

Lecture 14: 10.31.05 Batteries continued; Thermodynamic stability

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Reading:

- C.H.P. Lupis, *Chemical Thermodynamics of Materials*, 'Stability of one-component systems,' pp. 34-35.
- H.B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 'Stability of Thermodynamic Systems,' pp. 202-212
- Engel and Reid 6.2 (Maxwell relations)

Supplementary Reading: -

ANNOUNCEMENTS :

PS 5 WILL BE POSTED LATER TODAY ; DUE 1 WEEK FROM THIS THURS. (11/10/05)

Thermodynamics of a battery, continued

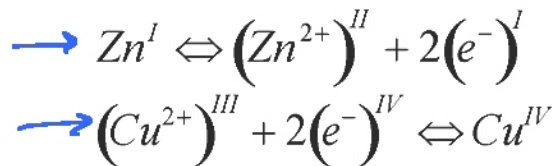
- Last time, we began the analysis of how a battery converts chemical work into electrical work (transport of electrons). This system introduces a new form of internal energy, arising from the transport of charged species, which is incorporated into the fundamental equation for a system as the electrochemical potential:

$$\tilde{\mu}_i = \mu_i + z_i F \phi_i = \mu_i^{\circ}(T) + RT \ln a_i + z_i F \phi_i$$

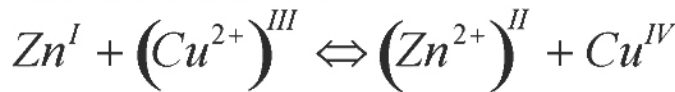
↑ VALENCY OF i
↑ POTENTIAL OF i

- The script F in this expression is the Faraday constant: $F = 96,485 \frac{C}{\text{mole } e^-}$
- We applied this new term for electrochemical potentials in our analysis of the Daniell cell.

Half-cell reactions:



Total reaction for system:



$$\Delta \bar{G}_{rxn} = \mu_{Cu}^{IV} + \tilde{\mu}_{Zn^{2+}}^{II} - \mu_{Zn}^I - \tilde{\mu}_{Cu^{2+}}^{III}$$

- We showed last time that the electrical potential difference obtained across the electrodes I and IV is related to the free energy of reaction by the Nernst Equation:

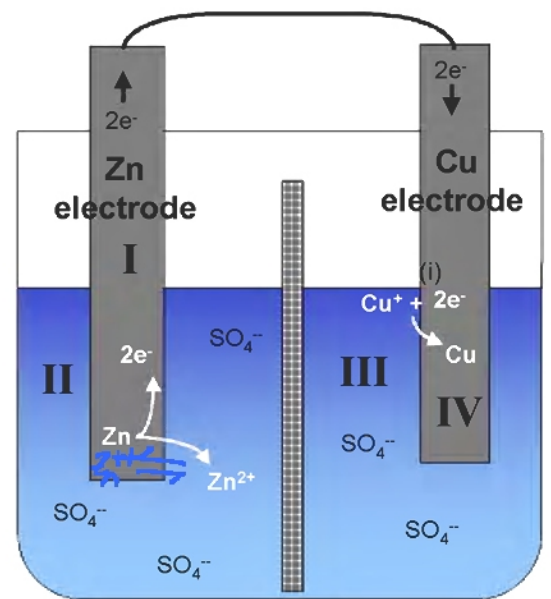
NERNST EQUATION:

$$\Delta \phi = - \frac{\Delta \bar{G}_{rxn}}{n F}$$

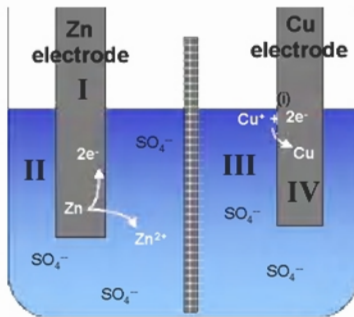
↑ # OF e^- TRANSPORTED PER MOLE OF Rxn

$$\Delta \bar{G}_{rxn} = \mu_{Cu}^{IV} + \underbrace{\mu_{Zn^{2+}}^{II} + 2 F \phi^{II}} - \mu_{Zn}^I - \underbrace{\mu_{Cu^{2+}}^{III} - 2 F \phi^{III}}$$

Daniell cell discharge reactions



- How can we further simplify this expression? Recall that we have **sulfate ion equilibration through the membrane between the aqueous solutions II and III:**



$$\left(\tilde{\mu}_{SO_4^{2-}}\right)^{II} = \left(\tilde{\mu}_{SO_4^{2-}}\right)^{III}$$

$$\mu_{SO_4^{2-}}^{II} - 2\phi^{II}F = \mu_{SO_4^{2-}}^{III} - 2\phi^{III}F \quad (c) \quad \phi^{II} = \phi^{III}$$

$$N_{SO_4^{2-}}^{II} \approx N_{SO_4^{2-}}^{III}$$

PURE SOLIDS!

$$\begin{aligned} \therefore \Delta \bar{G}_{RAN} &= N_{Cu}^{IV} + N_{Zn^{2+}}^{II} - N_{Zn}^I - N_{Cu^{2+}}^{III} \\ &= \Delta \bar{G}_{RAN}^{\circ} + RT \ln Q = \Delta \bar{G}_{RAN}^{\circ} + RT \ln \frac{a_{Cu}^{II} a_{Zn^{2+}}^{II}}{a_{Zn}^I a_{Cu^{2+}}^{III}} \end{aligned}$$

↑ RAN QUOTIENT

- For a reversible reaction, we call the potential difference the electromotive force, or EMF:

$$E \equiv EMF \equiv \Delta \phi_{TOT} = - \frac{\Delta \bar{G}_{RAN}}{nF}$$

STANDARD POTENTIAL!

$$E^{\circ} = - \frac{\Delta \bar{G}_{RAN}^{\circ}}{nF}$$

- The U.S. convention is that EMF is positive when reactions are written to proceed spontaneously from left to right (i.e. Zn is the left electrode).

FOR THE DANIELL CELL:

$$E = - \frac{\Delta \bar{G}_{RAN}}{2F} = - \frac{1}{2F} \left[\Delta \bar{G}_{RAN}^{\circ} + RT \ln \frac{a_{Zn^{2+}}^{II}}{a_{Cu^{2+}}^{III}} \right]$$

$$E = E^{\circ} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}^{II}}{a_{Cu^{2+}}^{III}} \rightarrow a_i = \gamma_i X_i$$

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \quad \dots \text{IN GENERAL}$$

An example calculation: Thermodynamics of a fuel cell

- Consider again a fuel cell similar to the one shown schematically in the last lecture notes. A more simplified schematic is shown below:

(Silbey et al.)

- The Half-cell reactions and overall reaction are:

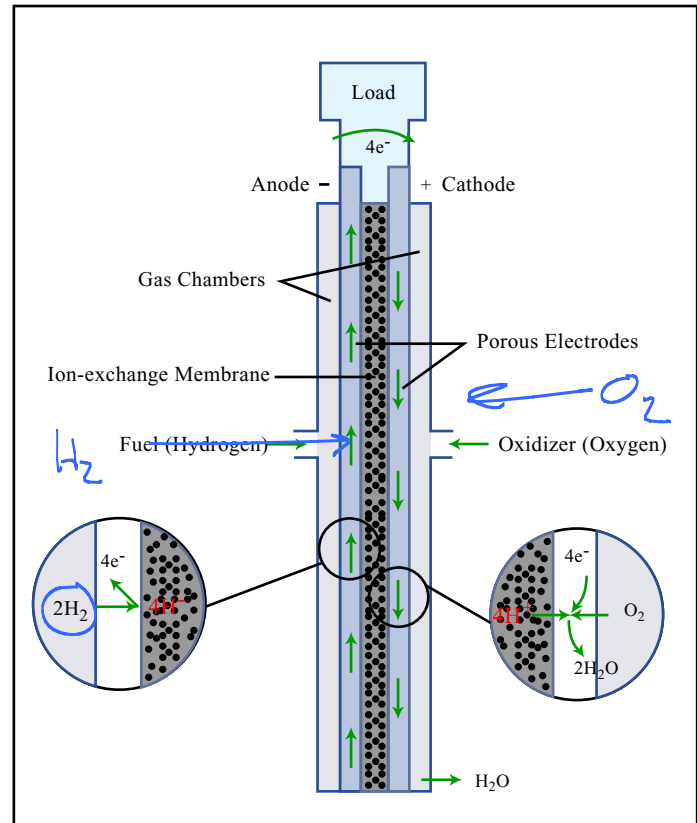
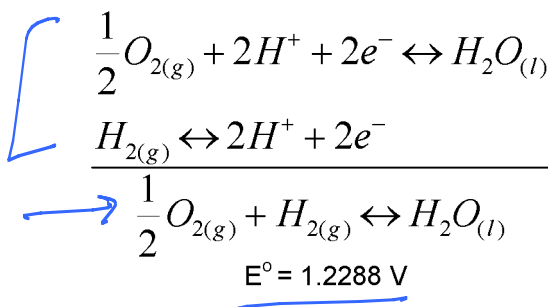


Figure by MIT OCW.

- If a certain fuel cell runs with $P_{O_2} = P_{H_2} = 5000 \text{ psi (340 atm)}$, what voltage is achieved by the cell? Assume the gases can be treated as ideal.

$$\Delta \bar{G}_{RXN} = \Delta \bar{G}_{RXN}^\circ + RT \ln \frac{P_{H_2O}}{(P_{O_2})^{1/2} (P_{H_2})} \quad \text{AT } T=298\text{K}$$

$$= \Delta \bar{G}_{RXN}^\circ - RT \ln \left(\frac{P_{O_2}}{P^\circ} \right)^{1/2} \left(\frac{P_{H_2}}{P^\circ} \right)$$

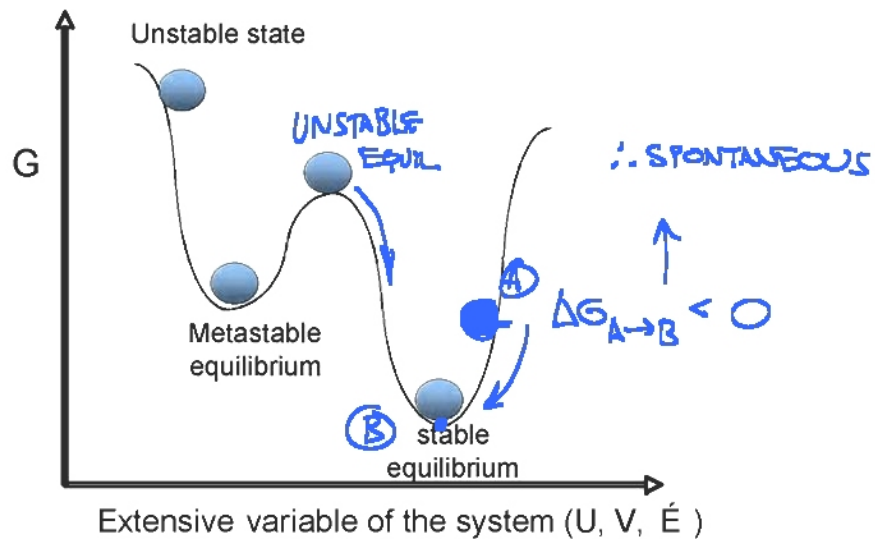
$$\begin{aligned} E &= E^\circ + \frac{RT}{2F} \ln \left(\frac{P_{O_2}}{P^\circ} \right)^{1/2} \left(\frac{P_{H_2}}{P^\circ} \right) \\ &= 1.2288 \text{ V} + 0.1172 \text{ V} = \underline{1.346 \text{ V}} \\ & \quad \quad \quad \uparrow \\ & \quad \quad \quad T=298\text{K} \end{aligned}$$

Implications of stability requirements for the properties of materials

Le Chatelier's principle

- Materials are most useful in stable equilibrium states- conditions where the material is resistant to change if the system experiences small fluctuations in its state. For example, if the temperature and pressure are held constant at (T_0, P_0) , then stable equilibrium is identified by finding the minimum value of G in the landscape of possible U , S , and V values taken by the system. Using a figure from our first lecture:

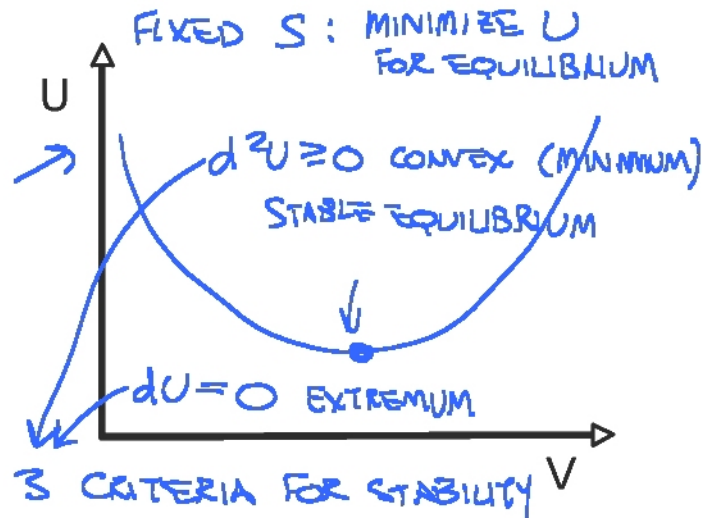
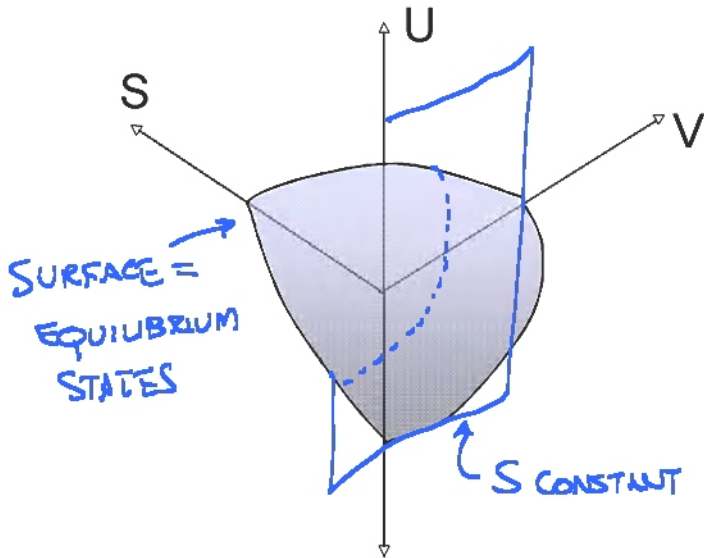
$$G = H - TS = U - T_0S + P_0V$$



- Le Chatelier's principle** states that a system perturbed by a small fluctuation will feel a thermodynamic driving force to return to the stable equilibrium state.

Constraints on thermodynamic properties ensure stability: example of internal energy constraints

- MAIN IDEA:** Many of the thermodynamic properties of materials can only have certain values if the material is in a stable equilibrium state.
- Recall the equilibrium condition in terms of internal energy: For conditions of fixed total entropy, the internal energy of the system is minimized. Graphically, this means:



- The surface drawn in the diagram represents all of the possible equilibrium states of some system. The mathematical requirements for a stable equilibrium are:

For equilibrium to be stable against fluctuations in S only or V only:

SIMPLE SYSTEM: $U = U(S, V)$ (ASSUME n FIXED)

$$\textcircled{1} \left[\left(\frac{\partial^2 U}{\partial V^2} \right)_{S, n} \geq 0 \right]$$

$$\textcircled{2} \left[\left(\frac{\partial^2 U}{\partial S^2} \right)_{V, n} \geq 0 \right]$$

For equilibrium to be stable against coupled fluctuations in both S and V:

$$d^2U \geq 0 \quad d^2U = \left(\frac{\partial^2 U}{\partial S^2} \right)_{V, n} dS^2 + \left(\frac{\partial^2 U}{\partial V^2} \right)_{S, n} dV^2 + 2 \left(\frac{\partial^2 U}{\partial S \partial V} \right) dS dV \geq 0$$

EQUIVALENT TO:

$$\left[\left(\frac{\partial^2 U}{\partial S^2} \right) dS + \left(\frac{\partial^2 U}{\partial S \partial V} \right) dV \right]^2 + \left[\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V} \right)^2 \right] dV^2 \geq 0$$

ALWAYS > 0!

$$\textcircled{3} \left[\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V} \right)^2 \geq 0 \right]$$

- These requirements on the shape of the internal energy surface are linked to values of thermodynamic parameters of the system:

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_{V,n} \geq 0 \quad \frac{\partial}{\partial S} \left[\left(\frac{\partial U}{\partial S} \right)_{V,n} \right] = \left(\frac{\partial T}{\partial S} \right)_{V,n} \stackrel{\uparrow}{=} \frac{T}{C_V} \geq 0$$

ABSOLUTE $T > 0$ BY DEF'N!

$$\therefore \boxed{C_V \geq 0} \text{ FOR STABILITY}$$

$$C_V \equiv T \left(\frac{\partial S}{\partial T} \right)_V$$

$$\boxed{S \uparrow \text{ AS } T \uparrow}$$

- **This is the requirement for thermal stability.** Since the absolute temperature must be > 0 the heat capacity must also be greater than 0. In addition, the entropy must increase if the temperature increases, for stability.

- Next, we have:

$$\left(\frac{\partial^2 U}{\partial V^2} \right)_{S,n} \geq 0$$

T IS ALWAYS ≥ 0

$$\therefore \boxed{K_S \geq 0}$$

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial V} \right)_{S,n} \right] = - \left(\frac{\partial P}{\partial V} \right)_{S,n} \stackrel{\uparrow}{=} \frac{1}{K_S V} \geq 0$$

$$K_S = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{S,n} \text{ ISENTROPIC COMPRESSIBILITY}$$

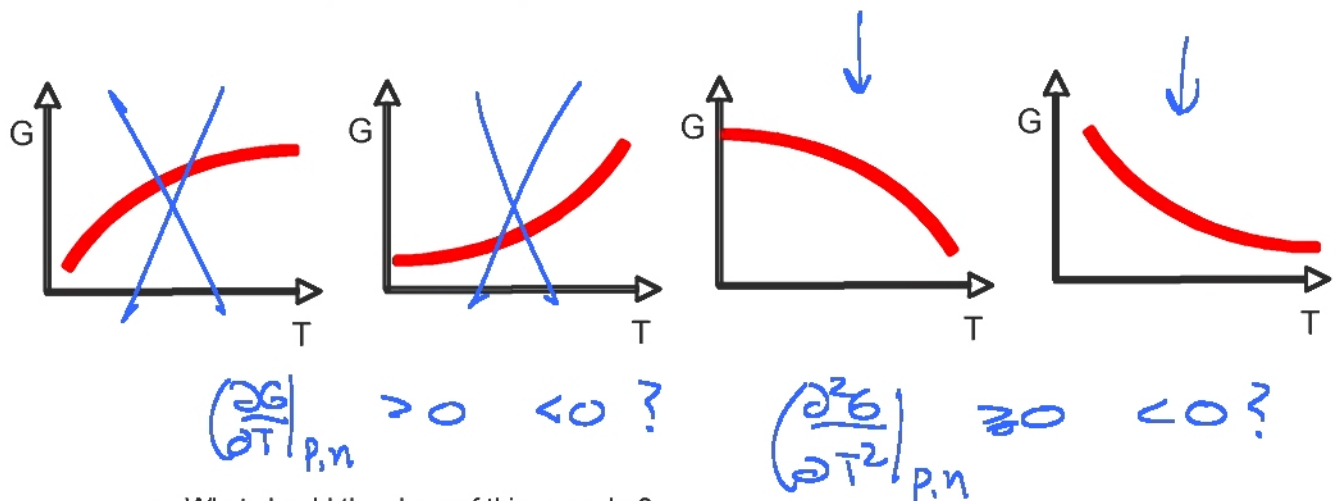
- **This is the condition for mechanical stability.**

- From this analysis, we see that **many properties of materials may only have certain values if the material is to be stable.** There are numerous other examples that can be derived using the other thermodynamic functions. In summary, one can prove:

$$\boxed{\begin{aligned} C_P &\geq C_V \geq 0 \\ K_T &\geq K_S \geq 0 \end{aligned}}$$

Requirements for the shape of free energy curves

- What does the free energy as a function of typical experimental parameters look like- for example, what does a plot of G vs. T look like? What about G vs. P ? Do we know anything (qualitatively) about how it must look? The answer is yes: the relationships between the Gibbs free energy and other thermodynamic parameters tell us numerous things about how plots of G vs. various thermodynamic variables must behave in stable thermodynamic systems:
 - Consider a plot of G vs. temperature:



- What should the slope of this curve be?
 - Using our differential expression for G :

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

- ...and combining this with the algebraic definition of the differential for $G(T,P,N)$:

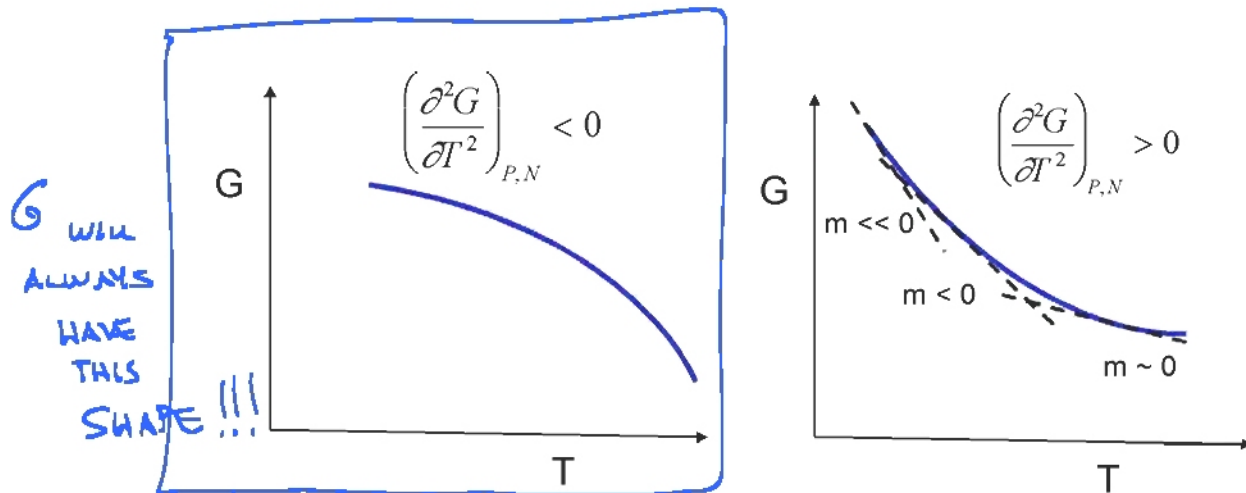
$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \sum_{j=1}^P \sum_{i=1}^C \left(\frac{\partial G}{\partial n_i^j}\right)_{T,N,j,i} dn_i^j$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad \text{SINCE } S \geq 0 \text{ FOR STABILITY, THEN SLOPE } \leq 0$$

- ...thus, the slope of the curve is $-S$.

- what is the curvature of G vs. T ?

- The curvature is given by the second derivative of G vs. T - it is the rate of change of the slope:



- The curvature is also related to known thermodynamic quantities:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,N} = \left[\frac{\partial(-S)}{\partial T}\right]_{P,N} = -\left(\frac{\partial S}{\partial T}\right)_{P,N} = -\frac{C_p}{T} \leq 0$$

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

- The heat capacity and the absolute temperature must always be ≥ 0 , thus the curvature must be < 0 . **Thus plots of the free energy vs. temperature at constant pressure must always have the general shape shown at left above.**
- Similar analyses may be applied to predict the shape of other free energy curves of interest.

Maxwell Relations

The Euler Relationship and Maxwell Relations

- We've already discussed some of the useful properties of state functions like U, S, and H- they are path independent and integrable. An additional useful characteristic is that state functions must obey the Euler reciprocal relationship, which is expressed mathematically for a multivariable function f(x,y) as:

$$\left[\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial^2 f(x,y)}{\partial y \partial x} \right] \quad \text{FOR ANY STATE FUNCTION!} \quad \text{EULER RELATIONSHIP}$$

- The Euler relationship can be used to identify identities between thermodynamic variables that are not obvious; these are called the *Maxwell relations*.
- A set of Maxwell relations can be derived for each thermodynamic state function. For example, starting with the internal energy U(S,V,N):

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \quad \leftarrow \text{N FIXED}$$

$$\left(\frac{\partial T}{\partial V} \right)_{S,N} = \left[\frac{\partial}{\partial S} \left[\frac{\partial U}{\partial V} \right]_{S,N} \right]_{V,N} = - \left(\frac{\partial P}{\partial S} \right)_{V,N}$$

- Maxwell's relations can help us further derive thermodynamic quantities from measurable parameters of our materials.
- Another example is the Maxwell relation obtained by taking second derivatives of the enthalpy H(S,P,N):

$$\frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P}$$

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

- Summarizing these relationships for each of our main thermodynamic functions:

U	$-\left(\frac{\partial P}{\partial S}\right)_{V,n} = \left(\frac{\partial T}{\partial V}\right)_{S,n}$
$H \equiv U + PV$	$\left(\frac{\partial V}{\partial S}\right)_{P,n} = \left(\frac{\partial T}{\partial P}\right)_{S,n}$
$G \equiv H - TS$	$-\left(\frac{\partial S}{\partial P}\right)_{T,n} = \left(\frac{\partial V}{\partial T}\right)_{P,n}$
$F \equiv U - TS$	$\left(\frac{\partial S}{\partial T}\right)_{V,n} = \left(\frac{\partial P}{\partial V}\right)_{T,n}$

References

Reference Type: Book

Record Number: 34

Author: Silbey, R.J.; Alberty, R.A.; Bawendi, M.G.

Year: 2005

Title: Physical Chemistry

City: New York

Publisher: John Wiley

Number of Pages: 944

Edition: 4th

Reference Type: Electronic Source

Record Number: 1

Author: Carter, W.C.

Year: 2002

Title: 3.00 Thermodynamics of Materials Lecture Notes

URL: <http://pruffle.mit.edu/3.00/>