Lecture 3

Maxwell relations

Consider $f = f(x, y)$:

$$df = \underbrace{\left(\frac{\partial f}{\partial x}\right)_y}_{\equiv a} dx + \underbrace{\left(\frac{\partial f}{\partial y}\right)_x}_{\equiv b} dy$$

$$\Downarrow$$

$$\underbrace{\left(\frac{\partial a}{\partial y}\right)_x}_{=\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x} = \underbrace{\left(\frac{\partial b}{\partial x}\right)_y}_{=\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y}$$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$$

In particular,

one species for simplicity

(1) $dA = -S\,dT - p\,dV + \mu\,dn$ yields

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{V,n}$$ Maxwell relation

(2) $dG = -S\,dT + V\,dp + \mu\,dn$ yields

$$\left(\frac{\partial S}{\partial p}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

Ex. 1 Heat capacity:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,n}.$$

Then $\left(\frac{\partial C_V}{\partial V}\right)_{T,n} = T\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_{V,n}\right)_{T,n} =$

$$= T\left(\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial S}{\partial V}\right)_{T,n}}_{=\left(\frac{\partial p}{\partial T}\right)_{V,n}}\right)_{V,n} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_{V,n}.$$

Ex. 2 Consider $C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,n}$

Assume $n = \text{const}$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV, \quad \text{or}$$

$$\left(\frac{\partial S}{\partial T}\right)_{p,n} = \left(\frac{\partial S}{\partial T}\right)_V + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{=\left(\frac{\partial p}{\partial T}\right)_V}\left(\frac{\partial V}{\partial T}\right)_p,$$

$$\frac{C_p}{T} = \frac{C_V}{T} + \left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$$

now, consider $\begin{cases} f = f(x,y) \\ x = x(f,y) \\ y = y(f,x) \end{cases}$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy =$$

$$= \left(\frac{\partial f}{\partial x}\right)_y \left[\left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy \right] + \left(\frac{\partial f}{\partial y}\right)_x dy =$$

$$= \underbrace{\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial f}\right)_y}_{=1} df + \left[\underbrace{\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f + \left(\frac{\partial f}{\partial y}\right)_x}_{=0} \right] dy.$$

Hence, $$\boxed{\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1} \quad (*)$$

Using Eq. (*), we obtain:

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p, \text{ yielding}$$

$$C_p - C_V = -T\left(\frac{\partial p}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2$$

Isothermal compressibility:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

Coeff. of thermal expansion:

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Thus, $C_p - C_v = -T\left(-\frac{1}{\kappa_T V}\right)\left[\alpha_v V\right]^2 =$

$$= \frac{V T \alpha_v^2}{\kappa_T}.$$

Extensive functions

Def. Homogeneous f'n of degree n:

$$f(\lambda x) = \lambda^n f(x).$$

Note that $E(\lambda S, \lambda \vec{X}) = \lambda E(S, \vec{X})$:

$E(S, \vec{X}) \Rightarrow n=1$ homog. f'n of S & $\vec{X}$.

Now, consider $f(x_1, \ldots, x_n) \Rightarrow n=1$ homog. f'n of $x_1, \ldots, x_n$

If $u_i = \lambda x_i$,

$$f(u_1, \ldots, u_n) = \lambda f(x_1, \ldots, x_n).$$

Then
$$\left(\frac{\partial f(u_1, \ldots, u_n)}{\partial \lambda}\right)_{\underbrace{x_i}_{\text{all } x_i\text{'s fixed}}} = f(x_1, \ldots, x_n) \quad (1)$$

Further, $df(u_1, \ldots, u_n) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial u_i}\right)_{u_{j \neq i}} du_i$, or

$$\left(\frac{\partial f}{\partial \lambda}\right)_{x_i} = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial u_i}\right)_{u_j} \underbrace{\left(\frac{\partial u_i}{\partial \lambda}\right)_{x_i}}_{= x_i} \quad (2)$$

Combine (1) & (2):

$$f(x_1,\dots,x_n)=\sum_{i=1}^{n}\left(\frac{\partial f}{\partial u_i}\right)_{u_j} x_i \quad , \forall\lambda .$$

For $\lambda=1$, we have:

$$f(x_1,\dots,x_n)=\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)_{x_j} x_i .$$

<u>Euler's theorem</u>
for $n=1$ homog. f's

<u>Ex.</u> $f(x,y)=\alpha x+\beta y$
$\quad\quad '' \left(\frac{\partial f}{\partial x}\right)_y x+\left(\frac{\partial f}{\partial y}\right)_x y=\alpha x+\beta y .$

In particular,

$$E=\left(\frac{\partial E}{\partial S}\right)_{\vec{X}} S+\left(\frac{\partial E}{\partial \vec{X}}\right)_S\cdot\vec{X}=TS+\vec{f}\cdot\vec{X} .$$

If $\vec{f}\cdot d\vec{X}=-p\,dV+\sum_{i=1}^{r}\mu_i\,dn_i$, then

$$dE=T\,dS-p\,dV+\sum_i \mu_i\,dn_i$$
$$\hookrightarrow E=E(S,V,n_1,\dots,n_r)$$

Euler's theorem:

$$E=TS-pV+\sum_i\mu_i n_i$$

But then

$$dE = TdS + SdT - pdV - Vdp + \sum_i [\mu_i dn_i + n_i d\mu_i],$$

yielding

$$\underline{\underline{SdT - Vdp + \sum_i n_i d\mu = 0}}$$

↑

Gibbs–Duhem equation

Next, consider

$$G = E - TS + pV =$$

$$= (TS - pV + \sum_i \mu_i n_i) - TS + pV =$$

$$= \underline{\underline{\sum_i \mu_i n_i}} .$$

If $r = 1$, $\mu = \frac{G}{n} \Leftarrow \mu$ is G per mole

In general, if

$$X(T, p, \lambda n_1, \dots, \lambda n_r) = \lambda X(T, p, n_1, \dots, n_r) :$$

$$X(T, p, n_1, \dots, n_r) = \sum_{i=1}^{r} x_i n_i \quad , \text{where}$$

$$x_i = \left(\frac{\partial X}{\partial n_i}\right)_{T, p, n_{j \neq i}}$$

Intensive functions

are $n=0$ homog. f's of the extensive vars.

For ex., $p = p(S, V, n_1, \ldots, n_r) =$

$$= p(\lambda S, \lambda V, \lambda n_1, \ldots, \lambda n_r).$$

If $\lambda = \frac{1}{\sum_{i=1}^{r} n_i} = \frac{1}{n}$,

$$p = p\Big(\frac{S}{n}, \frac{V}{n}, \underbrace{\frac{n_1}{n}, \ldots, \frac{n_r}{n}}_{\text{mole fractions } x_i = \frac{n_i}{n}}\Big)$$

Note that $\sum_i x_i = 1$, giving

$$p = p\Big(\underbrace{\frac{S}{n}, \frac{V}{n}, x_1, \ldots, x_{r-1}}_{r+1 \text{ indep. vars}}, 1 - x_1 - \ldots - x_{r-1}\Big)$$

For extensive vars, $r+2$ vars are needed $\Rightarrow$ one less DoF for intensive vars b/c they are indep. of system size.