

# **Thermodynamics**

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# Extensive Function

- A macroscopic property is extensive if it depends linearly on the size of the system
- Consider the internal energy  $E$ , which is extensive, how it depends upon  $S$  and  $\underline{X}$ , which are also extensive.

$$E(\lambda S, \lambda \underline{X}) = \lambda E(S, \underline{X})$$

- Thus,  $E(S, \underline{X})$  is a first order homogeneous function of  $S$  and  $\underline{X}$ .

# Extensive Function

- Euler's theorem gives,

$$\begin{aligned} E &= (\partial E / \partial S)_{\underline{X}} S + (\partial E / \partial \underline{X})_S \underline{X} \\ &= TS + \underline{f} \cdot \underline{X} \end{aligned}$$

- And work is

$$\underline{f} \cdot d\underline{X} = -pdV + \sum \mu_i dn_i$$

- This flow naturally to give,

$$dE = TdS - pdV + \sum_{i=1}^r \mu_i dn_i$$

# Extensive Function

- This is,  $E = E(S, V, n_1, \dots, n_r)$ , and Euler's theorem yields

$$E = TS - pV + \sum_{i=1}^r \mu_i dn_i$$

- Its total differential is

$$dE = TdS + SdT - pdV - Vdp + \sum_{i=1}^r (\mu_i dn_i + n_i d\mu_i)$$

- Therefore,

$$0 = SdT - Vdp + \sum_{i=1}^r (n_i d\mu_i)$$

**This is the Gibbs-Duhem Equation**

# Extensive Function

- Recall the definition of Gibbs free energy

$$G = E - TS - (-pV)$$

- Apply Euler's theorem gives,

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

- For one component system  $\mu = G/n$ ,  
Gibbs free energy per mole

# 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

- **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,**

$$\begin{aligned} dG &= \left( \frac{\partial G}{\partial T} \right)_{P, N_i} dT + \left( \frac{\partial G}{\partial P} \right)_{P, N_i} dP + \sum_i^c \left( \frac{\partial G}{\partial N_i} \right)_{P, N_i} dN_i \\ &= -SdT + VdP + \sum_i^c \bar{G}_i dN_i \end{aligned} \quad \text{(CP1)}$$

# 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

$$d(nG)^{\alpha} = -(nS)^{\alpha} dT + (nV)^{\alpha} dp + \sum_{i=1} \mu_i^{\alpha} dn_i^{\alpha}$$

$$d(nG)^{\beta} = -(nS)^{\beta} dT + (nV)^{\beta} dp + \sum_{i=1} \mu_i^{\beta} dn_i^{\beta}$$

# Chemical Potential and Phase Equilibrium

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

$$d(nG) = -(nS)dT + (nV)dp + \sum_{i=1} \mu_i^{\alpha} dn_i^{\alpha} + \sum_{i=1} \mu_i^{\beta} dn_i^{\beta}$$

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

# 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 ( $\theta$ )

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

- It is a *response function*, representing the change of total property  $\theta$  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,

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

# Partial Molar Property

- Or

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

So that, by the product rule of differentiation,

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

- 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**

# 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  $\theta$  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,**

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

- **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,**

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

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

$$0 = - \left( \frac{\partial \bar{\theta}_i}{\partial T} \right)_{p, N_i} dT - \left( \frac{\partial \bar{\theta}_i}{\partial p} \right)_{T, N_i} dp + \sum_{j=1}^C x_i \left[ \left( \frac{\partial \bar{\theta}_i}{\partial T} \right)_{p, \underline{x}} dT + \left( \frac{\partial \bar{\theta}_i}{\partial p} \right)_{T, \underline{x}} dp + \sum_{j=1}^{C-1} \left( \frac{\partial \bar{\theta}_i}{\partial x_j} \right)_{T, p} d\underline{x}_j \right]$$

# 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**

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

- **For Binary**

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

# Ideal-Gas Mixtures

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

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

- $p_i$  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

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

- 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

$$S_i^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

$$S_i^{ig} - \sum_i y_i S_i^{ig} = R \sum_i y_i \ln \frac{1}{y_i}$$

- 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

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

$$\overline{G}_i^{ig} = H_i^{ig} - TS_i^{ig} + RT \ln y_i$$

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

# 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  $G^{ig} = H^{ig} - TS^{ig}$ ,