

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:

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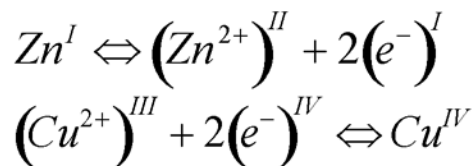
Thermodynamics of a battery, continued

- 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:

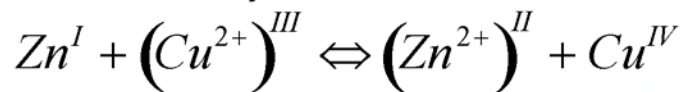
- The script F in this expression is the Faraday constant: $F = 96,485 \frac{C}{\text{mole } e^-}$

- We applied this new term for electrochemical potentials in our analysis of the Daniell cell.

Half-cell reactions:



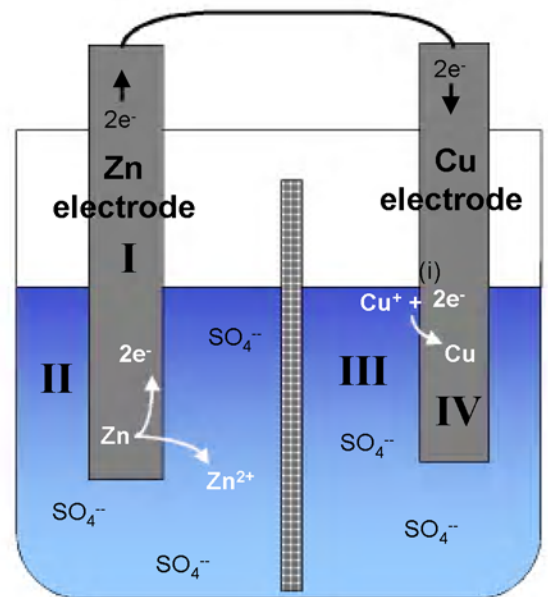
Total reaction for system:



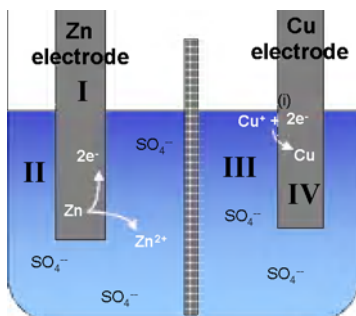
$$\Delta \bar{G}_{rxn} = \mu_{\text{Cu}}^{IV} + \tilde{\mu}_{\text{Zn}^{2+}}^{II} - \mu_{\text{Zn}}^I - \tilde{\mu}_{\text{Cu}^{2+}}^{III}$$

- 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:

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**:



$$\left(\tilde{\mu}_{\text{SO}_4^{2-}}\right)^{\text{II}} = \left(\tilde{\mu}_{\text{SO}_4^{2-}}\right)^{\text{III}} \quad (\text{c}) \quad \phi^{\text{II}} = \phi^{\text{III}}$$

$$\mu_{\text{SO}_4^{2-}}^{\text{II}} - 2\phi^{\text{II}}F = \mu_{\text{SO}_4^{2-}}^{\text{III}} - 2\phi^{\text{III}}F$$

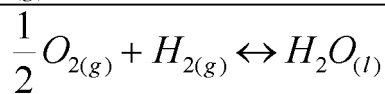
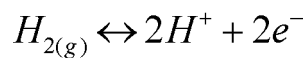
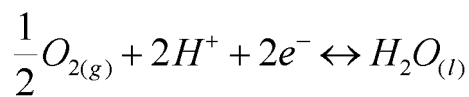
- For a reversible reaction, we call the potential difference the electromotive force, or EMF:
- The U.S. convention is that EMF is positive when reactions are written to proceed spontaneously from left to right (i.e. Zn is the left electrode).

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:

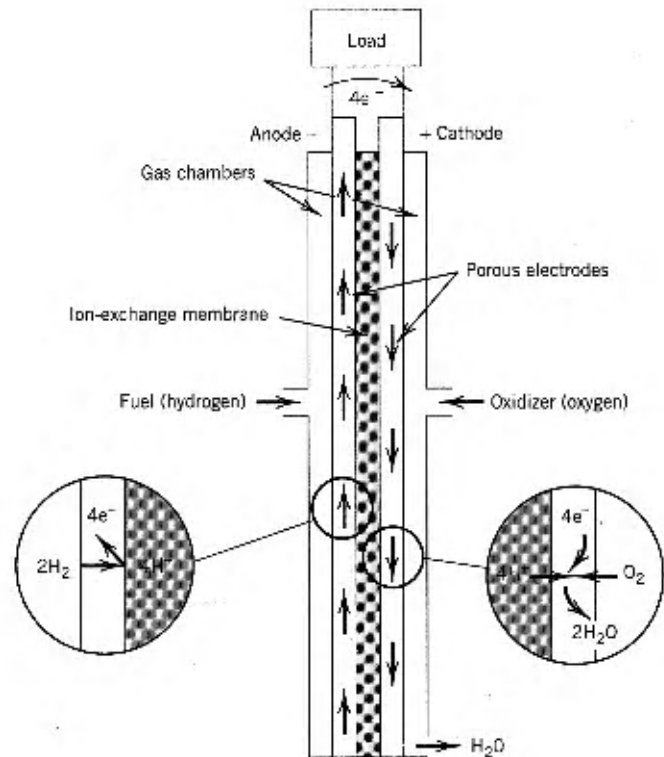
(Silbey et al.)

- The Half-cell reactions and overall reaction are:



$$E^\circ = 1.2288 \text{ V}$$

- 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.

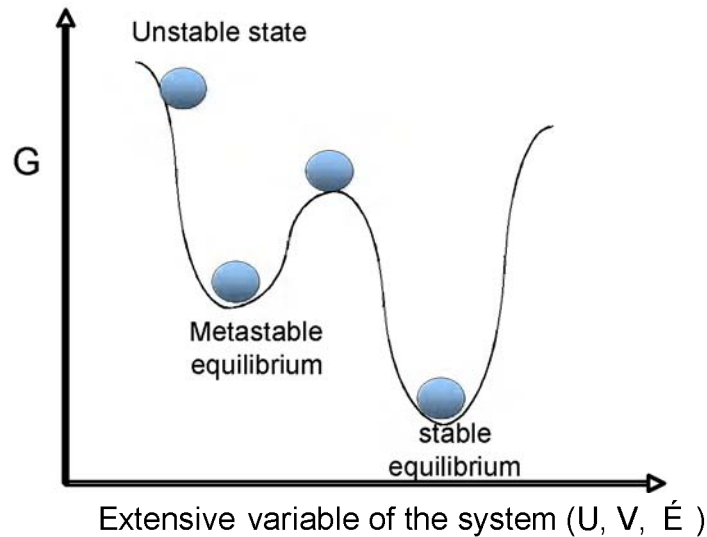


Implications of stability requirements for the properties of materials

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:

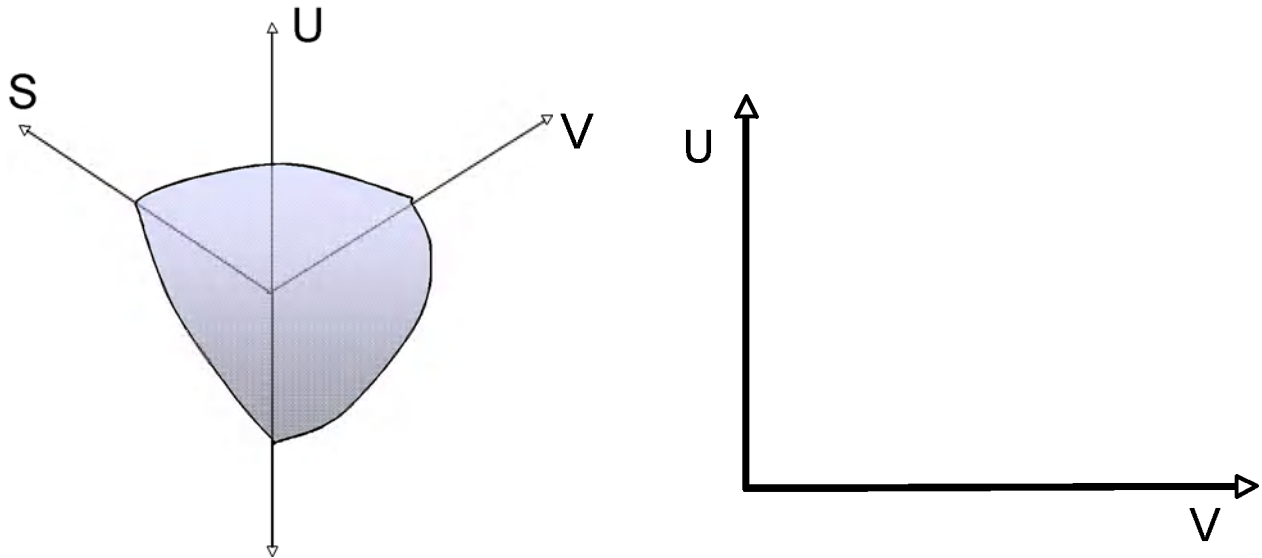
$$G = H - TS = U - T_0S + P_0V$$



- 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:

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

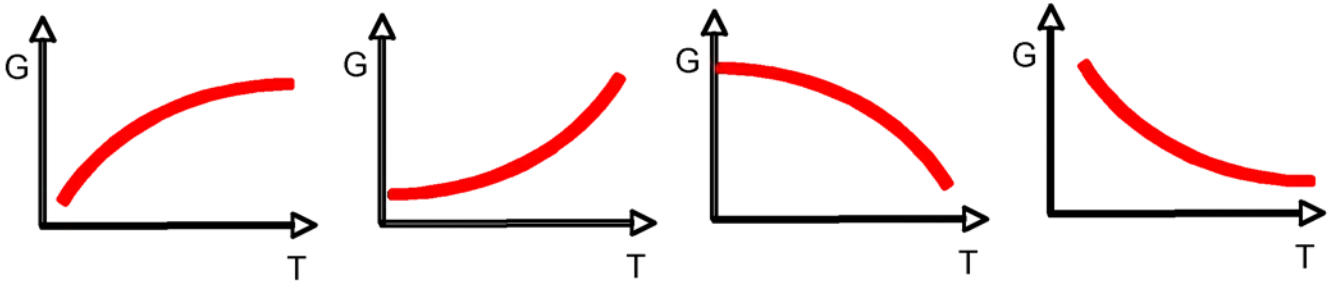
- These requirements on the shape of the internal energy surface are linked to values of thermodynamic parameters of the system:
 - ***This is the requirement for thermal stability.*** Since the absolute temperature must be > 0 the heat capacity must also be greater than 0. In addition, the entropy must increase if the temperature increases, for stability.
- Next, we have:
 - ***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:

$$C_P \geq C_V \geq 0$$

$$K_T \geq K_S \geq 0$$

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:



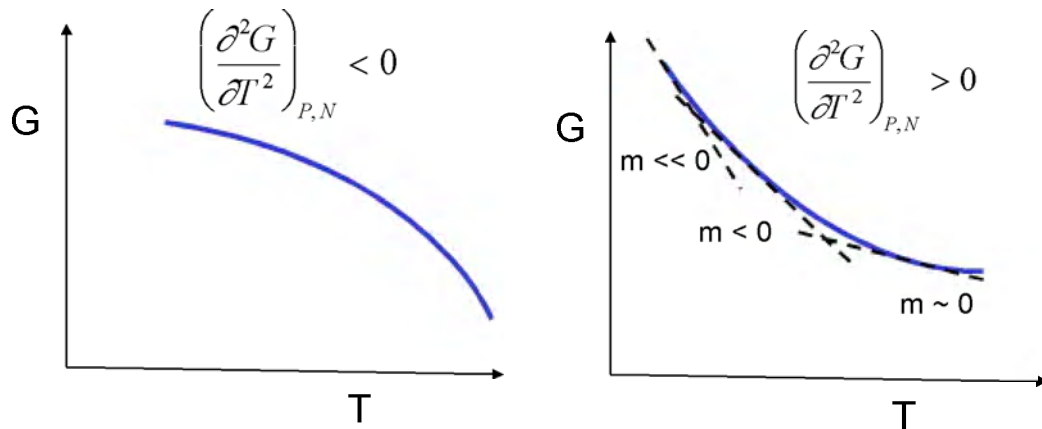
- What should the slope of this curve be?
 - Using our differential expression for G :

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

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

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

- ...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:
 - 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:

$$\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial^2 f(x,y)}{\partial y \partial x}$$

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 $U(S,V,N)$:
 - 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 $H(S,P,N)$:

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

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

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/>