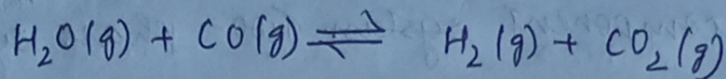


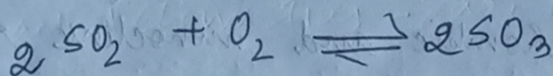
## Chemical Equilibrium

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



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.



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

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

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

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

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

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

Q → Derive Clapeyron equation.

(3)

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 boiling point of liquid.
- (iii) Solid and vapour,  $S \rightleftharpoons V$  at the sublimation temp<sup>r</sup> 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 temp<sup>r</sup> 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,  $G_A = G_B$ .

ie.  $\Delta G = G_B - G_A = 0$ .

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  $\rightarrow$

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

and for phase B  $\rightarrow$

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

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  $q_h$  is the heat exchanged reversibly per mole of the substance during the phase transformation at Temp<sup>r</sup>  $T$ , then the change in entropy ( $\Delta S$ ) in this process is given by -  $\Delta S = \frac{q_h}{T}$

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

$\Rightarrow \frac{dP}{dT} = \frac{q_h}{T(V_B - V_A)}$  ⑥

eqn ⑥ is called the Clapeyron equation. This eqn gives the change in pressure 'dP' with change in Temp<sup>r</sup> 'dT' in the case of a system containing two phase of a pure substance in equilibrium with each other.

①  $T b_A^2 - q b_A V = 0$

②  $T b_B^2 - q b_B V = 0$

$T b_A^2 - q b_A V = T b_B^2 - q b_B V$

$q b_A V - q b_B V = T b_A^2 - T b_B^2$

$(b_A - b_B) q V = (b_A^2 - b_B^2) T$

③  $\frac{(b_A - b_B) q V}{b_A V - b_B V} = \frac{(b_A^2 - b_B^2) T}{b_A^2 - b_B^2}$

④  $\frac{q}{V} = \frac{T}{b_A - b_B}$