Some Interesting Factoids Regarding Partial Molar Quantities

1 . State function differentials for systems of variable composition

$$U(S,V,n_1,....,n_N) \qquad dU = TdS - PdV + \sum_{i=1}^{N}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j\neq n_i} dn_i$$

$$H(S,P,n_1,....,n_N) \qquad dH = TdS + VdP + \sum_{i=1}^{N}\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j\neq n_i} dn_i$$

$$A(T,V,n_1,....,n_N) \qquad dA = -SdT - PdV + \sum_{i=1}^{N}\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j\neq n_i} dn_i$$

$$G(T,P,n_1,....,n_N) \qquad dG = -SdT + VdP + \sum_{i=1}^{N}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j\neq n_i} dn_i$$

2 . The partial molar Gibbs free energy, the chemical potential plays a central role

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

thus

$$dG = -SdT + VdP + \sum_{i=1}^{N}\mu_i dn_i$$

also

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j\neq n_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j\neq n} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j\neq n} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j\neq n}$$

PROOF:

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i$$

$$dG = dH - TdS - SdT$$

$$dH = TdS + VdP + \sum_{i=1}^{N} \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i} dn_i$$

$$\underbrace{-SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i}_{dG} = \underbrace{TdS + VdP + \sum_{i=1}^{N} \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i} dn_i}_{dH} - TdS - SdT$$

$$-SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i = TdS + VdP + \sum_{i=1}^{N} \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i} dn_i - TdS - SdT$$

$$\sum_{i=1}^{N} \left(\mu_i - \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i} \right) dn_i = 0$$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i}$$

and similarly for

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j \neq n} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq n}$$

3. **An extensive property of a multi-component system is the sum of partial molar contributions from each of the components**

$$V_{total} = \sum_{i}^{N} n_i \bar{V}_i = n_1 \bar{V}_1 + n_2 \bar{V}_2 + \cdots$$

$$G = \sum_{i}^{N} n_i \bar{G}_i$$

$$H = \sum_{i}^{N} n_i \bar{H}_i \quad note: \bar{H} \quad note: \bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq n_i} \neq \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i} = \mu_i$$

etc

PROOF: ***[done for partial molar volume; holds for any extensive state function]***

At constant T and P the volume of the material will change by a factor of λ if the number of moles of each component is changed by the same factor λ.

$$\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right) = \lambda \mathrm{V}_{T,P}\left(n_1, n_2, n_3\ \ldots\right)$$

taking the differential of the l.h.s. (V is state function):

$$d\left[\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right)\right] = \sum_i \left(\frac{\partial\left[\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right)\right]}{\partial\left(\lambda n_i\right)}\right)_{T.P,\lambda n_{j\neq i}} d\left(\lambda n_i\right)$$

and "dividing" by $\partial\lambda$ n_{ALL} constant

$$\left(\frac{\partial\left[\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right)\right]}{\partial\lambda}\right)_{n_{ALL}} = \sum_i \left(\frac{\partial\left[\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right)\right]}{\partial\left(\lambda n_i\right)}\right)_{T.P,\lambda n_{j\neq i}} \left(\frac{\partial \lambda n_i}{\partial\lambda}\right)_{n_{ALL}}$$

$$\left(\frac{\partial\left[\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right)\right]}{\partial\lambda}\right)_{n_{ALL}} = \sum_i \left(\frac{\partial\left[\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right)\right]}{\partial\left(\lambda n_i\right)}\right)_{T.P,\lambda n_{j\neq i}} n_i$$

taking the derivative of the r.h.s. w.r.t λ:

$$\left(\frac{\partial\left[\lambda \mathrm{V}_{T,P}\left(n_1, n_2, n_3\ \ldots\right)\right]}{\partial\lambda}\right)_{n_{ALL}} = \mathrm{V}_{T,P}\left(n_1, n_2, n_3\ \ldots\right)$$

equating the two derivatives and setting λ=1:

$$\mathrm{V}_{T,P}\left(n_1, n_2, n_3\ \ldots\right) = \sum_i \left(\frac{\partial\left[\mathrm{V}_{T,P}\left(\lambda n_1, \lambda n_2, \lambda n_3\ \ldots\right)\right]}{\partial\left(\lambda n_i\right)}\right)_{T.P,\lambda n_{j\neq i}} n_i$$

setting $\lambda=1$

$$\mathrm{V}_{T,P}\left(n_1, n_2, n_3\ \ldots\right) = \sum_i \left(\frac{\partial\left[\mathrm{V}_{T,P}\left(n_1, n_2, n_3\ \ldots\right)\right]}{\partial n_i}\right)_{T.P,n_{j\neq i}} n_i = \sum_i n_i \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$\mathrm{V}_{T,P}\left(n_1, n_2, n_3\ \ldots\right) = \sum_i n_i \bar{V}_i \quad \text{Q.E.D}$$

we obtain the desired result !!!

4 . **Relationships among thermodynamic quantities derived for one-component systems often hold for partial molar quantities**

$$G \equiv H - TS \quad \Rightarrow \quad \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

or

$$H \equiv U + PV \quad \Rightarrow \quad \bar{H}_i = \bar{U}_i + P\bar{V}_i$$

proofs

$$dG = dH - TdS - SdT$$

"divide by dn_i holding $T, P, n_j \neq n_i$ constant"

$$\underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\bar{G}_i} = \underbrace{\left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\bar{H}_i} - T\underbrace{\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\bar{S}_i} - S\underbrace{\left(\frac{\partial T}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{=0}$$

$$\bar{G}_i = \bar{H}_i - T\bar{S}_i \qquad \text{Q.E.D}$$

and

$$dH = dU + PdV + VdP$$

"divide by dn_i holding $T, P, n_j \neq n_i$ constant"

$$\underbrace{\left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\bar{H}_i} = \underbrace{\left(\frac{\partial U}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\bar{U}_i} + P\underbrace{\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\bar{V}_i} + V\underbrace{\left(\frac{\partial P}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{=0}$$

$$\bar{H}_i = \bar{U}_i + P\bar{V}_i \qquad \text{Q.E.D}$$

another example and another technique

we have shown:

$$\left(\frac{\partial G}{\partial T}\right)_{P,n_{all}} = -S$$

Prove:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_{all}} = -\bar{S}_i = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j \neq n_i}$$

so

$$\left(\frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial T}\right)_{P,n_{all}}\right]\right)_{T,P,n_j \neq n_i} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j \neq n}$$

reverse order of differentiation

$$\left(\frac{\partial}{\partial T}\left[\underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\mu_i}\right]\right)_{P,n_{all}} = \underbrace{-\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j \neq n}}_{\bar{S}_i}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_{all}} = -\bar{S}_i$$

5 . **The Gibbs-Duhem relationship shows that partial molar quantities for substances in a mixture can not vary independently**

in general:

$$\sum_{i=1}^{N} X_i \left(\frac{\partial \bar{Q}_i}{\partial n_k}\right)_{T,P,n_j \neq n_k} = 0$$ where $\bar{Q}_i$ is partial molar value of property Q for component ***i***

and n_k is number of moles of any **one** component

example: $\bar{V}_i$ for a two component mixture e.g. EtOH + H_2O

$$X_A \left(\frac{\partial \bar{V}_A}{\partial n_B}\right)_{T,P,n_A} + X_B \left(\frac{\partial \bar{V}_B}{\partial n_B}\right)_{T,P,n_A} = 0$$

$$X_A \left(\frac{\partial \bar{V}_A}{\partial n_B}\right)_{T,P,n_A} = -X_B \left(\frac{\partial \bar{V}_B}{\partial n_B}\right)_{T,P,n_A}$$

$$X_{H_2O} \left(\frac{\partial \bar{V}_{H_2O}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}} = -X_{EtOH} \left(\frac{\partial \bar{V}_{EtOH}}{\partial n_{EtOH}}\right)_{T,P,n_{H_2O}}$$

[note : the variation is with respect to one of the components (∂n_{EtOH} in both denominators)]

PROOF:

$$V = \sum_{i=1}^{N} n_i \bar{V}_i \quad \text{see factoid 3}$$

$$dV = \sum_{i=1}^{N} \left(n_1 d\bar{V}_i + \bar{V}_i dn_i \right)$$

and with $V\left(T, P, n_1, \cdots, n_N\right)$ also

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n_{all}} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n_{all}} dP + \sum_{i=1}^{N} \underbrace{\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j \neq n_i}}_{\bar{V}_i} dn_i$$

at T and P constant

$$dV = \sum_{i=1}^{N} \bar{V}_i dn_i$$

thus

$$\sum_{i=1}^{N} \left(n_i d\bar{V}_i + \bar{V}_i dn_1 \right) = \sum_{i=1}^{N} \bar{V}_i dn_i$$

and

$$\sum_{i=1}^{N} n_i d\bar{V}_i = 0$$

divide every term by ∂n_A with T,P, $n_j \neq n_A$ constant

$$\sum_{i=1}^{N} n_i \left(\frac{\partial \bar{V}_i}{\partial n_A}\right)_{T,P,n_j \neq n_A} = 0$$

divide each term by n_{total} with $X_i = \frac{n_i}{n_{total}}$

$$\sum_{i=1}^{N} X_i \left(\frac{\partial \bar{V}_i}{\partial n_A}\right)_{T,P,n_j \neq n_A} = 0 \qquad \text{Q.E.D.}$$

note the derivative of every $\bar{V}_i$ is with respect to the same composition variable n_A