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Course 565/665 Lecture Number _____ Date 3/7/03

Lecturer Dr. Silvia Cavagnaro Note Taker Eric Fulmer

Last Time: Maxwell Relations

$$T = \left(\frac{\partial U}{\partial S} \right)_V ; \quad P = - \left(\frac{\partial U}{\partial V} \right)_S$$

$$\Rightarrow \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S$$

$$\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right)_S = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right)_V$$

Can Switch the Order

$$- \left(\frac{\partial P}{\partial S} \right)_S = \left(\frac{\partial T}{\partial V} \right)_S$$

← A Maxwell Relation

Correction To The Lecture

$$\frac{P}{T} = + \left(\frac{\partial S}{\partial V} \right)_{u, N}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial N_2} \right)_{u, N_1, T, V}$$

The signs were reversed.

After a show of democracy, the exam will remain at Friday, 5:30pm (and not moved to Thursday).
Vote 11 to 4.

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Procedure to Find the Desired Maxwell Relation

- ① Identify relevant independent variables.

$$\left(\frac{\partial S}{\partial P}\right)_{T,N}$$

↑ ↑ ↑

In this case $f(T, P, N)$, these are the independent variables in this case.

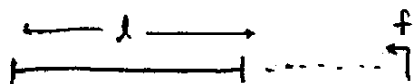
- ② Find the natural function for these independent variables.

$$G = G(T, P, N)$$

In this case, it is Gibbs free energy.

- ③ Write down the total differential for natural function. $G(T, P, N)$.

- ④ Based on the Euler relations, set mixed derivatives equal.

Course 565/665 Lecture Number _____ Date 3/7/03Lecturer Cavagnero Note Taker FulmerExample: The thermodynamics of a rubber band. f = retraction force (a restoring force) l = the length of rubber band.

$$dG = d(H - TS) = d(U + PV - TS)$$

$$= \cancel{TdS} - \cancel{PdV} + fdl + \cancel{PdV} + Vdp - \cancel{TdS} - SdT$$

$\underbrace{\hspace{2cm}}$
 We include this term because there is another work term in our system.

$$dG = -SdT + Vdp + fdl$$

At constant T, P $dG = fdl = \left(\frac{\partial G}{\partial l}\right)_{T,P} dl$

$$f = \left(\frac{\partial G}{\partial l}\right)_{T,P}$$

A Maxwell Relation:

$$-\left(\frac{\partial f}{\partial T}\right)_{l,N} = \left(\frac{\partial S}{\partial l}\right)_{T,N}$$

because:
$$-\frac{\partial^2 G}{\partial T \partial l} = -\frac{\partial^2 G}{\partial l \partial T}$$

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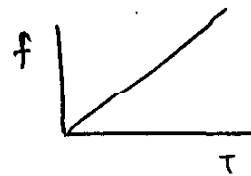
The fl work is just another type of work, just as PV is a type of work.

$$\delta W_{PV} = -P dV$$

$$\delta W_{fl} = f dl$$

In the case of the previous Maxwell relation,

$$-\left(\frac{\partial S}{\partial l}\right)_{T,P,N} = \left(\frac{\partial f}{\partial T}\right)_{l,T,N}$$



If the restoring force increases with an increase in T , then we know from the above relation that the entropy of the system decreases with the increase in length of the rubber band. This makes intuitive sense because the monomers are stretched out and thus more ordered in the band ($\Delta S < 0$).

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Thermal Expansion Coefficient

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Thermal Expansion Coefficient (α)

For an Ideal Gas

$$\alpha = \frac{P}{NkT} \cdot \frac{Nk}{P} = \frac{1}{T}$$

$$V = \frac{NkT}{P}$$

$$\alpha = \frac{1}{T}$$

for an Ideal Gas.

Measure V vs $T \Rightarrow$ get slope.

Isothermal Compressibility (κ)

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Isothermal Compressibility (κ)

Example 9.4: S vs. P changes.

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Course 565/665 Lecture Number _____ Date 3/7/03Lecturer Cavagnero Note Taker FulmerPartial Molar Quantities

→ Important when we talk about mixtures and systems with changes in N_j .

$$v = \frac{V}{n} \quad \# \text{ moles}$$

$$g = \frac{G}{n}$$

↳ partial molar volumes.

More Rigorously:

$$v_j = \left(\frac{\partial V}{\partial n_j} \right)_{T, P, n_i \neq j}$$

Partial Molar Volume.

For a multicomponent System:

$$dV = \sum_{j=1}^M \left(\frac{\partial V}{\partial n_j} \right)_{T, P, n_i \neq j} dn_j$$

$$dn_j = \sum_{j=1}^M v_j dn_j$$

EtOH + H₂O. A decrease in the apparent volume.
This is called electrostriction.

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How are partial molar quantities of different components related?

$$dV = \sum_{j=1}^M v_j dn_j \quad (1)$$

$$V = \sum_{j=1}^M n_j \left(\frac{\partial V}{\partial N_j} \right) = \sum_{j=1}^M n_j v_j$$

$$dV = \sum_{j=1}^M (n_j dv_j + v_j dn_j) \quad (2)$$

Set (1) = (2)

$$\sum_{j=1}^M n_j dv_j = 0$$

For ~~total~~ chemical potentials =

$$\sum_{j=1}^M N_j d\mu_j = 0$$

Gibbs-Duhem Relation.