Thermodynamics II

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Recap Mixture/solution

- From postulate of internal energy to the definition of heat and the First Law.

$$dE = d\!\!\!/Q + d\!\!\!/W$$

- From the Newton's Second Law

$$d\!\!\!/W = \underline{f} \; d\underline{X}$$

- In the reversible case plus

$$\underline{f} \; d\underline{X} = -pdV + \sum_i m_i dn_i$$

Recap Mixture/solution

- **From postulate of entropy to the definition of temperature**

$$(\P S / \P E)_{\underline{X}} > 0, \text{ or } (\P E / \P S)_{\underline{X}} \neq 0$$

$$T \equiv (\P E / \P S)_{\underline{X}} \neq 0$$

- **and the Second Law**

$$dS = (1/T)dE - (\underline{f} / T)\ d\underline{X}$$

$$dE = TdS + \underline{f}\ d\underline{X}$$

$$(\Delta S)_{adiabatic} \neq 0$$

Recap Mixture/solution

- **Combine the First and Second Law,**
- **Euler's theorem lead to Gibbs-Duhem Equation**
- **From the Legendre transformation lead to Helmholtz free energy**
- **And Gibbs free energy**

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

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

$$dA = -SdT - pdV + \sum_{i=1}^{r} m_i dn_i$$

$$dG = -SdT - Vdp + \sum_{i=1}^{r} m_i dn_i$$

Recap Mixture/solution

- From the definition of chemical potential,
- we introduced partial molar property
- This allow the calculation of mixture properties at a small deviation

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

$$\overline{V}_i = \left[\frac{\partial (nV)}{\partial n_i}\right]_{p,T,n_{i\neq j}}$$

$$dv\big|_{T,p} = \overline{V}_1 dn_1 + \overline{V}_2 dn_2 + \cdots,$$

$$V\big|_{T,p} = \overline{V}_1 n_1 + \overline{V}_2 n_2 + \cdots.$$

Recap Mixture/solution

- **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.**
- **This leads to**

$$\overline{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i) \quad when\ M_i^{ig} \;„\; V_i^{ig}$$

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

Nonideal gas mixtrures

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