 \times 0.014 \\ &= 0.028\text{M}\end{aligned}$$

5. A gas X dissociates on heating to set up an equilibrium

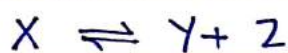


A quantity of X was heated at constant pressure P at a certain temperature. The equilibrium partial pressure of X was found to be $\frac{1}{7}P$. What is the equilibrium constant K_p at this temperature.

Ans: $\frac{9}{7}P$

Explanation:

We assume that total pressure, P_T of the gases at equilibrium is P



Mole of Y = Mole of Z (At Equilibrium)

Partial Pressure of Y, P_Y = Partial Pressure of Z, P_Z

Since equilibrium partial pressure of X, P_X is $\frac{1}{7}P$, it means that the other $\frac{6}{7}P$ of pressure must be shared equally among Y and Z.

Thus

$$P_Y = \frac{3}{7}P$$

$$P_Z = \frac{3}{7}P$$

$$K_p = \frac{(P_Y)(P_Z)}{(P_X)}$$

$$= \frac{(\frac{3}{7}P)(\frac{3}{7}P)}{(\frac{1}{7}P)}$$

$$K_p = \frac{9}{7}P$$

* PREDICTION OF DIRECTION OF REACTION

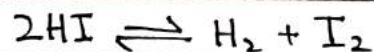
• The ratio of conc. of products to reactants at any particular time is called reaction quotient.

→ If $Q_c = K_c$, the reaction is at equilibrium.

→ If $Q_c > K_c$, the system is not at equilibrium and the net reaction will occur in the reverse direction until equilibrium is reached.

→ If $Q_c < K_c$, the system is not at equilibrium and the net reaction will occur in the forward direction until equilibrium is established.

• For the dissociation of HI



K_c at 520°C is 1.6×10^{-2} . Predict the direction in which the system will move to attain the equilibrium if the initial concentrations of HI is 1.02M and that of H_2 and I_2 are 0.01M and 0.01M respectively

Sol:

$$Q_c = \frac{[\text{H}_2]_0 [\text{I}_2]_0}{[\text{HI}]_0^2}$$
$$= \frac{[0.01]_0 [0.01]_0}{[1.02]_0^2}$$

$$Q_c = 9.61 \times 10^{-5}$$

Since the initial conc. ratio 9.61×10^{-5} is less than given value of K_c 1.6×10^{-2} , hence the reaction will proceed in forward direction and HI will dissociate further

PREDICTION OF THE EXTENT OF A CHEMICAL REACTION

1. Larger value of K_c favors forward reaction.
2. Smaller value of K_c favors backward reaction.
3. Neither very small, nor very large value of K_c favor equilibrium.

→ If K_c is very small then products will be very much unstable

→ If K_c is very large then products will be stable.

LE CHATELIER'S PRINCIPLE

"If a system at equilibrium is subjected to a stress by a change in temperature, pressure or concentration, the system tends to adjust itself so as to minimize the effect of that change"

The point at which a reversible reaction reaches the state of equilibrium is called position of equilibrium.

1. EFFECT OF CHANGE IN CONCENTRATION

- The addition of substance among the reactants, or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction.
- The addition of a substance among the products or the removal of a substance among the reactants will drive the equilibrium towards the backward direction.

NOTE: The reaction shifts in any direction on the addition of any substance just to keep the value of K_c constant.

2. EFFECT OF CHANGE IN PRESSURE

- The change in pressure or volume is important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.
- The increase of pressure or decrease in volume shifts the reaction in direction of less number of moles and vice versa.

3. EFFECT OF CHANGE IN TEMPERATURE

(1) ON ENDOTHERMIC REACTIONS

→ By increasing the temperature, reaction is favored in forward direction and vice versa.

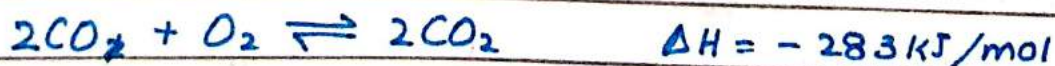
e.g



(2) ON EXOTHERMIC REACTIONS

→ By decreasing the temperature, reaction is favored in forward direction and vice versa.

e.g

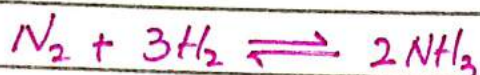


The formation of NO_2 is endothermic. Thus according to Le Chatelier Principle, a high temperature will favour the formation of NO_2 . Practically, the temperature used for its formation is about 3000°C .

BOSCH - HABER PROCESS

Reaction:

Preparation of ammonia



$$\Delta H = -92.38 \text{ kJ}$$

(Exothermic)

CONDITIONS FOR MAXIMUM PRODUCTION:

1. Removal of ammonia after regular intervals by Liquefaction
2. Increase in pressure
3. Decrease in temperature

CATALYST:

Finely divided iron

OPTIMUM CONDITIONS:

Pressure = 200 - 500 atm

Temperature = 450°C

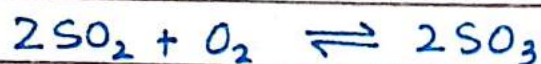
NOTE:

- No chance to obtain 100% yield due to dynamic equilibrium
- High temp is used for fast rate of reaction and attain equilibrium in earlier time.

SYNTHESIS OF SO_3 FOR MANUFACTURE OF H_2SO_4

In contact process H_2SO_4 is prepared

REACTION:



$$\Delta H = -94.58 \text{ kJmol}^{-1}$$

(Exothermic)

CONDITIONS FOR MAXIMUM PRODUCTION:

1. Continuous supply of O_2
2. Increase in pressure
3. Decrease in temperature

CATALYST:

V_2O_5 , NO or Pt are used as catalyst

FAVOURABLE CONDITIONS:

Pressure = 1.5 - 1.7 atm

Temperature = 400 - 500°C

SOLUBILITY PRODUCT (K_{sp})

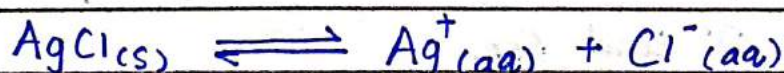
The solubility product constant is a heterogeneous equilibrium constant, a specific form of equilibrium constant. It is relevant in saturated solutions in which ionic compound has not fully dissolved.

The solubility product K_{sp} applies to situation where salts do not fully dissolve in a solvent. The solvent is generally water.

The solubility product constant, K_{sp} is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. The more soluble a substance is, the higher the K_{sp} value it has.

K_{sp} represent the maximum extent that a solid that can be dissolved in solution.

A substance's solubility product is the mathematical product of its dissolved ion concentrations raised to the power of their stoichiometric coefficients.



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

K_{sp} AND TEMPERATURE

K_{sp} is usually very small quantity at room temperature. The value of K_{sp} is temperature dependant.

K_{sp} increase with increase in temperature.

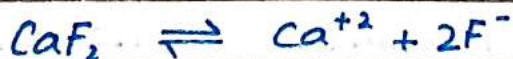
* SOLUBILITY AND K_{sp}

The smaller the solubility product of a substance, the lower is its solubility

* SOLUBILITY AND PRECIPITATION

To predict whether a precipitate will form when two solutions are mixed we use the term ionic product (Q'). It is obtained by substituting initial concentrations instead of equilibrium concentration in the expression of K_{sp}.

e.g



$$Q' = [\text{Initial conc. of Ca}^{+2}] [\text{Initial conc. of F}^{-}]^2$$

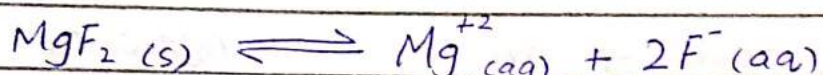
If we add a solution containing Ca⁺² ions to a solution containing F⁻ ions, precipitate may or may not form. To predict whether a precipitation will occur, we compare Q' and K_{sp}.

- 1) If $Q' > K_{sp}$, precipitation occurs and will continue until the conc. satisfy K_{sp}
- 2) If $Q' < K_{sp}$, precipitation doesnot occur.

CALCULATIONS

1. What is the solubility product constant expression for MgF_2 ?

Sol:

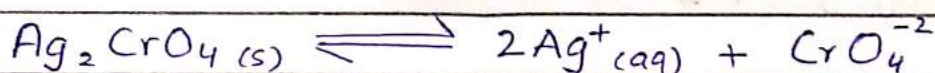


So

$$K_{sp} = [Mg^{+2}][F^{-}]^2$$

2. What is the solubility product constant expression for Ag_2CrO_4 ?

Sol:

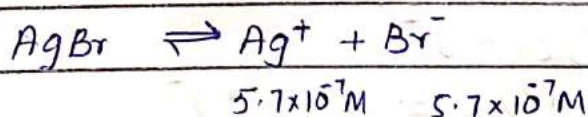


So

$$K_{sp} = [Ag^{+}]^2 [CrO_4^{-2}]$$

3. Determine the K_{sp} of silver bromide given that its molar solubility is 5.71×10^{-7} moles per litre.

Sol:



$$K_{sp} = [Ag^{+}][Br^{-}]$$
$$= (5.7 \times 10^{-7})(5.7 \times 10^{-7})$$

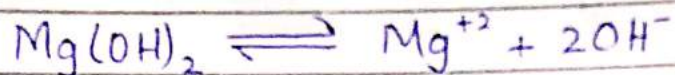
$$K_{sp} = 3.26 \times 10^{-13}$$

→ Above calculation is used when numbers of positive and negative ions are 1:1

when number of positive and negative ions is not 1:1
↓

4. The solubility of magnesium hydroxide at 298K is $1.71 \times 10^{-4} \text{ mol dm}^{-3}$. Calculate solubility product.

Sol:



For every mole of magnesium hydroxide that dissolves, you will get one mole of magnesium ions, but twice that number of hydroxide ions.

So the concentration of dissolved Mg^{2+} ions is the same as the dissolved magnesium hydroxide.

$$[\text{Mg}^{2+}] = 1.71 \times 10^{-4} \text{ mol dm}^{-3}$$

The concentration of dissolved hydroxide ions is twice that:

$$\begin{aligned} [\text{OH}^-] &= 2 \times 1.71 \times 10^{-4} \\ &= 3.42 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

Now

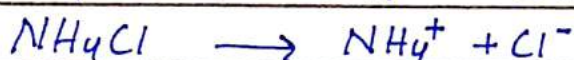
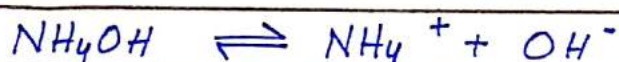
$$\begin{aligned} K_{sp} &= [\text{Mg}^{2+}][\text{OH}^-]^2 \\ &= (1.71 \times 10^{-4})(3.42 \times 10^{-4})^2 \\ K_{sp} &= 2 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-3} \end{aligned}$$

COMMON ION EFFECT

It is the phenomenon in which the solubility of one electrolyte is suppressed by the addition of another strong electrolyte having a common ion.

The shift of equilibrium, caused by the addition of an electrolyte having an ion in common with the dissolved salt is called common ion effect.

1) Addition of NH_4Cl suppresses the ionization of NH_4OH .



$$K_{sp} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

Since the conc. of NH_4^+ ions increases by adding NH_4Cl , so equilibrium shifts to the left to keep the value of K_{sp} constant and ionization of NH_4OH is suppressed.

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

PURIFICATION OF NaCl

Purification of NaCl is carried out by passing HCl gas through a saturated solution of NaCl.



Cl^- is a common ion due to which equilibrium shifts to the backward direction whereby NaCl precipitates