Intensive Properties

- So far, mostly written equations/laws in terms of extensive properties
  - easily applied to constant composition CM systems
- For open CV systems and reacting/phase change processes, more convenient to work with intensive (e.g., mole or mass specific) properties
  - applicable to all systems (closed too)
- Examine mole specific properties
  - **molar property** ≡ property of substance per mole of mixture
  - **partial molar property** ≡ property of substance per mole of one species in mixture

Molar Properties of Mixture

- Examples

$$\hat{u} \equiv U/n;\ \hat{s} \equiv S/n;\ \hat{h} \equiv H/n;\ \hat{v} \equiv V/n$$

- What do state equations look like for molar properties?
- Gibb's equation example

$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

  - extensive properties in terms of molar properties

$$dU = \hat{u}dn + nd\hat{u} \qquad dS = \hat{s}dn + nd\hat{s} \qquad dV = \hat{v}dn + nd\hat{v}$$

  - so Gibb's becomes

$$nd\hat{u} + \hat{u}dn = Tnd\hat{s} + T\hat{s}dn - pnd\hat{v} - p\hat{v}dn + \sum_i \mu_i dn_i$$

$$nd\hat{u} = Tnd\hat{s} - pnd\hat{v} + \sum_i \mu_i dn_i - \underbrace{\left(\hat{u} - T\hat{s} + p\hat{v}\right)}_{\equiv \hat{g} = G/n} dn$$

Molar Properties of Mixture

- So $$d\hat{u} = Td\hat{s} - pd\hat{v} - \frac{1}{n}\left(\frac{G}{n}dn - \sum_i \mu_i dn_i\right)$$
  - use $n = \sum_i n_i$; $dn = \sum_i dn_i$ and $G = \sum_i \mu_i n_i$

$$d\hat{u} = Td\hat{s} - pd\hat{v} - \underbrace{\left(\sum_i \frac{dn_i}{n}\left\{\left(\sum_j n_j \mu_j\right)\Big/ n - \mu_i\right\}\right)}$$

  - with $n_i = \chi_i n$
    $\Rightarrow$ $dn_i = \chi_i dn + n d\chi_i$

$$= \sum_i \left[\left(\chi_i \frac{dn}{n} + d\chi_i\right)\left(\sum_j \chi_j \mu_j - \mu_i\right)\right]$$

$$= \sum_i \left[\chi_i \frac{dn}{n}\sum_j \chi_j \mu_j - \chi_i \frac{dn}{n}\mu_i + d\chi_i \sum_j \chi_j \mu_j - d\chi_i \mu_i\right]$$

$$= \left[\sum_j \chi_j \mu_j \left(\frac{dn}{n}\underbrace{\sum_i \chi_i}_{1} + \underbrace{\sum_i d\chi_i}_{0}\right) - \frac{dn}{n}\sum_i \chi_i \mu_i - \sum_i d\chi_i \mu_i\right]$$

Molar Properties of Mixture

- So $$d\hat{u} = Td\hat{s} - pd\hat{v} - \left[\left(\frac{dn}{n}\right)\underbrace{\left\{\sum_j \chi_j \mu_j - \sum_i \chi_i \mu_i\right\}}_{0} - \sum_i d\chi_i \mu_i\right]$$

$$\boxed{d\hat{u} = Td\hat{s} - pd\hat{v} + \sum_i \mu_i d\chi_i}$$

$$d\hat{u} = Td\hat{s} - pd\hat{v}$$

for single component substance

- Similarly

$$\boxed{d\hat{h} = Td\hat{s} + \hat{v}dp + \sum_i \mu_i d\chi_i}$$

$$d\hat{h} = Td\hat{s} + \hat{v}dp$$

$$\boxed{d\hat{g} = d\mu = -\hat{s}dT + \hat{v}dp + \sum_i \mu_i d\chi_i}$$

$$d\hat{g} = -\hat{s}dT + \hat{v}dp$$

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Partial Molar Properties

- Let B be any extensive property
  - then partial molar version of B is
  - note, it is possible for $\hat{b}_i \neq \bar{b}_i \neq \hat{b}_{i,pure}$

$$\boxed{\bar{b}_i \equiv \left.\frac{\partial B}{\partial n_i}\right|_{p,T,n_{j\neq i}}}$$

- For fixed conditions (T, p) , can apply same proof used to examine Gibbs Free Energy

$$B(T,p,\lambda n_1,\lambda n_2,\ldots)=\lambda B(T,p,n_1,n_2,\ldots)$$

  - take partial derivative with respect to λn_i
  - then let λ=1

$$B=\sum_i \left.\frac{\partial B}{\partial n_i}\right|_{T,p,n_{j\neq i}} n_i$$

$$\boxed{B=\sum_i \bar{b}_i n_i}$$

$\bar{b}_i$ is B per mole of i in mixture, for given mixture composition

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Partial Molar Property Example

- Take partial molar of enthalpy

$$\left.\frac{\partial H}{\partial n_i}\right|_{p,T,n_{j\neq i}}=\left.\frac{\partial (U+pV)}{\partial n_i}\right|_{p,T,n_{j\neq i}}=\left.\frac{\partial U}{\partial n_i}\right|_{p,T,n_{j\neq i}}+p\left.\frac{\partial V}{\partial n_i}\right|_{p,T,n_{j\neq i}}$$

note: no p partial deriv. because p held constant

- So $\bar{h}_i=\bar{u}_i+p\,\bar{v}_i$
- Similarly $\bar{g}_i=\bar{h}_i-T\,\bar{s}_i=\mu_i$

already showed

$$\mu_i=\left.\frac{\partial G}{\partial n_i}\right|_{p,T,n_{j\neq i}}\equiv \bar{g}_i$$

  - Maxwell Relations (reciprocity) $-\bar{s}_i=-\left.\frac{\partial S}{\partial n_i}\right|_{T,p,n_{j\neq i}}=\left.\frac{\partial \mu_i}{\partial T}\right|_{p,\chi_i,\chi_j}$
  - so also $\bar{g}_i=\bar{h}_i+T\left.\frac{\partial \mu_i}{\partial T}\right|_{p,\chi_i,\chi_j}$

Partial Molar State Equations

- What are differential equations of state in terms of partial molar quantities
- Example Gibbs Free Energy (based on T, p)

$$d\bar{g}_i = d\mu_i = \left.\frac{\partial \mu_i}{\partial p}\right|_{T,\chi_j} dp + \left.\frac{\partial \mu_i}{\partial T}\right|_{p,\chi_j} dT + \sum_{k=1}^{m-1} \left.\frac{\partial \mu_i}{\partial \chi_k}\right|_{T,p,\chi_{j\neq k}} d\chi_k$$

again from Maxwell Relations

$$= \left.\frac{\partial V}{\partial n_i}\right|_{T,p,n_{j\neq i}} \equiv \bar{v}_i \qquad = -\bar{s}_i$$

$$\boxed{d\bar{g}_i = d\mu_i = \bar{v}_i dp - \bar{s}_i dT + \sum_{k=1}^{m-1} \left.\frac{\partial \mu_i}{\partial \chi_k}\right|_{T,p,\chi_{j\neq k}} d\chi_k}$$

  - compare to molar version $\quad d\hat{g} = d\mu = \hat{v}dp - \hat{s}dT + \sum_{i=1}^{m} \mu_i d\chi_i$

Partial Molar State Equations

- Similarly

$$\boxed{d\bar{u}_i = T_i d\bar{s}_i - p d\bar{v}_i + \sum_{k=1}^{m-1} \left.\frac{\partial \mu_i}{\partial \chi_k}\right|_{T,p,\chi_{j\neq k}} d\chi_k} \quad \boxed{d\bar{h}_i = T_i d\bar{s}_i + \bar{v}_i dp + \sum_{k=1}^{m-1} \left.\frac{\partial \mu_i}{\partial \chi_k}\right|_{T,p,\chi_{j\neq k}} d\chi_k}$$

- All these differential state equations give *relative change* in property from one state to another
  - okay, that is usually what we need to know
  - also consistent, e.g., can't define absolute energy in TD
  - "absolute" values of u, h, g often reported, but based on some (arbitrarily chosen) datum where u (or h) and s =0
    - example datum: u (298 K, 1 bar) = 0
  - for chemically reacting systems with different compositions, can define arbitrary composition datum
    - certain species defined to have "zero" chemical energy