AGENDA

1. **Equilibrium and Chemical potential**
2. **Calculating Equilibrium Composition**

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1. Equilibrium and Chemical potential

Consider a two phase, isolated system:

$$dS' = \left(\frac{1}{T^{\alpha}} - \frac{1}{T^{\beta}}\right) dU'^{\alpha} + \left(\frac{P^{\alpha}}{T^{\alpha}} - \frac{P^{\beta}}{T^{\beta}}\right) dV'^{\alpha} - \left(\frac{\mu^{\alpha}}{T^{\alpha}} - \frac{\mu^{\beta}}{T^{\beta}}\right) dn'^{\alpha}$$

At Equilibrium, entropy at maximum: $dS' = 0$

Thus, we have:

Thermal Equilibrium: $T^{\alpha} = T^{\beta}$

Mechanical Equilibrium: $P^{\alpha} = P^{\beta}$

Chemical Equilibrium: $\mu^{\alpha} = \mu^{\beta}$

In general:

(1) Entropy is maximized in **isolated systems** at equilibrium while the internal energy is minimized.

(2) Enthalpy is minimized in **closed, adiabatic systems at constant pressure** at equilibrium.

(3) Helmholtz free energy is minimized in **closed, isothermal systems with rigid walls** at equilibrium.

(4) Gibbs free energy is minimized for **closed, constant pressure, isothermal systems** at equilibrium

For detailed derivation, please refer to the lecture notes 21.

Chemical potential:

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_l} \longrightarrow dG = -SdT + VdP + \sum_i \mu_i dn_i \Rightarrow \begin{cases} dU = TdS - PdV + \sum_i \mu_i dn_i \\ dH = TdS + VdP + \sum_i \mu_i dn_i \\ dF = -SdT - PdV + \sum_i \mu_i dn_i \\ dG = -SdT + VdP + \sum_i \mu_i dn_i \end{cases}$$

$$U \xrightarrow{+PV} H, \quad U \xrightarrow{-TS} F, \quad H \xrightarrow{-TS} G, \quad F \xrightarrow{+PV} G$$

$$X = \sum_i n_i \overline{X}_i \longrightarrow G = \sum_i n_i \mu_i \Rightarrow \begin{cases} U = TS - PV + \sum_i \mu_i n_i \\ H = TS + \sum_i \mu_i n_i \\ F = -PV + \sum_i \mu_i n_i \\ G = \sum_i \mu_i n_i \end{cases}$$

$$\sum_i n_i d\mu_i = -SdT + VdP$$

Gibbs-Duhem equation

2. Calculating Equilibrium Composition

Evaluating Chemical Potentials:

For an idea gas mixture:

$$s(T_2, p_2) - s(T_1, p_1) = \underbrace{\int_{T_1}^{T_2} c_p(T) \frac{dT}{T}}_{s^o(T_2) - s^o(T_1)} - R \ln \frac{p_2}{p_1}$$

$$s(T, p) = s(T, p_{ref}) - R \ln \frac{p}{p_{ref}}$$

$$\overline{s}_i(T, p) = \overline{s}_i^0(T) - \overline{R} \ln \frac{y_i p}{p_{ref}}$$

So we have:

$$\mu_i = \bar{h}_i(T) - T\bar{s}_i(T, p_i)$$

$$= \bar{h}_i(T) - T\left[\bar{s}_i^0(T) - \bar{R}\ln\frac{y_i p}{p_{ref}}\right]$$

$$= \underbrace{\bar{h}_i(T) - T\bar{s}_i^0(T)}_{\bar{g}_i^0} + \bar{R}T\ln\frac{y_i p}{p_{ref}}$$

$$\mu_i = \bar{g}_i^0 + \bar{R}T\ln\frac{y_i p}{p_{ref}}, \quad \bar{g}_i^0 = \bar{h}_i(T) - T\bar{s}_i^0(T)$$

where $\bar{g}_i^0$ is the Gibbs function of component i evaluated at temperature T and a pressure of 1 atm. The p_{ref} is 1 atm.

Equation of Reaction Equilibrium:

Consider a closed system containing five components, A,B,C,D, and E, at a given temperature and pressure, subject to a single chemical reaction of the form

$$v_A A + v_B B \rightleftarrows v_C C + v_D D$$

The equation of reaction equilibrium is:

$$v_A\mu_A + v_B\mu_B = v_C\mu_C + v_D\mu_D$$

Using $\mu_i = \bar{g}_i^0 + \bar{R}T\ln\frac{y_i p}{p_{ref}}$, we can derive the **Equilibrium constant K:**

$$\Rightarrow -\frac{\Delta G^0}{\bar{R}T} = \ln\left[K(T)\right]$$

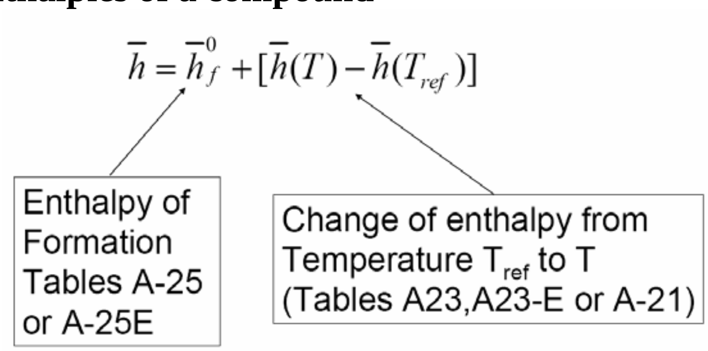
$$K(T) = \frac{y_C^{v_C} y_D^{v_D}}{y_A^{v_A} y_B^{v_B}}\left(\frac{p}{p_{ref}}\right)^{v_C + v_D - v_A - v_B}$$

Where

$$\Delta G^0 = v_C \bar{g}_C^0 + v_D \bar{g}_D^0 - v_A \bar{g}_A^0 - v_B \bar{g}_B^0$$
$$= v_C(\bar{h}_C - T\bar{s}_C{}^0) + v_D(\bar{h}_D - T\bar{s}_D{}^0) - v_A(\bar{h}_A - T\bar{s}_A{}^0) - v_B(\bar{h}_B - T\bar{s}_B{}^0)$$
$$= (v_C\bar{h}_C + v_D\bar{h}_D - v_A\bar{h}_A - v_B\bar{h}_B) - T(v_C\bar{s}_C{}^0 + v_D\bar{s}_D{}^0 - v_A\bar{s}_A{}^0 - v_B\bar{s}_B{}^0)$$

Where $\bar{h} = \bar{h}_f^0 + \Delta\bar{h}$

Evaluating enthalpies of a compound



Here, we choose T_{ref} as $25^\circ C$ or **298 K**. Note the formation enthalpies for H_2, O_2, N_2 and C are 0.

In general, we can employ one of the following methods to calculate $\Delta\bar{h}$

For a solid or liquid: Use $\Delta\bar{h} = \bar{c}_p \Delta T$, as we used in HW 10.

For gases:
Method 1: Assume an ideal gas with constant specific heat so that $\Delta\bar{h} = \bar{c}_p \Delta T$;
Method 2: Assume an ideal gas and use table.

The energy rate balance for a control volume at steady state neglecting kinetic and potential energy effects can be written as:

$$0 = \frac{\dot{Q}_{cv}}{\dot{n}_{cv}} - \frac{\dot{W}_{cv}}{\dot{n}_{cv}} + \sum_i n_i \bar{h}_i(T_i) - \sum_e n_e \bar{h}_e(T_e)$$

where $\bar{h} = \bar{h}_f^0 + \Delta\bar{h}$