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CHEMICAL EQUILIBRIUM

Types of Reaction

	Reversible	Irreversible
(i)	A reaction in which not only the reactants react to form products but also the products react to form reactants under the same conditions is called reversible reaction.	A reaction which cannot take place in the reverse direction is called an irreversible reaction
(ii)	A few examples are given as $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $N_2O_4(g) \rightleftharpoons 2NO_2(g)$	A few examples are given as $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$ $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$

Characteristics of Equilibrium State

- A reaction (or a process) is said to be in equilibrium when the rate of forward reaction (process) becomes equal to the rate of backward reaction (process).
- At equilibrium the concentration of each of the reactants and products become constant.
- An equilibrium is dynamic in nature and not static *i. e.*, even after equilibrium is attained, the forward as well as the backward reaction take place but at equal speeds.
- A chemical equilibrium can be established only if none of the products is allowed to escape out.
- Chemical equilibrium can be attained from either direction.
- When reaction attain equilibrium at certain temperature and pressure, $\Delta_r G = 0$
- Catalyst increases rate of reaction in forward as well as backward direction upto same extent.

Law of Mass Action

It was put forward by Guldberg and Waage. It sates that the rate at which a substance reacts is directly proportional to its active mass and hence the rate at which substances react together is directly proportional to the product of their active masses. Active mass means molar concentration.

Law of Chemical Equilibrium

For the reaction $aA(aq) + bB(aq) \rightleftharpoons xX(aq) + yY(aq)$

$$K_c = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Where K_c is called equilibrium constant at constant temperature.

Types of Equilibrium Constant

K_c = Equilibrium constant in terms of molar concentration $= \dfrac{[X]^x [Y]^y}{[A]^a [B]^b}$

K_p = Equilibrium constant in terms of pressure $= \dfrac{p_X^x \cdot p_Y^y}{p_A^a \cdot p_B^b}$

K_x = Equilibrium constant in terms of mole fraction $= \dfrac{(X_x)^x (X_y)^y}{(X_A)^a (X_B)^b}$

Unit of Equilibrium Constant

Unit of $K_p = (\text{atm})^{\Delta n_g}$ (where Δn_g = change in gas mole of reaction)

Unit of $K_c = M^{\Delta n_g}$

Unit of K_x = Unitless

Relationship between K_p and K_c: $K_p = K_c(RT)^{\Delta n_g}$

where R = universal gas constant, T = temperature

Relationship between K_p and K_x: $K_p = K_x(P)^{\Delta n_g}$

where P = equilibrium pressure in container.

Types of Chemical Equilibria

- Homogeneous equilibrium. When in an equilibrium reaction, all the reactants and products are present in the same phase (*i.e.* gaseous or liquid), it is called homogeneous equilibrium.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_3(l) + H_2O(l)$ etc.

- Heterogeneous equilibrium. When in an equilibrium reaction, the reactants and the products are present in two or more than two phases, it is called a heterogeneous equilibrium.

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$; $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$ etc.

Expression of *K* for Equilibrium Reaction

- **Homogeneous equilibria in gases**

Example: (i) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

(ii) $3O_2(g) \rightleftharpoons 2O_3(g)$

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

Equilibrium constant expression for them are

(i) $K_c = \dfrac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$; [] represents concentration in mol/ litre at equilibrium.

(ii) $K_c = \dfrac{[O_3]^2}{[O_2]^3}$; $K_p = \dfrac{P_{O_3}^2}{P_{O_2}^3}$ (iii) $K_C = \dfrac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}$; $K_p = \dfrac{P_{CO_2}^3 \cdot P_{H_2O}^4}{P_{C_3H_8} \cdot P_{O_2}^5}$

Note: Equilibrium constant for gaseous homogeneous equilibrium can be expressed in two ways K_p and K_C. This means value of equilibrium constant depends upon choice of standard state in which concentration of reactants and products are expressed.

- **Heterogeneous equilibria**

If reactants and product are found in two or more phases, the equilibria describing them is called heterogeneous equilibrium.

Example: (i) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

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

(iii) $Br_2(l) \rightleftharpoons Br_2(g)$

Equilibrium expression for them can be written as

(i) $K_C = [Ag^+(aq)][I^-(aq)]$ (ii) $K_P = \dfrac{1}{P_{CO_2}}$; $K_C = \dfrac{1}{[CO_2(g)]}$

(iii) $K_P = P_{Br_2}(g)$; $K_C = [Br_2(g)]$

Predicting the Extent of a Reaction

High value of equilibrium constant indicates that product(s) concentration is high and its low value indicates that concentration of the product(s) in equilibrium mixture is low.

Large value of K_P or K_C (larger than about 10^3), favour the products strongly. For intermediate values of K (approximately in the range of 10^{-3} to 10^3), the concentrations of reactants and products are comparable. Small values of equilibrium constant (smaller than 10^{-3}), favour the reactants strongly.

Predicting the Direction of the Reaction

For this purpose, we calculate the reaction quotient, Q. The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_C, or with partial pressure to give Q_P) at any stage of reaction. For a general reaction

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

$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^d}$$

Then, if $Q_C > K_C$, the reaction will proceed towards direction of reactants.

If $Q_C < K_c$, the reaction will move towards direction of the products.

If $Q_C = K_c$, the reaction mixture is at equilibrium

Important Point about Equilibrium Constant

- If the reaction is reversed, the value of equilibrium constant is inversed *e.g.*,

$$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l), \text{ Equilibrium constant} = K$$

then for $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$, Equilibrium constant = $1/K$

- If the reaction is divided by 2, equilibrium constant is the square root of the original e.g.

for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, Equilibrium constant $= K$

then for $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$, Equilibrium constant $= \sqrt{K}$

If the reaction is multiplied by 2, equilibrium constant is the square of the original.

- If the reaction is written in two steps, equilibrium constant is equal to the product of the equilibrium constants of the step reactions *e.g.*, if for

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g), \text{ Equilibrium constant} = K$$

and for the same reaction taking place in steps *i.e.*,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g), \text{ Equilibrium constant} = K_1$$

and $NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, Equilibrium constant $= K_2$

then $K = K_1 \times K_2$

- Effect of temperature: According to van't Hoff equation, $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

where K_1 and K_2 are the equilibrium constants at temperatures T_1 and T_2 respectively and ΔH is the molar enthalpy change in the temperature range T_1 to T_2.

For exothermic reaction, as temperature increases K decreases.

For endothermic reaction, as temperature increases K increases.

Relationship Between Degree of Dissociation (α) and Vapour Density

- For dissociation reaction: $A_n(g) \rightleftharpoons nA(g)$

$$\text{Degree of dissociation } (\alpha) = \frac{\text{No. of moles dissociated}}{\text{Total no. of moles taken}} = \frac{D - d}{d(n-1)} = \frac{M_t - M_0}{M_0(n-1)}$$

where M_t = theoretical (calculated) molecular weight

M_0 = observed (experimental) molecular weight

D = theoretical vapour density, d = observed vapour density.

n = number of moles of product formed from 1 mole reactant

$$\text{Density of gas mixture} = \frac{PM}{RT}$$

- For polymerization reaction

$$nA(g) \rightleftharpoons A_n(g), \text{ where } n \geq 2$$

$$\alpha = \frac{D - d}{d\left(\frac{1}{n} - 1\right)} = \frac{M_t - M_0}{M_0\left(\frac{1}{n} - 1\right)}$$

Le Chatelier's Principle

"If a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed."

- Effect of change in concentration on equilibrium

  As we add or remove reactant (or product) the ratio of equilibrium concentration become 'Q' (reaction quotient)

  $Q < K$: equilibrium will shift in forward direction.

  $Q > K$: equilibrium will shift in backward direction.

- Effect of change in pressure

  If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The equilibrium will shift in the direction in which there is decrease in number of moles *i.e.*, towards the direction in which there is decrease in volume.

- **Effect of change in pressure on melting point:** There are two types of solids:

  (i) Solids whose volume decreases on melting, *e.g.*, ice, diamond, carborundum, magnesium nitride and quartz.

  Solid (higher volume) $\rightleftharpoons$ Liquid (lower volume)

  The process of melting is facilitated at high pressure, thus melting point is lowered.

  (ii) Solid whose volume increase on melting, *e.g.*, Fe, Cu, Ag, Au, etc.

  Solid (lower volume) $\rightleftharpoons$ Liquid (higher volume)

  In this case the process of melting becomes difficult at high pressure, thus melting point becomes high.

- **Solubility of substances :** When solid substance are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

  (i) For endothermic solubility process, solubility increase with increase in temperature.

  (ii) For exothermic solubility process, decrease with increase in temperature.

- **Solubility of gases in liquids :** When a gas dissolves in liquid, there is decrease in volume. Thus increase of pressure will favour the dissolution of gas in liquid.

- **Effect of temperature:** For endothermic reaction as temperature increases reaction shift in forward direction. For exothermic reaction as temperature increases reaction shift in backward direction.

- **Addition of inert gas**

  (i) For reactions in which $n_p = n_r$ there is no effect of adding an inert gas at constant volume or at constant pressure on the equilibrium.

  (ii) For reactions in which $n_p \neq n_r$, there is no effect of adding inert gas on the equilibrium at constant volume but at constant pressure, equilibrium shifts towards larger mole side.

Applying Le Chatelier's principle, the favourable conditions for the dissociation of NH_3 by Haber's process

i.e., $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),\ \Delta H = -92.5\ \text{kJ}$

are (i) High temperature (ii) Low pressure (iii) Removal of N_2 and H_2 (iv) Addition of inert gas at constant pressure.

❖ Physical Equilibrium

Only physical changes are involved.

Example : (i) Solid liquid equilibria

$$H_2O(s) \rightleftharpoons H_2O(l)$$

At equilibrium: Net rate of conversion of ice into water = Net rate of conversion of water into ice.

For $H_2O(l)$ normal freezing point is 273 K.

(ii) Liquid vapour equilibria :

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Equilibrium is characterized by constant value of vapour pressure of $H_2O(l)$ at certain temperature.

For $H_2O(l)$ normal boiling point is 373 K.

Level 1

1. A reversible reaction is one which :
   (a) Proceeds in one direction
   (b) Proceeds in both directions
   (c) Proceeds spontaneously
   (d) All the statements are wrong
2. The equilibrium constant K_c for the reaction
   $$P_4(g) \rightleftharpoons 2P_2(g)$$
   is 1.4 at 400°C. Suppose that 3 moles of $P_4(g)$ and 2 moles of $P_2(g)$ are mixed in 2 litre container at 400°C. What is the value of reaction quotient (Q_c)?
   (a) $\frac{3}{2}$
   (b) $\frac{2}{3}$
   (c) 1
   (d) None of these
3. In a chemical reaction equilibrium is established when :
   (a) Opposing reaction ceases
   (b) Concentrations of reactants and product are equal
   (c) Velocity of opposing reaction is the same as that of forward reaction
   (d) Reaction ceases to generate heat
4. The equilibrium constant for a reaction is K, and the reaction quotient is Q. For a particular reaction mixture, the ratio $\frac{K}{Q}$ is 0.33. This means that :
   (a) the reaction mixture will equilibrate to form more reactant species
   (b) the reaction mixture will equilibrate to form more product species
   (c) the equilibrium ratio of reactant to product concentrations will be 3
   (d) the equilibrium ratio of reactant to product concentrations will be 0.33
5. Consider the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ for which $K_c = 278\ M^{-1}$. 0.001 mole of each of the reagents $SO_2(g)$, $O_2(g)$ and $SO_3(g)$ are mixed in a 1.0 L flask. Determine the reaction quotient of the system and the spontaneous direction of the system :
   (a) $Q_c = 1000$; the equilibrium shifts to the right
   (b) $Q_c = 1000$; the equilibrium shifts to the left
   (c) $Q_c = 0.001$; the equilibrium shifts to the left
   (d) $Q_c = 0.001$; the equilibrium shifts to the right
6. In Q. No. 5, if the mixture of gases was allowed to come to equilibrium. The volume of the reaction vessel was then rapidly increased by a factor of two. As a result of the change the reaction quotient (Q_c) would :
   (a) increase because of the pressure decrease
   (b) decrease because of the pressure decrease
   (c) remain the same because the equilibrium constant is independent of volume
   (d) increase because the reaction is endothermic
7. For the reaction $A(g) + 3B(g) \rightleftharpoons 2C(g)$ at 27°C, 2 moles of A, 4 moles of B and 6 moles of C are present in 2 litre vessel. If K_c for the reaction is 1.2, the reaction will proceed in :
   (a) forward direction
   (b) backward direction
   (c) neither direction
   (d) none of these

8. For a reversible gaseous reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium, if some moles of H_2 are replaced by same number of moles of T_2 (T is tritium, isotope of H and assume isotopes do not have different chemical properties) without affecting other parameters, then :

(a) The sample of ammonia obtained after sometime will be radioactive.

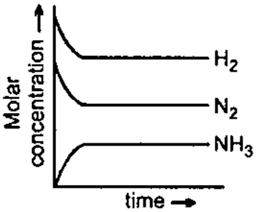
(b) Moles of N_2 after the change will be different as compared to moles of N_2 present before the change

(c) The value of K_p or K_c will change

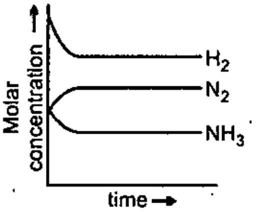
(d) The average molecular mass of new equilibrium will be same as that of old equilibrium

9. For the synthesis of ammonia by the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ in the Haber's process, the attainment of equilibrium is correctly predicted by the curve

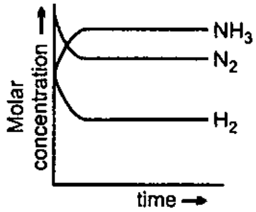
(a)



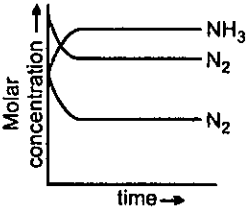
(b)



(c)



(d)

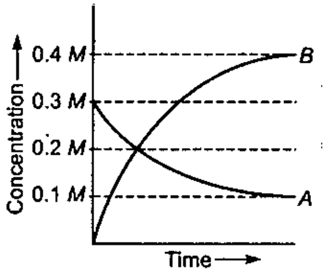


10. The figure shows the change in concentration of species A and B as a function of time.

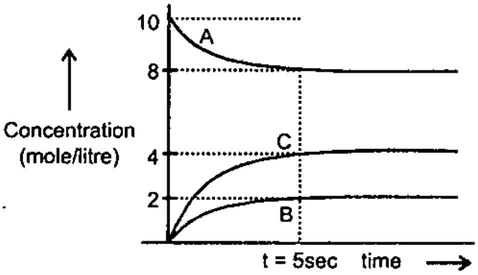
The equilibrium constant K_c for the reaction $A(g) \rightleftharpoons 2B(g)$ is:

(a) $K_c > 1$ (b) $K < 1$

(c) $K = 1$ (d) data insufficient



11. Attainment of the equilibrium $A(g) \rightleftharpoons 2C(g) + B(g)$ gave the following graph. Find the correct option. (% dissociation = fraction dissociated ×100)



(a) At $t = 5$ sec equilibrium has been reached and $K_c = 40$ (mol/litre)^2
(b) At $t = 5$ sec equilibrium has been reached and % dissociation of A is 20%
(c) At $t = 5$ sec equilibrium has been reached and % dissociation of A is 30%
(d) None of these

12. Using molar concentrations, what is the unit of K_c for the reaction?

$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

(a) M^{-2} (b) M^2 (c) M^{-1} (d) M

13. What is the unit of K_p for the reaction?

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

(a) atm (b) atm^{-2} (c) atm^2 (d) atm^{-1}

14. What is the equilibrium expression for the reaction $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$
(a) $K_c = [O_2]^5$ (b) $K_c = [P_4O_{10}] / 5[P_4][O_2]$
(c) $K_c = [P_4O_{10}] / [P_4][O_2]^5$ (d) $K_c = 1/[O_2]^5$

15. At 527°C, the reaction given below has $K_c = 4$

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

What is the K_p for the reaction?

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

(a) $16 \times (800\,R)^2$ (b) $\left(\frac{800R}{4}\right)^{-2}$ (c) $\left(\frac{1}{4 \times 800R}\right)^2$ (d) None of these

16. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature (T) is 4×10^{-4}. The value of K_c for the reaction $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is :
(a) 4×10^{-4} (b) 50 (c) 2.5×10^2 (d) 0.02

17. The equilibrium constant K_c for the following reaction at 842°C is 7.90×10^{-3}. What is K_p at same temperature?

$$\frac{1}{2}F_2(g) \rightleftharpoons F(g)$$

(a) 8.64×10^{-5} (b) 8.26×10^{-4} (c) 7.90×10^{-2} (d) 7.56×10^{-2}

18. The equilibrium constant K_p for the following reaction at 191°C is 1.24. What is K_c?

$$B(s) + \frac{3}{2}F_2(g) \rightleftharpoons BF_3(g)$$

(a) 6.7 (b) 0.61 (c) 8.30 (d) 7.6

19. For the equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$, what is the temperature at which $\frac{K_p\ (\text{atm})}{K_c\ (\text{M})} = 3$?
(a) 0.027 K (b) 0.36 K (c) 36.54 K (d) 273 K

20. For the reversible reaction,

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

at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c with concentration in mole litre^{-1}, is:

(a) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$
(b) $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$
(c) $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$
(d) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

21. For the reaction $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ the value of $\frac{K_c}{K_p}$ is equal to :

(a) $\sqrt{RT}$
(b) RT
(c) $\frac{1}{RT}$
(d) 1.0

22. The concentration of a pure solid or liquid phase is not included in the expression of equilibrium constant because :

(a) solid and liquid concentrations are independent of their quantities.
(b) solids and liquids react slowly.
(c) solids and liquids at equilibrium do not interact with gaseous phase.
(d) the molecules of solids and liquids cannot migrate to the gaseous phase.

23. A catalyst is a substance which :

(a) increases the equilibrium concentration of the product.
(b) changes the equilibrium constant of the reaction.
(c) shortens the time to reach equilibrium.
(d) supplies energy to the reaction.

24. What will be the effect on the equilibrium constant on increasing temperature, if the reaction neither absorbs heat nor releases heat?

(a) Equilibrium constant will remain constant.
(b) Equilibrium constant will decrease.
(c) Equilibrium constant will increase.
(d) Can not be predicted.

25. The equilibrium constant for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 4×10^{-4} at 200 K. In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant in presence of the catalyst at 200 K is :

(a) 40×10^{-4}
(b) 4×10^{-4}
(c) 4×10^{-3}
(d) difficult to compute without more data

26. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant changes with :

(a) total pressure
(b) catalyst
(c) concentration of H_2 and I_2
(d) temperature

27. Consider the reactions

(i) $2CO(g) + 2H_2O(g) \rightleftharpoons 2CO_2(g) + 2H_2(g)$; Eqm. Constant $= K_1$

(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; Eqm. Constant $= K_2$

(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; Eqm. Constant $= K_3$

Which of the following relation is correct?

(a) $K_3 = \frac{K_1}{K_2}$ (b) $K_3 = \frac{K_1^2}{K_2^2}$ (c) $K_3 = K_1K_2$ (d) $K_3 = \sqrt{K_1} \cdot K_2$

28. For the reaction $2NO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons N_2O_5(g)$, if the equilibrium constant is K_p, then the equilibrium constant for the reaction $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$ would be :

(a) K_p^2 (b) $\frac{2}{K_p}$ (c) $\frac{1}{K_p^2}$ (d) $\frac{1}{\sqrt{K_p}}$

29. The equilibrium constant (K_c) for the reaction

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

is 4×10^{-34} at 25°C. What is the equilibrium constant for the reaction?

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$$

(a) 2×10^{-17} (b) 2.5×10^{33} (c) 5×10^{6} (d) None of these

30. At a certain temperature, the following reactions have the equilibrium constants as shown below:

$$S(s) + O_2(g) \rightleftharpoons SO_2(g); \quad K_c = 5 \times 10^{52}$$

$$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); \; K_c = 10^{29}$$

What is the equilibrium constant K_c for the reaction at the same temperature ?

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

(a) 2.5×10^{76} (b) 4×10^{23} (c) 4×10^{-77} (d) None of these

31. Consider the following gaseous equilibria given below :

(I) $N_2 + 3H_2 \rightleftharpoons 2NH_3$; Eqm. Constant $= K_1$

(II) $N_2 + O_2 \rightleftharpoons 2NO$; Eqm. Constant $= K_2$

(III) $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$; Eqm. Constant $= K_3$

The equilibrium constant for the reaction, $2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$ in terms of K_1, K_2 and K_3 will be :

(a) $K_1K_2K_3$ (b) $\frac{K_1K_2}{K_3}$ (c) $\frac{K_1K_3^2}{K_2}$ (d) $\frac{K_2K_3^3}{K_1}$

32. In the reaction $X(g) + Y(g) \rightleftharpoons 2Z(g)$, 2 mole of X, 1 mole of Y and 1 mole of Z are placed in a 10 litre vessel and allowed to reach equilibrium. If final concentration of Z is 0.2 M, then K_c for the given reaction is :

(a) 1.60 (b) $\frac{80}{3}$ (c) $\frac{16}{3}$ (d) None of these

33. An equilibrium mixture of the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ had 0.5 mole H_2S, 0.10 mole H_2 and 0.4 mole S_2 in one litre vessel. The value of equilibrium constant (K) in mol litre^{-1} is :

(a) 0.004 (b) 0.008 (c) 0.016 (d) 0.160

34. Given $[CS_2] = 0.120\,M, [H_2] = 0.10, [H_2S] = 0.20$ and $[CH_4] = 8.40 \times 10^{-5}\,M$ for the following reaction at 900°C, at eq. Calculate the equilibrium constant (K_c).

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

(a) 0.0120 (b) 0.0980 (c) 0.280 (d) 0.120

35. The equilibrium constant for the following reaction is 10.5 at 500 K. A system at equilibrium has $[CO] = 0.250\,M$ and $[H_2] = 0.120\,M$. What is the $[CH_3OH]$?

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

(a) 0.0378 (b) 0.0435 (c) 0.546 (d) 0.0499

36. When sulphur (in the form of S_8) is heated at temperature T, at equilibrium, the pressure of S_8 falls by 30% from 1.0 atm, because $S_8(g)$ is partially converted into $S_2(g)$.
Find the value of K_p for this reaction.

(a) 2.96 (b) 6.14 (c) 204.8 (d) None of these

37. 9.2 grams of $N_2O_4(g)$ is taken in a closed one litre vessel and heated till the following equilibrium is reached $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium, 50% $N_2O_4(g)$ is dissociated. What is the equilibrium constant (in mol litre^{-1}) (molecular weight of $N_2O_4 = 92$)

(a) 0.1 (b) 0.4 (c) 0.2 (d) 2

38. Two moles of NH_3 when put into a previously evacuated vessel (one litre), partially dissociated into N_2 and H_2. If at equilibrium one mole of NH_3 is present, the equilibrium constant is :

(a) 3/4 $\text{mol}^2\text{litre}^{-2}$ (b) 27/64 $\text{mol}^2\text{litre}^{-2}$ (c) 27/32 $\text{mol}^2\text{litre}^{-2}$ (d) 27/16 $\text{mol}^2\text{litre}^{-2}$

39. In the presence of excess of anhydrous $SrCl_2$, the amount of water taken up is governed by $K_p = 10^{12}\ \text{atm}^{-4}$ for the following reaction at 273 K

$$SrCl_2 \cdot 2H_2O(s) + 4H_2O(g) \rightleftharpoons SrCl_2 \cdot 6H_2O(s)$$

What is equilibrium vapour pressure (in torr) of water in a closed vessel that contains $SrCl_2 \cdot 2H_2O(s)$?

(a) 0.001 torr (b) 10^3 torr (c) 0.76 torr (d) 1.31 torr

40. $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g); K_p = 4 \times 10^{-4}\ \text{atm}^2$. If the vapour pressure of water is 38 torr then percentage of relative humidity is : (Assume all data at constant temperature)

(a) 4 (b) 10 (c) 40 (d) None of these

41. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

The equilibrium pressure at 25°C is 0.660 atm. What is K_p for the reaction?

(a) 0.109 (b) 0.218 (c) 1.89 (d) 2.18

42. For the reaction $2A(g) \rightleftharpoons B(g) + 3C(g)$, at a given temperature, $K_c = 16$. What must be the volume of the flask, if a mixture of 2 mole each of A, B and C exist in equilibrium?
(a) $\frac{1}{4}$ (b) $\frac{1}{2}$ (c) 1 (d) None of these

43. One mole of pure ethyl alcohol was treated with one mole of pure acetic acid at 25°C. One-third of the acid changes into ester at equilibrium. The equilibrium constant for the reaction will be :
(a) $\frac{1}{4}$ (b) 2 (c) 3 (d) 4

44. $I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$. We started with 1 mole of I_2 and 0.5 mole of I^- in one litre flask. After equilibrium is reached, excess of $AgNO_3$ gave 0.25 mole of yellow precipitate. Equilibrium constant is :
(a) 1.33 (b) 2.66 (c) 2.0 (d) 3.0

45. At 87°C, the following equilibrium is established.

$$H_2(g) + S(s) \rightleftharpoons H_2S(g); \; K_c = 0.08$$

If 0.3 mole hydrogen and 2 mole sulphur are heated to 87°C in a 2 L vessel, what will be the concentration of H_2S at equilibrium?
(a) 0.011 M (b) 0.022 M (c) 0.044 M (d) 0.08 M

46. In the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, the partial pressure of SO_2, O_2 and SO_3 are 0.662, 0.10 and 0.331 atm respectively. What should be the partial pressure of oxygen so that the equilibrium concentrations of SO_2 and SO_3 are equal?
(a) 0.4 atm (b) 1.0 atm (c) 0.8 atm (d) 0.25 atm

47. When heated, ammonium carbamate decomposes as follows :

$$NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

At a certain temperature, the equilibrium pressure of the system is 0.318 atm. K_p for the reaction is :
(a) 0.128 (b) 0.426 (c) 4.76×10^{-3} (d) None of these

48. In a system $A(s) \rightleftharpoons 2B(g) + 3C(g)$, if the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to :
(a) two times the original value (b) one half of its original value
(c) $2\sqrt{2}$ times to the original value (d) $\frac{1}{2\sqrt{2}}$ times the original value

49. $A + B \rightleftharpoons C + D$. If finally the concentration of A and B are both equal but at equilibrium concentration of D will be twice of that of A then what will be the equilibrium constant of reaction ?
(a) $\frac{4}{9}$ (b) $\frac{9}{4}$ (c) $\frac{1}{9}$ (d) 4

50. The equilibrium constant K_c for the reaction $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$ is 16. If 1 mole of each of all the four gases is taken in 1 dm^3 vessel, the equilibrium concentration of NO would be :
(a) 0.4 M (b) 0.6 M (c) 1.4 M (d) 1.6 M

51. On increasing the temperature, the rate of a reaction :
(a) always increases
(b) always decreases
(c) first increases and then decreases
(d) may increase or decrease depending upon the nature of the reaction

52. A catalyst increases the rate of a reaction by :
(a) increasing the activation energy of the reaction
(b) increasing the value of rate constants (k_f and k_b)
(c) increasing the enthalpy change of the reaction
(d) decreasing the enthalpy change of the reaction

53. At a certain temperature, only 50% HI is dissociated at equilibrium in the following reaction :

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

The equilibrium constant for this reaction is :
(a) 0.25 (b) 1.0 (c) 3.0 (d) 0.5

54. The equilibrium constant K_p for the reaction

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

is 4.0 at 1660°C. Initially 0.80 mole H_2 and 0.80 mole CO_2 are injected into a 5.0 litre flask. What is the equilibrium concentration of $CO_2(g)$?
(a) 0.533 *M* (b) 0.0534 *M* (c) 0.535 *M* (d) None of these

55. At 273 K and 1 atm, 10 litre of N_2O_4 decomposes to NO_2 according to equation

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

What is degree of dissociation (α) when the original volume is 25% less than that of existing volume?
(a) 0.25 (b) 0.33 (c) 0.66 (d) 0.5

56. The equilibrium constant for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 5. How many moles of CO_2 must be added to 1 litre container already containing 3 moles each of CO and H_2O to make 2M equilibrium concentration of CO?
(a) 15 (b) 19 (c) 5 (d) 20

57. A nitrogen-hydrogen mixture initially in the molar ratio of 1 : 3 reached equilibrium to form ammonia when 25% of the N_2 and H_2 had reacted. If the total pressure of the system was 21 atm, the partial pressure of ammonia at the equilibrium was :
(a) 4.5 atm (b) 3.0 atm (c) 2.0 atm (d) 1.5 atm

58. Ammonia under a pressure of 15 atm at 27°C is heated to 347°C in a closed vessel in the presence of a catalyst. Under the conditions, NH_3 is partially decomposed according to the equation,

$2NH_3 \rightleftharpoons N_2 + 3H_2$ the vessel is such that the volume remains effectively constant where as pressure increases to 50 atm. Calculate the percentage of NH_3 actually decomposed :
(a) 65% (b) 61.3% (c) 62.5% (d) 64%

59. 0.1 mole of $N_2O_4(g)$ was sealed in a tube under one atmospheric conditions at 25°C. Calculate the number of moles of $NO_2(g)$ present, if the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $(K_p = 0.14)$ is reached after some time :

(a) 1.8×10^2 (b) 2.8×10^2 (c) 0.034 (d) 2.8×10^{-2}

60. 5 moles of SO_2 and 5 moles of O_2 are allowed to react. At equilibrium, it was found that 60% of SO_2 is used up. If the pressure of the equilibrium mixture is one atmosphere, the partial pressure of O_2 is:

(a) 0.52 atm (b) 0.21 atm (c) 0.41 atm (d) 0.82 atm

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

For the reaction initially the mole ratio was 1 : 3 of $N_2 : H_2$. At equilibrium 50% of each has reacted. If the equilibrium pressure is P, the partial pressure of NH_3 at equilibrium is :

(a) $\frac{P}{3}$ (b) $\frac{P}{4}$ (c) $\frac{P}{6}$ (d) $\frac{P}{8}$

62. 2.0 mole of PCl_5 were introduced in a vessel of 5.0 L capacity of a particular temperature. At equilibrium, PCl_5 was found to be 35% dissociated into PCl_3 and Cl_2. The value of K_c for the reaction

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

(a) 1.89 (b) 0.377 (c) 1.33 (d) 13.3

63. At certain temperature compound $AB_2(g)$ dissociates according to the reaction

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

With degree of dissociation α, which is small compared with unity. The expression of K_p, in terms of α and initial pressure P is :

(a) $P\frac{\alpha^3}{2}$ (b) $\frac{P\alpha^2}{3}$ (c) $P\frac{\alpha^3}{3}$ (d) $\frac{P\alpha^2}{2}$

64. For the reaction

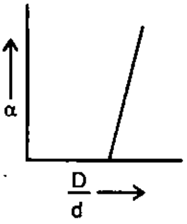
$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$. If the initial concentration of $[H_2] = [CO_2]$ and x moles/litre of hydrogen is consumed at equilibrium, the correct expression of K_p is :

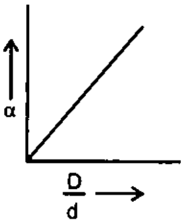
(a) $\frac{x^2}{(1-x)^2}$ (b) $\frac{(1+x)^2}{(1-x)^2}$ (c) $\frac{x^2}{(2+x)^2}$ (d) $\frac{x^2}{1-x^2}$

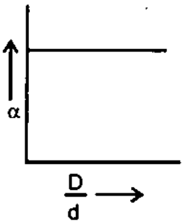
65. If D_T and D_O are the theoretical and observed vapour densities at a definite temperature and α be the degree of dissociation of a substance. Then, α in the terms of D_O, D_T and n (number of moles of products formed from 1 mole reactant) is calculated by the formula :

(a) $\alpha = \frac{D_O - D_T}{(1-n)\,D_T}$ (b) $\alpha = \frac{D_T - D_O}{(n-1)\,D_T}$ (c) $\alpha = \frac{D_T - D_O}{(n-1)\,D_O}$ (d) $\alpha = \frac{D - D_T}{(n-1)\,D_T}$

66. For the dissociation of PCl_5 into PCl_5 and Cl_2 in gaseous phase reaction, if d is the observed vapour density and D the theoretical vapour density with 'α' as degree of dissociation. Variation of D/d with 'α' is given by which graph?

(a)


(b)


(c)


(d) None of these

67. At 27°C and 1 atm pressure, N_2O_4 is 20% dissociation into NO_2. What is the density of equilibrium mixture of N_2O_4 and NO_2 at 27°C and 1 atm?
(a) 3.11 g/litre (b) 2.11 g/litre (c) 4.5 g/litre (d) None of these

68. $COCl_2$ gas dissociates according to the equation, $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$. When heated to 700 K the density of the gas mixture at 1.16 atm and at equilibrium is 1.16 g/litre. The degree of dissociation of CO_2 at 700 K is :
(a) 0.28 (b) 0.50 (c) 0.72 (d) 0.42

69. The degree of dissociation of I_2 molecule of 1000°C and under atmospheric pressure is 40% by volume. If the dissociation is reduced to 20% at the same temp. total equilibrium pressure on the gas is :
(a) 1.57 atm (b) 2.57 atm (c) 3.57 atm (d) 4.57 atm

70. Determine the value of equilibrium constant (K_c) for the reaction

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

If 10 moles of A_2; 15 moles of B_2 and 5 moles of AB are placed in a 2 litre vessel and allowed to come to equilibrium. The final concentration of AB is 7.5 M :
(a) 4.5 (b) 1.5 (c) 0.6 (d) None of these

71. At 87°C, the following equilibrium is established

$$H_2(g) + S(s) \rightleftharpoons H_2S(g); \quad K_p = 7 \times 10^{-2}$$

If 0.50 mole of hydrogen and 1.0 mole of sulphur are heated to 87°C in 1.0 L vessel, what will be the partial pressure of H_2S at equilibrium?
(a) 0.966 atm (b) 1.38 atm (c) 0.0327 atm (d) 1 atm

72. Pure PCl_5 is introduced into an evacuated chamber and comes to equilibrium at 247°C and 2.0 atm. The equilibrium gaseous mixture contains 40% chlorine by volume.
Calculate K_p at 247°C for the reaction

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

(a) 0.625 atm (b) 4 atm (c) 1.6 atm (d) None of these

73. For the reaction

$$SnO_2(s) + 2H_2(g) \rightleftharpoons 2H_2O(g) + Sn(l)$$

calculate K_p at 900 K, where the equilibrium steam-hydrogen mixture was 45% H_2 by volume :
(a) 1.49 (b) 1.22 (c) 0.67 (d) None of these

74. For the reaction $XCO_3(s) \rightleftharpoons XO(s) + CO_2(g)$, $K_p = 1.642$ atm at 727°C. If 4 moles of $XCO_3(s)$ was put into a 50 litre container and heated to 727°C.
What mole percent of the XCO_3 remains unreacted at equilibrium?
(a) 20 (b) 25 (c) 50 (d) None of these

75. $Fe_2O_3(s)$ may be converted to Fe by the reaction

$$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2Fe(s) + 3H_2O(g),$$

for which $K_c = 8$ at temp. 720°C.
What percentage of the H_2 remains unreacted after the reaction has come to equilibrium?
(a) $\simeq 22\%$ (b) $\simeq 34\%$ (c) $\simeq 66\%$ (d) $\simeq 78\%$

76. $AB_3(g)$ is dissociates as $AB_3(g) \rightleftharpoons AB_2(g) + \frac{1}{2}B_2(g)$.

When the initial pressure of AB_2 is 800 torr and the total pressure developed at equilibrium is 900 torr. What fraction of $AB_3(g)$ is dissociated?
(a) 10% (b) 20% (c) 25% (d) 30%

77. At 1000 K, a sample of pure NO_2 gas decomposes as :

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

The equilibrium constant K_p is 156.25 atm. Analysis shows that the partial pressure of O_2 is 0.25 atm at equilibrium. The partial pressure of NO_2 at equilibrium is :
(a) 0.01 (b) 0.02 (c) 0.04 (d) None of these

78. Pure nitrosyl chloride (NOCl) gas was heated to 240°C in a 1.0 L container. At equilibrium the total pressure was 1.0 atm and the NOCl pressure was 0.64 atm. What would be the value of K_p?
(a) 1.02 atm (b) 16.875×10^{-3} atm
(c) 16×10^{-2} atm (d) None of these

79. At a certain temperature the equilibrium constant K_c is 0.25 for the reaction

$$A_2(g) + B_2(g) \rightleftharpoons C_2(g) + D_2(g)$$

If we take 1 mole of each of the four gases in a 10 litre container, what would be equilibrium concentration of $A_2(g)$?
(a) 0.331 *M* (b) 0.033 *M* (c) 0.133 *M* (d) 1.33 *M*

80. At 200°C PCl_5 dissociates as follows :

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

It was found that the equilibrium vapours are 62 times as heavy as hydrogen. The degree of dissociation of PCl_5 at 200°C is nearly :
(a) 10% (b) 42% (c) 50% (d) 68%

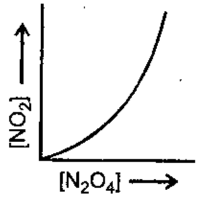
81. For the dissociation reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the degree of dissociation (α) in terms of K_p and total equilibrium pressure P is :

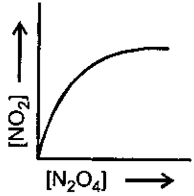
(a) $\alpha = \sqrt{\frac{4P + K_P}{K_P}}$ (b) $\alpha = \sqrt{\frac{K_P}{4P + K_P}}$ (c) $\alpha = \sqrt{\frac{K_P}{4P}}$ (d) None of these

82. The graph which represents all the equilibrium concentrations for the reaction

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

Then the select the correct graph for concentrations of NO_2 against concentrations of NO_4:

(a)


(b)


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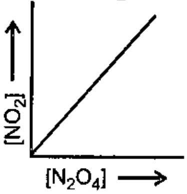

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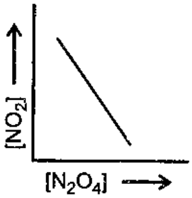


83. The vapour pressure of mercury is 0.002 mm Hg at 27°C. K_c for the process $Hg(l) \rightleftharpoons Hg(g)$ is :

(a) 0.002 (b) 8.12×10^{-5} (c) 6.48×10^{-5} (d) 1.068×10^{-7}

84. Calculate the equilibrium constant (K_c) for the reaction below if they are present at equilibrium 5.0 mole of A_2, 3 mole of B_2 and 2 mole of AB_2 at 8.21 atm and 300 K

$$A_2(g) + 2B_2(g) \rightleftharpoons 2AB_2(g) + \text{Heat}$$

(a) 1.333 (b) 2.66 (c) 20 (d) None of these

85. For the reaction (1) and (2)

$$A(g) \rightleftharpoons B(g) + C(g) \qquad \ldots(1)$$

$$X(g) \rightleftharpoons 2Y(g) \qquad \ldots(2)$$

Given, $K_{P_1} : K_{P_2} = 9:1$

If the degree of dissociation of $A(g)$ and $X(g)$ be same then the total pressure at equilibrium (1) and (2) are in the ratio :

(a) 3 : 1 (b) 36 : 1 (c) 1 : 1 (d) 0.5 : 1

86. Given the following reaction at equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected?

(a) More $NH_3(g)$ is produced (b) Less $NH_3(g)$ is produced

(c) No affect on the equilibrium (d) K_p of the reaction is decreased

87. Change in volume of the system does not alter the number of moles in which of the following equilibrium :

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

88. For the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H = -93.6 \text{ kJ mol}^{-1}$$

the number of moles of H_2 at equilibrium will increase if :

(a) volume is increased (b) volume is decreased

(c) argon gas is added at constant volume (d) NH_3 is removed

89. The volume of the reaction vessel containing an equilibrium mixture is increased in the following reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

When equilibrium is re-established :

(a) the amount of $Cl_2(g)$ remains unchanged
(b) the amount of $Cl_2(g)$ increases
(c) the amount of $SO_2Cl_2(g)$ increases
(d) the amount of $SO_2(g)$ decreases

90. Some inert gas is added at constant volume to the following reaction at equilibrium

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Predict the effect of adding the inert gas :

(a) the equilibrium shifts in the forward direction
(b) the equilibrium shifts in the backward direction
(c) the equilibrium remains unaffected
(d) the value of K_p is increased

91 Consider the reaction where $K_p = 0.497$ at 500 K

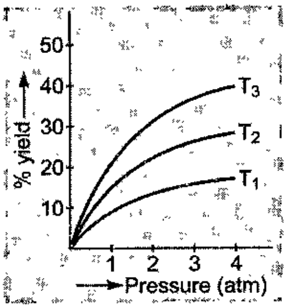
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If the three gases are mixed in a rigid container so that the partial pressure of each gas in initially 1 atm. Which is true ?

(a) More PCl_5 will be produced
(b) More PCl_3 will be produced
(c) Equilibrium will be established when 50% reaction is complete
(d) None of the above

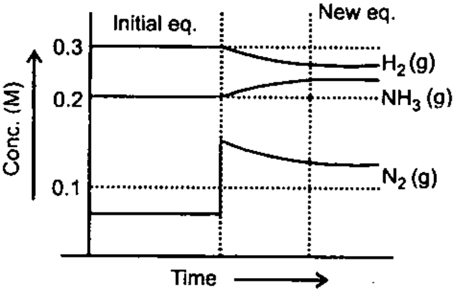
92. The preparation of $SO_3(g)$ by reaction $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is an exothermic reaction. If the preparation follows the following temperature-pressure relationship for its % yield, then for temperatures T_1, T_2 and T_3. The correct option is :

(a) $T_3 > T_2 > T_1$
(b) $T_1 > T_2 > T_3$
(c) $T_1 = T_2 = T_3$
(d) Nothing could be predicted about temperature through given information

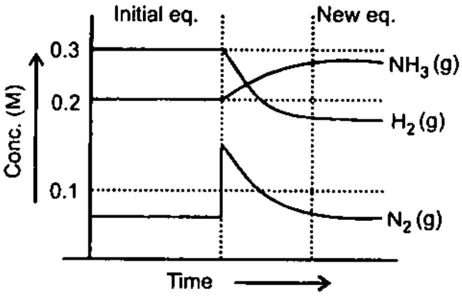


93. An equilibrium mixture at 700 K of $0.05M$ $N_2(g)$, $0.3M$ $H_2(g)$ and $0.2M$ $NH_3(g)$ is present in a container. Now if this equilibrium is disturbed by adding $N_2(g)$ so that its concentration becomes $0.15M$ just after addition then which of the following graphs represents the above situation more appropriately:

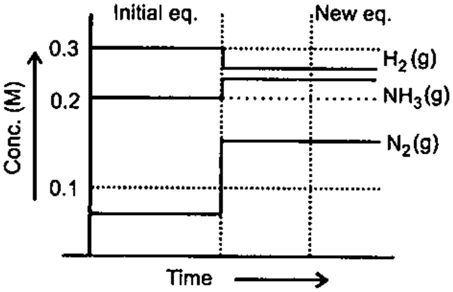
(a)



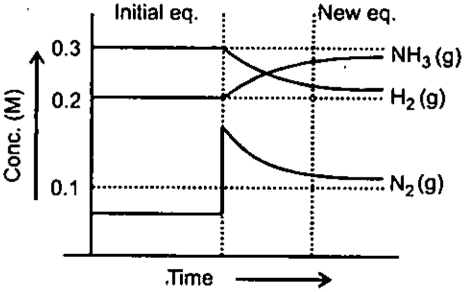
(b)



(c)



(d)



94. In a vessel containing N_2, H_2 and NH_3 at equilibrium, some helium gas is introduced so that total pressure increase while temperature and volume remain constant. According to Le Chatelier's principle, the dissociation of NH_3 :

(a) increases (b) decreases

(c) remains unaltered (d) changes unpredictably

95. Le-Chatelier principle is not applicable to :

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (b) $Fe(s) + S(s) \rightleftharpoons FeS(s)$

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

96. Consider the following reactions. In which cases is the product formation favoured by decreased pressure?

(1) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$; $\Delta H° = +172.5$ kJ

(2) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H° = -91.8$ kJ

(3) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; $\Delta H° = 181$ kJ

(4) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $\Delta H° = 484.6$ kJ

(a) 2, 3 (b) 3, 4 (c) 2, 4 (d) 1, 4

97. Consider the following reactions. In which cases is product formation favoured by decreased temperature?

(1) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; $\Delta H° = 181$ kJ

(2) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$; $\Delta H° = 566$ kJ

(3) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $\Delta H° = -9.4$ kJ

(4) $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$; $\Delta H° = -541$ kJ

(a) 1, 2 (b) 2 only (c) 1, 2, 3 (d) 3, 4

98. For which of the following reactions is product formation favoured by low pressure and high temperature?

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $\Delta H^\circ = -9.4$ kJ

(b) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$; $\Delta H^\circ = 172.5$ kJ

(c) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH$; $\Delta H^\circ = -21.7$ kJ

(d) $3O_2(g) \rightleftharpoons 2O_3(g)$; $\Delta H^\circ = 285$ kJ

99. For which of the following reaction is product formation favoured by low pressure and low temperature?

(a) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$; $\Delta H^\circ = 172.5$ kJ

(b) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH$; $\Delta H^\circ = -21.7$ kJ

(c) $2O_3(g) \rightleftharpoons 3O_2(g)$; $\Delta H^\circ = -285$ kJ

(d) $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$; $\Delta H^\circ = -541$ kJ

100. Consider the following reactions at equilibrium and determine which of the indicated changes will cause the reaction to proceed to the right.

(1) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ (add CH_4)

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

(3) $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$ (add F_2)

(4) $BaO(s) + SO_3(g) \rightleftharpoons BaSO_4(s)$ (add BaO)

(a) 2, 3 (b) 1, 4 (c) 2, 4 (d) 2, 3, 4

101. If the pressure in a reaction vessel for the following reaction is increased by decreasing the volume, what will happen to the concentrations of CO and CO_2?

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) + \text{Heat}$$

(a) both the [CO] and [CO_2] will decrease

(b) neither the [CO] nor the [CO_2] will change

(c) the [CO] will decrease and the [CO_2] will increase

(d) both the [CO] and [CO_2] will increase

102. Consider the following reaction and determine which of the conditions will shift the equilibrium position to the right?

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + \text{Heat}$$

(a) increasing the temperature (b) increasing the pressure

(c) adding a catalyst (d) none of the above is correct

103. The conversion of ozone into oxygen is exothermic. Under what conditions is ozone the most stable?

$$2O_3(g) \rightleftharpoons 3O_2(g)$$

(a) At low pressure and low temperature (b) At high pressure and high temperature

(c) At high pressure and low temperature (d) At low pressure and high temperature

104. A system at equilibrium is described by the equation of fixed temperature *T*.

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

What effect will an increases in the total pressure caused by a decrease in volume have on the equilibrium?

(a) Concentration of $SO_2Cl_2(g)$ increases (b) Concentration of $SO_2(g)$ increases
(c) Concentration of $Cl_2(g)$ increases (d) Concentration of all gases increases

105. The reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ is an exothermic equilibrium. This means that :
(a) equilibration of this gas mixture will be slower at high temperature
(b) a mole of N_2O_4 will occupy twice the volume of a mole of NO_2 at the same
(c) the equilibrium will move to the right if an equilibrium mixture is cooled
(d) the position of equilibrium will move to the left with increasing gas pressure

106. Densities of diamond and graphite are 3.5 and 2.3 gm/mL.

$\text{C (diamond)} \rightleftharpoons \text{C (graphite)}; \quad \Delta_r H = -1.9 \text{ kJ/mol}$

favourable conditions for formation of graphite are :
(a) high pressure and low temperature (b) low pressure and high temperature
(c) high pressure and high temperature (d) low pressure and low temperature

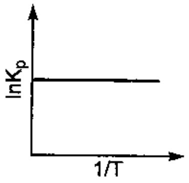
107. For an equilibrium $H_2O(s) \rightleftharpoons H_2O(l)$, which of the following statements is true?
(a) The pressure changes do not affect the equilibrium
(b) More of ice melts if pressure on the system is increased
(c) More of liquid freezes if pressure on the system is increased
(d) The pressure changes may increase or decrease the degree of advancement of the process

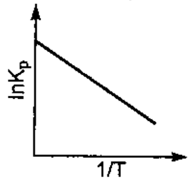
108. A pressure cooker reduces cooking time for food because:
(a) the higher pressure inside the cooker crushes the food material
(b) cooking involves chemical changes helped by a rise in temperature
(c) heat is more evenly distributed in the cooking space
(d) boiling point of water involved in cooking is increased

109. The vapour pressure of a liquid in a closed container depends on :
(1) temperature of liquid
(2) quantity of liquid
(3) surface area of the liquid
(a) 1 only (b) 2 only (c) 1 and 3 only (d) 1, 2 and 3

110. The pressure on a sample of water at its triple point is reduced while the temperature is held constant. Which phases changes are favoured?
(I) melting of ice
(II) sublimation of ice
(III) vaporization of liquid water
(a) I only (b) III only (c) II only (d) II and III

111. An exothermic reaction is represented by the graph :

(a)


(b)


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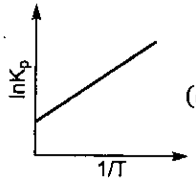

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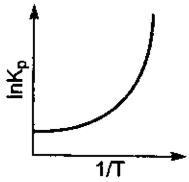
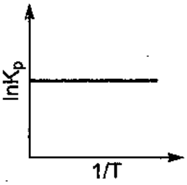
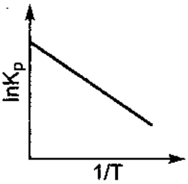
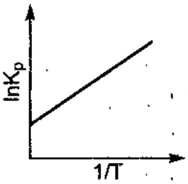
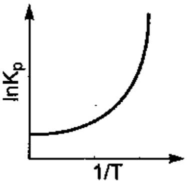


112. An endothermic reaction is represented by the graph :

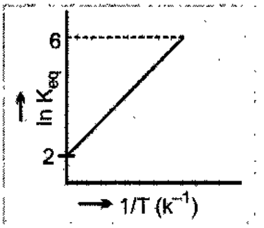
(a) 

(b) 

(c) 

(d) 

113. A schematic plot of ln K_{eq} *versus* inverse of temperature for a reaction is shown below



the reaction must be :

(a) Exothermic

(b) Endothermic

(c) One with negligible enthalpy change

(d) Highly spontaneous at ordinary temperature

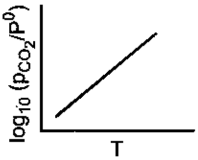
114. What is the correct relationship between free energy change and equilibrium constant of a reaction :

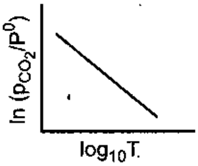
(a) $\Delta G^\circ = RT \ln K$ (b) $\Delta G^\circ = -RT \ln K$

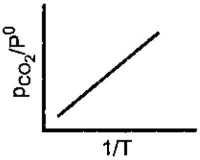
(c) $\Delta G = RT \ln K$ (d) $\Delta G = -RT \ln K$

115. For the chemical equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, ΔH_r^0 can be determined from which one of the following plots ?

(a) 

(b) 

(c) 

(d) 

116. K_p has the value of 10^{-6} atm^3 and 10^{-4} atm^3 at 298 K and 323 K respectively for the reaction

$$CuSO_4 \cdot 3H_2O(s) \rightleftharpoons CuSO_4(s) + 3H_2O(g)$$

$\Delta_r H^\circ$ for the reaction is :

(a) 7.7 kJ/mol (b) −147.41 kJ/mol

(c) 147.41 kJ/mol (d) None of these

117. van't Hoffs equation shows the effect of temperature on equilibrium constants K_c and K_p. The K_p varies with temperature according to the relation :

(a) $\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{2.303\,R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$ (b) $\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

(c) $\log \frac{K_{p2}}{K_{p_1}} = \frac{\Delta E°}{2.303\,R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$ (d) None of these

118. For a reaction, the value of K_p increases with increase in temperature. The ΔH for the reaction would be :

(a) positive (b) negative
(c) zero (d) cannot be predicted

119. The most stable oxides of nitrogen will be :

(a) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $K = 6.7 \times 10^{16}$ mol L^{-1}
(b) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g)$; $K = 1.2 \times 10^{24}$ mol^5 L^{-5}
(c) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $K = 2.2 \times 10^{30}$
(d) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$; $K = 3.5 \times 10^{33}$ mol L^{-1}

120. When 1 mole of pure ethyl alcohol (C_2H_5OH) is mixed with 1 mole of acetic acid at 25°C, the equilibrium mixture contains 2/3 mole each of ester and water

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

The $\Delta G°$ for the reaction at 298 K is :

(a) 3435 J (b) 4 J (c) –3435 J (d) Zero

121. The value of $\Delta G°$ for a reaction in aqueous phase having $K_c = 1$, would be :

(a) $-RT$ (b) –1 (c) 0 (d) $+RT$

122. A plot of Gibbs energy of a reaction mixture against the extent of the reaction is :

(a) minimum at equilibrium (b) zero at equilibrium
(c) maximum at equilibrium (d) None of these

123. For the reaction at 300 K

$$A(g) \rightleftharpoons V(g) + S(g)$$

$$\Delta_r H° = -30\ \text{kJ/mol},\ \Delta_r S° = -0.1\ \text{kJ.K}^{-1}.\text{mol}^{-1}$$

What is the value of equilibrium constant?

(a) 0 (b) 1 (c) 10 (d) None of these

124. Solid $Ca(HCO_3)_2$ decomposes as

$Ca(HCO_3)_2(s) \rightleftharpoons CaCO_3(s) + CO_2(g) + H_2O(g)$

If the total pressure is 0.2 bar at 420 K, what is the standard free energy change for the given reaction ($\Delta_r G°$)?

(a) 840 kJ/mol (b) 3.86 kJ/mol (c) 6.98 kJ/mol (d) 16.083 kJ/mol

125. The standard free energy change of a reaction is $\Delta G° = -115$ kJ at 298 K. Calculate the value of $\log_{10} K_p$ ($R = 8.314$ JK^{-1} mol^{-1})

(a) 20.16 (b) 2.303 (c) 2.016 (d) 13.83

Level 2

1. The following equilibrium constants were determined at 1120 K :

$$2CO(g) \rightleftharpoons C(s) + CO_2(g); \qquad K_{p_1} = 10^{-14}\ \text{atm}^{-1}$$

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g); \qquad K_{p_2} = 6 \times 10^{-3}\ \text{atm}^{-1}$$

What is the equilibrium constant K_c for the following reaction at 1120 K :

$$C(s) + CO_2(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g)$$

(a) $3.31 \times 10^{11}\ M^{-1}$ (b) $5.5 \times 10^{10}\ M^{-1}$ (c) $5.51 \times 10^{6}\ M^{-1}$ (d) None of these

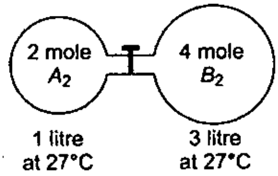
2. One mole of $N_2(g)$ is mixed with 2 moles of $H_2(g)$ in a 4 litre vessel. If 50% of $N_2(g)$ is converted to $NH_3(g)$ by the following reaction :

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

What will be the value of K_c for the following equilibrium?

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

(a) 256 (b) 16 (c) $\frac{1}{16}$ (d) None of these

3. 

The gas A_2 in the left flask allowed to react with gas B_2 present in right flask as $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; $K_c = 4$ at 27°C. What is the concentration of AB when equilibrium is established?

(a) 1.33 M (b) 2.66 M (c) 0.66 M (d) 0.33 M

4. Assume that the decomposition of HNO_3 can be represented by the following equation

$$4HNO_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$$

and the reaction approaches equilibrium at 400 K temperature and 30 atm pressure. At equilibrium partial pressure of HNO_3 is 2 atm.

Calculate K_c in $(\text{mol/L})^3$ at 400 K :

(Use : $R = 0.08$ atm-L/mol-K)

(a) 4 (b) 8 (c) 16 (d) 32

5. For the equilibrium

$$LiCl \cdot 3NH_3(s) \rightleftharpoons LiCl \cdot NH_3(s) + 2NH_3(g);$$

$K_p = 9\ \text{atm}^2$ at 37°C. A 5 litre vessel contains 0.1 mole of $LiCl \cdot NH_3$. How many moles of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion?

Use : $R = 0.082$ atm-L/mol K

(a) 0.2 (b) 0.59 (c) 0.69 (d) 0.79

6. Ammonium carbamate dissociates as

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In a closed vessel containing ammonium carbamate in equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of partial pressure of CO_2 now to the original partial pressure of CO_2 :

(a) 4 (b) 9 (c) $\frac{4}{9}$ (d) $\frac{2}{9}$

7. For the reaction $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

K_p is 5×10^{-2} atm. Calculate the mole per cent of $C_2H_6(g)$ at equilibrium if pure C_2H_6 at 1 atm is passed over a suitable catalyst at 900 K :

(a) 20 (b) 33.33 (c) 66.66 (d) None of these

8. $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$. If nitrosyl bromide (NOBr) is 40% dissociated at certain temp. and a total pressure of 0.30 atm. K_p for the reaction $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$ is :

(a) 45 (b) 25 (c) 0.022 (d) 0.25

9. Consider the partial decomposition of A as

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

At equilibrium 700 mL gaseous mixture contains 100 mL of gas C at 10 atm and 300 K. What is the value of K_p for the reaction?

(a) $\frac{40}{7}$ (b) $\frac{1}{28}$ (c) $\frac{10}{28}$ (d) $\frac{28}{10}$

10. At a certain temperature and 2 atm pressure equilibrium constant (K_p) is 25 for the reaction

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

Initially if we take 2 moles of each of the four gases and 2 moles of inert gas, what would be the equilibrium partial pressure of NO_2?

(a) 1.33 atm (b) 0.1665 atm (c) 0.133 atm (d) None of these

11. 0.020 g of selenium vapour at equilibrium occupying a volume of 2.463 mL at 1 atm and 27°C. The selenium is in a state of equilibrium according to reaction

$$3Se_2(g) \rightleftharpoons Se_6(g)$$

What is the degree of association of selenium?

(At. wt. of Se = 79)

(a) 0.205 (b) 0.315 (c) 0.14 (d) None of these

12. Determine the degree of association (polymerization) for the reaction in aqueous solution

$$6HCHO \rightleftharpoons C_6H_{12}O_6$$

If observed (mean) molar mass of HCHO and $C_6H_{12}O_6$ is 150 :

(a) 0.50 (b) 0.833 (c) 0.90 (d) 0.96

13. A reaction system in equilibrium according to reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ in one litre vessel at a given temperature was found to be 0.12 mole each of SO_2 and SO_3 and 5 mole of O_2. In another vessel of one litre contains 32 g of SO_2 at the same temperature. What mass of O_2 must be added to this vessel in order that at equilibrium 20% of SO_2 is oxidized to SO_3?

(a) 0.4125 g (b) 11.6 g (c) 1.6 g (d) None of these

14. The equilibrium constant K_p for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \text{ is } 4.5$$

What would be the average molar mass (in g/mol) of an equilibrium mixture of N_2O_4 and NO_2 formed by the dissociation of pure N_2O_4 at a total pressure of 2 atm?

(a) 69 (b) 57.5 (c) 80.5 (d) 85.5

15. A flask containing 0.5 atm pressure of $A_2(g)$, some solid AB added into flask which undergoes dissociation according to $2AB(s) \rightleftharpoons A_2(g) + B_2(g)$ $K_p = 0.06 \text{ atm}^2$

The total pressure (in atm) at equilibrium is :

(a) 0.70 (b) 0.6 (c) 0.10 (d) None of these

16. A vessel of 250 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain the equilibrium at 440°C as

$$Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$$

After equilibrium, the H_2S formed was analysed by dissolved it in water and treating with excess of Pb^{2+} to give 1.19 g of PbS as precipitate. What is the value of K_c at 440°C?

(a) 1 (b) 2 (c) 4 (d) 8

17. For the reaction $2A(g) + B(g) \rightleftharpoons C(g) + D(g); K_c = 10^{12}$. If the initial moles of A, B, C and D are 2, 1, 7 and 3 moles respectively in a one litre vessel. What is the equilibrium concentration of A?

(a) 4×10^{-4} (b) 2×10^{-4} (c) 10^{-4} (d) 8×10^{-4}

18. The equilibrium constant for the reaction in aqueous solution

$$H_3BO_3 + \text{glycerin} \rightleftharpoons (H_3BO_3 - \text{glycerin}) \text{ is } 0.90.$$

How many moles of glycerin should be added per litre of 0.10 M H_3BO_3 so that 80% of the H_3BO_3 is converted to the boric-acid-glycerin complex?

(a) 4.44 (b) 4.52 (c) 3.6 (d) 0.08

19. Rate of diffusion of ozonized oxygen is $0.4\sqrt{5}$ times that of pure oxygen. What is the per cent degree of association of oxygen assuming pure O_2 in the sample initially?

(a) 20 (b) 40 (c) 60 (d) None of these

20. One mole of SO_3 was placed in a two litre vessel at a certain temperature. The following equilibrium was established in the vessel

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

the equilibrium mixture reacted with 0.2 mole $KMnO_4$ in acidic medium. Hence, K_c is :

(a) 0.50 (b) 0.25
(c) 0.125 (d) None of these

21. At 800°C, the following equilibrium is established as

$$F_2(g) \rightleftharpoons 2F(g)$$

The composition of equilibrium may be determined by measuring the rate of effusion of the mixture through a pin hole. It is found that at 800°C and 1 atm mixture effuses 1.6 times as fast as SO_2 effuses under the similar conditions. (At. wt. of F = 19). What is the value of K_p (in atm)?

(a) 0.315 (b) 0.685
(c) 0.46 (d) 1.49

22. The equilibrium constant for the ionization of $RNH_2(g)$ in water as

$$RNH_2(g) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$

is 8×10^{-6} at 25°C. Find the pH of a solution at equilibrium when pressure of $RNH_2(g)$ is 0.5 bar :

(a) ≈ 12.3 (b) ≈ 11.3 (c) ≈ 11.45 (d) None

23. Calculate $\Delta_r G$ for the reaction at 27°C

$$H_2(g) + 2Ag^+(aq) \rightleftharpoons 2Ag(s) + 2H^+(aq)$$

Given : $P_{H_2} = 0.5$ bar; $[Ag^+] = 10^{-5}\ M$;

$[H^+] = 10^{-3}\ M$; $\Delta_r G°[Ag^+(aq)] = 77.1$ kJ/mol

(a) −154.2 kJ/mol (b) −178.9 kJ/mol

(c) −129.5 kJ/mol (d) None of these

24. When N_2O_5 is heated at certain temperature, it dissociates as $N_2O_5(g) \rightleftharpoons N_2O_3(g) + O_2(g)$; $K_c = 2.5$. At the same time N_2O_3 also decomposes as : $N_2O_3(g) \rightleftharpoons N_2O(g) + O_2(g)$. If initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to dissociation, concentration of O_2 at equilibrium is 2.5 M. Equilibrium concentration of N_2O_5 is :

(a) 1.0 M (b) 1.5 M (c) 2.166 M (d) 1.846 M

25. Two solid compounds X and Y dissociates at a certain temperature as follows

$$X(s) \rightleftharpoons A(g) + 2B(g);\ K_{p_1} = 9 \times 10^{-3}\ \text{atm}^3$$

$$Y(s) \rightleftharpoons 2B(g) + C(g);\ K_{p_2} = 4.5 \times 10^{-3}\ \text{atm}^3$$

The total pressure of gases over a mixture of X and Y is :

(a) 4.5 atm (b) 0.45 atm (c) 0.6 atm (d) None of these

Level 3

PASSAGE 1

For a gaseous reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

equilibrium constant K_c, K_p and K_x are represented by the following relations

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b};\quad K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b} \text{ and } K_x = \frac{x_C^c \cdot x_D^d}{x_A^a \cdot x_B^b}$$

where $[A]$ represents molar concentration of A, p_A represents partial pressure of A and P represents total pressure, x_A represents mole fraction of A

1. On the basis of above work-up. Select write option

(a) $K_p = K_c\,(RT)^{\Delta n_g}; K_x = K_p\,(RT)^{\Delta n_g}$ (b) $K_c = K_p\,(RT)^{-\Delta n_g}; K_p = K_x P^{\Delta n_g}$

(c) $K_c = K_x P^{\Delta n_g}; K_p = K_x P^{\Delta n_g}$ (d) $K_c = K_p\,(RT)^{-\Delta n_g}; K_x = K_p\,(RT)^{\Delta n_g}$

2. For the reaction $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g), K_p > K_x$ is obtained at :

(a) 0.5 atm (b) 0.8 atm (c) 1 atm (d) 2 atm

3. For the following equilibrium relation between K_c and K_x (in terms of mole fraction) is

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

(a) $K_c = K_x\,(RT)^{-1}$ (b) $K_c = K_x\,(RT)$ (c) $K_c = K_x\left(\frac{RT}{P}\right)$ (d) $K_p = K_x\left(\frac{P}{RT}\right)$

PASSAGE 2

Variation of equilibrium constant K with temperature is given by van't Hoff equation

$$\ln K = \frac{\Delta S_r{}^\circ}{R} - \frac{\Delta H_r{}^\circ}{RT}$$

from this equation, $\Delta H_r{}^\circ$ can be evaluated if equilibrium constants K_1 and K_2 at two temperature T_1 and T_2 are known.

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_r{}^\circ}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

1. For an isomerization $X(g) \rightleftharpoons Y(g)$, the temperature dependency of equilibrium constant is given by :

$$\ln K = 2 - \frac{1000}{T}$$

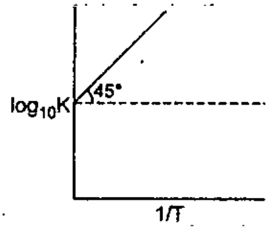
The value of $\Delta_r S^\circ$ at 300 K is :

(a) $2R$ (b) $\frac{2}{R}$ (c) $1000\,R$ (d) None of these

2. Select the correct statement :

(a) Value of K_{eq} always increases with increasing temperature
(b) For exothermic reaction value of K_{eq} increases with decreasing in temperature
(c) For endothermic reaction value of K_{eq} increases with decreasing in temperature
(d) For exothermic reaction slope is ($\log K$ *Vs* $.1/T$) negative

3. Variation of $\log_{10} K$ with $\frac{1}{T}$ is shown by the following graph in which straight line is at 45°C, hence $\Delta H°$ is :



(a) –4.606 kJ/mol (b) –19.147 kJ/mol (c) 8.314 kJ/mol (d) 10 kJ/mol

4. The equilibrium constant K_p for the reaction

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

is 1 at 27°C and 4 at 47°C. For the reaction calculate enthalpy change for the $B(g) + C(g) \rightleftharpoons A(g)$ (Given : $R = 2$ cal/mol-K)

(a) – 13.31 kcal/mol (b) 13.31 kcal/mol (c) – 19.2 kcal/mol (d) 55.63 kcal/mol

PASSAGE 3

N_2O_3 is an unstable oxide of nitrogen and it docomposes into $NO(g)$ and $NO_2(g)$ where $NO_2(g)$ is further dimerise into N_2O_4 as

(i) $N_2O_3(g) \rightleftharpoons NO_2(g) + NO(g)$; $K_{p_1} = 2.5$ bar

(ii) $2NO_2(g) \rightleftharpoons N_2O_4(g)$; K_{p_2}

A flask is initially filled with pure $N_2O_3(g)$ having pressure 2 bar and equilibria were established.

At equilibrium partial pressure of $NO(g)$ was found to be 1.5 bar.

1. The equilibrium partial pressure of $N_2O_3(g)$ is:

(a) 0.5 bar (b) 1.0 bar (c) 1.5 bar (d) 0.1 bar

2. The equilibrium partial pressure of $NO_2(g)$ is:

(a) 0.066 bar (b) 0.133 bar (c) 0.423 bar (d) 0.83 bar

3. The value of K_{p_2} is:

(a) 0.16 bar^{-1} (b) 0.32 bar^{-1} (c) 0.48 bar^{-1} (d) 0.64 bar^{-1}

PASSAGE 4

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way so as to minimise the effect of that change.

Effect of change in concentration on equilibrium:

As we add or remove reactant (or product) the ratio of equilibrium concentration become 'Q' (reaction quotient) and depending upon.

$Q < K$: equilibrium will shift in forward direction

$Q > K$: equilibrium will shift in backward direction

Effect of change in pressure :

If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, then equilibrium will shift in the direction in which there is decrease in number of moles *i.e.*, towards the direction in which there is decrease in volume.

Effect of change in pressure on melting point : There are two types of solids :

(a) Solids whose volume decreases on melting, *e.g.*, ice, diamond, carborundum, magnesium nitride and quartz.

Solid (higher volume) $\rightleftharpoons$ Liquid (lower volume)

The process of melting is facilitated at high pressure, thus melting point is lowered.

(b) Solid whose volume increase on melting, *e.g.*, Fe, Cu, Ag, Au, etc.

Solid (lower volume) $\rightleftharpoons$ Liquid (higher volume)

In this case the process of melting becomes difficult at high pressure, thus melting point becomes high.

(c) **Solubility of substances :** When solid substance are dissolved in water, either heat is evolved.

For endothermic solubility process solubility increase with increase in temperature.

For exothermic solubility decrease with increase in temperature.

(d) **Solubility of gases in liquids :** When a gas dissolves in liquid, there is decrease in volume. Thus increase of pressure will favour the dissolution of gas in liquid.

Effect of temperature : For endothermic reaction as temperature increases reaction shift in forward direction. For exothermic reaction as temperature increases reaction shift in backward direction.

1. A 'X' (g) solute when dissolved in water heat is evolved. Then solubility of 'X' will increase :

(a) High temperature, low pressure
(b) Low temperature, high pressure
(c) High temperature, high pressure
(d) Low temperature, low pressure

2. $Fe(l) \rightleftharpoons Fe(s)$

Above equilibrium is favoured at :

(a) High pressure, low temperature
(b) High pressure, high temperature
(c) Low pressure, high temperature
(d) Low pressure, low temperature

3. For the reaction

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

If pressure is increased by reducing the volume of the container then :

(a) Total pressure at equilibrium will remain same

(b) Concentration of all the component at equilibrium will change

(c) Concentration of all the component at equilibrium will remain same

(d) Equilibrium will shift in the backward direction

ONE OR MORE ANSWERS IS/ARE CORRECT

1. A catalyst :

(a) increases the average kinetic energy of reacting molecules

(b) decreases the activation energy

(c) can alters the reaction mechanism

(d) can change pre-exponential factor

2. Which of the following is correct about the chemical equilibrium?

(a) $(\Delta G)_{T,P} = 0$

(b) Equilibrium constant is independent of initial concentration of reactants

(c) Catalyst has no effect on equilibrium state

(d) Reaction stops at equilibrium

3. For the reaction

$$AB_2(g) \rightleftharpoons AB(g) + B(g)$$

If α is negligiable w.r.t. 1 then degree of dissociation (α) of AB_2 is proportional to :

(a) $\frac{1}{P}$ (b) $\frac{1}{V}$ (c) $\frac{1}{\sqrt{P}}$ (d) $\sqrt{V}$

4. Consider the reactions given below. In which cases will the reaction proceed toward right by increasing the pressure?

(a) $4HCl(g) + O_2(g) \longrightarrow 2Cl_2(g) + 2H_2O(g)$

(b) $Cl_2(g) + H_2O(g) \longrightarrow 2HCl(g) + \frac{1}{2}O_2(g)$

(c) $CO_2(g) + 4H_2(g) \longrightarrow CH_4(g) + 2H_2O(g)$

(d) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

5. Ammonia is a weak base that reacts with water according to the equation

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Select the correct option(s) that can increase the moles of ammonium ion in water:

(a) Addition of HCl (b) Addition of NaOH

(c) Addition of NH_4Cl (d) Addition of H_2O

6. Consider the reaction $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + \text{Heat}$

Under what conditions shift is undeterminable?

(a) Addition of O_2 and decrease in volume

(b) Addition of CO and removal of CO_2 at constant volume

(c) Increase in temperature and decrease in volume
(d) Addition of CO and increase in temperature at constant volume

7. What will be the effect of addition of catalyst at constant temperature?
(a) The equilibrium constant will remain constant
(b) ΔH of the reaction will remain constant
(c) k_f and k_b will increase upto same extent
(d) equilibrium composition will change

8. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperature is favoured by:
(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container

9. For the reaction : $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$; $\Delta H = -329$ kJ, dissociation of $ClF_3(g)$ will be favoured by :
(a) increasing the temperature
(b) increasing the volume of the container
(c) adding of F_2 gas
(d) adding of inert gas at constant pressure

10. Increase in the pressure for the following equilibrium : $H_2O(l) \rightleftharpoons H_2O(g)$, result in the:
(a) formation of more $H_2O(l)$
(b) formation of more $H_2O(g)$
(c) increase in b.p. of $H_2O(l)$
(d) decrease in b.p. of $H_2O(l)$

11. Heating a II group metal carbonate leads to decomposition as :
$BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$
Equilibrium will shift left
(a) by addition of BaO(s)
(b) by addition of $CO_2(g)$
(c) by decreasing the temperature
(d) by decreasing the volume of the vessel

12. $N_2(g)$ and $H_2(g)$ are allowed to react in a closed vessel at given temp. and pressure for the formation of $NH_3(g)[N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.4\text{ kcal}]$ if $He(g)$ is added at equilibrium at constant pressure then which is/are correct ?
(a) Concentration of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ decrease.
(b) Moles of $NH_3(g)$ decreases.
(c) The extent of cooling depends on amount of $He(g)$ added.
(d) Concentration of N_2 and H_2 increases and concentration of NH_3 decreases.

MATCH THE COLUMN

Column-I and **Column-II** contains four entries each. Entries of Column-I are to be matched with some entries of Column-II. One or more than one entries of Column-I may have the matching with the same entries of Column-II.

1.

Column-I	**Column-II**
(A) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(P) $K_p > K_c$ above room temperature
(B) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$	(Q) $K_p = K_c$ above room temperature
(C) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(R) $K_p < K_c$ above room temperature
(D) $HCl(g) \rightleftharpoons H^+(aq) + Cl^-(aq)$	(S) K_p and K_c not defined

2.

Column-I	**Column-II**
(A) $3O_2(g) \rightleftharpoons 2O_3(g)$	(P) no unit
(B) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$	(Q) $atm^{-1/2}$
(C) $2HF(g) \rightleftharpoons H_2(g) + F_2(g)$	(R) atm^{-1}
(D) $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$	(S) atm^{-2}

3.

Column-I **(Reaction)**	**Column-II** **(If α is negligiable w.r.t. 1)**
(A) $2X(g) \rightleftharpoons Y(g) + Z(g)$	(P) $\alpha = 2 \times \sqrt{K_c}$
(B) $X(g) \rightleftharpoons Y(g) + Z(g)$	(Q) $\alpha = 3 \times \sqrt{K_c}$
(C) $3X(g) \rightleftharpoons Y(g) + Z(g)$	(R) $\alpha = (2K_c)^{1/3}$
(D) $2X(g) \rightleftharpoons Y(g) + 2Z(g)$	(S) $\alpha = \sqrt{K_c}$

4.

Column-I	**Column-II**
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H = -ve$	(P) K increases with increase in temperature
(B) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \Delta H = +ve$	(Q) K decreases with increase in temperature
(C) $A(g) + B(g) \rightleftharpoons 2C(g) + D(g);$ $\Delta H = +ve$	(R) Pressure has no effect
(D) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); \Delta H = +ve$	(S) Product moles, increases due to addition of inert gas at constant pressure

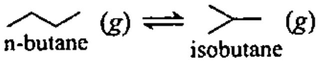
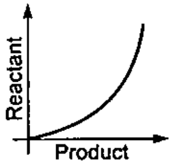
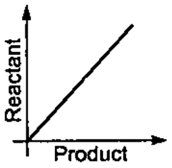
5.

Column-I	Column-II
(A) $\frac{K_{10+T°C}}{K_{T°C}}=2$	(P) Endothermic
(B) $\frac{K_{10+T°C}}{K_{T°C}}=\frac{1}{2}$	(Q) Not affected by pressure
(C) $A(g)+B(g) \rightleftharpoons C(g)$	(R) Exothermic
(D) $X(s)+Y(g) \rightleftharpoons Z(g)$	(S) Affected by volume

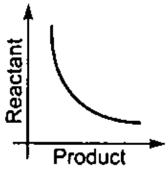
6.

Column-I	Column-II
(A) Pressure increased in $2NO(g) \rightleftharpoons N_2(g)+O_2(g)$	(P) Equilibrium shifted in forward direction
(B) Pressure increased in $CH_4(g)+H_2O(g) \rightleftharpoons CO(g)+3H_2(g)$	(Q) Equilibrium shifted in backward direction
(C) Temp. increased and pressure increased $3O_2(g) \rightleftharpoons 2O_3(g)$; $\Delta H = 285$ kJ	(R) Equilibrium remains unaffected
(D) Pressure decrease and moles of N_2 increased $N_2(g)+2O_2(g) \rightleftharpoons 2NO_2(g)$; $\Delta H = 66.4$ kJ	(S) Theoretically we cannot predict

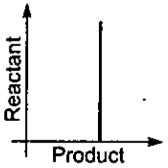
7.

Column-I (Reactions)	Column-II (Equilibrium States)
(A) (A)  n-butane (g) ⇌ isobutane (g)	(P) 
(B) $I_2(s) \rightleftharpoons I_2(aq)$	(Q) 

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



(D) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ (S)



ASSERTION-REASON TYPE QUESTIONS

Each question contains STATEMENT-1 (Assersion) and STATEMENT-2 (Reason).

Examine the statements carefully and mark the correct answer according to the instructions given below :

(A) If both the statements are TRUE and STATEMENT-2 is the correct explanation of STATEMENT-1

(B) If both the statements are TRUE but STATEMENT-2 is NOT the correct explanation of STATEMENT-1

(C) If STATEMENT-1 is TRUE and STATEMENT-2 is FALSE

(D) If STATEMENT-1 is FALSE and STATEMENT-2 is TRUE

1. **STATEMENT-1 :** The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.

   STATEMENT-2 : When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

2. **STATEMENT-1 :** The melting point of ice decreases with increase of pressure.

   STATEMENT-2 : Ice contracts on melting.

3. **STATEMENT-1 :** The equilibrium of $A(g) \rightleftharpoons B(g) + C(g)$ is not affected by changing the volume.

   STATEMENT-2 : K_c for the reaction does not depend on volume of the container.

4. **STATEMENT-1 :** For a chemical reaction at initial stage rate of forward reaction (r_f) is greater than rate of reversed reaction (r_b)

   STATEMENT-2 : When $r_f = r_b$, chemical reaction is at equilibrium.

5. **STATEMENT-1 :** For the reaction $A(g) \rightleftharpoons B(g) + C(g)$, $K_p = 1$ atm. If we start with equal moles of all gases at 9 atm of initial pressure, then at equilibrium partial pressure of A increases.

   STATEMENT-2 : Reaction quotient $Q_p > K_p$ hence equilibrium shifts in backward direction.

6. **STATEMENT-1 :** The gas phase reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ shifts to the right on increasing pressure.

   STATEMENT-2 : When pressure increases, equilibrium shifts towards more number of moles.

7. **STATEMENT-1 :** For a reaction at equilibrium, the Gibb's free energy of reaction is minimum at constant temp. and pressure.

   STATEMENT-2 : The Gibb's free energy of both reactants and products increases and become equal at equilibrium.

8. **STATEMENT-1 :** The physical equilibrium is not static but dynamic in nature.

   STATEMENT-2 : The physical equilibrium is a state in which two opposing process are proceeding at the same rate.

9. **STATEMENT-1 :** Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

   STATEMENT-2 : Eqilibrium constant depends upon the way in which the reaction is written.

10. **STATEMENT-1 :** If $Q_p < K_p$ reaction moves in direction of reactants.

    STATEMENT-2 : Reaction quotient is defined in the same way as equilibrium constant at any stage of the reaction.

11. **STATEMENT-1 :** For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ if the volume of vessel is reduced to half of its original volume, equilibrium concentration of all gases will be doubled.

    STATEMENT-2 : According to Le-Chatelier's principle, reaction shifts in a direction that tends to minimized the effect of the stress.

12. **STATEMENT-1 :** The equilibrium constant of the exothermic reaction at high temperature decreases.

    STATEMENT-2 : Since $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ and for exothermic reaction,

    $\Delta H^\circ = -$ve and thereby; $\frac{K_2}{K_1} < 1$

13. **STATEMENT-1 :** For the reaction at certain temperature

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

    there will be no effect by addition of inert gas at constant volume.

    STATEMENT-2 : Molar concentration of all gases remains constant.

14. **STATEMENT-1 :** For the physical equilibrium $H_2O(s) \rightleftharpoons H_2O(l)$ on increasing temperature and increasing pressure more water will form.

    STATEMENT-2 : Since forward reaction is endothermic in nature and volume of water is greater than that of the volume of ice.

15. **STATEMENT-1 :** The catalyst does not alter the equilibrium constant.

    STATEMENT-2 : Because for the catalysed reaction and uncatalysed reaction ΔH remains same and equilibrium constant depends on ΔH.

SUBJECTIVE PROBLEMS

1. If 50% of CO_2 converts to CO at the following equilibrium :

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

and the equilibrium pressure is 12 atm. Calculate K_p.

2. Calculate partial pressure of B at equilibrium in the following equilibrium

$$A(s) \rightleftharpoons B(g)+2C(g);\ K_p = 32\,\text{atm}^3.$$

3. In a gaseous reaction $A+2B \rightleftharpoons 2C+D$ the initial concentration of B was 1.5 times that of A. At equilibrium the concentrations of A and D were equal. Calculate the equilibrium constant K_C.

4. For the reaction $A(g) \rightleftharpoons B(g);\ K_C = 10$

$$B(g) \rightleftharpoons C(g);\ K_C = 2$$

$$C(g) \rightleftharpoons D(g);\ K_C = 0.01$$

Calculate K_C for the reaction $D(g) \rightleftharpoons A(g)$.

5. 5 litre vessel contains 2 moles of each of gases A and B at equilibrium. If 1 mole each of A and B are removed. Calculate K_C for the reaction $A(g) \rightleftharpoons B(g)$.

6. Calculate K_p for the reaction $A(g) \rightleftharpoons B(s)+2C(g)$; $K_C = 0.2$ at 305 K.

7. A mixture of 3 moles of SO_2, 4 moles of NO_2, 1 moles of SO_3 and 4 moles of NO is placed in a 2.0L vessel. $SO_2(g)+NO_2(g) \rightleftharpoons SO_3(g)+NO(g)$.
At equilibrium, the vessel is found to contain 1 mole of SO_2. Calculate the value of K_C.

8. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 373.5K is 2.0g/L. Calculate K_C for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

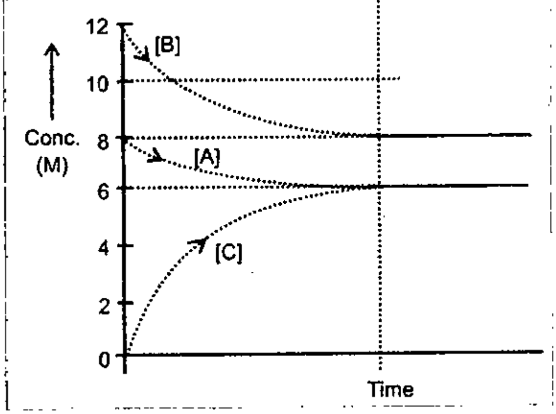
9. If chemical equilibrium is attained at standard states then what is the value of $\Delta G°$?

10. Calculate the equilibrium concentration ratio of C to A if equimolar ratio of A and B were allowed to come to equilibrium at 300K.

$$A(g)+B(g) \rightleftharpoons C(g)+D(g)\ ;\ \Delta G° = -830\,\text{cal}.$$

11. A definite amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.1 atm pressure. NH_4HS decomposes to give NH_3 and H_2S and at equilibrium total pressure in flask is 1.1 atm. If the equilibrium constant K_p for the reaction $NH_4HS(s) \rightleftharpoons NH_3(g)+H_2S(g)$ is represented as $z \times 10^{-1}$ then find the value of z.

12. The gaseous reaction : $A(g) + nB(g) \rightleftharpoons mC(g)$ is represented by following curves



What is the value of $n + m$?

ANSWERS

Level 1

1. (b)	2. (b)	3. (c)	4. (a)	5. (b)	6. (a)	7. (a)	8. (a)	9. (a)	10. (a)
11. (b)	12. (b)	13. (b)	14. (d)	15. (c)	16. (b)	17. (d)	18. (d)	19. (c)	20. (d)
21. (b)	22. (a)	23. (c)	24. (a)	25. (b)	26. (d)	27. (d)	28. (c)	29. (d)	30. (c)
31. (d)	32. (c)	33. (c)	34. (c)	35. (a)	36. (a)	37. (c)	38. (d)	39. (c)	40. (c)
41. (a)	42. (b)	43. (a)	44. (a)	45. (a)	46. (a)	47. (c)	48. (d)	49. (d)	50. (d)
51. (a)	52. (b)	53. (a)	54. (b)	55. (b)	56. (b)	57. (b)	58. (b)	59. (c)	60. (c)
61. (a)	62. (d)	63. (a)	64. (a)	65. (c)	66. (a)	67. (a)	68. (c)	69. (d)	70. (a)
71. (a)	72. (c)	73. (a)	74. (d)	75. (b)	76. (c)	77. (b)	78. (b)	79. (c)	80. (d)
81. (b)	82. (b)	83. (d)	84. (b)	85. (b)	86. (b)	87. (a)	88. (a)	89. (b)	90. (c)
91. (a)	92. (b)	93. (a)	94. (c)	95. (b)	96. (d)	97. (d)	98. (b)	99. (c)	100. (a)
101. (d)	102. (d)	103. (b)	104. (d)	105. (c)	106. (d)	107. (b)	108. (d)	109. (a)	110. (d)
111. (c)	112. (b)	113. (a)	114. (b)	115. (a)	116. (c)	117. (b)	118. (a)	119. (a)	120. (c)
121. (c)	122. (a)	123. (b)	124. (d)	125. (a)					

Level 2

1. (a)	2. (c)	3. (c)	4. (d)	5. (d)	6. (c)	7. (c)	8. (a)	9. (c)	10. (c)
11. (b)	12. (d)	13. (b)	14. (b)	15. (a)	16. (a)	17. (a)	18. (b)	19. (c)	20. (c)
21. (d)	22. (b)	23. (c)	24. (d)	25. (b)					

Level 3

Passage-1: 1. (b) 2. (d) 3. (c)

Passage-2: 1. (a) 2. (b) 3. (b) 4. (a)

Passage-3: 1. (a) 2. (d) 3. (c)

Passage-4: 1. (b) 2. (a) 3. (b)

One or More Answers is/are correct

1. (b,c,d) 2. (a,b,c) 3. (c,d) 4. (a,c) 5. (a,c,d) 6. (c,d) 7. (a,b,c) 8. (c,d)

9. (a,b,d) 10. (a,c) 11. (b,c,d) 12. (a,b,c)

Match the Column

1. A → P; B → R; C → Q; D → S
2. A → R; B → Q; C → P; D → S
3. A → P; B → S; C → Q; D → R
4. A → Q; B → P, R; C → P, S; D → P, S
5. A → P; B → R; C → S; D → Q
6. A → R; B → Q; C → P; D → S
7. A → Q; B → S; C → P; D → S

Assertion-Reason Type Questions

1. (D) 2. (A) 3. (D) 4. (B) 5. (A) 6. (C) 7. (C) 8. (A) 9. (A) 10. (D)

11. (B) 12. (A) 13. (A) 14. (C) 15. (A)

Subjective Problems

1. 4 2. 2 3. 4 4. 5 5. 1 6. 5 7. 9 8. 2 9. 0 10. 2

11. 3 12. 5

Hints and Solutions

Level 1

2. (b) $Q_C = \frac{[P_2(g)]^4}{[P_4(g)]} = \frac{(1)^2}{(3/2)} = \frac{2}{3}$

7. (a) $Q_C = \frac{\left(\frac{6}{2}\right)^2}{\left(\frac{2}{2}\right)\left(\frac{4}{2}\right)^3} = \frac{9}{8}$

$Q_c < K_c$ so reaction will proceed in forward direction.

36. (a) $K_p = \frac{P^4_{S_2(g)}}{P_{S_8(g)}} = \frac{(4 \times 0.3)^4}{0.70} = 2.96$

39. (c) $K_p = \frac{1}{P^4_{H_2O(g)}}$

$\Rightarrow \quad P_{H_2O(g)} = \left(\frac{1}{K_p}\right)^{1/4}$

$\Rightarrow \quad (10^{-12})^{1/4} = 10^{-3}$ atm

$\therefore \quad K_p = 10^{-3} \times 760 = 0.76$ torr

40. (c) $P_{H_2O} = 2 \times 10^{-2}$ atm

$\text{R. H.} = \frac{2 \times 10^{-2} \times 760}{38} \times 100$

$= 40\%$

42. (b) $K_c = \frac{n_B n_C^3}{n_A^2} \times \frac{1}{V^2}$

$\Rightarrow \quad 16 = \frac{2 \times 2^3}{2^2 \times V^2}$

$\Rightarrow \quad V = \frac{1}{2}$

45. (a) $K_c = \frac{[H_2S(g)]}{[H_2(g)]}$

$\Rightarrow \quad 8 \times 10^{-2} = \frac{x}{0.3 - x}$

$\Rightarrow \quad x = 0.022$

$[H_2S(g)] = \frac{0.022}{2}$

$= 0.011\,M$

47. (c) $P_{\text{total}} = 3P$

$\Rightarrow \quad P = \frac{0.318}{3} = 0.106$

$\therefore \quad K_p = 4P^3 = 4.76 \times 10^{-3}$

54. (b) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

moles of eqm $0.8 - x \quad 0.8 - x \quad x \quad x$

conc. at eqm $\frac{0.8 - x}{5} \quad \left(\frac{0.8 - x}{5}\right) \left(\frac{x}{5}\right) \left(\frac{x}{5}\right)$

$\because \quad \Delta n_g = 0$

$\therefore \quad K_c = \frac{\left(\frac{x}{5}\right)^2}{\left(\frac{0.8 - x}{5}\right)^2}$

$\Rightarrow \quad 2 = \frac{x}{0.8 - x}$

$\Rightarrow \quad x = 0.533$

$[CO_2(g)] = \frac{0.8 - 0.533}{5}$

55. (b) For ideal gas mole % ≡ volume %

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

Initial moles $a \quad 0$

at eqm $a(1 - \alpha) \quad 2a\alpha$

As per given original volume

$= \frac{75}{100} \times \text{Volume at eqm}$

at constant T and P : $V \propto n$

$\therefore \quad a = 0.75 \times a(1 + \alpha)$

$\Rightarrow \quad \alpha = 0.33$

56. (b) $CO + H_2O \rightleftharpoons CO_2 + H_2$

Initial conc. $3 \quad 3 \quad x \quad 0$

At eqm $2 \quad 2 \quad (x + 1) \quad 1$

$5 = \frac{(x + 1)}{4} = 20 = x + 1$

$\Rightarrow \quad x = 19$

67. (a) $\alpha = \frac{M_T - M_O}{(n - 1)M_O}$

$\Rightarrow \quad 0.2 = \frac{92 - M_O}{M_O}$

$$\Rightarrow \quad M_O = 76.66$$

$$d_{\text{mixture}} = \frac{PM_{\text{mixture}}}{RT}$$

$$= \frac{1 \times 76.66}{0.821 \times 300} = 3.11 \text{ g/litre}$$

68. (c)
$$M_O = \frac{dRT}{P} = 57.47$$

$$\alpha = \frac{99 - 57.47}{57.47} = 0.72$$

70. (a)
$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

Initial conc.	$10/2$	$15/2$	$5/2$
at eqm	$5 - x$	$7.5 - x$	$2.5 + 2x$

$$\because \quad 2.5 + 2x = 7.5$$

$$\Rightarrow \quad x = 2.5$$

$$K_c = \frac{(7.5)^2}{2.5 \times 5} = 4.5$$

71. (a)
$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

Conc. at eqm	$0.5 - x$	—	x

$$K_c = \frac{[H_2S]}{[H_2]}$$

$$\Rightarrow \quad 7 \times 10^{-2} = \frac{x}{0.5 - x}$$

$$\Rightarrow \quad x = 0.0327$$

$$P_{H_2S} = \left(\frac{n_{H_2S}}{V}\right) RT$$

$$= 0.0327 \times 0.0821 \times 360 = 0.966$$

72. (c) The gaseous mixture contains 40% Cl_2 and 40% PCl_3, since they are produced in 1 : 1 mole ratio. The PCl_5 % is 20.

For ideal gases mole % ≡ volume %

$$P_{Cl_2} = P_{PCl_3}$$

$$\Rightarrow \quad 2 \times 0.40 = 0.80 \text{ atm}$$

$$P_{PCl_5} = 2 \times 0.2 = 0.40 \text{ atm}$$

$$\therefore \quad K_p = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$$

$$= \frac{0.80 \times 0.80}{0.40}$$

$$= 1.6 \text{ atm}$$

73. (a) For an ideal gas mole % ≡ volume %

$$K_p = \frac{P_{H_2O}^2}{P_{H_2}^2} = \frac{(0.55)^2}{(0.45)^2} = 1.49$$

74. (d) Moles of CO_2 present at equilibrium

$$= \frac{1.642 \times 50}{0.0821 \times 1000} = 1$$

Mole % of XCO_3 decomposed

$$= \frac{1}{4} \times 100 = 25\%$$

Hence, 75% remains undecomposed.

75. (b) Let initial moles of $H_2(g)$ is 1

$$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2Fe(s) + 3H_2O(g)$$

at eqm	—	$1 - 3x$	—	$3x$

$$K_c = \frac{\left(\frac{3x}{V}\right)^3}{\left(\frac{1 - 3x}{V}\right)^3}$$

$$\Rightarrow \quad 8 = \left(\frac{3x}{1 - 3x}\right)^3$$

$$\Rightarrow \quad x = 0.22$$

% of H_2 unreacted

$$= \frac{1 - 3 \times 0.22}{1} \times 100 = 34$$

76. (c)
$$AB_3(g) \rightleftharpoons AB_2(g) + \frac{1}{2}B_2(g)$$

At eqm	$800 - x$	x	$x/2$

$$800 - x + x + \frac{x}{2} = 900 \Rightarrow x = 200$$

$$\% \text{ dissociated} = \frac{200}{800} \times 100 = 25$$

77. (b) Let P is initial pressure of NO_2

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

At eqm	$P - 2x$	$2x$	x

as per given $x = 0.25$

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

$$\Rightarrow \quad 156.25 = \frac{(0.5)^2 (0.25)}{P_{NO_2}^2}$$

$$\Rightarrow \quad P_{NO_2} = 0.02$$

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

At eqm	$P - 2x$	$2x$	x

$$P + x = 1; \quad P - 2x = 0.64, \quad x = 0.12$$

$$K_p = \frac{(0.24)^2 (0.12)}{(0.64)^2}$$

$$= 16.875 \times 10^{-3} \text{ atm}$$

79. (c) $Q_c = \dfrac{1 \times 1}{1 \times 1} = 1$

$\because$ $Q_c > K_c$ so reaction will proceed in backward direction

$$A_2(g) + B_2(g) \rightleftharpoons C_2(g) + D_2(g)$$

Conc. eqm	$\frac{1+x}{10}$	$\frac{1+x}{10}$	$\frac{1-x}{10}$	$\frac{1-x}{10}$

$$0.25 = \frac{\left(\frac{1-x}{10}\right)^2}{\left(\frac{1+x}{10}\right)^2} \Rightarrow x = 0.333$$

$$[A_2(g)] = \frac{1+x}{10} = \frac{1.333}{10} = 0.133$$

83. (d) $K_c = [Hg(g)]; P = CRT$

$$C = \left(\frac{0.002}{760}\right) \times \frac{1}{(0.0821 \times 300)}$$

$$= 1.068 \times 10^{-7}\ M$$

84. (b) $K_c = \dfrac{n^2_{AB_2}}{n_{A_2} \cdot n^2_{B_2}} \times V = \dfrac{n^2_{AB_2}}{n_{A_2} \cdot n^2_{B_2}} \times \left(\dfrac{n_{\text{total}}RT}{P}\right)$

$$= \frac{2^2}{5 \times 3^2} \times \left(\frac{10 \times 0.0821 \times 300}{8.21}\right)$$

104. (d) Concentration of all gases increases and equilibrium shifts toward less no. of moles but new equilibrium concentration of every gas would be higher than earlier.

116. (c) $\ln \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta H^\circ}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

$$= \ln\left(\frac{10^{-4}}{10^{-6}}\right) = \frac{\Delta H^\circ}{8.314}\left(\frac{25}{298 \times 323}\right)$$

$$\Delta_r H^\circ = 147.41 \text{ kJ/mol}$$

123. (a) $\Delta_r G^\circ = \Delta_r H^\circ - T \cdot \Delta_r S^\circ$

$$= -30 - 300 \times 0.1 = 0$$

$$\Delta_r G^\circ = -2.303\,RT \log K$$

$$K = 1$$

124. (d) $P_{\text{total}} = 0.2$ bar

At equilibrium $P_{CO_2} = P_{H_2O} = 0.1$ bar

$K_p = (0.1)^2 = 0.01$

$\Delta_r G^\circ = -RT \ln K_p$

$$= -8.314 \times 420 \ln (0.01)$$

$$= 16083.6 \text{ J/mol or } 16.083 \text{ kJ/mol}$$

Level 2

1. (a) $C(s) + CO_2(g) \rightleftharpoons 2CO(g);$ ...(1)

$$K_{P_1} = 10^{14} \text{ atm}$$

$2CO(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g);$ ...(2)

$$K_{P_2} = (6 \times 10^{-3})^2 \text{ atm}^{-2}$$

Add (1) and (2)

$$C(s) + CO_2(g) + 2Cl_2(g) \rightleftharpoons 2COCl_2(g);$$

$$K_p = 10^{14} \times 36 \times 10^{-6}$$

$$= 36 \times 10^8$$

For given reaction $\Delta n_g = -1$

$\therefore$ $K_c = K_p(RT)$

$$= 36 \times 10^8 \times 0.0821 \times 1120$$

$$K_c = 3.31 \times 10^{11}\ M^{-1}$$

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

Initial moles	1	2	0
at eqm	$1-x$	$2-3x$	$2x$

where $x = 0.5$

$$K_c = \frac{(1/4)^2}{\left(\frac{0.5}{4}\right)\left(\frac{0.5}{4}\right)^3} = 256$$

equilibrium constant for the reaction

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

$$K_c^1 = \frac{1}{\sqrt{K_c}} = \frac{1}{16}$$

3. (c) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

Moles at eqm	$2-x$	$4-x$	$2x$

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

$$\Rightarrow \quad x = \frac{32}{24} = 1.33 \text{ mole}$$

$$[AB(g)] = \frac{2 \times 1.33}{4} = 0.66\ M$$

4. (d) $P_{\text{total}} = P_{HNO_3} + P_{NO_2} + P_{H_2O} + P_{O_2}$

$\because$ $P_{NO_2} = 4P_{O_2}$ and $P_{H_2O} = 2P_{O_2}$

$\therefore$ $P_{\text{total}} = P_{HNO_3} + 7P_{O_2}$

$\Rightarrow$ $30 - 2 = P_{O_2} \times 7$

$$\Rightarrow \qquad P_{O_2} = \frac{28}{7} = 4$$

$$K_p = \frac{P^4_{NO_2} \cdot P_{H_2O} \cdot P_{O_2}}{P^4_{HNO_3}}$$

$$= \frac{(4 \times 4)^4 \times (2 \times 4)^2 \times 4}{2^4} = 2^{20}$$

$$K_p = K_c\,(RT)^{\Delta n_g} = K_c\,(0.08 \times 400)^3$$

$$\Rightarrow \qquad K_c = \frac{2^{20}}{(32)^3} = 32$$

5. (d) $LiCl \cdot 3NH_3(s) \rightleftharpoons LiCl \cdot NH_3(s) + 2NH_3(g)$;

$[K_p = 9 \text{ atm}^2]$

Therefore,

$LiCl \cdot NH_3(s) + 2NH_3(g) \rightleftharpoons LiCl \cdot 3NH_3(s)$;

Initial moles	0.1	a	0
Final moles at eqm	0	$(a - 0.2)$	0.1

$$\left[K'_p = \frac{1}{9}\,(\text{atm})^{-2}\right]$$

Let initial moles of NH_3 is a for completion of reaction.

At eqm $K'_p = \dfrac{1}{(P'_{NH_3})^2}$ or $\dfrac{1}{9} = \dfrac{1}{(P'_{NH_3})^2}$

$\therefore \quad P'_{NH_3} = 3$ atm

$\because \quad PV = nRT \Rightarrow 3 \times 5 = n \times 0.0820 \times 310$

$\therefore \quad n = 0.59$ *i.e.*, $(a - 0.2) = 0.59$

$\therefore$ initial moles of $NH_3 = 0.79$

6. (c) $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

Let partial pressure at equilibrium of CO_2 be P, then $P_{NH_3} = 2P$ and total pressure at equilibrium $= 3P$

$$K_p = (2P)^2 \times P = 4P^3 \qquad \ldots(1)$$

If NH_3 is added and the pressure of NH_3 after addition at equilibrium is $3P$

$$K_p = 4P^3 = (P'_{NH_3})^2 \times P'_{CO_2}$$

$$\Rightarrow \qquad P'_{CO_2} = \frac{4}{9}P$$

$\therefore$ ratio of $\dfrac{P'_{CO_2}}{P_{CO_2}} = \dfrac{4}{9}$

7. (c) $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

At eqm	$1 - x$	x	x

$$K_p = \frac{P_{C_2H_4} \cdot P_{H_2}}{P_{C_2H_6}} \Rightarrow \frac{x^2}{1 - x} = 5 \times 10^{-2}$$

$$x^2 + 0.05\,x - 0.05 = 0$$

$$x = \frac{-0.05 + \sqrt{(0.05)^2 + 4 \times 0.05}}{2} = 0.20 \text{ atm}$$

Partial pressure of C_2H_6 = mole fraction × total pressure

$\Rightarrow \quad 0.80$ = mole fraction $\times 1.2$

$\therefore$ mole % of $C_2H_6 = \dfrac{0.8}{1.2} \times 100 = 66.66$

8. (a) $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

Initial pressure	P	0	0
at eqm	$P - 2x$	$2x$	x

where $2x = 0.40\,P$

$\Rightarrow \quad x = 0.20\,P$;

$\Rightarrow \quad 1.20\,P = 0.30$

$\Rightarrow \quad P = 0.25$ atm

$$K_p = \frac{P^2_{NO} \cdot P_{Br_2}}{P^2_{NOBr}}$$

$$= \frac{(0.4P)^2\,(0.2P)}{(0.6P)^2} = 0.0222$$

$\therefore$ K_p for the reaction

$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$

is $\dfrac{1}{0.0222} = 45$

9. (c) $\because$ Initially only A is present so at eqm B and C should be present in 2 : 1

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

At eqm	400 mL	200 mL	100 mL

for ideal gases volume % ≡ mole %

$$K_p = \frac{\left(\dfrac{200}{700} \times 10\right)^2 \left(\dfrac{100}{700} \times 10\right)}{\left(\dfrac{400}{700} \times 10\right)^2} = \frac{10}{28}$$

10. (c) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

Initial moles	2	2	2	2
at eqm	$2 - x$	$2 - x$	$2 + x$	$2 + x$

$(\because Q_p < K_p)$

Total no. of moles of gases at equilibrium

$= 8 + 2 = 10$

$$K_p = \frac{P_{SO_3} \cdot P_{NO}}{P_{SO_2} \cdot P_{NO_2}}$$

$$\Rightarrow \qquad 25 = \frac{\left(\dfrac{2 + x}{10} \times P\right)^2}{\left(\dfrac{2 - x}{10} \times P\right)^2}$$

$$\Rightarrow \qquad 5 = \frac{2+x}{2-x}$$

$$\Rightarrow \qquad x = 1.33$$

Partial pressure of $NO_2 = \frac{2-x}{10} \times P_{total}$

$$= \frac{0.666}{10} \times 2$$

$$= 0.133 \text{ atm}$$

11. (b) $3Se_2(g) \rightleftharpoons Se_6(g)$

$$\begin{array}{lll} \text{moles at eqm} & a(1-\alpha) & \frac{a\alpha}{3} \end{array}$$

$$\frac{\text{Observed no. of moles at equilibrium}}{\text{Initial no. of moles of reactant}} = \frac{M_T}{M_O},$$

$$\Rightarrow \qquad \frac{a(1-\alpha)+\frac{a\alpha}{3}}{a} = \frac{M_T}{M_O} = \alpha = 0.315$$

where molar mass of Se_2

$(M_T) = 79 \times 2 = 158$

and molar mass of mixture

$$(M_O) = \frac{wRT}{PV} = \frac{0.02 \times 24.63}{1 \times 2.463 \times 10^{-3}} = 200$$

12. (d) $6HCHO \rightleftharpoons C_6H_{12}O_6$

$$\begin{array}{lll} \text{Conc. at eqm} & C(1-\alpha) & \frac{C\alpha}{6} \end{array}$$

$$\frac{\text{Observed moles concentration}}{\text{Initial moles concentration}} = \frac{M_T}{M_O}.$$

M_T = Theoretical molar mass of HCHO

$$\frac{C(1-\alpha)+\frac{C\alpha}{6}}{C} = \frac{M_T}{M_O} = \frac{30}{150}$$

$$\Rightarrow \qquad \alpha = 0.96$$

13. (b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K_c = \frac{(0.12)^2}{(0.12)^2 \times 5} = 0.2$$

Another vessel

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

$$\begin{array}{llll} \text{moles at eqm} & 0.5-2x & y-x & 2x \end{array}$$

as per given $2x = \frac{20}{100} \times 0.5 = 0.1$

$$K_c = \frac{(0.1)^2}{(0.4)^2\,(y-0.05)} = 0.20$$

$y = 0.3625$ mole

$\therefore$ mass of O_2 added $= 11.6$ g

14. (b) Let initial mole of $N_2O_4(g)$ is one

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

$$\begin{array}{lll} \text{Initial moles} & 1 & 0 \\ \text{At equilibrium} & 1-\alpha & 2\alpha \end{array}$$

Total no. of moles at equilibrium $= 1 + \alpha$

$$P_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P$$

$$P_{NO_2} = \frac{2\alpha}{(1+\alpha)} \times P$$

Hence, $K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{4\alpha^2}{(1-\alpha^2)} \times P$

$$\therefore \qquad 4.5 = \frac{4\alpha^2}{(1-\alpha^2)} \times 2$$

$$\Rightarrow \qquad \alpha = 0.6$$

Mole fraction of N_2O_4 :

$$X_{N_2O_4} = \frac{1-\alpha}{1+\alpha} = 0.25$$

$$\therefore \qquad X_{NO_2} = 0.75$$

Average molar mass of mixture

$$= 0.25 \times 92 + 0.75 \times 46 = 57.5$$

15. (a) $2AB(s) \rightleftharpoons A_2(g) + B_2(g)$

$$\begin{array}{ll} 0.5+x & x \end{array}$$

$$K_p = P_{A_2} \cdot P_{B_2}$$

$$\Rightarrow \qquad 0.06 = (0.5+x)\,x$$

$$= x^2 + 0.5x - 0.06$$

$$\Rightarrow \qquad x = 0.1$$

$P_{total} = P_{A_2} + P_{B_2} = 0.6 + 0.1 = 0.70$ atm

16. (a) $Sb_2S_3(s) + 3H_2(g) \longrightarrow 2Sb(s) + 3H_2S(g)$

$$\begin{array}{llll} 0.01-x & 0.01-3x & 2x & 3x \end{array}$$

where $3x = 0.005$

$$H_2S + Pb^{2+} \longrightarrow PbS + 2H^+$$

no. of moles of PbS formed

$$= \frac{1.19}{238} = 0.005 \text{ mole}$$

At eqm $[H_2] = \left[\frac{0.005}{250}\right] = \left(\frac{.01 - .005}{250}\right);$

$$K_c = \left(\frac{0.005}{0.005}\right)^3 = 1$$

17. (a) $2A(g) + B(g) \rightleftharpoons C(g) + D(g)$

$$\begin{array}{lllll} \text{Initial moles} & 1 & 1 & 7 & 3 \\ \text{at eqm} & 2-2x & 1-x & 7+x & 3+x \end{array}$$

Due to very high value of K_c we can assume that reactant almost converted into products so

$$1 - x = y; \quad 2 - 2x = 2y \Rightarrow \quad x \simeq 1$$

$$10^{12} = \frac{8 \times 4}{(2y)^2 y}$$

$$\Rightarrow \qquad y^3 = 8 \times 10^{-12}$$

$\therefore$ equilibrium concentration of

$$A = 2y = 4 \times 10^{-4}$$

18. (b) $K_c = \dfrac{[\text{complex}]}{[H_3BO_3][\text{glycerin}]} = 0.90$

$$\Rightarrow \qquad \frac{[\text{complex}]}{[H_3BO_3]} = \frac{80}{20}$$

$$\therefore \qquad [\text{glycerin}] = \frac{80}{20 \times 0.9} = 4.44\,M$$

$$\begin{array}{llll} & H_3BO_3 & + \text{ glycerin} & \rightleftharpoons (H_3BO_3 - \text{glycerin}) \\ \text{At eq}^m & 0.1 - x & a - x & x \end{array}$$

$$x = 0.1 \times \frac{80}{100} = 0.08;$$

$$a - x = 4.44$$

$$\Rightarrow \qquad a = 4.44 + 0.08 = 4.52\,M$$

or Initial moles = 4.52

19. (c) $\dfrac{r_{mix}}{r_{O_2}} = \sqrt{\dfrac{32}{M_{mix}}} = 0.4\sqrt{5}$

$$\Rightarrow \qquad M_{mix} = 40\text{g/mol}$$

$$\begin{array}{lll} & O_2(g) & \rightleftharpoons \frac{2}{3}O_3(g) \\ \text{Initial moles} & 1 & 0 \\ \text{at eqm} & 1 - \alpha & \frac{2}{3}\alpha \end{array}$$

$$\frac{32}{40} = \frac{1 - \alpha + \frac{2}{3}\alpha}{1}$$

$$\Rightarrow \qquad \alpha = 0.6$$

$$\therefore \qquad \% \alpha = 60$$

20. (c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

$$\begin{array}{llll} \text{moles at eqm} & 1 - 2x & 2x & x \end{array}$$

Only SO_2 (O. No. = 4) will oxidized so equivalent of SO_2 = equivalent of $KMnO_4$

$$2x \times 2 = 0.2 \times 5$$

$$\Rightarrow \qquad 2x = 0.5$$

$$K_c = \frac{\left(\frac{0.5}{2}\right)^2 \left(\frac{0.25}{2}\right)}{\left(\frac{0.5}{2}\right)^2} = 0.125$$

21. (d) $\dfrac{r_{mix}}{r_{SO_2}} = \sqrt{\dfrac{M_{SO_2}}{M_{mix}}}$

$$\Rightarrow \qquad 2.56 = \frac{64}{M_{mix}}$$

$$\Rightarrow \qquad M_{mixture} = 25$$

Let mole fraction of F_2 is x

$$25 = \frac{38 \times x + (1 - x) \times 19}{1}$$

$$x = 0.315;$$

$$\Rightarrow \quad K_p = \frac{P_F^2}{P_{F_2}} = \frac{(0.685\,P)^2}{(0.315\,P)} = 1.49\text{atm}$$

22. (b) $8 \times 10^{-6} = \dfrac{x^2}{0.5}$

$$\Rightarrow \qquad x = 2 \times 10^{-3}$$

$$\therefore \qquad pOH = 2.7$$

So, $\qquad pH = 11.3$

23. (c) $\Delta_r G^\circ = 0 - 77.1 \times 2 = -154.2\,\text{kJ/mol}$

$$Q = \frac{[H^+]^2}{P_{H_2} \cdot [Ag^+]^2}$$

$$= \frac{10^{-6}}{0.5 \times (10^{-10})} = 2 \times 10^4$$

$$\Delta G = \Delta_r G^\circ + RT \ln Q$$

$$\Delta_r G = -154.2 + \frac{8.314 \times 300 \ln(2 \times 10^4)}{1000}$$

$$= -129.5\,\text{kJ/mol}$$

24. (d)

$$\begin{array}{ccccc} N_2O_5 & \rightleftharpoons & N_2O_3 & + & O_2 \\ 4 - x & & x - y & & x + y \\ N_2O_3 & \rightleftharpoons & N_2O & + & O_2 \\ x - y & & y & & y + x \end{array}$$

$$\because \quad [O_2] = x + y = 2.5$$

and $\quad 2.5 = \dfrac{(x + y)(x - y)}{4 - x}$

$$\therefore \qquad x = 2.166$$

$$[N_2O_5] = 4 - x = 1.846$$

25. (b) Let x is partial pressure of A and y is partial pressure of C when both equilibrium simultaneously established in a vessel

$$\begin{array}{lcccc} X(s) & \rightleftharpoons & A(g) & + & 2B(g) \\ & & x & & (2x + 2y); \end{array}$$

$$K_{P_1} = P_A \cdot P^2_{B(\text{total})}$$

$$\begin{array}{lcccc} Y(s) & \rightleftharpoons & C(g) & + & 2B(g) \\ & & y & & (2y + 2x); \end{array}$$

$$K_{p_2} = P_C \cdot P^2_{B(\text{total})}$$

$$\frac{K_{P_1}}{K_{P_2}} = \frac{x}{y} \Rightarrow x = 2y$$

$$K_{P_1} = x(2x + 2y)^2$$

$$\Rightarrow \quad x = 0.1 \text{ atm};$$

$$\therefore \quad y = 0.05 \text{ atm}$$

$$\text{Total pressure of gases} = P_A + P_B + P_C$$
$$= 3(x + y)$$
$$= 0.45 \text{ atm.}$$

Level 3

Passage-3

$$N_2O_3(g) \rightleftharpoons NO_2(g) + NO(g) \; ; \; K_{P_1} = 2.5 \text{ bar}$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \; ; \; K_{P_2}$$

$$x - y \qquad y/2$$

$$P_{NO} = x = 1.5 \text{ b}$$

$$\therefore \; K_{P_1} = \frac{P_{NO} \cdot P_{NO_2}}{P_{N_2O_3}}$$

$$2.5 = \frac{x(x-y)}{2-x} = \frac{1.5(1.5-y)}{2-1.5} = 4.5 - 3y$$

$$\Rightarrow \; y = \frac{2}{3} \text{ Bar}$$

(1) $P_{N_2O_3} = 2 - x = 2 - 0.5 = 0.5 \text{ b}$

(2) $P_{NO_2} = x - y = 1.5 - \frac{2}{3} = \frac{2.5}{3} \text{ b}$

(3) $K_{P_2} = \dfrac{y}{2(x-y)^2} = \dfrac{2/3}{2\left(\frac{2.5}{3}\right)^2} = 0.48 \text{ b}^{-1}$

One or More Answers is/are correct

6. (c, d) Le Chatelier's principle is not quantitative. If both stress would cause the same direction of shift, the shift is determinable. If the two stresses would cause shifts in opposite directions, no deduction is possible.

Subjective Problems

11. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

At eqm. $\quad - \quad (0.1 + P) \quad P \quad ;$

As per given $0.1 + 2P = 1.1$; $P = 0.5$

$$K_P = P_{NH_3} \cdot P_{H_2S} = (0.1 + P) \times P$$
$$= 0.6 \times 0.5 = 0.3 = 3 \times 10^{-1} = 3$$

12. $A + nB \rightleftharpoons mC$

$t = 0 \quad 8M \quad 12M$

$t = t_{eq.} \quad 8 - x \quad 12 - nx \quad mx$

Given: $[A]_{eq} = 6M$

$$8 - x = 6$$
$$x = 2M$$
$$[B]_{eq} = 8M$$
$$12 - nx = 8$$
$$n(2) = 4$$
$$n = 2$$
$$[C]_{eq} = 6M$$
$$mx = 6$$
$$m(2) = 6$$
$$m = 3$$
$$\therefore \quad m + n = 3 + 2 = 5$$