Day-8

→ $H_2 + \frac{1}{2}O_2 \longrightarrow aH_2O + bOH + cO_2 + dH_2 + eO + fH$

(Others: O_3, H_2O_2, HO_2)

2 eqn's from atom balance

Rest: Formation equilibria reactions

$\cancel{H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O}$

$\frac{1}{2}O_2 \rightleftharpoons O$

$\frac{1}{2}H_2 \rightleftharpoons H$

$\frac{1}{2}O_2 + \frac{1}{2}H_2 \rightleftharpoons OH$

$$\Delta S = \int_R \frac{dQ}{T} + S_{gen}$$

For isolated system, $\Delta S \geq 0$

→ Criteria for chemical equilibrium:

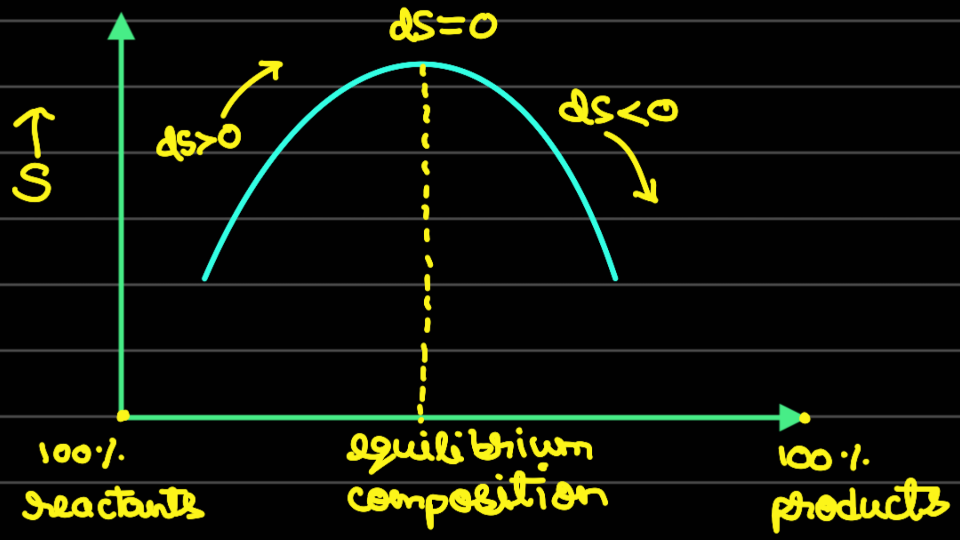
A reaction chamber contains a mixture of CO, CO_2 + O_2 at a given T and P.

$CO + \frac{1}{2}O_2 \longrightarrow CO_2$

$CO + \frac{1}{2}O_2 \longrightarrow aCO + bCO_2 + cO_2$

$CO + \frac{1}{2}O_2 \longrightarrow CO + \frac{1}{2}O_2$

$dS_{sys} \geq \frac{dQ}{T}$ (Clausius inequality)



not convenient.

→ Gibb's function:

$$G = H - TS$$

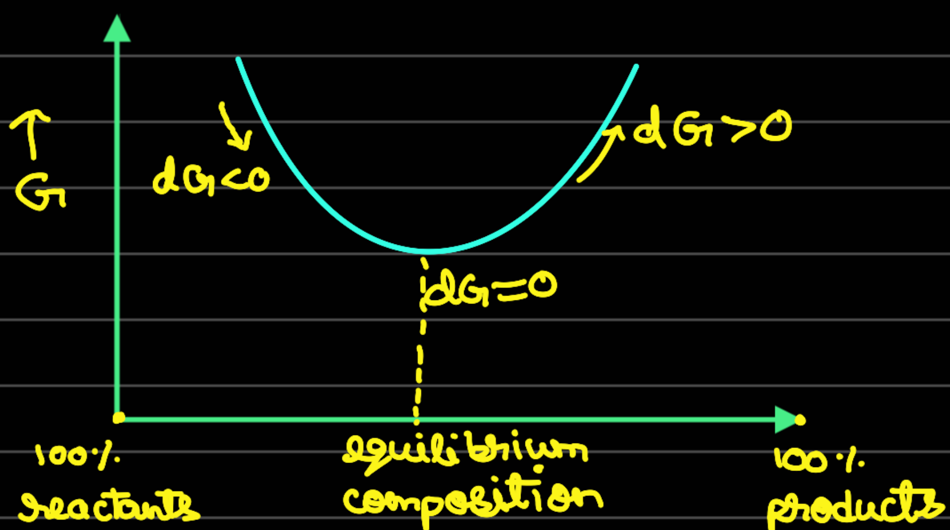
$$\delta Q = dU + PdV$$
$$dS = \frac{\delta Q_{rev}}{T}$$

$$\Rightarrow dU + PdV - TdS \leq 0$$

$$\Rightarrow d(U + PV) - d(TS) + SdT - VdP \leq 0$$

$T, P \rightarrow$ constant, $VdP = SdT = 0$

$$\Rightarrow d(H - TS) \leq 0$$
$$\Rightarrow dG \leq 0$$



At equilibrium at a given P and T,

$$\Delta G_{P,T} = 0$$

Absolute entropy values at P other than $P_0 = 1$ atm for any temp.,

$$S(T,P) = \bar{S}^{\circ}(T,P_0) - R_u \ln \frac{P}{P_0}$$

$\bar{S}^{\circ}$ = Abs. entropy at a given temp. at 1 atm.

For gaseous mixture (ideal gas behaviour)

$$S_i(T,P_i) = \bar{S}_i^{\circ}(T,P_0) - R_u \ln P_i/P^{\circ}$$

$P^{\circ} \longrightarrow 1$ atm

$P_i \longrightarrow$ partial pressure of ith component

$$dG_{T,P} \leq 0$$

For a mixture of ideal gases, Gibb's func^n for ith species is given by

$$\bar{g}_{i,T} = \bar{g}^{\circ}_{i,T} + R_u T \ln(P_i/P_0)$$

$\bar{g}^{\circ}_{i,T}$ = Gibb's func^n of ith species at std. state pressure (1 atm)

Proof:

$$G = H - TS$$

$$\Rightarrow dG = dH - TdS - \cancel{SdT} \quad \xrightarrow{} 0 \text{ for } T \to \text{const.}$$

$$\Rightarrow dG = -VdP$$

$$\Rightarrow \int dG = \int_{P_0}^{P_i} -V\,dP$$

In dealing with reacting system, a gibb's func^n of formation is defined

$$\bar{g}^\circ_{f,i}(T) = \bar{g}^\circ_i(T) - \sum_j \nu_j' \,\bar{g}^\circ_j(T)$$

$\nu_j' \rightarrow$ stoichiometric coeff. of elements required to form 1 mole compound of interest.