Mathematical Property Relationships

- We have started to define certain TD properties
  - $m, V, U, S, T, p, H, G, F$
- and the relationships between them
  - state relationships/equations
- How can we use basic mathematical **identities** to help
- For example,

$$dS = dU/T + p/T\,dV + \frac{1}{T}\sum_{i=1}^{k}\mu_i dn_i \Rightarrow dU = TdS - pdV + \sum_{i=1}^{k}\mu_i dn_i$$

- Similarly

$$H = U + pV \Rightarrow \qquad dH = TdS + Vdp + \sum_{i=1}^{k}\mu_i dn_i$$

$$G = H - TS \Rightarrow \qquad dG = Vdp - SdT + \sum_{i=1}^{k}\mu_i dn_i$$

$$F = U - TS \Rightarrow \qquad dF = -SdT - pdV + \sum_{i=1}^{k}\mu_i dn_i$$

Identities

$$dU = TdS - pdV + \sum_{i=1}^{k}\mu_i dn_i \qquad dH = TdS + Vdp + \sum_{i=1}^{k}\mu_i dn_i$$

$$dG = Vdp - SdT + \sum_{i=1}^{k}\mu_i dn_i \qquad dF = -SdT - pdV + \sum_{i=1}^{k}\mu_i dn_i$$

- These are exact differentials, so we can deduce the following (i.e., from $dZ = \left.\frac{\partial Z}{\partial X}\right|_Y dX + \ldots$)

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,n_i} = \left.\frac{\partial H}{\partial S}\right|_{p,n_i} \qquad p = -\left.\frac{\partial U}{\partial V}\right|_{S,n_i} = -\left.\frac{\partial F}{\partial V}\right|_{T,n_i}$$

$$V = \left.\frac{\partial H}{\partial p}\right|_{S,n_i} = \left.\frac{\partial G}{\partial p}\right|_{T,n_i} \qquad S = -\left.\frac{\partial G}{\partial T}\right|_{p,n_i} = -\left.\frac{\partial F}{\partial T}\right|_{V,n_i}$$

van't Hoff Relation

- Consider $\left.\dfrac{\partial}{\partial T}\left(\dfrac{G}{T}\right)\right)_{p,n_i} = \left.\dfrac{\partial G}{\partial T}\right|_{p,n_i}\dfrac{1}{T} + G\left.\dfrac{\partial(1/T)}{\partial T}\right|_{p,n_i}$

$$= -S\frac{1}{T} + G\left(-\frac{1}{T^2}\right)$$

$$= (-TS - G)/T^2$$

$$\boxed{\left.\frac{\partial(G/T)}{\partial T}\right|_{p,n_i} = \frac{-H}{T^2}}$$

- Then for 2 states with same T

$$\left.\frac{\partial(G_2/T)}{\partial T}\right|_{p,n_i} - \left.\frac{\partial(G_1/T)}{\partial T}\right|_{p,n_i} = \frac{-H_2}{T^2} - \frac{-H_1}{T^2}$$

$$\left.\frac{\partial((G_2-G_1)/T)}{\partial T}\right|_{p,n_i} = \frac{-(H_2-H_1)}{T^2} \Rightarrow \left.\frac{\partial(\Delta G_{12}/T)}{\partial T}\right|_{p,n_i} = \frac{-\Delta H_{12}}{T^2}$$

Maxwell Relations

- For smooth, continuous functions, we have the following relation from Calculus
  - if we can write an exact differential

$$dF = x_1 dy_1 + x_2 dy_2 + \ldots + x_i dy_i \qquad x_1 = \left.\frac{\partial F}{\partial y_1}\right|_{y_{j\neq 1}};\ etc.$$

  - then

$$\left.\frac{\partial x_i}{\partial y_j}\right|_{y_{k\neq j}} = \left.\frac{\partial x_j}{\partial y_i}\right|_{y_{k\neq i}}$$

Reciprocity Relation

- Apply this to previous exact differentials (dU, dH, etc.)

$dU = TdS - pdV + \sum_{i=1}^{k}\mu_i dn_i \Rightarrow$

$$\boxed{\left.\frac{\partial T}{\partial V}\right|_{S,n_i} = -\left.\frac{\partial p}{\partial S}\right|_{V,n_i} \qquad \left.\frac{\partial V}{\partial T}\right|_{p,n_i} = -\left.\frac{\partial S}{\partial p}\right|_{T,n_i}}$$

$\Leftarrow dG = Vdp - SdT + ..$

$dH = TdS + Vdp + .. \Rightarrow$

$$\boxed{\left.\frac{\partial T}{\partial p}\right|_{S,n_i} = \left.\frac{\partial V}{\partial S}\right|_{p,n_i} \qquad \left.\frac{\partial p}{\partial T}\right|_{V,n_i} = \left.\frac{\partial S}{\partial V}\right|_{T,n_i}}$$

$\Leftarrow dF = -pdV - SdT + ..$

for simple compress. substance

Maxwell Relations

- Can get similar results from the chemical potential terms, e.g.,

$$dG = Vdp - SdT + \sum \mu_i dn_i \Rightarrow \quad \left.\frac{\partial \mu_i}{\partial p}\right|_{T,\cancel{n_i,n_j}\ \chi_i,\chi_j} = \left.\frac{\partial V}{\partial n_i}\right|_{T,p,n_{j\neq i}}$$

$$dF = -pdV - SdT + \sum \mu_i dn_i \Rightarrow \quad \left.\frac{\partial \mu_i}{\partial T}\right|_{p,\cancel{n_i,n_j}\ \chi_i,\chi_j} = -\left.\frac{\partial S}{\partial n_i}\right|_{T,p,n_{j\neq i}}$$

Example

- One use of Maxwell Relations is construction of equation-of-state information
  – e.g., how to relate U to measureable properties (p, T, V)
- For non-reacting mixture, let's assume we can measure (T,V)

$$dU = \left.\frac{\partial U}{\partial T}\right|_V dT + \left.\frac{\partial U}{\partial V}\right|_T dV$$

  – Gibb's

$$dS = \frac{1}{T}dU + \frac{p}{T}dV \Rightarrow \quad dS = \underbrace{\frac{1}{T}\left.\frac{\partial U}{\partial T}\right|_V}_{=\left.\frac{\partial S}{\partial T}\right|_V} dT + \underbrace{\frac{1}{T}\left\{\left.\frac{\partial U}{\partial V}\right|_T + p\right\}}_{=\left.\frac{\partial S}{\partial V}\right|_T} dV$$

- From Maxwell Relations

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V \longrightarrow \boxed{\left.\frac{\partial U}{\partial V}\right|_T = T\left.\frac{\partial p}{\partial T}\right|_V - p}$$

so can use purely p, T information to find this derivative

Variable Transformations

- Another useful mathematical relation
  - *cyclic rule* (comes from chain rule)
- If we have a 3D surface function
  - $f(x, y, z) = 0$

    $\Rightarrow x = x(y, z);\ \ y = y(x, z)$ then $\boxed{\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial z}{\partial x}\right|_y \left.\frac{\partial y}{\partial z}\right|_x = -1}$
- Also $\boxed{\left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\left.\partial y/\partial x\right|_z}}$ $\boxed{\frac{\partial}{\partial z}\left(\frac{\partial x}{\partial y}\right) = \frac{\partial^2 x}{\partial y \partial z} = \frac{\partial}{\partial y}\left(\frac{\partial x}{\partial z}\right)}$
- Example: if we need $\left.\frac{\partial U}{\partial p}\right|_T$ and we know $\left.\frac{\partial T}{\partial U}\right|_p$ & $\left.\frac{\partial p}{\partial T}\right|_U$

$$\left.\frac{\partial U}{\partial p}\right|_T \cdot \left.\frac{\partial T}{\partial U}\right|_p \cdot \left.\frac{\partial p}{\partial T}\right|_U = -1 \Rightarrow \left.\frac{\partial U}{\partial p}\right|_T = -\left(\left.\frac{\partial T}{\partial U}\right|_p \cdot \left.\frac{\partial p}{\partial T}\right|_U\right)^{-1} = -\left.\frac{\partial U}{\partial T}\right|_p \cdot \left.\frac{\partial T}{\partial p}\right|_U$$