

< Thermochemistry III >

o Second law of thermodynamics applied to Reacting Systems

* Entropy, S .

- Entropy points the direction in time for physical and chemical processes

- Second law: for an isolated system, i.e. one that does not exchange energy (heat transfer and work) or mass with surroundings, entropy must increase or remain constant.

$$\boxed{dS_{\text{isolated}} \geq 0.}$$

- At equilibrium, the entropy of an isolated system will be the maximum possible value.

$$dS_{\text{isolated}} = 0 \Rightarrow S \rightarrow S_{\text{max.}}$$

o Formulation.

An isolated system, comprising N chemical species, undergoing chemical reactions.

$$S = S(U, V, N_1, \dots, N_N)$$

N_i : mole # of species i .

Total derivative of S . $\equiv dS$.

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V, N}}_{\equiv \frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U, N}}_{\equiv \frac{P}{T}} dV + \underbrace{\sum_{i=1}^N \left(\frac{\partial S}{\partial N_i}\right)_{U, V, N_j \neq N_i}}_{\equiv -\frac{\bar{\mu}_i}{T}} dN_i$$

$\bar{\mu}_i$: chemical potential of a species i

Thermodynamic definitions.

$$\therefore dS = \left(\frac{1}{T}\right) \cdot dU + \left(\frac{P}{T}\right) \cdot dV - \sum_{i=1}^N \left(\frac{\bar{M}_i}{T}\right) \cdot dN_i$$

⇒ General form of Gibbs equation for a reacting mixture.

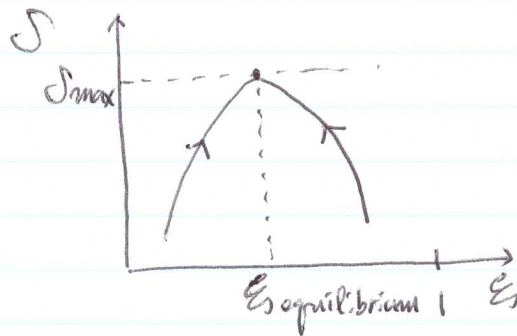
no heat transfer and no work.

$$\Rightarrow dU = dV = 0.$$

$$\therefore dS_{u,v} = - \sum_{i=1}^N \left(\frac{\bar{M}_i}{T}\right) \cdot dN_i = - \sum_{i=1}^N \left(\frac{\bar{M}_i}{T}\right) (\nu_i' - \nu_i) d\xi$$

where, $dN_i = (\nu_i' - \nu_i) d\xi$

progress variable
or the degree of advancement,
0 (reactants) to 1 (products)

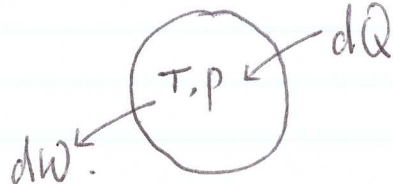


$$\therefore \left(\frac{dS}{d\xi}\right)_{u,v} = 0 = - \sum_{i=1}^N \frac{\bar{M}_i}{T} \cdot (\nu_i' - \nu_i) \text{ @ equilibrium.}$$

In combustion process, T/P or T/V constant assumption is possible.

$$\therefore \sum_i \bar{M}_i (\nu_i' - \nu_i) = 0.$$

* Control mass with heat transfer and work (PdV) interaction
T/P constant.



- First law.

$$\delta W - \delta Q + dU = PdV - \delta Q + dU = 0$$

- Second law.

$$dS - \frac{\delta Q}{T} \geq 0$$

→ Combine the two above gives.

$$TdS - dU - PdV \geq 0$$

→ T and P are constant

$$\therefore TdS - dU - PdV = d[TS - U - PV] = d[TS - H] \geq 0.$$

$= -H$

$$d[H - TS] \leq 0$$

$\equiv G$: Gibbs function.

$$\therefore dG_{T,p} \leq 0.$$

at equilibrium, $G_{T,p}$ is minimum.

why?

$dG_{T,p} \leq 0 \Rightarrow G_{T,p}$ is decreasing.

and $G_{T,p}$ should be constant at equilibrium.

* Total derivative of $G = G(P, T, N_1, \dots, N_M)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, N_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N_i} dP + \sum_{i=1}^M \left(\frac{\partial G}{\partial N_i}\right)_{P, T, N_j \neq N_i} \cdot dN_i$$

$\equiv \bar{g}_i$: partial molal Gibbs energy of species i .

$$\text{Now, } dG = d[H - TS] = dH - Tds - SdT.$$

$$\text{and } dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV - \sum_{i=1}^M \left(\frac{\mu_i}{T}\right) \cdot dN_i$$

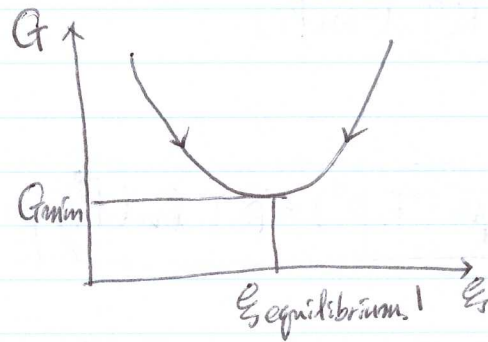
$$dG = -SdT + VdP + \sum \bar{\mu}_i dN_i$$

$$\therefore \bar{\mu}_i = \bar{g}_i$$

For T/P constant.

$$dG_{T,P} = \sum_i \bar{\mu}_i dN_i = \sum_i \bar{\mu}_i (v_i' - v_i) d\xi$$

at equilibrium $G_{T,P} = G_{\min}$ and $\frac{dG_{T,P}}{d\xi} = 0 = \sum_i \bar{\mu}_i (v_i' - v_i)$



ex) Water - Gas reaction



@ equilibrium

$$\sum_i \bar{\mu}_i (v_i' - v_i) = -\bar{\mu}_{\text{CO}} - \bar{\mu}_{\text{H}_2\text{O}} + \bar{\mu}_{\text{CO}_2} + \bar{\mu}_{\text{H}_2} = 0$$

$$G = \sum_i g_i(T, p_i) N_i$$

$$g_i = h_i(T) - T s_i(T, p_i)$$

$$d\bar{\mu}_i = dg_i = dh_i(T) - s_i(T, p_i) dT - T ds_i(T, p_i)$$

for fixed T.

$$dg_i = -T ds_i(T, p_i)$$

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For fixed T. & Perfect Gas.

$$ds_i = -\hat{R} \left(\frac{dp_i}{p_i} \right)$$

$$\therefore d\bar{\mu}_i = \hat{R} T d(\ln p_i)$$

 $p^\circ = 1 \text{ bar}$: reference pressure.

$$\int_{T, p^\circ}^{T, p_i} d\bar{\mu}_i = \int_{T, p^\circ}^{T, p_i} \hat{R} T d(\ln p_i)$$

$$\boxed{\bar{\mu}_i(T, p_i) - \bar{\mu}_i(T, p^\circ) = \hat{R} T \ln(p_i/p^\circ)}$$

$$\sum_i (\nu_i' - \nu_i) \bar{\mu}_i(T, p_i^*) = \sum_i (\nu_i' - \nu_i) \bar{\mu}_i(T, p^\circ) + \sum_i (\nu_i' - \nu_i) \hat{R} T \ln p_i$$

\uparrow
 equilibrium partial press.

$\underline{= 0}$

$$\Rightarrow \prod_i \left(\frac{p_i^*}{p^\circ} \right)^{\nu_i' - \nu_i} = \exp \left\{ \underbrace{- \sum_i (\nu_i' - \nu_i) \bar{\mu}_i(T, p^\circ)}_{\equiv \Delta_r G^\circ} / RT \right\}$$

$$\Delta_r G_i^\circ \equiv g_i - \sum_j \nu_j g_j^\circ$$

\downarrow
 reference elements at 1 bar, T.
 Gibbs func. of species i at 1 bar, T.

$$\Delta_r G^\circ \equiv \sum_i (\nu_i' - \nu_i) \Delta_r G_i^\circ \equiv \Delta_r G^\circ$$

$$\Delta_r G^\circ = + \sum_i (\nu_i' - \nu_i) \left(\Delta_r G_i^\circ + \sum_j \nu_j g_j^\circ \right)$$

$$\Rightarrow \sum_i \left\{ (\nu_i' - \nu_i) \sum_j \nu_j g_j^\circ \right\} = 0 \quad \text{reactant \& product have same ref. species}$$

K_p , K_c & K_x
 mole fraction $p_i = x_i P$
 molar concentration

$$p_i = C_i \bar{R} T$$

$$\Delta N \equiv \sum_i (\nu_i' - \nu_i)$$

$$K_p = K_c (\bar{R} T / p^\circ)^{\Delta N}$$

$$K_p = K_x (P / p^\circ)^{\Delta N}$$

when $\Delta N = 0$, $K_p = K_c = K_x$

* Van't Hoff eqn.

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta \hat{H}^\circ(T)}{\bar{R} T^2} \rightarrow \text{Not a strong func. of } T.$$

$\Delta \hat{H}^\circ$: heat of reaction

< 0 exothermic

> 0 endothermic