Exercise

Multiple choice questions

Choose the Correct Answer.

1. **K. is independent of**

(a) Tempreature (b) Pressure

(c) Both Temperature and Pressure (d) K_p

2. **For which of the following reactions, Kc has units of concentration**

$(a)\ 2A(g) \rightleftharpoons B(g)$ $(b)\ A(g) \rightleftharpoons B(g)$

$(c)\ A(g) \rightleftharpoons 2B(g)$ $(d)\ 3(g) \rightleftharpoons 2C(g)$

3. **For the following reaction**

$2A(g) + B(g) \rightleftharpoons 3C(g)$

We can write

$(a)\ K_c > K_p$ $(b)\ K_c < K_p$

$(c)\ K_p - K_c = 0$ $(d)\ K_p - K_c = -1$

4. **When a catalyst is added to an equilibrium mixture, it decreases**

(*a*) Reverce reaction (*b*) Forwerd reaction

(*c*) Concentration of reaction mixture (*d*) Enthalpy of reaction

(*e*) *it* has no effect

5. **If** $K_{SP} = \left[M^{+2}\right]^3 \left[X^{-3}\right]^2$ **the chemical formula of compound is**

$(a) MX_2$ $(b) M_2X_3$
$(c) M_3X_2$ (d) None of these

6. NaCl can be purified by passing HCl gas through the_________ solution of NaCl

(a) *Dilute* (b) *Concentrated*
(c) *Hot* (d) *Cold*

7. .$K_C = K_P$, when an is equal to

(a) *Zero* $(b) +1$
$(c) -1$ $(d) -2$

8. Consider the following reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \Delta H^0 - 198KJ$$

Yield of sulphur trioxide can be increased

(a) Increasing Pressure (b) increasing temperature
(c) adding caralyst (d) increasing concentration of oxygen

Answer

1. **d**	2. **c**	3. **c**	4. **e**
5. **b**	6. **b**	7. **a**	8. **d**

2. Define chemical equilibrium?

Ans. Chemical Equilibrium:

"It is the state of a reversible reaction at which composition of the reaction mixture do not change and the rate of both forward and reverse reaction is same that stage of reaction is called chemical equilibrium."

3. State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.

Ans: Conditions for Equilibrium

Important features of equilibration constant expression are as follows:

- **i.** K_C applies only at equilibrium. The subscript c indicates the concentrations of reactants and products are in moles per dm' at equilibrium state.
- **ii.** K_C is independent of initial concentrations of reactants and products but depends upon temperature. At a given temperature, it has only one value. Whether we start reaction with pure reactants or pure products or any composition in between, the value of K_C remains unchanged.
- **iii.** K_C is related to the coefficients of the balanced equation. The concentrations of the products are placed in the numerator and those of reactants in the denominator. Each concentration is raised to a power equal to coefficient the balanced equation.
- **iv.** The magnitude of K_C indicates the position of equilibrium. When K_C is less than 1, the denominator is greater magnitude than the numerator This means the concentration of the reactants are greater than those of products when the equilibrium is established Whereas, when K_C Is greater than I, the numerator is greater in magnitude than the denominator. This means the concentrations of the products are greater than those of the reactants at equilibrium.

Ways to Recognize Equilibrium and Determination of Equilibrium Constant:

Equilibrium constant expression can be determined by two methods:

a. Physical Method (spectrometric method)

b. Chemical Method

a. Physical Method (spectrometric method):

This method, is based on the measurement of a physical property of a physical property of the reaction mixture. This physical property is measured during the course of reaction without removing the saturation of the mixture.

Explanation:

This method is applicable if a reactant or product absorbs ultraviolet, Visible or infrared radiation. The concentration can be determined by measuring the amount of radiation absorbed

Example:

Equilibrium constant for $N_2 0_4$-NO_2, system can be determined by the spectrophotometer.

$$N_2 0_4(g) \rightleftharpoons 2NO_2(g)$$

N_2O_4, is a colorless gas whereas NO_2 is reddish brown gas. The progress of the reaction can be studied by measuring the absorbance at regular interval Absorbance is proportional to the concentration of NO_2

At equilibrium spectrometer will show constant value of absorbance. Suppose reaction is started with "a" mole of N_2O_4, at 100°C, and x moles of it is converted to NO_2. By applying stoichiometry, the amount of NO_2 present equilibrium will be 2x, which is measured by the spectrophotometer.

Mathematically:

Suppose the volume of the reaction mixture is V dm^3 then we can write

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Initial Conc (in mole)	a	zero
Eq. Conc (in mole)	$a-x$	$2x$
Eq Conc (mole/dm^3)	$\frac{a-x}{V}$	$\frac{2x}{V}$

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

$$K_C = \frac{\left(\frac{2x}{v}\right)^2}{\frac{(a-x)}{V}}$$

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

b. Chemical Method:

In this method, the amount of a reactant or product is determined by a b) suitable chemical reaction

Explanation:

Consider the reaction between acetic acid and ethanol to form ethyl acetate and water it is an example of reversible reaction in the solution state,

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_20(l)$$

Suppose this reaction is started by taking 'a' mole of acetic acid and 'b moles of ethanol in a stoppered flask at room temperature. A small amount of mineral acid is added in the mixture to catalyze the reaction

The progress of the reaction can be studied by determining the concentration of acetic acid after regular intervals. For this purpose, small portion of mixture is withdrawn

The concentration of acetic acid is determined by titrating it against a standard solution of NaOH using phenolphthalein as indicator. Concentration of acetic acid will decrease until equilibrium is attained. Suppose x moles of acetic acid has been reacted with ethanol, since one mole of acetic reacts with one mole of ethanol, the amount of ethanol reacted with acetic acid will also be x moles. As one mole of each of the product is formed, at equilibrium x moles of ethyl acetate and x moles of water are produced.

Mathematically:

Reaction initial Conc (in mole)

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_20(l)$$

a b zero zero

Eq Conc (in mole) a-x b-x x x

$$K_C = \frac{[CH_3COOC_2H_5][H_20]}{[CH_3COOH][C_2H_5OH]}$$

$$K_C = \frac{(x)(x)}{(a-x)(b-x)}$$

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

4. Describe the microscopic events that occur when a chemical system is in equilibrium.

Ans: Microscopic events:

The microscopic events take place in an equilibrium system are given below.

i. The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules.

ii. At equilibrium the numbers of effective collisions for the forward and reverse reactions are equal.

Number of effective collisions:

Increase in concentration of reactant increases such collisions for the forward reaction, Thus equilibrium shift towards right with the formation of more molecules of products.

Therefore, the number of effective collisions for the reverse process also increases. As time passes the effective collisions of reactant molecules decreased, lowering the rate of forward reaction.

Ultimately the number of effective collisions for both the processes again becomes equal and equilibrium is re-established.

5. Define and explain the following terms:

i. **Common ion effect**

ii. **Reaction quotient**

iii. **Solubility product**

iv. **Ion product**

Ans: (i). Reaction quotient (Q):

The ratio of concentrations of products to reactant at any particular time is called reaction quotient. It is obtained by applying the law of mass action, using initial concentrations or concentrations at any particular time instead of equilibrium concentration.

$$| \; Q = \frac{\text{Products}}{\text{reactant}}$$

The value Q leads to one of the following possibilities.

Q< K_C

This indicates that more product is needed to acquire equilibrium.

Therefore, system must shift to the right until equilibrium is attained

Q> Kc

This indicates that less product or more reactant is needed to acquire equilibrium Therefore system must shift to the left until equilibrium in reached.

This shows that reaction is at equilibrium. No shift will occur

(ii) Solubility product:

It is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balanced equation.

Explanation:

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and remaining compound settle at the bottom Dynamic equilibrium is established between undisclosed solid compound and its ions in the saturated solution

Example:

For example, when CaF_2 is mixed with water. Following equilibrium is established

$$CaF_2(s) \rightleftharpoons Ca^{+2}(aq) + 2F(aq)$$

Mathematically:

K_C for the equilibrium can be written as

$$K_C = \frac{[Ca^{+2}][F^-]^2}{[CaF_2]}$$

Since CaF_2 is slightly soluble salt its concentration almost remains constant.

Therefore
$$K_C[CaF_2] = [Ca^{+2}][F^-]^2$$
$$K_{SP} = [Ca^{+2}][F^-]^2$$

Where K_{SP} is a constant known as the solubility product constant.

iii. Common iron effect:

Common iron effect:

The phenomenon in when the degree of ionization or solubility of an electrolyte suppressed by the addition of highly soluble electrolyte containing a common ion is called **common ion effect.**

Explanation.

Consider a solution of weak acid, hydrofluoric acid K_a = 7.2 sodium fluoride produces the common ion.

$$HF(aq) \xrightleftharpoons{H_2O} H^+(aq) + F^-(aq)$$
$$NaF(s) \xrightleftharpoons{H_2O} Na^+(aq) + F^-(aq)$$

- Since HF is a weak electrotype. slightly dissociates
- NaF being strong electrolyte breaks up completely into its ions.
- The common ion F is produced by NaF will upset its equilibrium
- This will increase concentration of F ions
- According, to the Le Chatellier's principle. the equilibrium will shift to the left use some of F ions
- This will decrease the dissociation of HF Thus dissociation of HF will decrease in the presence of dissolved NaF

- This means as a result of equilibrium shift, the concentration of HF will increase
- Similarly, when a highly soluble salt is added to the saturated solution of less soluble salt containing a common ion
- The degree of dissociation of less soluble salt decreases. Therefore, it causes to decrease its solubility

iv. Heterogeneous equilibrium:

Equilibrium which involve more than one phases are called Heterogeneous equilibria. For example

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$
$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

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

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$
$$K_C = [H_2]^2[O_2]$$
$$and \qquad \mathrm{K}_P = p_{H_2}^2 \times p_{O_2}$$

v. Ion product:

It is the product of the initial concentration of ions each raised to a power equal to the co-efficient of the on in the balanced chemical equation.

6. Explain industrial application of Le Chatellier's principle using Haber's process as an example.

Ans: Industrial Application of Le Chatellier's Principle (Synthesis of Ammonia by Haber's Process):

The manufacture of ammonia by Haber's process is represented by the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$\Delta H^o = -92.46KJ$$

This equation provides the following information

i. The reaction is exothermic
ii. The react proceeds with a decrease in number of molecules or moles. Le Chatellier's principle suggests three ways to get maximum yield of ammonia.

i. **Low Temperature:**
The forward reaction is exothermic therefore, low temperature will favor the formation of ammonia the suitable temperature in 400°C

ii. **High Pressure:**
Since four molecules (one of N_2 and three of H_2) react to produce two molecules of NH_3. Thus high pressure will shift the equilibrium to the right side ie formation of NH_3. The most suitable pressure is 200 - 300 atm.

Optimum condition:
Thus optimum condition for equilibrium production of ammonia is low temperature and high pressure. Although at low temperature yield of ammonia is high, but the rate of its formation is so slow that the process becomes uneconomical. Therefore, a catalyst is used to increase the rate of reaction Usually a piece of iron with other metal oxides is used as catalyst. The equilibrium mixture contains 35% NH_3 by volume.

iii. **Continual removal of ammonia:**
A final factor which greatly increases the production of ammonia is the continuous removal of ammonia as it is formed. This is done by liquefying ammonia.

The equilibrium mixture is cooled by refrigeration coils until ammonia condenses at -33.4°C and is removed. N_2 and H_2 which do not liquefy at this temperature are recycled into the reaction chamber
The stress caused by the continual removal of ammonia shifts the equilibrium toward the production of more ammonia. In fact the mixture needs not to be allowed to come to equilibrium at all. In this way practically 100% conversion of N_2 and H_2, to NH_3, is possible

7. Propose microscopic events that account for observed macroscopic changes that take place during a shift in equilibrium.

Ans. Microscopic events:

The microscopic events that take place in an equilibrium system are given below.

- The rate of chemical reaction depends on the numbers of effective collisions between the reacting molecules.
- At equilibrium the numbers of effective collisions for the forward and reverse reactions are equal.

Number of effective collisions:

Increase in concentration of reactant increases such collisions for the forward reaction, Thus equilibrium shift towards right with the formation of more molecules of products.

Therefore, the number of effective collisions for the reverse process also increases, as time passes the effective collisions of reactant molecules decreased, lowering the rate of forward reaction.

Ultimately the number of effective collisions for both the processes again becomes equal and equilibrium is re-established

8. 50 cm' of acetic acid (d = 1.049 gcm^{-3}) is mixed with 50 cm^{-3} of ethanol (d=0.789 gcm^{-3}) what is the equilibrium composition of the mixture at 25°C (K_C=4). (Ans:CH_3COOH=31.68 g, C_2H_5OH=32.506 g, CH3COOC_2H_5 =30.448 g, H_20= 6.22 g)

Solution:

Equilibrium constant = K_C = 4 at 25°C

Volume of acetic acid = 50 cm?

Density of acetic acid = 1.049 g cm?

Mass of acetic acid = density x Volume = 1 049x50 = 52.45 g

Molar mass of acetic acid = 60 g mole

Number of moles of CH3COOH = 60 = 0.874 mole

Number of moles of CH_3COOH = $\frac{52.45}{46} = 0.858 mole$

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initial concentration (in moles)

0.874	0.858	zero	zero

Equation concentration (in moles)

0.874-x	0.858-x	x	x

K_C will be

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

$$4 = \frac{(x)(x)}{(0.874-x)(0.858-x)}$$

$$(0.874-x)(0.858-x)4 = x^2$$

$$x^2 = 4\left(0.750 - 0.874x - 0.858x + x^2\right)$$

$$x^2 = 4\left(0.750 - 1.732x + x^2\right)$$

$$x^2 = 3 - 6.928x + 4x^2$$

$$x^2 - 3 + 6.928x - 3 = 0$$

$$-3x^2 + 6.928x - 3 = 0$$

Taking negative sign common on both side

$3x^2 - 6.928x + 3 = 0$

Using quadratic formula

$a = 3, b = -6.928, c = 3$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-6.928) \pm \sqrt{(-6.928)^2 - 4(4\times3\times3)}}{2\times3}$$

$$x = \frac{6.928 \pm \sqrt{11.997}}{6}$$

Thus

$$x = \frac{6.928 + \sqrt{11.997}}{6}, \quad \text{or} \quad x = \frac{6.928 - \sqrt{11.997}}{6}$$

X=1.73 moles or x=0.577 moles

x=1.73 moles is not possible because it is greater than the initial concentral of reactants.

X=0.577 moles

The equilibrium concentration in moles are as follows

$[CH_3OOH] = 0.874 - x = -.874 - 0.577 = 0.297 moles$

Mass of $[CH_3COOH]$ in grams =0.297moles×60g mole = 17.82g

$[C_2H_5OH]$ =0.858-x=0.858-0.577=0.281 moles

Mass of $[C_2H_5OH]$ in grams. =0.281 moles×46g moles^{-1} = 12.93*g*

$[CH_3COOC_2H_5]$ = x =0.577moles

Mass of $[CH_3COOC_2H_5]$ =0.577moles × 88g mole^{-1} = 50.78 g

$[H_2O]$ =x=0.577 moles

Mass of $[H_2O]$ =0.577 moles × 18g mol^{-1} = 10.39*g*

9. Write K_C and K_P expressions for the following reactions

i. $SO_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

ii. $H_2O(g)+Cl_2O(g) \rightleftharpoons 2HOCl(g)$

iii. $O_3(g) \rightleftharpoons O_2(g)+O(g)$

iv. $O_3(g) \rightleftharpoons \frac{3}{2}O_2(g)$

v. $Fe_3O_4(s)+H_2(g) \rightleftharpoons 3FeO(s)+H_2O(g)$

vi. $2NO(g)+Cl_2(g) \rightleftharpoons 2NOCl(g)$

vii. $CaCO_3(s) \rightleftharpoons CaO(s)+CO_2(g)$

viii. $C(s)+H_2O(g) \rightleftharpoons O(g)+H_2(g)$

Solution:

i. $SO_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$$Kc=\frac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}},(and)K_C=\frac{P_{SO_3}}{P_{SO_2}\times P_{O_2}^{1/2}}$$

ii. $H_2O(g)+Cl_2O(g) \rightleftharpoons 2HOCl(g)$

$$K_C=\frac{[HOCl]^2}{[H_2O][Cl_2O]},(and)K_C=\frac{P_{HOCl}^2}{P_{H_2O}\times PCl_2O}$$

iii. $O_3(g) \rightleftharpoons O_2(g)+O(g)$

$$K_C=\frac{[O_2][O]}{[O_3]},(and)K_C=\frac{P_{O_2}\times P_O}{P_{O_3}}$$

iv. $O_3(g) \rightleftharpoons \frac{3}{2}O_2(g)$

$$K_C=\frac{[O_2]^{3/2}}{[O_3]},(and)K_C=\frac{P_{O_2}^{\frac{3}{2}}}{P_{O_3}}$$

v. $Fe_3O_4(s)+H_2(g) \rightleftharpoons 3FeO(s)+H_2O(g)$

As the equilibrium is heterogeneous therefore only gas phase is included in equilibrium constant expression. Therefore

$$K_C = \frac{[H_2O]}{[H_2]}, (and)\, K_P = \frac{P_{H_2O}}{P_{H_2}}$$

vi. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

$$K_C = \frac{[NOCl]^2}{[NO]^2[Cl_2]}, (and)\, K_P = \frac{P^2_{NOCl}}{P^2_{NO} \times PCl_2}$$

vii. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_C = [CO_2], (and) K_P = P_{CO_2}$$

viii. $C(s) + H_2O(g) \rightleftharpoons O(g) + H_2(g)$

$$K_C = \frac{[CO][H_2]}{[H_2O]}, (and)\, K_P = \frac{P_{CO} \times P_{H_2}}{P_{H_2O}}$$

10. $K_C = 2.6 \times 10^{-5}$ at $125^O C$ for the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ calculate K_P at this temprature. $(\text{Ans: } K_P = 284.4078)$

Solution:

$T = 125^o C + 273 = 398K$

$K_C = 2.6 \times 10^{-5}\, at 125^O C$

$\Delta n = (1+3) - 2 = 2$

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

as we know that

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

Putting values

$K_P = 2.6 \times 10^{-5}(0.0821 \times 398)^2$

$K_p = 2.78 \times 10^{-2}$

11. At a particular temperature atm. Which of the following conditions corresponds to equilibrium position for the reaction.

A(g) $\rightleftharpoons$ 2B(g)

a. $P_B = 0.175$ atm, $P_A = 0.102$ atm

b. $P_B = 0.064$ atm, $P_A = 0.0308$ atm

c. $P_B = 0.144$ atm, $P_A = 0.156$ atm

(Ans: b and c)

Solution:

$K_p = 0.133 atm$

as we know that

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

(a). $P_B = 0.175$ atm, $P_A = 0.102$ atm

$$K_p = \frac{P_B^2}{P_A} = \frac{(0.175)^2}{(0.102)} = 0.30 atm$$

As this value does not correspond with the given value therefore the reaction Is not at equilibrium

(b). $P_B = 0.064$ atm, $P_A = 0.0308$ atm

$$K_p = \frac{P_B^2}{P_A} = \frac{(0.064)^2}{(0.0308)} = 0.133 atm$$

As this value correspond with the given value therefore the reaction Is at equilibrium

(c). $P_B = 0.144$ atm, $P_A = 0.156$ atm

$$K_P = \frac{P_B^2}{P_A} = \frac{(0.144)^2}{(0.156)} = 0.113atm$$

As this value correspond with the given value therefore the reaction Is at equilibrium

12. Write the expression for K, and K, for the following processes.

a. Blue vitriol is deep blue solid copper (II) sulphate pentahydrate is heated to drive off water vapors to form white solid copper (II) sulphate.

b. The decomposition of solid phosphorus pentachloride to gaseous phosphorus trichloride and chlorine gas.

Solution:

a. The balance chemical equation for process (a) is given below.

$$CuSO_4 5H_2 0\ (s) \rightleftharpoons 5H_2 0\ (g) + CuSO_4\ (s)$$

As the equilibrium is heterogeneous therefore only gas phase is included equilibrium constant expression

$$K_C = [H_2O]^5$$
$$K_P = P_{H_2O}^5$$

b. The balance chemical equation for process (b) is given below

$$PCl_5\,(s) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

As the equilibrium is heterogeneous therefore only gas phase is included (b) equilibrium constant expression.

$$K_C = [PCl_3][Cl_2]$$
$$K_P = P_{PCl_3} \times P_{Cl_2}$$

13. Predict the shift in equilibrium position that will occur for each the following processes when the volume is reduced.

i. $PCl_3(g)+2NH_3(g) \rightleftharpoons P(NH_2)_3(g)+3HCl(g)$

ii. $2NO(g)+O_2(g) \rightleftharpoons 2NO_2(g)$

iii. $4NH_3(g)+5O_2(g) \rightleftharpoons 4NO(g)+6H_2O(g)$

Ans. Principle:

According to Le-Chatellier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus, the equilibrium will shift in a direction where the numbers of molecules are less.

i. $PCl_3(g)+2NH_3(g) \rightleftharpoons P(NH_2)_3(g)+3HCl(g)$

In this reaction three molecules are present on reactant side $(PCl_3, 2NH_3)$ while four molecules are present on product side $(P(NH_2)_3, 3HCl)$.

Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in backward direction to reduce the number of molecules. and compensate the change.

ii. $2NO(g)+O_2(g) \rightleftharpoons 2NO_2(g)$

In this reaction three molecules are present on reactant side (2NO, O_2) and two molecules (2NO_2) are present on product side

Therefore when the volume decreases by increasing pressure then the equilibrium will shift in forward direction to reduce the number of molecules, and to compensate the change

iii. $4NH_3(g)+5O_2(g) \rightleftharpoons 4NO(g)+6H_2O(g)$

In this reaction, nine molecules are present on reactant side ($4NH_3$, $5O_2$) and ten molecules are present on product side ($4NO$, $6H_2O$)

Therefore, when the volume decreases by increasing pressure then the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change.

14. For each of the following reactions, predict how the value of K_C changes as the temperature is increased.

(a). $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H^O = 180KJ$

(b). $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^O = -198KJ$

(c). $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^O = 58KJ$

(d). $CH_4(g)+H_2O(g) \rightleftharpoons CO(g)+3H_2(g)$ $\Delta H^O = 356KJ$

Ans:

Principles:

i. High temperature favours endothermic reactions.

ii. Low temperature favours exothermic reactions.

iii. In exothermic reactions heat is written on the right side of the equation.

iv. In endothermic reactions heat is written on the left side of the equation.

(a). $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H^O = 180KJ$

As the reaction is endothermic therefore heat is written on the left side of the equation.

$N_2(g) + O_2(g) + Heat \rightleftharpoons 2NO(g)$

According to Le-Chatellier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of NO will increase while that of N_2 and O_2 will decrease.

$$K_C = \frac{[NO]^2 \longleftarrow decrease}{[N_2][O_2] \longleftarrow increas}$$

Hence, in this case the value of K_C will increase with increase in temperature.

(b). $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H^O = -198KJ$

As the reaction is exothermic therefore, heat is written on the right side of the equation. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + heat$

According to Le-Chatellier's principle, when temperature is increased this reaction will shift in the reverse direction in order to compensate the added heat. Thus, concentration of SO_2 and O_2 will increase while that of SO_3 will decrease.

$$K_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Hence, in this case the value of K_C will decrease with increase in temperature.

(c). $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^O = 58KJ$

As the reaction is endothermic therefore heat is written on the left side of the equation.

$N_2O_4(g) + Heat \rightleftharpoons 2NO_2(g)$

According to Le-Chatier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat. Therefore, concentration of NO_2 will increase while that of N_2O_4 will decrease

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

Hence, in this case the value of K will increase with increase in temperature

(d). $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^O = 356KJ$

According to Le-Chatellier's principle, when temperature increases the reaction will shift in forward direction in order to compensate the added heat.

Therefore, concentration of CO and H; will increase while that of CH_4 and H_20 will decrease.

$$K_C = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

Hence, in this case the value of K_C will increase with increase in temperature

15. What is the difference between an equilibrium with a K_C value larger than one compared with an equilibrium that has a K_C smaller than one.

Ans: K_C is very large:

Many reactions have very large equilibrium constant.

Example:

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \qquad K_C = 5.4 \times 10^{18}$ at 25°C

If concentration of each of the reactant at equilibrium is 1 mole then concentration of HBr would be

$$\frac{[HBr]^2}{[x]} = 5.4\times10^{18}$$
$$[HBr] = \sqrt{5.4\times10^{18}}$$
$$=2.32\times10^{9}M$$

Conclusion:

It means that the concentration of HBr is very large as compared to that of reactants. At equilibrium the mixture will have mainly products. Thus large value of K_C indicates that the reaction goes virtually to completion.

(b). K_C is very small:

Reactions having very small K_C do not proceed appreciably in the forward direction

Example:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_C = 1.0x10^{-30} \text{ at } 25°C$$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = 1.0\times10^{-30}$$

If one mole of each of the reactant is present at equilibrium. Then the concentration of NO would be

$$\frac{[NO]^2}{1\times1} = 1\times10^{-30}$$
$$[NO] = \sqrt{1\times10^{-30}}$$
$$[NO] = 1\times10^{-15}\,moles$$

Conclusion:

Thus concentration of NO will be very small. Equilibrium mixture will have mainly reactants. Therefore, small value of K_C indicates that the reaction has very little tendency to move in the forward direction.

16. Describe the behavior of the following equilibrium with the stated changes

(a) Increasing pressure on

$C_3H_8(g)+5O_2(g) \rightleftharpoons 3CO_2(g)+4H_2O(g)$

(b) Adding $I_2(g)$ to $2HI(g) \rightleftharpoons I_2(g)+H_2(g)$

(c) Removing heat from

$CO_2(g) \rightleftharpoons CO(g)+\frac{1}{2}O_2(g) \quad \Delta H^O = 284KJ$

(d) Decreasing pressure on

$C_2H_6(g) \rightleftharpoons H_2(g)+C_2H_4(g)$

Ans.

(a) Incresing pressure on

$C_3H_8(g)+5O_2(g) \rightleftharpoons 3CO_2(g)+4H_2O(g)$

According to Le-Chatellier's principle, when pressure increases then the system will reduce its volume by reducing the number of molecules present. Thus the equilibrium will shift in a direction where the numbers of molecules are less.

According to the given reaction, six molecules are present on reactant side $(C_3H_8, 5O_2)$ and seven molecules $(3CO_2, 4H_2O)$ are present on product side.

Therefore, when the pressure increases the volume must decreases and the equilibrium will shift in backward direction to reduce the number of molecules and to compensate the change.

(b) Adding $I_2(g)$ to $2HI(g) \rightleftharpoons 3CO_2(g)+H_2(g)$

According to Le-Chatellier's principle, the addition of I_2 increases the concentration of product and to compensate it the equilibrium will shift in the backward reaction.

(c) Removing heat from

$$CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^o = 284KJ$$

As the reaction is endothermic therefore heat is written on the left side of the equation.

$$CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$$

According to Le-Chatellier's principle, when temperature is decreased this reaction will shift in backward direction in order to compensate the decrease in heat Therefore, the concentration of CO, will decrease while that of CO and O_2 will decrease.

$$K_C = \frac{[CO][O_2]^{\frac{1}{2}} \longleftarrow decreas}{[CO_2] \longleftarrow increas}$$

(d) Decreasing pressure on

$$C_2H_6(g) \rightleftharpoons H_2(g) + C_2H_4(g)$$

In the given reaction one molecule is present on reactant side (C_2H_6) and two molecules are present on product side (H… C_2H_4.) So, when pressure is decreased, the equilibrium will shift in forward direction to compensate the change.

17. A solution is prepared by mixing $50cm^3$ **of** $5\times10^3 M$ NaCl **with** $50cm^3$ **of** $2\times10^{-2} M$ $Pb(NO_3)_2$ **. will a precipitation of** $PbCl_2$ **form?** K_{SP} **For** $PbCl_2$ **is** 1.7×10^{-5}**.**

Solution:

Molarity of $Pb(NO_3)_2$ solution = 2×10^{-2} M

Molarity of NaCl solution = $5\times10^{-3} M$

Precipitate of $PbCl_2$ =?

K_{SP} for $PbCl_2 = 1.7\times10^{-5}$

Volume of NaCl solution = $50cm^3$ =$0.05dm^3$

Volume of $Pb(NO_3)_2$ solution = $50cm^3$ =$0.05dm^3$

Total volume of solution = $0.05dm^3 + 0.05dm^3 = 0.1dm^3$

Concentration of Cl^-:

$NaCl \rightleftharpoons Na^+(aq) + Cl^-(aq)$

$5\times10^{-3}M$ $5\times10^3 M$ $5\times10^3 M$

1 dm^3 of NaCl solution contains Cl^- ions = $5\times10^3 M$ moles

0 05 dm^3 of NaCl solution contains Cl^- ions $=5\times10^3\times0.05$

$= 25\times10^4$ moles

Now total volume is 0 1 dm^3 therefore

0.1 dm^3 of total solution contains Cl^- ions = 25×10^4 moles

1 dm of total solution contains Cl^- ions = $\frac{25 \times 10^4}{0.1} = 25 \times 10^3$ moles

Concentration of Pb^{+2}:

$Pb(NO_3)_2 \rightleftharpoons Pb^{+2}(aq) + 2NO_3(aq)$

2×10^2 M 2×10^2M $2\times2\times10^4 M$

1 dm^3 of $Pb(NO_3)_2$ Solution contains Pb^{+2} ions 2×10^2 moles moles

0.05 dm^3 of $Pb(NO_3)_2$ Solution contains Pp' ions = $2 \times 10^2 \times 0.05$

$= 1.0 \times 10^3$ moles

Now total volume is 0.1 dm^3 therefore

0.1 dm^3 of total solution contains Pb^{+2} ions = 1.0×10^3 moles

1 dm³ of total solution contains Pb^{+2} ions = $\frac{1.0\times10^{-3}}{0.1} = 1.0\times10^{-2}$ moles

$$\left[Pb^{+2}\right] = 1.0\times10^{-2} M$$

Precipitate of $PbCl_2$

Now for ionization of $PbCl_2$

$$PbCl_2 \rightleftharpoons Pb^{+2}(aq) + 2Cl^-(aq)$$

So,

$$Q' = \left[Pb^{+2}\right]\left[Cl^-\right]^2$$
$$= \left(1.0\times10^{-2}\right)\left(2.5\times10^{-3}\right)^2 = 6.25\times10^{-8}$$
$$K_{sp} = 1.7\times10^{-5}$$

Since, $Q' < K_{sp}$, therefore precipitation will not occur

18. When solid $PbCl_2$ is added to pure water at 25°C, the salt dissolves until the concentration of Pb^{+2} reaches 1.6×10^{-2} M. After this concentration is reached, excess solid remains undissolved. What is K_{sp} for this salt? (Ans: 1.6384×10^{-5})

Solution:

$$PbCl_2(s) \rightleftharpoons Pb^{+2}(aq) + 2Cl^-(aq)$$

$$\left[Pb^{+2}\right] = 1.6\times10^{-2} M$$
$$\left[Cl^-\right] = 2\times1.6\times10^{-2} M = 3.2\times10^{-2}$$
$$K_{SP} = \left[Pb^{+2}\right]\left[Cl^-\right]^2$$
$$K_{SP} = \left(1.6\times10^{-2}\right)\left(3.2\times10^{-2}\right)^2$$
$$K_{SP} = 1.6384\times10^{-5}$$

19. The equilibrium constant for the following reaction is 1.6×10^5 at 1000K

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

Find the equilibrium pressures of all the gases if 10.0 atm of HBr is introduced into a sealed container at 1000K

Solution:

$$H_2(g) \;+\; Br_2(g) \rightleftharpoons 2HBr\;(g)$$

Initial Concentration	*zero*	*zero*	**10**
Equation Concentration.	**X**		

$$K_P = \frac{P_{HBr}^2}{P_{H_2} \times P_{Br_2}}$$

$$1.6 \times 10^5 = \frac{(10-2x)^2}{(x)(x)}$$

$$1.6 \times 10^5 = \frac{(10-2x)^2}{x^2}$$

Taking square root of both the sides

$$\sqrt{1.6 \times 10^5} = \sqrt{\frac{(10-2x)^2}{x^2}}$$

$$400 = \frac{10-2x}{x}$$

$$400x = 10 - 2x$$

$$400x + 2x = 10$$

$$402x = 10$$

$$or$$

$$x = \frac{10}{402}$$

$$x = 0.0249$$

$$P_{H_2} = P_{Br_2} = x = 0.0249 \quad \text{atm}$$

$$P_{HBr} = 10 - 2 \times 0.0249 = 9.9502 \quad \text{atm}$$

20. Consider the following gas phase reaction. Describe four changes that would derive the equilibrium to left (backward direction).

$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g) + \text{Heat}$

Ans. According to Le-Chatellier's Principle following are the four changes that will drive the equilibrium in the reverse direction.

(i) Continual removal of reactants:
When any of the reactant is removed the equilibrium shift in the reverse direction to compensate the change

(ii) Low Pressure:
According to the given equation two molecules are present on reactant side (SO_2, Cl_2) and one molecule is present on product side (SO_4C_2) Thus when pressure decreased, the equilibrium will shift in the reverse direction to compensate the change.

(iii) High Temperature:
As the reaction is exothermic therefore, high temperature will not favor it and hence the reaction will proceed in the reverse direction with the increase in temperature

(iv) Addition of products:
Addition of products increases their concentration and the reaction will shift in the reverse direction to compensate this change i.e from right to left

21. How would you change the volume of the following reactions to inc increase the yield of products?

(i) $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl(g)$

(ii) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

Ans. (i) $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl(g)$

According to Le-Chatellier's principle when pressure increases then the system will reduce its volume by reducing the number of molecules present Thus the equilibrium will shift in a direction where the numbers of molecules are less.

According to the given reaction two molecules are present on both the According to Le-Chatellier's principle, when pressure increases then the reactant and the product side $(Cl_2, I_2,\ 2ICl)$

Thus the change in volume will not affect the equibrium position

(ii) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

(...pge#299...)

According to the given equation, two molecules are present un reactant side ($2NO_2$) and one molecule is present on product side (N_2O_4) When, we reduce volume by increasing pressure then the equilibrium will shift in forward direction and thus the yield increases.

Think Tank

22. A figurine device used to predict weather condition is blue on dry, sunny days and pink on damp, rainy days. These figurines are coated with substances containing chemical species that undergo following equilibrium.

$$2\left[Co(H_2O)_6\right]^{+2} + 4Cl^- \rightleftharpoons Co\left[CoCl_4\right]^{-2} + 12H_2O$$

a. **Identify the blue substance**

b. **Identify the pink substance**

c. **How is Le Chatellier's Principle applied here.**

Ans.

(a) Blue substance = $Co[CoCl_4]^{-2}$

(b) Pink substance = $\left[Co(H_2O)_6\right]^{+2}$

Appling Le Chatellier's Principle

Rainy days:

According to the reaction water is the product. On damp, rainy days the concentration of water is more in the surrounding and hence according to Le-Chatellier's principle, the equilibrium will shift in the reverse direction. Thus the concentration of $\left[Co(H_2O)_6\right]^{+2}$ Increases and the color of figurine becomes pink.

Sunny days:

According to the reaction water is the product. On a sunny day the concentration of water is low in the surrounding and therefore according to Le-Chatellier's principle, the equilibrium will shift in forward direction. Thus the formation of $Co[CoCl_4]^{-2}$ increases and the color of figurine become blue.

23. The combination of oxygen with hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction. For our purpose it can be represented by the simplified equation.

$$\mathbf{Hb(aq) + O_2(aq) \rightleftharpoons HbO_2\ (aq)}$$

where HbO_2 is oxyhemoglobin that actually transport oxygen to tissues. The equilibrium constant

expression is $K_C = \frac{[HbO_2]}{[Hb][O_2]}$

Scaling a 3km mountain can cause headache, nausea, extreme fatigue and other discomforts. Give possible explanation for it.

Ans:

$$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2\ (aq)$$

External pressure low on high mountains and thus the concentration of O_2 in the atmosphere also decreases. Hence, according to Le-Chatellier's principle, the given equilibrium will shift in reverse direction.

As a result, the concentration of HbO_2 decreases in order to give Hb and O_2 to compensate the change. Therefore, supply of oxygen to body is also decreased. This can cause headache, nausea, extreme fatigue and other discomforts.

24. Baking Soda undergoes thermal decomposition as follows

$$2NaHCO_3(s) \rightleftharpoons NaCO_3(s) + CO_2(g) + H_2O(g)$$

Would we obtain more CO_2 by adding extra baking soda to the reaction mixture in (a) a closed vessel (b) an open vessel?

Ans.

As pressure has very little effect on volume of solids so they almost remain same but pressure can affect the volume of gases.

(a) Closed vessel:

In close vessel volume does not change and therefore we cannot obtain more carbon dioxide gas by adding extra baking soda to the reaction mixture.

(b) Open vessel:

According to the reaction, there are two gaseous molecules on the product side (CO_2 and H_2O). Thus in this case according to Le-Chatellier's principle, when the volume increases then the equilibrium will shift in forward direction. Therefore, by adding baking soda more CO_2 will produce in an open vessel.

25. Potassium dichromate solution has beautiful clear orange colour. This is due to the colour of dichromate ion, $Cr_2O_7^{-2}$,. When a salt is dissolved in water, the following equilibrium is setup, on heating solution.

$$Cr_2O_7^{-2}\ (aq) + H_2O(l) \rightleftharpoons 2CrO_4^{-2}(aq) + 2H^+\ (aq)$$

(orange) (yellow)

What will happen if:

i. **dilute Sodium hydroxide is added to this solution.**
ii. **this is followed by dilute hydrochloric acid addition.**

Ans.

i. **Dilute Sodium hydroxide is added to this solution.**

NaOH is a base and it produces OH^- ions which will react with H^+ ion to form water.

Therefore the concentration of H^+ ions decreases and according to Le- Chatlier's principle, to compensate that change the dichromate/chromate equilibrium will shift in forward direction, As a result more orange $Cr_2O_7^{-2}$ ions react with H_2O to give yellow CrO_7^{-2} ions and the colour of solution changes from orange to yellow.

ii. This is followed by dilute hydrochloric acid addition.

HCl is a strong acid and it produces H^+ ions in the solution due to which an ases. Thus, according to Le-Chatellier's' principle, to the equilibrium will shift in backward direction. Thus, more yellow CrO_4^{-2} ions react with H^+ ions to give orange CrO_4^{-2} ions and the colour of solution changes from yellow to orange.

26. If 0.350 moles of SO_3 is placed in a 1.00 dm^3 flask and allowed to come to equilibrium at a high temperature, 0.207 mole of SO_3 remains. Calculate K_c for the reaction. (Ans: 14.64)

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

Solution:

	$2SO_3(g) \rightleftharpoons$	$2SO_2(g) +$	$O_2(g)$
Initial Concentration. (in moles dm^{-3})	0.350	zero	zero
Equation Concentration. (in moles dm^{-3})	0.350-x	2x	x

Given that at equilibrium, 0.207 moles of SO_3 remains

$$0.350 - 2x = 0.207$$
$$-2x = 0.207 - 0.350$$
$$-2x = -0.143$$
$$or$$
$$x = \frac{0.143}{2} = 0.0715$$

Equilibrium concentrations:

$$[SO_3] = 0.207 \text{ moles dm}^{-3}$$
$$[O_2] = x = 0.0715 \text{ moles dm}^{-3}$$
$$[SO_2] = 2x = 2\times0.0715 = 0.143 \text{ moles dm}^{-3}$$
$$K_C = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

Putting values

$$K_C = \frac{(0.143)^2(0.0715)}{(0.207)^2} = 0.0341$$

27. For the reaction between hydrogen and Iodine to form hydrogen Iodide, the value of K_C is 794 at 298K but 54 at 700K what can you 27. deduce from this information?

Ans.

$$\mathbf{H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)}$$

Given that the value of K_C decreased with the increase in temperature from 794 at 298K to 54 at 700K,

Conclusion:

Thus, this indicates that the reaction is exothermic and is not favored by high temperature. Therefore, the concentration of HI is decreased and that of H_2 and I_2 is increased by increase in temperature.

$$K_C = \frac{[HI]^2 \longleftarrow decrease}{[H_2][I_2] \longleftarrow increase}$$