**Illustration 18:** Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapours with a density of 15.0. What is the degree of dissociation of ammonium carbonate?

(a) 3/2   (b) 1/2   (c) 2   (d) 1   (e) 5/2   **(JEE MAIN)**

Sol: Write down the decomposition of ammonium carbamate, noting down the dissociated values of the reacting species. Using the vapour density, calculate degree of dissociation.

$$NH_2COONH_4 \longrightarrow 2NH_3 + CO_2$$
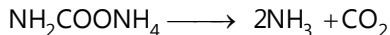
Initial 1 mole, After disso. $1-\alpha$ 2α α

      Total $= 1 + 2\alpha$

Theoretical density (D) $\propto \dfrac{1}{v}$; Observed density (d) $\propto \dfrac{1}{(1+2\alpha)V}$ $\therefore \dfrac{D}{d} = 1+2\alpha$ or $\alpha = \dfrac{1}{2}\left(\dfrac{D-d}{d}\right) = \dfrac{1}{2}\left(\dfrac{48-15.0}{15.0}\right) = 1.1$

PROBLEM-SOLVING TACTICS

(a) The equilibrium constant expression depends on the stoichiometry of the balanced reaction.

Table 5.6: Variation of Equilibrium Constant with Stoichiometric Coefficient

When the equation is	The new Equilibrium constant is
Reversed	1/K
Divided by 2	$\sqrt{K}$
Multiplied by 2	K^2
Divided into 2 steps	$K = K_1 \times K_2$

Case I: If $\Delta n(g) = 0$, $K_p = K_c$

Case II: If $\Delta n(g) = +ve$, $K_p > K_c$

Case III: If $\Delta n(g) = -ve$, $K_p < K_c$

Retain in Memory

For Δn, count only the gaseous species.

Δn may be positive, negative, zero, integer or a fraction. If $\Delta n = 0$, $K_p = K_c$.

Units of K_p and K_c

Unit of K_p = (unit of pressure)$^{\Delta n}$

Unit of K_c = (unit of concentration)$^{\Delta n}$

If $\Delta n = 0$; K_p or K_c have no units.

(b) If the partial pressures are taken in atmospheres, the value of R to be used in the above equation will be 0.0821 litre atmospheres/degree/mole. Temperature T will, of course be in degree Kelvin (K). If pressure is expressed in bars, R = 0.0831 litre bar K^{-1} mol^{-1}. (1 bar = 10^5 Pa = 10^5 Nm^{-2} = 0.987 atm). If the given value of K_p or K_c is dimensionless, use R = 0.0831 L bar K^{-1} mol^{-1}.

(c) Effect of temperature on equilibrium constant:

Case I: If $\Delta H = 0$, i.e. neither heat is evolved nor

absorbed, then $2.303\log_{10}\left(\dfrac{K_2}{K_1}\right) = 0$ or $\dfrac{K_2}{K_1} = 1$ or $K_2 = K_1$

i.e. equilibrium constant remains same at different temperature.

Case II: If ΔH = +ve, i.e., heat is absorbed during the course of reaction, then

$$2.303 \log \left(\frac{K_2}{K_1} \right) = +ve \quad or \quad \log K_2 > \log K_1 \text{ or } K_2 > K_1$$

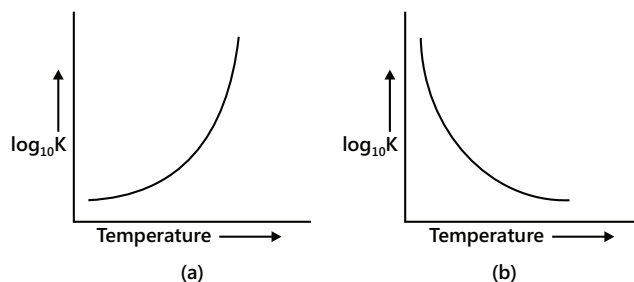i. e. , equilibrium constant increases with increase in temperature.

Figure 5.14: Plots of log K versus T
(a) Endothermic reaction (b) Exothermic reaction

Case III: If ΔH = – ve, i.e.heat is evolved during the course of reaction, then

$$2.303 \log \left(\frac{K_2}{K_1} \right) = -ve \quad or \quad \log K_2 < \log K_1 \text{ or } K_2 < K_1$$

i.e., equilibrium constant decreases with increase in temperature.

POINTS TO REMEMBER

Effect of adding an inert gas:

*   An inert gas (or noble gas) such as helium is one that does not react with other elements or compounds. At constant volume, addition of this inert gas does not affect the equilibrium.

*   According to Dalton's law, the partial pressures of the other gases remains same, which itself is the reason for the unchanged equilibrium.

*   But on increasing the volume, the partial pressures of all gases would decrease, resulting in a shift towards the side with the greater number of moles of gas.

Factors affecting the state of Equilibrium

Conditions	Shifts the Equilibrium
Increase in concentration of reactants	Forward direction
Increase in concentration of any product	Backward direction
Increase in temperature	In direction of endothermic reaction
Decrease in temperature	Direction of exothermic reaction
Increase in pressure	In direction of less number of gaseous moles
Decrease in pressure	In direction of large number of moles

Effect of temperature and Pressure :

Nature of Reaction	Effect of increase in T	Δn	Side with fewer mole	Side with fewer mole	Effect of increase on P
Exothermic concentration of reactants	Backward shift	0	Neither	neither	No shift
		-ve	Right	Forward	Forward
		+ve	Left	Backward	Backward
		-ve	Right	Forward	Forward
Endothermic concentration of any product	Forward shift	-ve	Right	Right	Forward
		+ve	Left	Forward	Forward
		0	Neither	No Shift	No shift