Chapter – 8

Physical and Chemical Equilibrium

Textbook Evaluation:

I. Choose the best answer:

Question 1.

If K_b and K_f for a reversible reaction are 0.8×10^{-5} and 1.6×10^{-4} respectively, the value of the equilibrium constant is,

- a) 20
- b) 0.2×10^{-1}
- c) 0.05
- d) None of these

Answer:

a) 20

Question 2.

At a given temperature and pressure, the equilibrium constant values for the equilibria

 $3A_2 + B_2 + 2Cr$ $2A_3BC$ and A_3BC $3/2[A_2] + 1/2B_2 + C$ The relation between K₁ and K₂ is

a)
$$K_1 = \frac{1}{\sqrt{K_2}}$$

b) $K_2 = K_1^{-1/2}$
C) $K_1^2 = 2K_2$
d) $\frac{K_1}{2} = K_2$

Answer:

b)K₂ =
$$\mathbf{K}_1^{-1/2}$$

Question 3.

The equilibrium constant for a reaction at room temperature is K_1 and that at 700 K is K_2 If $K_1 > K_2$, then

a) The forward reaction is exothermic

- b) The forward reaction is endothermic
- c) The reaction does not attain equilibrium
- d) The reverse reaction is exothermic

Answer:

a) The forward reaction is exothermic

Question 4.

The formation of ammonia from $N_2(g)$ and $H_2(g)$ is a reversible reaction

 $2NO(g) + O_2(g) \xrightarrow{\kappa_2} 2NO_2(g)$ + Heat What is the effect of increase of temperature on this equilibrium reaction

- a) equilibrium is unaltered
- b) formation of ammonia is favoured
- c) equilibrium is shifted to the left
- d) reaction rate does not change

Answer:

c) equilibrium is shifted to the left

Question 5.

Solubility of carbon dioxide gas in cold water can be increased by

- a) increase in pressure
- b) decrease in pressure
- c) increase in volume
- d) none of these

Answer:

a) increase in pressure

Question 6.

Which one of the following is incorrect statement?

a) for a system at equilibrium, Q is always less than the equilibrium constant

b) equilibrium can be attained from either side of the reaction

c) the presence of catalyst affects both the forward reaction and reverse reaction to the same extent

d) Equilibrium constant varied with temperature

Answer:

a) for a system at equilibrium, Q is always less than the equilibrium constant

Question 7.

 K_1 and K_2 are the equilibrium constants for the reactions respectively.

$$N_{2}(g) + O_{2}(g) \xrightarrow{\kappa_{1}} 2NO(g)$$
$$2NO(g) + O_{2}(g) \xrightarrow{\kappa_{2}} 2NO_{2}(g)$$

What is the equilibrium constant for the reaction NO₂(g) $\rightleftharpoons 1/2$ N₂(g) + O₂(g) a) $\frac{1}{\sqrt{K_1 K_2}}$

- b) $({
 m K}_1={
 m K}_2)^{1/2}$
- c) $\frac{1}{2 K_1 K_2}$

d)
$$\left(\frac{1}{K_1 K_2}\right)^{3/2}$$

Answer:

a)
$$\frac{1}{\sqrt{K_1 K_2}}$$

Question 8.

In the equilibrium, $2A(g) \rightleftharpoons 2B(g) + C_2(g)$ the equilibrium concentrations of A, B and C₂ at 400K are 1×10^{-4} M, 2.0×10^{-3} M, 1.5×10^{-4} M respectively. The value of K_c for the equilibrium at 400 K is a) 0.06

b) 0.09
c) 0.62
d) 3 × 10⁻²

Answer:

a) 0.06

Question 9.

An equilibrium constant of 3.2×10^{-6} for a reaction means, the equilibrium is a) largely towards forward direction

b) largely towards reverse direction

c) never established

d) none of these

Answer:

b) largely towards reverse direction

Question 10.

 $\frac{K_C}{K_P}$ for the reaction, N₂(g) + 3H₂(g) ≈ 2NH₃ (g) is a) $\frac{1}{RT}$ b) \sqrt{RT} c) RT d) (RT)²

Answer:

d) (RT)²

Question 11.

For the reaction AB (g) \rightleftharpoons A(g) + B(g), at equilibrium, AB is 20 % dissociated at a total pressure of P, the equilibrium constant K_p is related to the total pressure by the expression

a) $P = 24 K_p$ b) $P = 8 K_p$ c) $24 P = K_p$ d) none of these

Answer:

a) $P = 24 K_p$

Question 12.

In which of the following equilibrium, K_p and K_c are not equal? a) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ b) $SO_2(g) + NO_2 \rightleftharpoons SO_3(g) + NO(g)$ c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ d) $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$

Answer:

b) $SO_2(g) + NO_2 \rightleftharpoons SO_3(g) + NO(g)$

Question 13.

If x is the fraction of PCl₅ dissociated at equilibrium in the reaction PCl₅ \rightleftharpoons PCl₃ + Cl₂ then starting with 0.5 mole of PCl₅, the total number of moles of reactants and products at equilibrium is

a) 0.5 - x b) x + 0.5 c) 2x + 0.5 d) x + 1

Answer:

b) x + 0.5

Question 14.

The values of K_{p1} and K_{p2} ; for the reactions, $X \rightleftharpoons Y + Z$, $A \rightleftharpoons 2B$ are in the ratio 9 : 1 if degree of dissociation of X and A be equal then total pressure at equilibrium P_1 , and P_2 are in the ratio

- a) 36 : 1
- b) 1 : 1
- c) 3 : 1
- d) 1:9

Answer:

a) 36 : 1

Question 15.

In the reaction $Fe(OH)_3(S) \rightleftharpoons Fe^{3+} (aq) + 3OH^- (aq),$ if the concentration of OH- ions is decreased by 1/4 times, then the equilibrium concentration of Fe³⁺ will a) not changed b) also decreased by 1/4 times c) increase by 4 times d) increase by 64 times

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Answer:

d) increase by 64 times

Question 16.

Consider the reaction where $K_p = 0.5$ at a particular temperature $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ if the three gases are mixed in a container so that the partial pressure of each gas is initially 1 atm, then which one of the following is true. a) more PCl_3 will be produced

b) more Cl_2 will be produced

c) more PCl₅ will be produced

d) none of these

Answer:

c) more PCl₅ will be produced

Question 17.

Equimolar concentrations of H_2 and I_2 are heated to equilibrium in a 1 litre flask. What percentage of the initial concentration of H_2 has reacted at equilibrium if rate constant for both forward and reverse reactions are equal

- a) 33%
- b) 66%
- c) (33)²%
- d) 16.5 %

Answer:

a) 33%

Question 18.

In a chemical equilibrium, the rate constant for the forward reaction is 2.5 \times 10^{-2,} and the equilibrium constant is 50. The rate constant for the reverse reaction is,

a) 11.5

b) 50 c) 2×10^2 d) 2×10^{-3}

Answer:

b) 50

Question 19.

Which of the following is not a general characteristic of equilibrium involving physical process

a) Equilibrium is possible only in a closed system at a given temperature

b) The opposing processes occur at the same rate and there is a dynamic but stable condition

c) All the physical processes stop at equilibrium

d) All measurable properties of the system remains constant

Answer:

c) All the physical processes stop at equilibrium

Question 20.

For the formation of Two moles of $SO_3(g)$ from SO_2 and O_2 , the equilibrium constant is K1. The equilibrium constant for the dissociation of one mole of SO_3 into SO_2 and O_2 is

a)
$$1/K_1$$

b) K_1^2
c) $\left(\frac{1}{K_1}\right)^{1/2}$
d) $\frac{K_1}{2}$

Answer:

c)
$$\left(\frac{1}{K_1}\right)^{1/2}$$

Question 21.

Match the equilibria with the corresponding conditions: i) Liquid ≓ Vapour ii) Solid ≓ Liquid iii) Solid ≓ Vapour iv) Solute(s) \rightleftharpoons Solute (Solution)

- 1) Melting point
- 2) Saturated solution
- 3) Boiling point
- 4) Sublimation point
- 5) Unsaturated solution

251-111 (2622) (11	(i)	(ii)	(iii)	(iv)
(a)	1	2	3	4
(b)	3	1	4	2
(c)	2	1	3	4
(d)	3	2	4	5

Answer:

b) 3 1 4 2

Question 22.

Consider the following reversible reaction at equilibrium, $A + B \rightleftharpoons C$, If the concentration of the reactants A and B are doubled, then the equilibrium constant will

- a) be doubled
- b) become one fourth
- c) be halved
- d) remain the same

Answer:

d) remain the same

Question 23.

 $[Co(H_2O)_6]^{2+}$ (aq) (pink) + 4Cl⁻ (aq) \rightleftharpoons $[CoCl_4]^{2-}$ (aq) (blue) + 6 H₂O (l) In the above reaction at equilibrium, the reaction mixture is blue in colour at room temperature. On cooling this mixture, it becomes pink in color. On the basis of this information, which one of the following is true?

- a) $\Delta H > 0$ for the forward reaction
- b) $\Delta H = 0$ for the reverse reaction
- c) $\Delta H < 0$ for the forward reaction
- d) Sign of the ΔH cannot be predicted based on this information

Answer:

a) $\Delta H > 0$ for the forward reaction

Question 24.

The equilibrium constants of the following reactions are: $N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1 $N_2 + O_2 \rightleftharpoons 2NO$; K_2 $H_2 + 1/2O_2 \rightleftharpoons H_2O$; K_3

The equilbrium constant (K) for the reaction ; $2NH_3 + 5/2 O_2 \rightleftharpoons 2NO + 3H_2O$, will be

a) K₂³ K₃/K₁
b) K₁ K₃³/K₂
c) K₂K₃³/K₁
d) K₂K₃/K₁

Answer:

c) $K_2K_3^3/K_1$

Question 25.

A 20 litre container at 400 K contains CO_2 (g) at pressure 0.4 atm and an excess (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when the pressure of CO_2 attains its maximum value will be: Given that: $SrCO_3(S) \cong SrO + CO_2$ (g) $[K_p = 1.6 \text{ atm}]$

- a) 2 litre
- b) 5 litre
- c) 10 litre
- d) 4 litre

Answer:

b) 5 litre

II. Write brief answer to the following questions:

Question 26.

If there is no change in concentration, why is the equilibrium state considered dynamic?

Answer:

Rate of forward reaction = Rate of backward reaction

Question 27.

For a given reaction at a particular temperature, the equilibrium constant has constant value. Is the value of Q also constant? Explain.

Answer:

 K_c and Q_c are constant at equilibrium, both are temperature dependent. When K_c is constant at given temperature, Q_c also constant.

Question 28.

What is the relation between $K_{\rm p}$ and $K_{\rm c}?$ Given one example for which $K_{\rm p}$ is equal to $K_{\rm c}.$

Answer:

$$\begin{split} K_p &= K_c(RT)^{\Delta n_g} \\ H_2(g) + I_2(g) &\cong 2 HI \mbox{ (g) } ; \Delta n_g = 0 \mbox{ ;} \\ K_p &= K_c. \end{split}$$

Question 29.

For a gaseous homogeneous reaction at equilibrium, number of moles of products are greater than the number of moles of reactants. Is K_c is larger or smaller than K_p .

Answer:

 $K_p > K_c$ $n_p > n_R$

Question 30.

When the numerical value of the reaction quotient (Q) is greater than the equilibrium constant, in which direction does the reaction proceed to reach equilibrium?

Answer:

Q > K_c Reverse reaction is favoured.

Question 31.

For the reaction, $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; ΔH is -ve. the following molecular scenes represent different reaction mixture.(A-green, B-blue)



i) Calculate the equilibrium constant K_p and (K_c) .

ii) For the reaction mixture represented by scene (x), (y) the reaction proceed in which directions?

iii) What is the effect of increase in pressure for the mixture at equilibrium.

Answer:

 $K_c = \frac{[AB]^2}{[A_2][B_2]}$; A – green, B – blue

Given that 'V' is constant(closed system)

At equilbrium,

$$K_{c} = \frac{(-)}{\left(\frac{2}{V}\right)\left(\frac{2}{V}\right)} = \frac{16}{4} = 4$$
$$K_{p} = K_{c}(RT)^{\Delta n} = 4 (RT)^{0} = 4$$

At stage 'x',

$$Q = \frac{\left(\frac{6}{V}\right)^2}{\left(\frac{2}{V}\right)\left(\frac{1}{V}\right)} = \frac{36}{2} = 18$$

 $Q > K_c$ i.e., reverse reaction is favoured.

At stage 'y',

$$Q = \frac{\left(\frac{3}{\overline{V}}\right)^2}{\left(\frac{3}{\overline{V}}\right)\left(\frac{3}{\overline{V}}\right)} = \frac{9}{3 \times 3} = 1$$

 $K_c > Q$ i.e., forward reaction is favoured.

Question 32.

State Le – Chateller principle.

Answer:

"If a system at equilibrium is distributed, then the system shifts itself in a direction that nullifies the effect of that disturbance".

Question 33.

Consider the following reactions,

a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

c) $S(s) + 3 F_2(g) \rightleftharpoons SF_6(g)$

In each of the above reactions find out whether you have to increase (or) decrease the volume to increase the yield of the product.

Answer:

a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ In this reaction, there is no effect on changing the volume. $\Delta ng = 0$

b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ In this reaction, increases in volume favours forward reaction.

c) $S(s) + 3 F_2(g) \rightleftharpoons SF_6(g)$ In this reaction, decreases in volume favours forward reaction.

Question 34.

State law of mass action.

Answer:

The law states that, "At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant".

Rate \propto [Reactant]x Active mass = (n/V) mol dm⁻³ (or) mol L⁻¹

Question 35.

Explain how will you predict the direction of an equilibrium reaction.

Answer:

From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place for a given concentration or partial pressure of reactants and products.

Consider a general homogeneous reversible reaction,

 $xA + yB \rightleftharpoons lC + mD$

For the above reaction under non-equilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stiochiometric coefficients in the balanced chemical equation to that of the reactants.

Under non – equilibrium conditions, the reaction quotient Q can be calculated using the following expression.

$$\mathsf{Q} = \frac{[\mathsf{C}]^{1}[\mathsf{D}]^{\mathsf{m}}}{[\mathsf{A}]^{\mathsf{x}}[\mathsf{B}]^{\mathsf{y}}}$$

As the reaction proceeds, there is a continuous change in the concentration of reactants and products and also the Q value until the reaction reaches equilibrium. At equilibrium, Q is equal to K_c at a particular temperature. Once the equilibrium is attained, there is no change in the Q value. By knowing the Q value, we can predict the direction of the reaction by comparing it with K_c . If $Q = K_c$, the reaction is in equilibrium state.

If $Q > K_c$, the reaction will proceed in the reverse direction, i.e., formation of reactants.

If $Q < K_c$, the reaction will proceed in the forward direction i.e., formation of products.



reactants \rightarrow products equilibrium products \rightarrow reactants Predicting the direction of a reaction

Question 36.

Derive a general expression for the equilibrium constant Kp and Kc for the reaction, $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$.

Answer:

Let us consider the formation of ammonia in which, 'a' moles nitrogen and h' moles hydrogen gas are allowed to react in a container of volume V. Let 'x' moles of nitrogen react with 3 x moles of hydrogen to give 2x moles of ammonia.

 $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

	N ₂	H ₂	NH ₃
Initial number of moles	a	b	0
number of moles reacted	x	3x	0
Number of moles at equilibrium	a-x	b-3x	2x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

$$K_2 = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$
$$= \frac{\left(\frac{4x^2}{V^2}\right)}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

The equilibrium constant $K_{\rm p}\xspace$ can also be calculated as follows :

$$K_{p} = K_{c} (RT)^{(\Lambda ng)}$$

$$\Delta n_{g} = n_{p} - n_{r} = 2 - 4 = -2$$

$$K_{p} = \frac{4x^{2}V^{2}}{(a-x)(b-3x)^{3}} \times [RT]^{-2}$$

Total number of moles at equilibrium,

$$n = a - x + b - 3x + 2x = a + b - 2x$$

$$K_{p} = \frac{4x^{2}V^{2}}{(a - x)(b - 3x)^{3}} \times \left[\frac{PV}{n}\right]^{-2}$$

$$K_{p} = \frac{4x^{2}V^{2}}{(a - x)(b - 3x)^{3}} \times \left[\frac{n}{PV}\right]^{2}$$

$$K_{p} = \frac{4x^{2}V^{2}}{(a - x)(b - 3x)^{3}} \times \left[\frac{(a + b - 2x)}{PV}\right]^{2}$$

$$K_{p} = \frac{4x^{2}(a + b - 2x)^{2}}{P^{2}(a - x)(b - 3x)^{3}}$$

Question 37.

Write the balanced chemical equation for an equilibrium reaction for which the equilibrium constant is given by expression.

Answer:

$$K_{c} = \frac{[NH_{3}]^{4}[O_{2}]^{7}}{[NO]^{4}|H_{2}O]^{6}}$$

Balanced equation is: $4NO + 6H_2O \rightleftharpoons 4NH_3 + 7O_2$

Question 38.

What is the effect of added Inert gas on the reaction at equilibrium at constant volume?

Answer:

When an inert gas (i.e., a gas which does not react with any other species involved in equilibrium) is added to an equilibrium system at constant volume, the total number of moles of gases present in the container increases, that is, the total pressure of gases increases. The partial pressure of the reactants and the products are unchanged. Hence at constant volume, the addition of inert gas has no effect on the equilibrium.

Question 39.

Derive the relation between K_p and K_c .

Answer:

Let us consider the general reaction in which all reactants and products are ideal gases.

xA + yB ≈ lC + mD The equilibrium constant, K_c is, $K_{c} = \frac{[Cl^{l}[D]^{m}}{[A]^{x}[B]^{y}}$(1)

The ideal gas equation is, PV = nRTP = n/V RT since, Active mass = molar concentration = n/VP = active mass × RT

Based on the above expression the partial pressure of the reactants and products can be expressed as,

 $P_{A}^{x} = [A]^{x}[RT]^{x}$ $P_{B}^{y} = [A]^{y}[RT]^{y}$ $P_{C}^{1} = [A]^{1}[RT]^{1}$ $P_{D}^{m} = [A]^{m}[RT]^{m}$

On substituting in Eqn.(2).,

 $K_{p} = \frac{[C]^{l} [RT]^{l} [D]^{m} [RT]^{m}}{[A]^{x} [RT]^{x} [B]^{y} [RT]^{y}} - (3)$ $K_{p} = \frac{[C]^{l} [D]^{m} [RT]^{/+m}}{[A]^{x} [B]^{y} [RT]^{x+y}}$ $K_{p} = \frac{[C]^{l} [D]^{m}}{[A]^{x} [B]^{y}} [RT]^{(/+m)-(x+y)} - (4)$

By comparing equation (1) and (4), we get $K_{p\Delta ng} = K_c (RT) \dots (5)$ Where,

 Δn_g is the difference between the sum of number of moles of products and the sum of number of moles of reactants in the gas phase. The following relations become immediately obvious.

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when \Delta n_g = 0.

K_p = K_c (RT)^0 = K_c

Example :

H_2(g) + I_2(g) \rightleftharpoons 2HI(g)

N_2 + O_2 \rightleftharpoons 2NO(g)

when \Delta n_g = +ve

K_p = K_c (RT)^{+ve}

K_p > K_c

Example:
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2NH_{3}(g) \rightleftharpoons N_{2}(g) + 3H_{2}(g)
PCl_{5}(g) \rightleftharpoons PCl_{3}(g) + Cl_{2}(g)
When \Delta n_{g} = -ve
K_{p} = K_{c}(RT)^{-ve}
K_{p} < K_{c}
Example:

2H_{2}(g) + O_{2}(g) \rightleftharpoons 2H_{2}O(g)
2SO_{2}(g) + O_{2}(g) \rightleftharpoons 2SO_{3}(g)
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Question 40.

One mole of PCl_5 is heated in one litre closed container. If 0.6 mole of chlorine is found at equilibrium, Calculate the value of equilibrium constant.

Solution:

Given that,

$$\begin{split} [PCI_5]_{initial} &= \frac{1 \text{ mole}}{1 \text{ dm}^3} \\ [CI_2]_{eq} &= 0.6 \text{ mole } \text{dm}^{-3} \\ PCI_5 &\rightleftharpoons PCI_3 + CI_2 \\ [PCI_3]_{eq} &= 0.6 \text{ mole } \text{dm}^{-3} \\ [PCI_5]_{eq} &= 0.4 \text{ mole } \text{dm}^{-3} \\ &\therefore \text{ K}_c &= \frac{[PCI_3][CI_2]}{[PCI_5]} &= \frac{0.6 \times 0.6}{0.4} \\ &= 0.9 \text{ mole } \text{dm}^{-3} \end{split}$$

Question 41.

For the reaction SrCO₃ (s) \rightleftharpoons SrO(s) + CO₂(g) the value of equilibrium constant K_p = 2.2 × 10⁻⁴ at 1002 K. Calculate K_c for the reaction.

Solution:

For the reaction, $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$ $\Delta n_g = 1 - 0 = 1$ $\therefore K_p = K_c (RT)$ $2.2 \times 10^{-4} = K_c (0.0821) (1002)$ $K_c = \frac{2.2 \times 10^{-4}}{0.0821 \times 1002} = 2.674 \times 10^{-6}$

Question 42.

To study the decomposition of hydrogen iodide, a student fills an evacuated 3 litre flask with 0.3 mol of HI gas and allows the reaction to proceed at 500°C. At equilibrium he found the concentration of HI which is equal to 0.05 M. Calculate K_c and K_p for this reaction.

Solution:

$$V = 3 L$$

 $[HI]_{initial} = \frac{0.3 \text{ mol}}{3 \text{ L}} 0.1 \text{ M}$ $[HI]_{eq} = 0.05 \text{ M}$ $2 \text{ HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$

	HI (g)	H ₂ (g)	I ₂ (g)
Initial concentration	0.1	-	-
Reacted	0.05	-	-
Equilibrium concentration	0.05	0.025	0.025

$$K_{c} = \frac{[H_{2}][I_{2}]}{[HI]^{2}} = \frac{0.025 \times 0.025}{0.05 \times 0.05} = 0.25$$

$$K_{p} = K_{c}(RT)^{(\Delta n_{g})}$$

$$\Delta n_{g} = 2 - 2 = 0$$

$$K_{p} = 0.25(RT)^{0}$$

$$K_{p} = 0.25.$$

Question 43.

1 mol of CH₄, 1 mole of CS₂ and 2 mol of H₂S are 2 mol of H₂ are mixed in a 500 ml flask. The equilibrium constant for the reaction $K_c = 4 \times 10^{-2} \text{ mol}^2 \text{ lit}^{-2}$. In which direction will the reaction proceed to reach equilibrium ?

Solution:

 $CH_4(g) + 2 H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$ $K_c = 4 \times 10^{-2} \text{ mol}^2 \text{ lit}^{-2}$

Volume = 500 ml =
$$\frac{1}{2}$$
 L
[CH₄]_{in} = $\frac{1 \text{ mol}}{\frac{1}{2}L}$ = 2 mol L⁻¹;

$$[CH_{2}]_{in} = \frac{1 \text{ mol}}{\frac{1}{2}L} = 2 \text{ mol } L^{-1}$$

$$[H_{2}S]_{in} = \frac{2 \text{ mol}}{\frac{1}{2}L}; \qquad [H_{2}]_{in} = \frac{2 \text{ mol}}{\frac{1}{2}L}$$

$$= 4 \text{ mol } L^{-1} \qquad = 4 \text{ mol } L^{-1}$$

$$Q = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2} = \frac{[2][4]^4}{[2][2]^2}$$

= 64 mol² lit⁻²

 $Q > K_c$. \therefore The reaction will proceed in the reverse direction to reach the equilibrium

Question 44.

At particular temperature $K_c = 4 \times 10^{-2}$ for the reaction, $H_2S \rightleftharpoons 2H_2(g) + S_2(g)$. Calculate the K_c for each of the following reaction. i) $2H_2S(g) \rightleftharpoons 2H_2 + S_2(g)$ ii) $3H_2S(g) \rightleftharpoons 3H_2(g) + 3/2 S_2(g)$

Solution:

 $K_c = 4 \times 10^{\text{-}2}$ for the reaction,

$$H_{2}S \rightleftharpoons 2H_{2}(g) + S_{2}(g)$$

$$K_{c} = \frac{[H_{2}][S_{2}]^{1/2}}{[H_{2}S]}$$

$$\Rightarrow 4 \times 10^{-2} = \frac{[H_{2}][S_{2}]^{1/2}}{[H_{2}S]}$$
(i) $2H_{2}S(g) \rightleftharpoons 2H_{2} + S_{2}(g)$
For the reaction,
 $2H_{2}S(g) \rightleftharpoons 2H_{2} + S_{2}(g)$

$$K_{c} = \frac{[H_{2}]^{2}[S_{2}]}{[H_{2}S]^{2}}$$

$$= (4 \times 10^{-2})^{2} = 16 \times 10^{-4}$$

(ii)
$$3H_2S(g) \rightleftharpoons 3H_2(g) + 3/2 S_2(g)$$

For the reaction,
 $3H_2S(g) \rightleftharpoons 3H_2(g) + 3/2 S_2(g)$
 $K_c = \frac{[H_2]^3 [S_2]^{3/2}}{[H_2 S]^3}$
 $= (4 \times 10^{-2})^3 = 64 \times 10^{-6}$

Question 45.

28 g of Nitrogen and 6 g of hydrogen were mIed In a 1 litre closed container. At equIlibrium 17 g NH3 was produced. Calculate the weight of nitrogen, hydrogen at equilibrium.

Solution:

Given $m_{N2} = 28g$; $m_{H2} = 6g$; V = 1 L.

$$(n_{N_2})_{initial} = \frac{28}{28} = 1$$

$$(n_{H_2})_{initial} = \frac{6}{2} = 3$$

N₂(g) + 3 H₂(g) \rightleftharpoons 2NH₃(g)

	N ₂ (g)	H ₂ (g)	NH ₃ (g)
Initial concentrations	1	3	-
Reacted	0.5	1.5	-
Equilibrium concentration	0.5	1.5	1

$$\begin{split} [NH_3] &= 17/17 = 1 \text{ mol} \\ \text{Weight of } N_2 &= (\text{no. of moles of } N_2) \times (\text{molar mass of } N_2) \\ &= 0.5 \times 28 = 14g \\ \text{Weight of } H_2 &= (\text{no. of moles of } H_2) \times (\text{molar mass of } H_2) \\ &= 1.5 \times 2 = 3g \end{split}$$

Question 46.

The equilibrium for the dissociation of XY₂ is given as,

 $2 XY_2(g) \rightleftharpoons 2 XY(g) + Y_2(g)$

if the degree of dissociation x is so small compared to one. Show that 2 $K_p = PX^3$ where P is the total pressure and K_p is the dissociation equilibrium constant of XY₂.

Answer:

 $2 XY_2(g) \rightleftharpoons 2 XY(g) + Y_2(g)$

	XY ₂	XY	Y ₂
Initial no. of moles	. 1	-	•
No. of moles dissociated	x	-	-
No. of moles at equilibrium	(1- x) 1	x	$\frac{\mathbf{x}}{2}$

Total no. of moles = $1 - \mathbf{x} + \mathbf{x} + \frac{\mathbf{x}}{2} = 1 + \frac{\mathbf{x}}{2} \cong 1$

[:: Given that
$$x \ll 1$$
; $1-x \cong 1$ and $1 + \frac{x}{2} \cong 1$]

$$K_{p} = \frac{[P_{xy}]^{2}[P_{Y_{2}}]}{[P_{XY_{2}}]^{2}} = \frac{\left(\frac{x}{1} \times P\right)^{2} \left(\frac{X/2}{1} \times P\right)}{\left(\frac{1}{1} \times P\right)^{2}}$$
$$K_{p} = \frac{x^{2}P^{2} \times P}{2 P^{2}} ; 2K_{p} = x^{3}P$$

Question 47.

A sealed container was filled with 0.3 mol H₂(g), 0.4 mol I₂(g) and 0.2 mol HI(g) at 800 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that K = 870 for the reaction, H₂(g) + I₂(g) \rightleftharpoons 2 HI (g).

Solution:

 $A_2(g) + B_2(g) \rightleftharpoons 2 AB(g)$

	A ₂	B ₂	AB
Initial no. of moles	1	1	-
No. of moles reached	x	х	
No. of moles at equilibrium	1- x	1- x	2x

Total no. of moles = 1 - x + 1 - x + 2x = 2

$$K_{p} = \frac{[P_{AB}]^{2}}{[P_{A_{2}}][P_{B_{2}}]} = \frac{\left(\frac{2x}{2} \times P\right)^{2}}{\left(\frac{(1-x)}{2} \times P\right)\left(\frac{1-x}{2} \times P\right)}$$
$$= \frac{4x^{2}}{(1-x)^{2}}$$

Given that,
$$K_p = 1$$
;

$$\frac{4x^2}{(1-x)^2} = 1$$

$$\Rightarrow 4x^2 = (1-x)^2 = 1$$

$$\Rightarrow 4x^2 = 1 + x^2 - 2x$$

$$3x^2 + 2x - 1 = 0$$

$$x = \frac{-2 \pm \sqrt{4 - 4 \times 3 \times -1}}{2(3)}$$

$$= \frac{-2 \pm \sqrt{4 + 12}}{6}$$

$$= \frac{-2 \pm \sqrt{16}}{6} = \frac{-2 \pm 4}{6} ; \frac{-2 - 4}{6}$$

$$= \frac{2}{6} ; \frac{-6}{6}$$

$$x = 0.33 - 1 (\text{not possible})$$

$$\therefore [A_2]_{eq} = 1 - x = 1 - 0.33 = 0.67$$

$$[AB_2]_{eq} = 2x \times 0.33 = 0.66$$

Question 48.

Deduce the Vant Hoff equation.

Answer:

This equation gives that quantitative temperature dependence of equilibrium constant (K). The relation between standard free energy change (ΔG°) and equilibrium constant is $\Delta G^{\circ} = - \operatorname{RT} \operatorname{In} K$ (1)

We know that, $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ (2)

Substituting (1) in equation (2) – RT In K = $\Delta H^{\circ} - T\Delta S^{\circ}$ Rearranging, In K = $\frac{\Delta H^{0}}{RT} + \frac{\Delta S^{0}}{RT}$ (3) Differentiating equation (3) with respect to temperature, $\frac{d(\ln K)}{dT} = \frac{\Delta H^{0}}{RT^{2}}$ (4)

Equation (4) is known as differential form of van,t Hoff equation. On integrating the equation (4), between T_1 and T_2 with their respective equilbrium consatuts K_1 and K_2 .

$$\int_{K_{1}}^{K_{2}} d(\ln K) = \frac{\Delta H^{0}}{R} \int_{T_{1}}^{T_{2}} \frac{dT}{T^{2}}$$

$$[\ln K]_{K_{1}}^{K_{2}} = \frac{\Delta H^{0}}{R} \left[-\frac{1}{T} \right]_{T_{1}}^{T_{2}}$$

$$\ln K_{2} - \ln K_{1} = \frac{\Delta H^{0}}{R} - \left[\frac{1}{T_{2}} + \frac{1}{T_{1}} \right]$$

$$\ln \frac{K_{2}}{K_{1}} = \frac{\Delta H^{0}}{R} \left[\frac{T_{2} - T_{1}}{T_{2}T_{1}} \right]$$

$$\log \frac{K_{2}}{K_{1}} = \frac{\Delta H^{0}}{2.303 R} \left[\frac{T_{2} - T_{1}}{T_{2}T_{1}} \right] - ----(5)$$

Equation 5 is known as integrated form of Van't Hoff equation.

Question 49.

The equilibrium constant K_p for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 8.19 \times 10² at 298 K and 4.6 \times 10⁻¹ at 498 K. Calculate ΔH° for the reaction.

Solution:

$$\begin{split} K_{p1} &= 8.19 \times 10^2; \\ T_1 &= 298 \ K \\ K_{p1} &= 8.19 \times 10^2; \end{split}$$

$$\begin{split} T_1 &= 298 \text{ K} \\ K_{p2} &= 4.16 \times 10^{-1}; \\ T_2 &= 498 \text{ K} \\ & \log \frac{K_{P2}}{K_{p1}} = \frac{\Delta H^0}{2.303 \text{ R}} \left[\frac{T_2 - T_1}{T_2 T_1} \right] \\ & \log \left(\frac{4.6 \times 10^{-1}}{8.19 \times 10^2} \right) = \frac{\Delta H^0}{2.303 \times 8.314} \\ & \left(\frac{498 - 298}{498 \times 298} \right) \\ \left(\frac{-3.2505 \times 2.303 \times 8.314 \times 498 \times 298}{200} \right) = \Delta H^0 \\ \Delta H^0 &= -46181 \text{ J mol}^{-1} \\ \Delta H^0 &= -46.18 \text{ KJ mol}^{-1} \end{split}$$

Question 50.

The partial pressure of carbon dioxide in the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 1.017×10^{-3} atm at 500°C. Calculate K_p at 600°C for the reaction. H for the reaction is 181 KJ mol⁻¹ and does not change in the given range of temperature.

Solution:

$$\begin{split} P_{CO2} &= 1.017 \times 10^{-3} \text{ atm} \\ T &= 500^{\circ}\text{C}; \\ K_p &= P_{CO2} \\ \therefore & K_{p1} &= 1.017 \times 10^{-3}; \\ T &= 500 + 273 &= 773 \text{ K} \\ K_{p2} &= ? \\ T &= 600 + 273 &= 873 \text{ K} \\ \Delta \text{H}^{\circ} &= 181 \text{ KJ mol}^{-1} \end{split}$$

$$\log \left(\frac{K_{P_2}}{K_{P_1}}\right) = \frac{\Delta H^0}{2.303 \text{ R}} \left[\frac{T_2 - T_1}{T_2 T_1}\right]$$
$$\log \left(\frac{K_{P_2}}{1.017 \times 10^{-3}}\right) = \frac{181 \times 10^3}{2.303 \times 8.314}$$
$$= \left(\frac{873 - 773}{873 \times 773}\right)$$
$$\log \left(\frac{K_{P_2}}{1.017 \times 10^{-3}}\right) = \frac{181 \times 10^3 \times 100}{2.303 \times 8.314 \times 873 \times 773}$$
$$\left(\frac{K_{P_2}}{1.017 \times 10^{-3}}\right) = \text{anti log of (1.40)}$$
$$\frac{K_{P_2}}{1.017 \times 10^{-3}} = 25.12$$
$$\Rightarrow K_{P_2} = 25.12 \times 1.017 \times 10^{-3}$$
$$K_{P_2} = 25.54 \times 10^{-3}$$