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Frozen Equilibrium :-

To know the value of equilibrium constant (K_c) of a reaction, we have to measure the conc^n of at least one of the reactants and products. Generally concentration is measured by titrating the mixture with suitable titrant. But during titration equilibrium will be shifted. Therefore actual concentration at equilibrium cannot be measured.

To prevent shifting of equilibrium, the temp^n of the reaction mixture after reaching equilibrium is brought down to near about 0°C. Under this condition the equilibrium is called frozen equilibrium and concentration of all the components remain fixed in their values for quiete sometime.

Frozen equilibrium is necessary to determine the equilibrium constant of a reaction by chemical method.

Determination of equilibrium constant of a homogeneous gaseous reaction.

Equilibrium constant of a reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is determined by Bodensation in 1897 by following way.

A known amount of hydrogen and iodine was taken in a sealed glass tube and then heated at 730.7 K by when the equilibrium was attained, the bulb was suddenly cooled to freeze the equilibruim of the reaction. The ~~bulb is~~ reaction mixture so obtained was analysed by opening the bulb in KOH solution which observed unreacted Iodine and hydrogen iodide formed. The amount of hydrogen left was determined by measuring the volume. As initial amount of H_2 and I_2 is known, the amount of I_2 left

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and amount of HI formed at equilibrium can be determined.
Therefore for the above reaction equm. constant

$$\left[K = \frac{n_{HI}^2}{n_{H_2} \times n_{I_2}}\right]$$ can be determined.

Q. Consider endothermic dissociation of PCl_5

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

Indicate all the methods by which the equilibrium of the above reaction can be shifted from left to right. Justify your answer with the help of La Chatelier principle as well as equilibrium constant expression.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \quad \Delta H = +ve$$

Equilibrium of the above reaction can be shifted from left to right by the following ways

1) Increasing temperature
2) Decreasing pressure
3) By adding more PCl_5 at equilibrium or remaining Cl_2 or both from equilibrium
4) By adding inert gas at constant pressure

⇒ 1) As forward reaction is endothermic, according to La Chtelier principal equilibrium will be shifted from left to right by increasing temperature.

This can be explained by the following relation.

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \qquad \Delta H = +ve$$

$$\frac{d \ln K_p}{dT} = +ve$$

Therefore by increasing temp, K_p will increase. So equilibrium will be shifted from left to right by increasing temprature.

2.) As in forward reaction no of moles increases pressure also increases at constant volume. So according to La chatelier principle with decreasing pressure, the equilibrium will be shifted from left to right.

This can be explained by the following relation

$$\left[\frac{d \ln K_x}{dP}\right]_T = -\frac{\Delta n}{P}$$

for above reaction $\Delta n = +1$. So, $\left[\frac{d \ln K_x}{dP}\right]_T$ is '$-ve$'. Therefore by decreasing P, K_x will increase. So equm will be shifted from left to right by decreasing pressure.

3.) According to La chatelier principle equilibrium will be shifted from left to right if more PCl_5 is added at equm or the product PCl_3 or Cl_2 or both are removed from the equilibrium.

This can be explained by V. H. recn isotherm

$$\Delta G = -RT \ln K + RT \sum \nu \ln a$$

For the above reaction it can be written as

$$\Delta G = -RT \ln K_p + RT \ln \frac{P_{Cl_3} \cdot P_{Cl_2}}{P_{Cl_5}}$$

at equilibrium $\Delta G = 0$

If more PCl_5 is added or PCl_5 or Cl_2 or both are removed, the value of $\frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$ will decrease

Therefore $\Delta G = -ve$, Hence equilibrium will be shifted from left to right.

4.) The equilibrium of the above reaction can be shifted from left to right by adding inert gas at const pressure.

For the above reaction $K_p = \frac{n_{PCl_3} \cdot n_{Cl_2}}{n_{PCl_5}} \left(\frac{P}{\Sigma n}\right)$

By adding inert gas at constant pressure $[\Delta n = +1]$. Σn will increase, hence $\frac{P}{\Sigma n}$ will decrease. Therefore to keep K_p constant $\frac{n_{PCl_3} \cdot n_{Cl_2}}{n_{PCl_5}}$ will increase. It is possible if the equilibrium is shifted from left to right.

Q. A solute goes into solution with absorption of heat. How will the solubility of the solute change with temp.

=> As the process absorbs heat, it is endothermic recn.

$\Delta H = +ve$.

Process Solvent + solute → Soln - heat

1) According to Le. Chatelier principle with increase in temp. the rate of forward recn will increase because it absorbs heat. So at high temp, the salt will dissolve into soln. So it will be more soluble. Solubility of the solute will increase with increase in temp.

2) Vat Hoff equn $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$

$\Delta H = +ve$

$\frac{d \ln K}{dT} = +ve$. K value will increase with increase in temp, which is possible if solute goes more and more into soln, so solubility increases. With the increase in temp, solubility of the solute will increase.