

Solution thermodynamics

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Mixture/solution

- **Chemical Potential**
- **Partial Molar Property**
- **Partial Pressure**
- **Ideal-Gas Mixtures**
 - enthalpy of an ideal gas
 - entropy of an ideal gas
- **Gibbs energy of an ideal-gas mixture $G^{ig} = H^{ig} - TS^{ig}$,**

Mixture/solution

- **Because the properties of systems in chemical engineering depend strongly on composition as well as on temperature and pressure,**
- **Need to develop the theoretical foundation for applications of thermodynamics to gas mixtures and liquid solutions**

Mixture/solution

- **definition of a fundamental new property called the *chemical potential*, upon which the principles of phase and chemical-reaction equilibrium depend.**
- **This leads to the introduction of a new class of thermodynamic properties known as *partial properties*.**

Chemical potential

- **The total Gibbs energy of any closed system to its canonical variables, temperature and pressure is**

$$d(n\underline{G}) = (n\underline{V})dp - (n\underline{S})dT$$

- **and**

$$\left[\frac{\partial(n\underline{G})}{\partial p} \right]_{T,n} = n\underline{V} \quad \text{and} \quad \left[\frac{\partial(n\underline{G})}{\partial T} \right]_{p,n} = -n\underline{S}$$

Chemical potential

- **Gibbs free energy of a multicomponent mixture is a function of T , P and each species mole number, therefore, the total differential of the Gibbs free energy,**

$$d(n\underline{G}) = \left[\frac{\partial(n\underline{G})}{\partial p} \right]_{T,n} dp - \left[\frac{\partial(n\underline{G})}{\partial T} \right]_{p,n} dT + \sum_i \left[\frac{\partial(n\underline{G})}{\partial n_i} \right]_{p,T,n_j}$$

(CP1)

Chemical potential

- **Recall**

$$\begin{aligned} dG &= \left(TS - pV + \sum_{i=1}^r \mu_i dn_i \right) - TS - pV \\ &= \sum_{i=1}^r \mu_i dn_i \end{aligned}$$

- **in extensive function, therefore we have**

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i} \right]_{p,T,n_{i \neq j}}$$

Chemical Potential and Phase Equilibrium

- Consider a closed system consisting of two phases in equilibrium.
- Within this *closed* system, each individual phase is an *open* system, free to transfer mass to the other, that is

$$d(n\underline{G})^\alpha = -(n\underline{S})^\alpha dT + (n\underline{V})^\alpha dp + \sum_{i=1} \mu_i^\alpha dn_i^\alpha$$

$$d(n\underline{G})^\beta = -(n\underline{S})^\beta dT + (n\underline{V})^\beta dp + \sum_{i=1} \mu_i^\beta dn_i^\beta$$

Chemical Potential and Phase Equilibrium

- The change in the total Gibbs energy of the two-phase system is the sum of these equations.

$$d(n\underline{G}) = -(n\underline{S})dT + (n\underline{V})dp + \sum_{i=1} \mu_i^\alpha dn_i^\alpha + \sum_{i=1} \mu_i^\beta dn_i^\beta$$

$$\sum_{i=1} \mu_i^\alpha dn_i^\alpha + \sum_{i=1} \mu_i^\beta dn_i^\beta = 0$$

Chemical Potential and Phase Equilibrium

- And $dn_i^\alpha = -dn_i^\beta$
- Therefore,

$$\sum_{i=1} (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$$

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

- Thus, multiple phases at the same T and P are in equilibrium when the chemical potential of each species is the same in all phases.

Partial Molar Property

- Partial Molar Property ($\bar{\theta}$)

$$\mu_i / \bar{\theta} \equiv \left[\frac{\partial(n\underline{G} / \underline{\theta})}{\partial n_i} \right]_{p, T, n_{i \neq j}}$$

- It is a *response function*, representing the change of total property θ due to addition at constant T and P of a differential amount of species i to a finite amount of mixture/solution.

Partial Molar Property

- Let $\underline{\theta}$ be any molar property (molar volume, molar enthalpy, etc.) of a mixture consisting of N_i moles of species i ,
$$N = \sum_i^c N_i$$
- And partial molar thermodynamic property

$$\bar{\theta}_i = \bar{\theta}_i(T, P, \underline{x}) = \left. \frac{\partial (N \underline{\theta})}{\partial N_i} \right|_{T, P, N_{j \neq i}}$$

- Therefore,

$$\underline{\theta} = \sum_{i=1}^e x_i \bar{\theta}_i(T, P, \underline{x})$$

Partial Molar Property

• Or

$$N\underline{\theta} = \sum_{i=1}^e N_i \bar{\theta}_i$$

So that, by the product rule of differentiation,

$$d(N\underline{\theta}) = \sum N_i d\bar{\theta}_i + \sum \bar{\theta} dN_i \quad \text{PM 1}$$

• substitute G with $N\underline{\theta}$ into Eq. CP 1

Partial Molar Property

- substitute G with $N\bar{\theta}$ into Eq. CP 1

$$\begin{aligned}dN\bar{\theta} &= \left(\frac{\partial N\bar{\theta}}{\partial T} \right)_{P, N_i} dT + \left(\frac{\partial N\bar{\theta}}{\partial P} \right)_{T, N_i} dP + \sum_i^c \left(\frac{\partial N\bar{\theta}}{\partial N_i} \right)_{P, N_i} dN_i \\ &= N \left(\frac{\partial \bar{\theta}}{\partial T} \right)_{P, N_i} dT + N \left(\frac{\partial \bar{\theta}}{\partial P} \right)_{T, N_i} dP + \sum_i^c \bar{\theta}_i dN_i\end{aligned}$$

PM 2

Partial Molar Property

- **Subtracting PM 2 from PM 1,**

$$-N \left(\frac{\partial \bar{\theta}}{\partial T} \right)_{P, N_i} dT - N \left(\frac{\partial \bar{\theta}}{\partial P} \right)_{T, N_i} dP + \sum_i^c N_i d\bar{\theta}_i = 0$$

- **Or,**

$$-\left(\frac{\partial \bar{\theta}}{\partial T} \right)_{P, N_i} dT - \left(\frac{\partial \bar{\theta}}{\partial P} \right)_{T, N_i} dP + \sum_i^c x_i d\bar{\theta}_i = 0$$

This is the generalized Gibbs-Duhem Equation

Quiz XI

- What is the partial molar temperature?
- Express result in relation to T of the mixture.

Partial Molar Property

- For constant temperature and pressure,

$$\sum_{i=1}^e N_i d\bar{\theta}_i \Big|_{T,P} = 0$$

$$\sum_{i=1}^e x_i d\bar{\theta}_i \Big|_{T,P} = 0$$

- Substitute θ with G

$$SdT - VdP + \sum_{i=1}^e N_i d\bar{G}_i = 0$$

$$\underline{S}dT - \underline{V}dP + \sum_{i=1}^e x_i d\bar{G}_i = 0$$

Partial Molar Property

- At constant temperature and pressure,

$$\sum_{i=1}^e N_i d\bar{G}_i = 0$$

$$\sum_{i=1}^e x_i d\bar{G}_i = 0$$

- Recall Gibbs-Duhem Equation

$$-\left(\frac{\partial \bar{\theta}}{\partial T}\right)_{P, N_i} dT - \left(\frac{\partial \bar{\theta}}{\partial P}\right)_{T, N_i} dP + \sum_i^c x_i d\bar{\theta}_i = 0$$

Partial Molar Property

- **Rearrange and times n on both sides,**

$$- \left(\frac{\partial n\bar{\theta}}{\partial T} \right)_{p, N_i} dT - \left(\frac{\partial n\bar{\theta}}{\partial p} \right)_{T, N_i} dp + N_i d\bar{\theta}_i + \sum_j^{c-1} N_j d\bar{\theta}_j = 0$$

- **Derivative with respect to N_i**

$$- \left(\frac{\partial \bar{\theta}_i}{\partial T} \right)_{p, N_i} dT - \left(\frac{\partial \bar{\theta}_i}{\partial p} \right)_{T, N_i} dp + d\bar{\theta}_i + \sum_j^{c-1} dN_j \frac{d\bar{\theta}_j}{dN_i} = 0$$

$$- \left(\frac{\partial \bar{\theta}_i}{\partial T} \right)_{p, N_i} dT - \left(\frac{\partial \bar{\theta}_i}{\partial p} \right)_{T, N_i} dp + d\bar{\theta}_i + \sum_j^{c-1} dN_j \frac{\partial \bar{\theta}_i}{\partial N_j} = 0$$

Partial Molar Property

- **Rearrange,**

$$d\bar{\theta}_i = \left(\frac{\partial \bar{\theta}_i}{\partial T} \right)_{p, \underline{x}} dT + \left(\frac{\partial \bar{\theta}_i}{\partial p} \right)_{T, \underline{x}} dp - \sum_{j=1}^{c-1} \left(\frac{\partial \bar{\theta}_i}{\partial x_j} \right)_{T, p} dx_j$$

- **Substitute back to the Gibbs-Duhem Equation**

$$0 = - \left(\frac{\partial \underline{\theta}}{\partial T} \right)_{p, N_i} dT - \left(\frac{\partial \underline{\theta}}{\partial p} \right)_{T, N_i} dp$$

$$+ \sum_{j=1}^c x_j \left[\left(\frac{\partial \bar{\theta}_i}{\partial T} \right)_{p, \underline{x}} dT + \left(\frac{\partial \bar{\theta}_i}{\partial p} \right)_{T, \underline{x}} dp - \sum_{j=1}^{c-1} \left(\frac{\partial \bar{\theta}_i}{\partial x_j} \right)_{T, p} dx_j \right]$$

$$- \left(\frac{\partial \underline{\theta}}{\partial T} \right)_{p, N_i} dT - \left(\frac{\partial \underline{\theta}}{\partial p} \right)_{T, N_i} dp + \sum_i^c x_i d\bar{\theta}_i = 0$$

Partial Molar Property

- **Since**

$$\sum_{i=1}^c x_i \left(\frac{\partial \bar{\theta}_i}{\partial T} \right)_{p, \underline{x}} dT = \frac{\partial}{\partial T} \bigg|_{p, \underline{x}} \left(\sum_{i=1}^c x_i \bar{\theta}_i \right) dT = \left(\frac{\partial \theta}{\partial T} \right)_{p, \underline{x}} dT$$

- **Finally**

$$\sum_{i=1}^e x_i \sum_{j=1}^{e-1} \left(\frac{\partial \bar{\theta}_i}{\partial x_j} \right)_{T, P} dx_j = 0$$

- **For Binary**

$$\sum_{i=1}^2 x_i \sum_{j=1}^{c-1} \left(\frac{\partial \bar{\theta}_i}{\partial x_1} \right)_{T, P} dx_1 = 0 \quad x_1 \left(\frac{\partial \bar{\theta}_1}{\partial x_1} \right)_{T, P} + x_2 \left(\frac{\partial \bar{\theta}_2}{\partial x_1} \right)_{T, P} = 0$$

From calculus, partial differentiation x_i must be infinitely small and can not change independently !

Ideal-Gas Mixtures

- **Ideal gas** $p = \frac{nRT}{V^t}$ $p_i = \frac{n_i RT}{V^t}$

$$\frac{p_i}{p} = \frac{n_i}{n} = y_i \quad \text{or} \quad p_i = y_i p \quad (i = 1, 2, \dots, N)$$

- p_i is known as the *partial pressure* of species i

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

$$\frac{RT}{P} \left(\frac{\partial n}{\partial n_i} \right)_{n_j} = \frac{RT}{P}$$

Ideal-Gas Mixtures

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

$$\overline{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i) \text{ when } M_i^{ig} \neq V_i^{ig}$$

Ideal-Gas Mixtures

- Since the enthalpy of an ideal gas is **independent** of pressure,

$$\underline{H}_i^{ig}(T, p_i) = H_i^{ig}(T, p)$$

$$\underline{H}_i^{ig}(T, p) = H_i^{ig}(T, p)$$

$$H_i^{ig} = H_i^{ig} \text{ (pure value at mixture } T, p)$$

$$H^{ig} = \sum_i y_i H_i^{ig}$$

- For ideal gases, this *enthalpy change of mixing* is zero.

Ideal-Gas Mixtures

- The entropy of an ideal gas **does** depend on pressure, is given as

$$dS_i^{ig} = R d \ln p \quad \text{at const } T$$

$$dH = -TdS + Vdp + \sum_{i=1}^r \mu_i dn_i$$
$$dS|_{T,n_i} = \frac{V}{T} dp = \frac{R}{p} dp = R \ln p$$

- Therefore, **integration** from p_i to p

$$S_i^{ig}(T, p) - S_i^{ig}(T, p_i) = -R \ln \frac{p}{p_i} = R \ln y_i$$

$$\Delta S = n c_p \ln \frac{T_2}{T_1} - n R \ln \frac{p_2}{p_1}$$

Ideal-Gas Mixtures

- **Recall** $\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i)$ when $M_i^{ig} \neq V_i^{ig}$
- **Therefore,**

$$\bar{S}_i^{ig}(T, p) = S_i^{ig}(T, p) - R \ln y_i$$

$$\bar{S}_i^{ig} = S_i^{ig} - R \ln y_i$$

- **Where S_i^{ig} is the pure-species value at the mixture T and P .**

Ideal-Gas Mixtures

- **By the summability relation**

$$S^{ig} = \sum_i y_i \bar{S}_i^{ig} - R \sum_i y_i \ln y_i$$

$$S^{ig} - \sum_i y_i \bar{S}_i^{ig} = R \sum_i y_i \ln \frac{1}{y_i}$$

- **the left side of the second equation is the *entropy change of mixing* for ideal gases. Since $1/y_i > 1$, this quantity is always positive, **in agreement with the second law.****

Ideal-Gas Mixtures

- For the Gibbs energy of an ideal-gas mixture $G^{ig} = H^{ig} - TS^{ig}$,
- for partial properties is

$$\overline{G}_i^{ig} = \overline{H}_i^{ig} - T\overline{S}_i^{ig}$$

$$\overline{G}_i^{ig} = \overline{H}_i^{ig} - T\overline{S}_i^{ig} + RT \ln y_i$$

$$\mu_i^{ig} \equiv \overline{G}_i^{ig} = G_i^{ig} + RT \ln y_i$$

Recap Mixture/solution

- Gibbs free energy of a multicomponent mixture
- Chemical Potential
- Partial Molar Property
- Partial Pressure of Ideal-Gas
- Ideal-Gas Mixtures
 - enthalpy of an ideal gas
 - entropy of an ideal gas
- Gibbs energy of an ideal-gas mixture $G^{ig} = H^{ig} - TS^{ig}$,