Chemical Equilibrium

Q → What happens if we inject some $H_2O(g)$ molecules into the system at equilibrium?

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

Ans → If we increase the concentration of $H_2O(g)$, more H_2O is around, which means more collisions between H_2O and CO (reactant) molecules. Therefore, more $H_2(g)$ and $CO_2(g)$ is produced i.e. the equilibrium is shifted in the forward direction.

Q → At 400 K Temp, $SO_3(g)$, $SO_2(g)$, $O_2(g)$ are at eqm at volume 10 L.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

Given eqm constant $K_c = 10$, if no. of moles of SO_2 is equal to no. of moles of SO_3, then calculate ~~con~~ moles of O_2?

Soln → $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

$\because$ Given, $[SO_2] = [SO_3]$ [$\because$ no. of moles of SO_2 = SO_3]

$\therefore K_c = \dfrac{\cancel{[SO_3]^2}}{\cancel{[SO_3]^2}[O_2]}$

$\Rightarrow 10 = \dfrac{1}{[O_2]}$

$\Rightarrow [O_2] = \dfrac{1}{10}$ moles/L

In 10 L of flask no. of moles $[O_2] = 10 \times \frac{1}{10} = 1$ moles

Q→ Derive Clapeyron equation.

Soln. Clapeyron derived an important equation for one-component ~~system~~ Two-phase system from the second law of thermodynamics. This equation is known as Clapeyron equation.

The Two phases in equilibrium ~~can~~ may be any of the following —

(i) Solid and liquid, $S \rightleftharpoons L$ at the melting point of Solid.

(ii) Liquid and vapour, $L \rightleftharpoons V$ at the ~~p~~ boiling point of liquid.

(iii) Solid and vapour, $S \rightleftharpoons V$ at the sublimation Tempr of Solid.

(iv) One crystalline form and another crystalline form, as for example, rhombic and monoclinic sulphur,

$S_R \rightleftharpoons S_M$, at the Transition Temperature of the Two allotropic forms.

Consider, in general, the change of a pure substance from phase A to another phase B in equilibrium with it given Tempr and pressure.

If G_A = free energy per mole of the substance in the initial phase A.

G_B = free energy per moles of the substance in the final phase B.

At equilibrium, $G_A = G_B$.

i.e. $\Delta G = G_B - G_A = 0$

If the temperature of such a system is raised, say, from T to T+dT, the pressure will also have to change, say from P to P+dP in order to maintain the equilibrium. The relationship between dT and dP can be derived from thermodynamics.

Let the free energy per mole of the substance in phase A at the new temperature and be $G_A + dG_A$ and in phase B be $G_B + dG_B$. Since, the two phases are still in equilibrium, hence –

$$G_A + dG_A = G_B + dG_B$$

According to thermodynamics –

$$dG = VdP - SdT \quad \text{——— (1)}$$

For phase A →

$$dG_A = V_A dP - S_A dT \quad \text{——— (2)}$$

and for phase B →

$$dG_B = V_B dP - S_B dT \quad \text{——— (3)}$$

Since, $G_A = G_B$, hence –

$$V_A dP - S_A dT = V_B dP - S_B dT$$

$$\Rightarrow S_B dT - S_A dT = V_B dP - V_A dP$$

$$\Rightarrow dT(S_B - S_A) = dP(V_B - V_A)$$

$$\Rightarrow \frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} \quad \text{——— (4)}$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad \text{——— (5)}$$

where, $\Delta S = S_B - S_A$ = change in entropy

and $\Delta V = V_B - V_A$ = change in volume.

If q_r is the heat exchanged reversibly per mole of the substance during the phase transformation at Tempr T, then the change in entropy (ΔS) in this process is given by —

$$\Delta S = \frac{q_r}{T}$$

From eqn 5 $\Rightarrow$ $$\frac{dP}{dT} = \frac{q_r}{T\Delta V}$$

$$\Rightarrow \frac{dP}{dT} = \frac{q_r}{T(V_B - V_A)} \quad \text{——— (6)}$$

eqn 6 is called the Clapeyron equation. This eqn given the change in pressure 'dP' with change in Tempr 'dT' in the case of a system containing Two phase of a pure substance in equilibrium with each other.