CHEMICAL EQUILIBRIUM

1. For a reaction A→B

Time	0	5	10	15
[B]	1.6×10−4	1.6×10−4	1.6×10−4	1.6×10−4

The rate of the reaction is

(a) 1.6×10−4
(b) 3.2×10−4
(c) 1.6×10−4
(d) reaction is at equilibrium

Answer: (d)

As concentration of product is not changing with time, the reaction is at equilibrium.

2. The equilibrium constant for the reaction, N2(g) + O2(g)⇌2NO(g) is 4×10−4at 2000 K. In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is

(a) 4×10−3
(b) 4×10−4
(c) 4×10−5
(d) difficult to compute without more data

Answer: (b)

A catalyst does not affect the value of Equilibrium constant (Keq),it only reduces the time of attainment of equilibrium. In fact, it does not even change the position of equilibrium.

3. In which of the following cases does the reaction go farthest to completion

(a) K=103 (b) K=10−2 (c) K=10 (d) K=1

Answer: (a)

Extent of reaction depends upon value of Keq.Higher the Keq, higher is the extent of reaction.

4. For a reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the value of Kc would depend upon

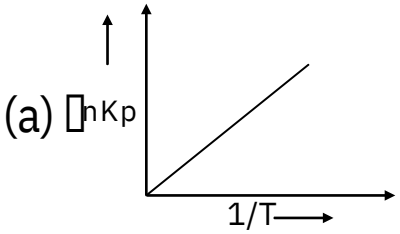
(a) initial concentration of the reactants (b) Pressure

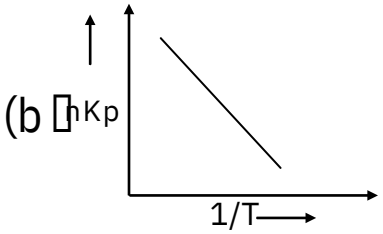
(c) temperature (d) all of the above

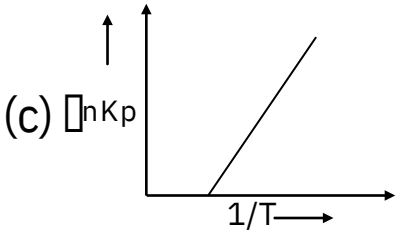
Answer: (c)

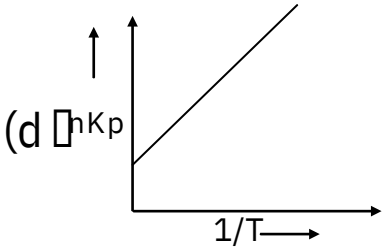
The equilibrium constant KC of a reaction depends only on temperature and nature of reactants.
Hence, (c) is the correct answer.

5. Which is not correct for an exothermic reaction

(a) 

(b 

(c) 

(d 

Answer: (b)

$$\ln K_p = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

For exothermic Reaction $\Delta H < 0$ hence slope > 0

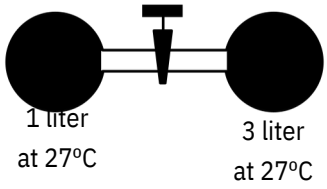
6. For the given reaction, $2A(s) \rightleftharpoons B(g) \rightarrow C(g) + 2D(s)$ E
degree of dissociation of B was found to be 20% at 300 K and 24% at 500 K. The rate of forward reaction
(a) increases with increase in pressure and temperature.
(b) increases with increase in pressure and decrease in temperature.
(c) depends on temperature only and increases with increase in temperature.
(d) increases with increasing the concentration of B and increasing the temperature.

Answer: (c)

As degree of dissociation, α increases with increase in temperature of reaction, the reaction is endothermic in nature. Therefore, on increase in temperature, Rate of forward reaction increases.

Also, $\Delta n_g = 0$ for the reaction, pressure has no effect on equilibrium.

7. The gas A2in the left flask allowed to react with gas B_2 present in right flask as



A2(g)+B2(g)⇌2AB(g); K_c=4 at 27°C

What is the concentration of AB when equilibrium is established?

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

Answer: (c)

	A2	B2	2AB
t=0	2	4	0
at equi.	2−x	4−x	2x

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

$$\Rightarrow x^2 = 8 - 6x + x^2$$

$$\Rightarrow x = \frac{8}{6} = 1.33$$

$$\Rightarrow [AB] = \frac{2x}{4} = \frac{x}{2} = 0.665$$

8. For the gas phase reaction, 2NO(g) ⇌ N2(g) + O2(g) , ΔH = −43.5 kcal, which one of the following is true for N2(g) + O2(g) ⇌ 2NO(g)

(a) K is independent of T (b) K decreases as T decreases (C) K increases as T decreases (d) K varies with addition of NO

Answer: (b)

The given reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is endothermic. Therefore, according to Le Chatelier's principle, high temperature favours forward reaction and hence K increases as T increases or K decreases as T decreases.

Hence, (b) is the correct answer.

9. The reactions, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ and $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ are simultaneously in equilibrium in an equilibrium box at constant volume. A few moles of CO(g) are later introduced into the vessel. After some time, the new equilibrium concentration of

(a) PCl_5 will remain unchanged (b) PCl_3 will become less
(c) PCl_5 will become less (d) $COCl_2$ will become less

Answer: (c)

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

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ ...(ii)

If some CO is added, the reaction (ii) will move in backward direction, this results in the decrease in concentration of Cl_2 and reaction (i) will move in forward

PCl5with, definitely decrease. Concentration of COCl2will increase and so will be the concentration of PCl3.

10. For the decomposition of PCl5(g)in a closed vessel, the degree of dissociation is 'x' at a total pressure 'P'.

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

Which among the following relations is correct?

(a) $x = \sqrt{\frac{Kp}{Kp+P}}$ (b) $x = \sqrt{\frac{K_p + P}{Kp}}$ (c) $x = \sqrt{Kp+P}$ (d) $x = \frac{1}{\sqrt{Kp+P}}$

Answer: (a)

	PCl_5	PCl_3	Cl_2
att 0	1	0	0
ateqb.	1 − x	x	x

Total number of moles $= 1 - x + x + x = (1 + x)$

$$K_p = \frac{\left(\frac{x}{1+x}\right)P \times \left(\frac{x}{1+x}\right)P}{\left(\frac{1-x}{1+x}\right)P} = \frac{x^2}{1-x^2} \times P$$

$$x = \sqrt{\frac{K_p}{K_p + P}}$$

11. The decomposition reaction, $4HNO_3(g) \rightleftharpoons 4NO_2(g) + 2H_2O(g) + O_2(g)$ is started with pure $HNO_3(g)$. If p is the total pressure at equilibrium, then

(a) $K_p = (p_{O_2})^7/(p - 7p_{O_2})^4$ (b) $K_p = 1024(p_{O_2})^7/(p - 7p_{O_2})^4$

(c) $Kp = 7p_{O_2}/(p - 4p_{O_2})$ (d) $K_p = (p - pO)^7/(p - 7pO)^4$

Answer: (b)

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

p_0 — — — —

$p_0 - 4p_{O_2}$ $4p_{O_2}$ $2p_{O_2}$ p_{O_2}

$\therefore \quad p_0 + 3p_{O_2} = p$

$\therefore \quad p_0 = (p - 3p_{O_2})$

$\therefore p_0 - 4p_{O_2} = p - 3p_{O_2} - 4p_{O_2} = p - 7p_{O_2}$

$\therefore \quad K_p = \frac{(4p_{O_2})^4 (2p_{O_2})^2 \times p_{O_2}}{(p - 7p_{O_2})^4} = \frac{1024 \times p_{O_2}^7}{(p - 7p_{O_2})^4}$

12. For the equilibrium, $SO_2(g) + \frac{1}{2}O_2(g) = SO_3(g); \Delta H = -99.0 kJ$.

extent of forward reaction can be increased by

(a) removing SO3 (b) using a catalyst

(c) raising the temperature (d) lowering the pressure

Answer: (a)

$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g); \Delta H = -99 kJ$

Equilibrium shifts in the forward direction by removing SO3,decreasing the temperature and increasing the pressure.

Catalyst does not disturb the equilibrium.

Therefore, extent of forward reaction increases by removing SO3.

13. Consider the following reaction,

C(s, diamond) ⇌ C(s, graphite) + heatand choose the correct option.

(a) An increase in temperature will shift the equilibrium to the right, and so will an increase in pressure.

(b) An increase in temperature and pressure will shift the equilibrium to the left.

(c) An increase in temperature will shift the equilibrium to the left and on increase in pressure to the right.

(d) Any increase in temperature and pressure will not shift the equilibrium.

Answer: (b)

The increase in temperature will favour the backward reaction, as the reaction is exothermic. With the increase of pressure on physical equilibria, the equilibrium will shift in that direction where the density is more. As the density of diamond is greater than graphite, thus increase in pressure will also favour backward reaction.

14. For the equilibrium,

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

which of the following statement 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 reaction depending upon the temperature of the system.

Answer: (b)

For heterogeneous physical equilibrium, with the increase of pressure, equilibrium shifts in the direction of physical state having higher density. This means that for the equilibrium,

$H_2O(s) \rightleftharpoons H_2O(l)$, more ice would melt on increasing the pressure of the system as density of water is more than ice.

15. Ammonia gas at 76 cm Hg pressure was connected to a manometer. After sparking in the flask, ammonia partially dissociated as follows $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$. The level in the mercury column of the manometer was found to show the difference of 18 cm. The partial pressure of H2(g)at equilibrium is

(a) 18 cm of Hg (b) 9 cm of Hg (c) 24 cm of Hg (d) 27 cm of Hg

Answer: (d)

	$2NH_3(g)$	$N_2(g)$	$3H_2(g)$
att 0	76cm	0	0
ateqb.	76 2x	x	3x

Total pressure at eqb., PT=76−2x+x+x

PT=76cm+18cm

76+2x=76+18

2x=18

x = 9 cm

Partial pressure of H2gas at eqb., $P_{H_2} = 3x = 27 cm of Hg$

16. For the equilibrium

$A(g) + 2B(g) \rightleftharpoons AB_2(g)$

the value of equilibrium constant at 300 k is 3×10^{-3} mole^{-2}L^2 and value of equilibrium constant at 500 k is 5×10^{-5} mole^{-2}L^2. What is the sign of enthalpy change for this reaction

(a) Positive

(b) Negative

(c) Data incomplete

(d) Both (a) and (b) are possible at lower temperature it is positive and at high temperature it is negative.

Answer: (b)

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Where, K1is equilibrium constant at temperature, T1and K2 is equilibrium constant at temperature T2.

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

If T1=300K&T2=500K

and K1=3×10^{-3}&K2=5×10^{-5}

then, we can either substitute the values in equation and solve the problem or we can apply a simple mathematical logic and find the answer.

Which is; log(x)<0ifx<1

and log(x)>0 if x>1

Here; $\frac{K_2}{K_1} = \frac{5\times10^{-5}}{3\times10^{-3}} < 1$

$$\log\left(\frac{K_2}{K_1}\right) < 0$$

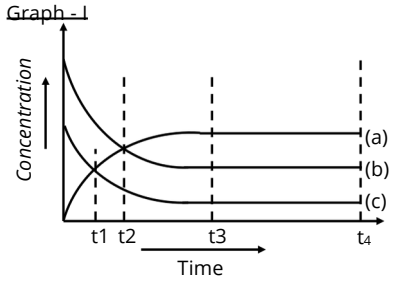
$$\frac{\Delta H}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) < 0 \quad \Delta H < 0 \text{ (as } T_2 - T_1 \text{ is positive)}$$

Alternately,

You can remember this fact and apply it in questions directly. The fact is that the value of Keqdecreases on increase in temperature and vice-versa in case of exothermic reaction. The value of Keqincreases on increase in temperature in case of endothermic reaction.

17. Following graph is plotted for the reaction:

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



In the graph the equilibrium state is reached at

(a) t1 (b) t2 (c) t3 (d) t4

Answer: (c)

At equilibrium, rate of forward reaction is equal to rate of backward reaction and at this situation concentration of each reactant and product becomes constant. Therefore, in graph-I at t3equilibrium is attained.

18. At −50°C, the self-ionization constant (ion product) of NH_3 is $K_{NH_3} = 10^{-30}\ M^2$. How many amide ions are present per mm^3 of pure liquid ammonia?

(a) 600 ions/mm3 (b) 6×106ions/mm3

(c) 6×104ions/mm3 (d) 60 ions/mm3

Answer: (a)

$2NH_3(l) \rightleftharpoons NH_4^+ + NH_2^-$

$1-x \quad x \quad x$

$K_{NH_3} = x^2 = 10^{-30}$

Thus, $x = 10^{-15} M = [NH_2^-]$

$[NH_2^-] = 10^{-15}$ moles/lit $= \frac{10^{-15}}{106}$ moles/mm^3

$[NH_2^-] = 10^{-21} \times 6 \times 1023$ ions/mm3 = 600 ions/mm3

19. The approach to the following equilibrium was observed kinetically from both directions.

$$[PtCl_4]^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^- + Cl^-$$

At 25°C, it was found that

$-\frac{d[PtCl_4^{2-}]}{dt} = (3.9 \times 10^{-5}\ s^{-1})[PtCl_4^{2-}] - (2.1 \times 10^{-3}\ L\ mol^{-1}.\ s^{-1})[Pt(H_2O)Cl_3^-][Cl^-]$

The value of K_c (equilibrium constant) for the complexation of the fourth Cl− by Pt(II) is

(a) 53.8 (b) 50 (c) 60 (d) 63.8

Answer: (a)

At equilibrium, the rate of change of concentration of any species (reactant or product) is zero.

The equilibrium reaction for the complexation of the fourth Cl– by Pt(II) is

$$[Pt(H_2O)Cl]_3^- + [Cl^-] \rightleftharpoons [PtCl_4]^{2-} + H_2O$$

$$K_{eq} = \frac{[PtCl_4^{2-}][H_2O]}{[Pt(H_2O)Cl_3^-][Cl^-]}$$

Since, water is a solvent in the given reaction, so its concentration remains constant.

$$\therefore \frac{K_{eq}}{[H_2O]} = \frac{[PtCl_4^{2-}]}{[Pt(H_2O)Cl_3^-][Cl^-]} = K_c$$

In the problem, expression of rate of change of concentration of [PtCl2–4]is given, which at equilibrium is zero.

$$-\frac{\Delta[PtCl_4^{2-}]}{\Delta t} = (3.9\times10^{-5})[PtCl_4]^{2-} - (2.1\times10^{-3})[Pt(H_2O)Cl_3^-][Cl^-] = 0$$

$$\therefore (3.9\times10^{-5})[PtCl]^{2-}_4 = (2.1\times10^{-3})[Pt(H_2O)Cl_3^-][Cl^-]$$

$$\frac{[PtCl_4^{2-}]}{[Pt(H_2O)Cl_3^-][Cl^-]} = K_c = \frac{2.1\times10^{-3}}{3.9\times10^{-5}} = 53.8$$

20. 20 ml of O2contracts to 17 ml when subjected to silent electric discharge in an ozoniser. What is the volume of O3 formed at equilibrium?

(a) 2 ml (b) 8 ml (c) 6 ml (d) 4 ml

Answer: (c)

	$3O_2(g)$	$2O_3(g)$
att 0	20 ml	0
at eqb.	20 – 3x	2x

$\therefore$ 20 – 3x + 2x = 17 ml

$\therefore\ x = 3$

$\therefore$ Volume of O_3 formed $= 2 \times 3 = 6$ ml

21. In a closed system: $A(s) \rightleftharpoons 2B(g) \rightleftharpoons 3C(g)$, if the partial pressure of C is doubled, then partial pressure of B will be

(a) two times the original pressure

(b) one half of its original value

(c) $\frac{1}{2\sqrt{2}}$ times to the original value

(d) $2\sqrt{2}$ times to the original value

Answer: (c)

$K\ 2p = (2p) \times (3p)^3 = 27 \times 4p^5$ where p is the original press.

$$A(s) \rightleftharpoons 2B(g) \rightleftharpoons 2C$$
$$p \qquad\qquad 6p$$

$\therefore\ (p')^2 \times (6p)^3 = 27 \times 4p^5$

or $(p')^2 = \frac{27 \times 4p^5}{3^3 \times 2^3 p} = \frac{p^2}{2}$

$\therefore\ p' = \frac{p}{\sqrt{2}}$ = final partial press. of B

$\therefore\ \frac{p'}{2p} = \frac{\text{final partial press of B}}{\text{initial partial press of B}} = \frac{p}{2\sqrt{2}p} = \frac{1}{2\sqrt{2}}$

22. The initial pressure of $COCl_2$ is 1000 torr. The total pressure of the system becomes 1500 torr, when the equilibrium $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ is attained at constant temperature. The value of K_p of a reaction is

(a) 1500 (b) 1000 (c) 2500 (d) 500

Answer: (d)

	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	$+$	$Cl_2(g)$
at t = 0	1000 torr		0		0
at eqb.	1000 − x		x		x

Total pressure eqb., $P_T = 1000 - x + x + x = 1500$

$x = 500$ torr

$$K_p = \frac{(P_{CO})(P_{Cl_2})}{(P_{COCl_2})}$$

$$K_p = \frac{(500)(500)}{(500)} = 500$$

23. Which set can explain chemical equilibrium?

(a) $\Delta G = 0, \Delta G^\circ \neq 0$ (b) $\Delta G \neq 0, \Delta G^\circ \neq 0$

(c) $\Delta G \neq 0, \Delta G^\circ = 0$ (d) $\Delta G = 0, \Delta S^\circ \neq 0$

Answer: (a)

At equilibrium $\Delta G = 0$ but $\Delta G^\circ = -RT \ln K_{eq}$

24. The first and second dissociation constants of an acid H2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be

(a) 0.2×10^{5} (b) 5.0×10^{-5} (c) 5.0×10^{5} (d) 5.0×10^{-15}

Answer: (d)

$H_2A \rightleftharpoons H^+ + HA^-$

$\therefore K_1 = 1.0\times10^{-5} = \frac{[H^+][HA^-]}{[H_2A]}$ (Given)

$HA^- \rightleftharpoons H^+ + A^{2-}$

$\therefore K_2 = 5.0\times10^{-10} = \frac{[H^+][A^{2-}]}{[HA^-]}$ (Given)

$K = \frac{[H^+]^2[A^{2-}]}{[HA]} = K_1 \times K_2$

$=(1.0\times10^{-5})\times(5\times10^{-10})=5\times10^{-15}$

25. The exothermic formation of CIF3is represented by the equation :

$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \Delta H = -329kJ$

Which of the following will increase the quantity of CIF3in an equilibrium mixture of Cl2,F2 and CIF3?

(a) Adding F2

(b) Increasing the volume of the container

(c) Removing Cl2

(d) Increasing the temperature

Answer: (a)

The reaction given is an exothermic reaction thus accordingly to i.e. chatalier's principle dowering of temperature, addition of F2and Cl2yarour the forward direction and hence the production of CIF3.

26. Which of the following equilibrium does not effected with the change in volume of the system?

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

Answer: (d)

In the nitric oxide formation reaction, both the reactants and the product possessequal moles. Hence, change in volume does not affect the equilibrium of reaction.

27. A saturated solution of iodine in water is 1.25×10–3(M).In any saturated solution of l2 concentration of l2is 1.25×10–3(M).In 1 L of 0.1 (M) solution I–,it is seen 51.25×10–3 mole of l2can be maximum dissolved. In the aqueous solution of l–(aq),l2(ag) undergoes complex formation, $I_2(aq) + I^- \rightleftharpoons I_3^-$.

What is the value of K C ?

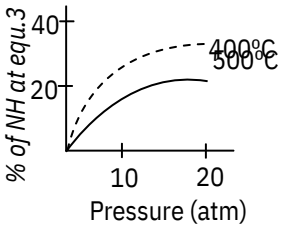
(a) 750 (b) 800 (c) $\frac{1000}{51.25}$ (d) 1

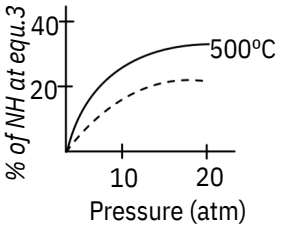
Answer: (b)

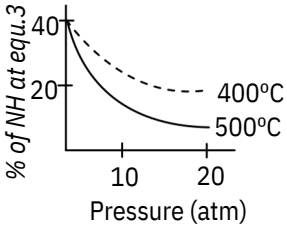
	I_2	+	I^-	$\rightleftharpoons$	I_3^-
	51.25×10^{-3}		0.1		
At equi.	1.25×10^{-3} (M)		50×10^{-3} (M)		50×10^{-3} (M)

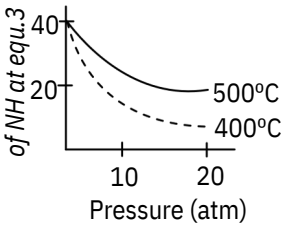
$$K_C = \frac{50 \times 10^{-3}}{50 \times 10^{-3} \times 1.25 \times 10^{-3}} = \frac{1000}{1.25} = 800$$

28. The percentage of ammonia obtainable, if equilibrium were to be established during the Haber process, is plotted against the operating pressure for two temperatures, 400°C and 500°C. Which of the following graph correctly represent the two process?

(a) 

(b) 

(c) 

(d) 

Answer: (a)

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H < 0$

By Le-Chatelier principle, higher pressure and lower temperature favour the forward reaction, i.e., higher % of NH_3.

29. Dissociation constants of CH_3COOH and NH_4OH are 1.8×10^{-5} each at 25°C. The equilibrium constant for the reaction of CH_3COOH and NH_4OH will be:

(a) $\frac{1.8 \times 1.8}{10^4}$ (b) $\frac{1.8}{10^{-9}}$ (c) $1.8 \times 1.8 \times 10^4$ (d) 3.24×10^{-10}

Answer: (c)

$$CH_3COOH \quad NH_4OH \rightleftharpoons CH_3COO^- NH_4^+ HO_2$$

$$K_a \quad K_b$$

$$K_C = \frac{[CH_3COO^-][NH_4^+]}{[CH_3COOH][NH_4OH]} = \frac{}{K_W} = 1.82 \times 10^4$$

30. In an aqueous solution of volume 500 ml, when the reaction of $2Ag + Cu \rightleftharpoons Cu^{2+} + 2Ag$ reached equilibrium the $[Cu^{2+}]$ was x M. When 500 ml of water is further added, at the equilibrium $[Cu^{2+}]$ will be

(a) 2 xM (b) x M

(c) between x M and x/2 M (d) less than x/2 M

Answer: (d)

$$2Ag + Cu \quad Cu^{2+} + 2Ag$$

Let $[Cu^{2+}] = xM$

$[Ag^+] = aM$

$$\therefore \quad k_c = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{x}{a^2}$$

On doubling volume

$$(Ag^+) \quad \frac{a}{2} \quad (Cu^{2+}) \quad \frac{x}{2}$$

$$\therefore \quad Q = \frac{\frac{x}{2}}{(a/2)^2} = \frac{2x}{a^2} > k_c$$

$\therefore$ Reaction go backward and concentration of $[Cu^{+2}] < x/2$.

31. The equilibrium, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is attained at 25°C in a closed container and an inert gas He is introduced. Choose the correct statement.

(a) Concentration of N_2, $3H_2$ and $2NH_3$ are changed.

(b) More N_2 is formed

(c) Concentration of NH_3 is reduced

(d) Nothing happens

Answer: (d)

Since formation of NH_3 is carried out in a closed container. When Inert gas (He) is introduced to the system in equilibrium at constant volume then no any change occurs in the partial pressures of N_2, $3H_2$ and $2NH_3$.

32. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm.

Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_P is:

(a) 3atm (b) 0.3atm (c) 0.18atm (d) 1.8atm

Answer: (d)

	$CO_2(g)$	+	$C(s)$		$2CO(g)$
att 0	0.5atm		+		0
ateqb.	(0.5 − x)atm		+		2xatm

As graphite is a pure solid, its concentration is invariable (or constant) during the course of reaction, it will not be a part of Kp'sexpression.

At equilibrium,

Total pressure, PT = 0.8atm

$P_T = 0.5 - x + 2x = 0.8\,atm$

$0.5 + x = 0.8$

$x = 0.3\ atm$

$(P_{CO_2})_{eq} = 0.5 - x = 0.2\,atm$

$(P_{CO})_{eq} = 2x = 0.6\,atm$

$K_P = \frac{(P_{CO})^2_{eq}}{(P_{CO_2})_{eq}} = \frac{(0.6)^2}{(0.2)} = 0.18\ atm$

33. 40% of a mixture of 0.2 mol of N2 and 0.6 mol of H2 react to give NH3 according to the equation, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, at constant temperature and pressure. Then the ratio of the final volume to the initial volume of gases are

(a) 4:5 (b) 5:4

(c) 7:10 (d) 8:5

Answer: (a)

$3H_2 \rightarrow 2NH_3$

0 2x

t = eq 0.2 0.6 − x − 3x

40% of N2 = 0.2 × 0.4 = 0.08

40% of H2 = 0.6 × 0.4 = 0.24

∴ Number of moles of N2 remaining = 0.2 – 0.08 = 0.12

Number of moles of H2 remaining = 0.6 – 0.24 = 0.36

Number of moles of NH3 formed = 0.16

Total number of moles = 0.12 + 0.36 + 0.16 = 0.64

$\therefore \frac{\text{Final volume}}{\text{Initial volume}} = \frac{\text{Final moles}}{\text{Initial moles}} = \frac{0.80}{5} = 0.644$

Hence, (a) is the correct answer.

34. One mole of ethanol is treated with one mole of ethanoic acid at 25°C.
One-fourth of the acid changes into ester at equilibrium.
The equilibrium constant for the reaction will be

(a) 1/9 (b) 4/9

(c) 9 (d) 9/4

Answer: (a)

$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Initially	1	1	0	0
At equilibrium	$1-\frac{1}{4}$	$1-\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$

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

$= \frac{\frac{1}{4} \times \frac{1}{4}}{\frac{3}{4} \times \frac{3}{4}} = \frac{1}{9}$

Hence, (a) is the correct answer.

35. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when N_2O_4 (g)

decomposes to NO2(g). If the resultant pressure is 2.4 atm, the percentage dissociation by mass of N2O4 (g) is

(a) 10% (b) 20%

(c) 30% (d) 40%

Answer: (b)

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

Equilibrium $1-\alpha$ 2α

where α is the degree of dissociation = $\frac{60}{0}$

($\because$ V is constant) $\frac{30}{0}$

$\therefore P_2 = 2$ atm

After dissociation of N2O4 at 600 K,

$P_{N_2O_4} = 2(1-\alpha)$

$= 2 - 2\alpha$

$P_{NO_2} = 2 \times 2\alpha$

$= 4\alpha$

Total pressure = $2 - 2\alpha + 4\alpha$

$= 2 + 2\alpha$

$2 + 2\alpha = 2.4$ (Given)

$\alpha = 0.2$

$\therefore$ Percentage dissociation = 20%

Hence, (b) is the correct answer.

36. K for the synthesis of HI(g) is 50. The degree of dissociation of HI is

(a) 0.10 (b) 0.14

(c) 0.18 (d) 0.22

Answer: (d)

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

$1-\alpha \qquad \frac{\alpha}{2} \qquad \frac{\alpha}{2}$

where α is the degree of dissociation

$$K_{diss} = \frac{1}{K_{synthesis}} = \frac{1}{50}$$

$$\frac{\frac{\alpha}{2} \times \frac{\alpha}{2}}{(1-\alpha^2)} = \frac{1}{50}$$

$$\frac{\alpha^2}{2(1-\alpha^2)} = \frac{1}{5\sqrt{2}}$$

$$5\sqrt{2}\alpha^2 = 2 - 2\alpha$$

$$2 + 5\sqrt{2}\alpha = 2$$

$$\alpha = \frac{2}{2 + 5\sqrt{2}} = 0.22$$

Hence, (d) is the correct answer.

37. For the reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, the value of Kp at 250°C is 0.61 atm–1. The value of Kc at this temperature will be

(a) 15 $(mol/l)^{-}$ (b) 26 (mol/l)–1

(c) 35 $(mol/l)^{1}$ (d) 52 (mol /l)–1

Answer: (b) $^{-}$

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

$\Delta n = -1$, $K_P = 0.61\ atm^{-1}$

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

$= 0.61 (0.0821 \times 523)+1 = 26$ mol /l.

Hence, (b) is the correct answer.

38. In the reaction $A_2(g) + 4B_2(g) \rightleftharpoons 2AB_4(g)$, $\Delta H > 0$. The decomposition of AB_4 (g) will be favoured at

(a) low temperature and high pressure

(b) high temperature and low pressure

(c) low temperature and low pressure

(d) high temperature and high pressure

Answer: (c)

$2AB_4(g) \rightleftharpoons A_2(g) + 4B_2(g)$ ΔH = –ve

It is an exothermic reaction and hence favoured at low temperature. Δn for the reaction is +3. Therefore low pressure will favour the forward reaction
Hence, (c) is the correct answer.

39. In a system, $A(s) \rightleftharpoons 2B(g) + 3C(g)$

If the conc. 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 the original value

(d) $1/2\sqrt{2}$ times the original value

Answer: (d)

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

Let, x and y be the concentrations of B and C at equilibrium respectively.

$\therefore K_c = xy^3$ .... (1)

Now, the concentration of C is changed from y to y′ such that y′ = 2y.

If x′ is the new concentration of B

$\therefore K_c = (x')^2(2y)^3 = 8(x')^2(y)^3$ ....(2)

From Eqs. (1) and (2)

$(x')^2(8y^3) = x^2y^3$

$\therefore x' = \sqrt{\frac{x^2}{8}} \quad x = \frac{}{2\sqrt{2}}$

∴ Equilibrium concentration of B changes to $\frac{1}{2\sqrt{2}}$ times the original value.

Hence, (d) is the correct answer.

40. For the following three reactions (i), (ii) and (iii), equilibrium constants are given

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; K

(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; K

(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; K

What is the relation between equilibrium constants of the three reactions?

(a) $K_1K_2 = K_3$ (b) $K_2K_3 = K_1$ (c) $K_3 = K_1K_2$ (d) $K_3K_3^2 = K_2^1$

Answer: (c)

Reaction (iii) can be obtained by adding reactions (i) and (ii) therefore K3 K1. K2.Hence (c) is the correct answer.

41. In the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the following amounts of substances were formed in 0.2 litre flask at equilibrium, C = 0.1 mole, CO = 0.05 mole, CO_2 = 0.06 mole. The equilibrium constant is

(a) 0.208 (b) 4.10

(c) 0.30 (d) 0.416

Answer: (a)

$$K = \frac{[CO]^2}{[CO_2]} = \frac{\left(\frac{0.05}{0.2}\right)^2}{\frac{0.06}{0.2}} = 0.208$$

42. Kp for a reaction at 25°C is 10 atm. The activation energy for forward and reverse reactions are 12 and 20 kJ/ mol respectively. The Kc for the reaction at 40°C will be

(a) 4.33×10^{-1} M (b) 3.33×10^{-2} M

(c) 3.33×10^{-1} M (d) 4.33×10^{-2} M

Answer: (c)

Enthalpy changed of a reaction is given by

$\Delta H = Ea(f) - Ea(b)$

where Ea(f) and Ea(b) are energies of activation for the forward and backward reactions.

$\Delta H = 12 - 20 = -8$ kJ/mol

Kp for the reaction at 25°C = 10 atm. Since Kp is expressed in atmosphere,

$\Delta n = +1$

$\therefore Kp = Kc(RT)^{\Delta n}$, $Kc = \frac{10}{0.0821 \times 298} = 0.4$ M

Kc at 40°C is given by

$$\log\frac{(Kc)_{40}}{(Kc)_{25}} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{-8 \times 1000}{2.303 \times 8.314} \times \frac{15}{298 \times 313} = -0.06719$$

$(Kc)40/(Kc)25 = 0.85$

$(Kc)40 = 0.85 \times 0.4 = 0.34$ M

Hence, (c) is the correct answer.

43. The vapour density of PCl_5 is 104.25 but when heated to 230°C, its vapour density is reduced to 62. The degree of dissociation of PCl_5 at this temperature will be

(a) 6.8% (b) 68%

(c) 46% (d) 64%

Answer: (b)

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

$1 + \alpha = \frac{D}{d}$

$1 + \alpha = \frac{104.25}{62}$

$1 + \alpha = 1.68$

$\therefore \alpha = 0.68$ or 68%

44. If equilibrium constant of

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ is 1.8×10^{-5} then equilibrium constant for

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$ is

(a) 6.63×10^{10} (b) 6.63×10^{-10}

(c) 1.8×10^{9} (d) 1.8×10^{-9}

Answer: (c)

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ $K_{a1} = 1.8 \times 10^{-5}$

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- K_{a2} = ?$

$$Ka_1 = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}, Kw = [H^+][OH^-] = 1 \times 10^{-14}$$

$$\therefore Ka_2 = \frac{Ka_1}{Kw} = \frac{1.8 \times 10^{-5}}{1 \times 10^{-14}} = 1.81 \times 10^{9}$$

45. For the decomposition reaction

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

The $K_p = 2.9 \times 10^{-5}\ atm^3$. The total pressure of gases at equilibrium when 1 mole of NH_2COONH_4 (s) was taken to start with would be

(a) 0.0194 atm (b) 0.0388 atm

(c) 0.0582 atm (d) 0.0766 atm

Answer: (c)

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

1 2 1

$K_p = 2.9 \times 10^{-5}\ atm^3$

If P is the total pressure at equilibrium

$$K_p = \left(\frac{2p}{3}\right)^2 \left(\frac{p}{3}\right)$$

$$\therefore P^3 = \frac{27 \times 2.9 \times 10^{-5}}{4} = 1.9575$$

$$P = \sqrt[3]{1.9575} = 0.0582$$

Hence, (c) is the correct answer.