

Thermodynamics II

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Solution Thermodynamics : theory

■ Objective

: lay the **theoretical foundation** for applications of thermodynamics to gas mixture and liquid solution

- Most of chemical process undergo composition changes by mixing separation.
=> **compositions** become essential variable along with T and P.
- Fundamental property relation become more comprehensive than eqn. (6.10)
 $dG = VdP - SdT.$

11.1 Fundamental Property Relation

- Eqn. (6.6) $d(nG) = (nV)dP - (nS)dT$ for **closed system of single phase**

$$\left[\frac{\partial(nG)}{\partial P} \right]_{T,n} = nV \quad \text{and} \quad \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} = -nS$$

- For a single-phase, **open system**

$$nG = f(P, T, n_1, n_2, \dots)$$

$$d(nG) = \left[\frac{\partial(nG)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_j} dn_i$$

By definition **chemical potential** of species i in the mixture

$$\mu_i = \sum_i \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_j} dn_i \quad [11.1]$$

$$\therefore d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i \quad [11.2]$$

For special case of **one mole** of solution $n=1$, $n_i = x_i$

$$dG = VdP - SdT + \sum_i \mu_i dx_i \quad (11.3)$$

$$\therefore G = G(T, P, x_1, x_2, \dots, x_i, \dots)$$

From (11.3)

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,x} \quad S = \left(\frac{\partial G}{\partial T}\right)_{P,x}$$

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_{P,x}$$

※ Gibbs energy plays a role of a **generating function**, providing the **means for calculation of all other thermodynamic properties** by simple mathematical operations.

11.2 The Chemical Potential and Phase Equilibria

- **Closed** systems consisting of two phase in **equilibrium**
each individual phase is open to the other => **mass transfer occur b/w phases**

Eqn.(11.2) applies to each phase

$$d(nG)^\alpha = (nV)^\alpha dP - (nS)^\alpha dT = \sum \mu_i^\alpha dn_i^\alpha$$

$$d(nG)^\beta = (nV)^\beta dP - (nS)^\beta dT = \sum \mu_i^\beta dn_i^\beta$$

Because two phases are in equilibrium \rightarrow T and P is uniform

Change of total Gibbs energy = sum of two equation $d(nG)^\alpha + d(nG)^\beta$

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta$$

$$(nM = (nM)^\alpha + (nM)^\beta)$$

at equilibrium $\sum \mu_i^\alpha dn_i^\alpha + \sum \mu_i^\beta dn_i^\beta = 0$

by mass conservation, $dn_i^\alpha + dn_i^\beta = 0$

$$\sum (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$$

At equilibrium μ of each phase is same ($\mu_i^\alpha = \mu_i^\beta$)

Thus, multiple phase at same T&P are in equilibrium when the chemical potential of each species is the same in the all phase

$$\therefore \mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad (i = 1, 2, 3, \dots, N)$$

(11-6)

11.3 Partial Properties

■ **Partial property** \overline{M}_i is defined by

$$\overline{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j} \quad (11-7)$$

Chemical potential is partial molar property of Gibbs Energy

$$\mu_i = \left(\frac{\partial(nG)}{\partial n_i} \right)_{P,T,n_j} = \overline{G}_i$$

※ Equations relating Molar and Partial molar properties

- From the knowledge of the partial properties, we can calculate solution properties or we can do reversely.
- Total thermo properties of homogeneous phase are functions of T, P and the numbers of moles of the individual species which comprise the phase

$$nM = \mu(T, P, n_1, n_2, \dots, n_i)$$

The total differential of nM is

$$d(nM) = \left[\frac{\partial(nM)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T} \right]_{P,n} dT + \sum_i \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j} dn_i$$

$$d(nM) = n \left(\frac{\partial(nM)}{\partial P} \right)_{T,x} dP + n \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \overline{M}_i dn_i \quad (11-9)$$

$$n_i = x_i n \rightarrow dn_i = x_i dn + n dx_i$$

$$d(nM) \equiv ndM + Mdn$$

$$\therefore ndM + Mdn = n \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + n \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \overline{M}_i (x_i dn + n dx_i)$$

The terms containing “n” are collected separated from those containing dn to yield

$$[dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum M_i dx_i]n + [M - \sum_i x_i M_i]dn = 0$$

$$\therefore dM = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i M_i dx_i \quad (11-10)$$

$$M = \sum_i x_i \overline{M}_i \quad (11-11)$$

Multiply Eqn.(11.11) by n yield

$$nM = \sum_i n_i M_i \quad (11-12)$$

(11.10) → special case of Eqn (11.9) by setting n=1

(11.11), (11.12) → summability relations

⇒ allow calculation of mixture from partial property

From Eqn (11.11) $M = \sum x_i \bar{M}_i$

$$dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i \quad \text{Compare this with (11.10)}$$

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0 \quad (11-13)$$

=> Gibbs/Duhem equation

$$\text{at const } T, P \quad \sum_i x_i d\bar{M}_i = 0 \quad (11-14)$$

■ Rationale for partial property

$$M = \sum x_i d\overline{M}_i \Rightarrow \text{Solution property is sum of its partial properties}$$

$$\lim_{x_i \rightarrow 1} M = \lim_{x_i \rightarrow 1} \overline{M}_i = M_i \quad (\text{in the limit as a solution become pure in species } i)$$

$$\text{By definition} \quad \lim_{x_i \rightarrow 0} \overline{M}_i = M_i^\infty$$

■ Summary of partial property

1. Definition $\overline{M}_i = \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j} \Rightarrow \text{yield partial properties from total property}$

2. summability $M = \sum_i x_i \overline{M}_i \Rightarrow \text{yield total properties from partial properties}$

3. Gibbs/Duhem $\sum_i x_i dM_i = \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + \left(\frac{\partial M}{\partial T} \right)_{P,x} dT$

\Rightarrow partial properties of species in solution \Rightarrow dependent one another

■ Partial properties in binary solutions

For binary solution (system), From summability relations $M = \sum x_i \overline{M}_i$

$$M = x_1 \overline{M}_1 + x_2 \overline{M}_2 \quad (\text{a}) \Rightarrow \quad dM = x_1 d\overline{M}_1 + \overline{M}_1 dx_1 + x_2 d\overline{M}_2 + \overline{M}_2 dx_2 \quad (\text{b})$$

at constant T, P by Gibbs/Duhem Egn.

$$x_1 d\overline{M}_1 + x_2 d\overline{M}_2 = 0 \quad (\text{c})$$

Because $x_1 + x_2 = 1$, $dx_1 = -dx_2$, Eliminating dx_2 in Eq (b)

$$dM = x_1 d\overline{M}_1 + \overline{M}_1 dx_1 + x_2 d\overline{M}_2 - \overline{M}_2 dx_1 \quad \text{by Egn (c)}$$

$$dM = \overline{M}_1 dx_1 - \overline{M}_2 dx_1 \quad \therefore \quad \frac{dM}{dx_1} = \overline{M}_1 - \overline{M}_2 \quad (\text{d})$$

$$\text{From Egn (a)} \quad M = (1 - x_2) \overline{M}_1 + x_2 \overline{M}_2 = \overline{M}_1 - x_2 (\overline{M}_1 - \overline{M}_2)$$

$$M = x_1 \overline{M}_1 + (1 - x_1) \overline{M}_2 = \overline{M}_2 + x_1 (\overline{M}_1 - \overline{M}_2)$$

$$\text{insert Egn (d)} \quad \overline{M}_1 = M + x_2 \frac{dM}{dx_1} \quad \overline{M}_2 = M - x_1 \frac{dM}{dx_1}$$

So, from the solution properties as a function of composition (at const T, P)

\Rightarrow Partial properties can be calculated

G/D can be written in derivative form

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0 \quad \Rightarrow \quad \frac{d\bar{M}_1}{dx_1} = -\frac{x_2}{x_1} \frac{d\bar{M}_2}{dx_1}$$

=> When \bar{M}_1 & \bar{M}_2 are plotted vs x_1 => sign of slope is opposite

Moreover from this Equation

$$\lim_{x_1 \rightarrow 1} \frac{d\bar{M}_1}{dx_1} = 0 \quad , \quad \lim_{x_2 \rightarrow 1} \frac{d\bar{M}_2}{dx_1} = 0$$

=> Plots of \bar{M}_1 and \bar{M}_2 vs x_1 => horizontal as each species approach purity

■ Relations among partial properties

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i \quad (\mu_i = \bar{G}_i)$$

$$\Rightarrow d(nG) = (nV)dP - (nS)dT + \sum_i \bar{G}_i dn_i$$

Apply criterion of exactness for differential expression

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = -\left(\frac{\partial S}{\partial P}\right)_{T,n} \quad \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,n} = -\left(\frac{\partial(nV)}{\partial n_i}\right)_{P,T,n_j} \Rightarrow \bar{V}_i$$

$$\left(\frac{\partial \bar{G}_i}{\partial T}\right)_{P,n} = -\left(\frac{\partial(nS)}{\partial n_i}\right)_{P,T,n_j} \Rightarrow -\bar{S}_i$$

※ Property relations used in const. composition solution has **their counterpart equations** for partial properties

For example, $H = U + PV$, for n mole
 $nH = nU + P(nV)$

Differentiation with respect to n_i at const T, P, n_j

$$\left[\frac{\partial(nH)}{\partial n_i}\right]_{P,T,n_j} = \left[\frac{\partial(nU)}{\partial n_i}\right]_{P,T,n_j} + P\left[\frac{\partial(nV)}{\partial n_i}\right]_{P,T,n_j} \Rightarrow \bar{H}_i = \bar{U}_i + P\bar{V}_i$$

$$d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT$$

11.4 Ideal Gas Mixtures

※ **Ideal gas mixture model** : Basis to build the structure of solution thermodynamics

Molar volume of Ideal Gas : $V = \frac{RT}{P}$

=> All ideal gas, whether pure or mixture have same molar volume at the same T, P

※ **Partial molar volume** of species i in ideal gas mixture

$$\bar{V}_i^{\text{ig}} = \left[\frac{\partial(nV^{\text{ig}})}{\partial n_i} \right]_{T,P,n_j} = \left[\frac{\partial(nRT/P)}{\partial n_i} \right] = \frac{RT}{P} \left(\frac{\partial n}{\partial n_i} \right)_{n_j} = \frac{RT}{P}$$

since $n = n_i + \sum n_j$

=> **partial molar volume = pure species molar volume = mixture molar volume**

$$\bar{V}_i^{\text{ig}} = V_i^{\text{ig}} = V^{\text{ig}} = \frac{RT}{P}$$

Partial pressure of ideal gas for n mol of ideal gas

$$P = \frac{nRT}{V^t}$$

for species i, $P_i = \frac{n_i RT}{V^t}$ (since $V^t = V_i^t$ in ideal

$$\frac{P_i}{P} = \frac{n_i}{n} = y_i \quad \therefore P_i = y_i P$$

In ideal gas, thermodynamic properties independent of one another

※ Gibbs theorem

A partial molar property (**except volume**) of a constituent in an ideal gas mixture is equal to the corresponding molar property of the species as a pure ideal gas but at a pressure equal to **its partial pressure**

$$\overline{M}_i^{\text{ig}}(T, P) = M_i^{\text{ig}}(T, P_i) \quad (11.21)$$

※ **H of Ideal Gas** => independent of P

$$H = C_p dT$$

$$\therefore \bar{H}_i^{\text{ig}}(T, P) = H_i^{\text{ig}}(T, P_i) = H_i^{\text{ig}}(T, P)$$

$$\therefore \bar{H}_i^{\text{ig}} = H_i^{\text{ig}} \quad \rightarrow \textcircled{1} \quad [11.22]$$

※ **S of an ideal gas** -> dependent on P and T

$$dS^{\text{ig}} = C_p^{\text{ig}} \frac{dT}{T} - R \frac{dP}{P} \quad [6.24]$$

at const T. $dS_i^{\text{ig}} = -R d \ln P = -R \frac{dP}{P}$

Integration from P_i to P $S_i^{\text{ig}}(T, P) - S_i^{\text{ig}}(T, p_i) = -R \ln \frac{P}{p_i} = -R \ln \frac{P}{y_i P} = R \ln y_i$

$\therefore S_i^{\text{ig}}(T, p_i) = S_i^{\text{ig}}(T, P) - R \ln y_i$ Since, $\bar{S}_i^{\text{ig}}(T, P) = S_i^{\text{ig}}(T, P_i)$ Gibbs theorem

$$\bar{S}_i^{\text{ig}} = S_i^{\text{ig}} - R \ln y_i \quad \rightarrow \textcircled{2} \quad [11.23]$$

For the Gibbs Energy of ideal gas mixture

$$G^{\text{ig}} = H^{\text{ig}} - TS^{\text{ig}} \Rightarrow \bar{G}^{\text{ig}} = \bar{H}^{\text{ig}} - T\bar{S}_i^{\text{ig}}$$

$$\bar{G}_i^{\text{ig}} = H_i^{\text{ig}} - TS_i^{\text{ig}} + RT \ln y_i \quad (\text{by using eqn. ① ②})$$

$$\text{or } \mu_i^{\text{ig}} \equiv \bar{G}_i^{\text{ig}} = G_i^{\text{ig}} + RT \ln y_i \quad \rightarrow \text{③} \quad (11.24)$$

By summability eqn ($M = \sum x_i \bar{M}_i$)

$$H^{\text{ig}} = \sum y_i H_i^{\text{ig}} \quad \rightarrow \text{④}$$

$$S^{\text{ig}} = \sum y_i S_i^{\text{ig}} - R \sum y_i \ln y_i \quad \rightarrow \text{⑤}$$

$$G^{\text{ig}} = \sum y_i G_i^{\text{ig}} + RT \sum y_i \ln y_i \quad \rightarrow \text{⑥}$$

$$\bullet H^{\text{ig}} - \sum y_i H_i^{\text{ig}} \quad (\text{enthalpy charge of mixing}) = 0$$

\Rightarrow no heat transfer for ideal gas mixing

$$\bullet S^{\text{ig}} - \sum y_i S_i^{\text{ig}} = R \sum y_i \ln \frac{1}{y_i} \quad (\text{entropy charge of mixing}) > 0$$

\Rightarrow agree with second law, mixing is irreversible

Alternative expression for μ_i^{ig}

$$dG_i^{\text{ig}} = V_i^{\text{ig}} dP - S_i^{\text{ig}} dT \Rightarrow V dP \quad (\text{at const } T)$$

$$\therefore dG_i^{\text{ig}} = V_i^{\text{ig}} dP = \frac{RT}{P} dP = RT d \ln P$$

By integration

$$G_i^{\text{ig}} = \Gamma_i(T) + RT \ln P \quad [11.28]$$

$$\therefore \mu_i^{\text{ig}} = \Gamma_i(T) + RT \ln(y_i P) \quad [11.29]$$

Applying summability relation

$$\therefore G^{\text{ig}} = \sum y_i \Gamma_i(T) + RT \sum y_i \ln(y_i P) \quad [11.30]$$