Lecture 14: 10.31.05 Batteries continued; Thermodynamic stability

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Reading:


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:

\[
\Delta G_{rxn} = \mu_{Ca}^{IV} + \mu_{Zn^{2+}}^{II} + 2\mu_{e}^{0} + \mu_{Cu^{2+}}^{III} + \mu_{Zn}^{I} + 2\mu_{e}^{0} + \mu_{Cu^{2+}}^{IV}
\]

- 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:

\[
\rightarrow Zn^{I} \rightleftharpoons (Zn^{2+})^{II} + 2(e^{-})^{I}
\]

\[
\rightarrow (Cu^{2+})^{III} + 2(e^{-})^{IV} \rightleftharpoons Cu^{IV}
\]

Total reaction for system:

\[
Zn^{I} + (Cu^{2+})^{III} \rightleftharpoons (Zn^{2+})^{II} + Cu^{IV}
\]

- 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:

\[
\Delta \phi = \frac{-\Delta G_{RXN}}{nF}
\]

\[
\Delta G_{RXN} = \mu_{Ca}^{IV} + \mu_{Zn^{2+}}^{II} + 2\mu_{e}^{0} - \mu_{Zn}^{I} - \mu_{Cu^{2+}}^{III} - 2\mu_{e}^{0} - \mu_{Cu^{2+}}^{IV}
\]
How can we further simplify this expression? Recall that we have sulfate ion equilibration through the membrane between the aqueous solutions II and III:

\[
\left( \mu_{SO_4^{2-}}^I \right)^{II} = \left( \mu_{SO_4^{2-}}^I \right)^{III}
\]

\[
\mu_{SO_4^{2-}}^I - 2\phi^I F = \mu_{SO_4^{2-}}^III - 2\phi^III F
\]

(C) \[ \phi^II = \phi^III \]

\[ \begin{align*}
N_{SO_4^{2-}}^I &= N_{SO_4^{2-}}^III \\
N_{Cu^{2+}}^I &= N_{Cu^{2+}}^III \\
N_{Zn^{2+}}^I &= N_{Zn^{2+}}^III
\end{align*} \]

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

\[
E = \text{EMF} = \Delta \phi^\text{REV} = -\frac{\Delta G^o_{\text{REV}}}{n^F}
\]

STANDARD POTENTIAL:

\[
E^0 = -\frac{\Delta G^o_{\text{REV}}}{n^F}
\]

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 DANIEL CELL:

\[
E = -\frac{\Delta G^o_{\text{REV}}}{2F} = -\frac{1}{2F} \left[ \Delta G^o_{\text{REV}} + RT \ln \frac{a_{Zn^{2+}}^{III}}{a_{Cu^{2+}}^{II}} \right]
\]

\[
E = E^0 - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}^{III}}{a_{Cu^{2+}}^{II}} \rightarrow a_i = Y_i X_i
\]

\[
E = E^0 - \frac{RT}{n^F} \ln Q \quad \text{... in general}
\]
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:

\[
\begin{align*}
\frac{1}{2} O_{2(g)} + 2H^+ + 2e^- & \leftrightarrow H_2O_{(l)} \\
H_{2(g)} & \leftrightarrow 2H^+ + 2e^- \\
\frac{1}{2} O_{2(g)} + H_{2(g)} & \leftrightarrow H_2O_{(l)}
\end{align*}
\]

\[E^0 = 1.2288 \text{ V}\]

- 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.

\[
\Delta G_{R,\text{xn}} = \Delta G_{R,\text{xn}}^0 + RT \ln \left( \frac{P_{O_2}}{P^0} \right)^{1/2} \left( \frac{P_{H_2}}{P^0} \right)^{1/2}
\]

\[E = E^0 + RT \ln \left( \frac{P_{O_2}}{P^0} \right)^{1/2} \left( \frac{P_{H_2}}{P^0} \right)^{1/2}
\]

\[= 1.2288 \text{ V} + 0.1172 \text{ V} = 1.346 \text{ V}
\]

\[T = 298 \text{ K}\]
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:
For equilibrium to be stable against fluctuations in S only or V only:

- Simple system: \( U = U(S, V) \) (Assume \( V \) fixed)
  1. \( \left( \frac{\partial^2 U}{\partial S^2} \right)_{V} \geq 0 \)
  2. \( \left( \frac{\partial^2 U}{\partial V^2} \right)_{S} \geq 0 \)

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

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

which is equivalent to:

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

Always \( \geq 0 \)

- \( \left( \frac{\partial^2 U}{\partial S^2} \right) - \left( \frac{\partial^2 U}{\partial S \partial V} \right)^2 \geq 0 \)
These requirements on the shape of the internal energy surface are linked to values of thermodynamic parameters of the system:

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

**Absolute \( T > 0 \) by def'n!**

\[c_V \geq 0 \quad \text{for stability}
\]

\[S^\uparrow \text{ as } T^\uparrow
\]

- **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:

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

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

\[k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,n}
\]

- **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:

\[
C_P \geq C_V \geq 0
\]

\[
\kappa_T \geq \kappa_S \geq 0
\]
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:

  o Consider a plot of G vs. temperature:

    ![Graphs showing the behavior of G vs. T]

    \[
    \left( \frac{\partial G}{\partial T} \right)_{P,N} \quad > \quad 0 \quad \text{or} \quad < \quad 0 \quad ?
    \]
    \[
    \left( \frac{\partial^2 G}{\partial T^2} \right)_{P,N} \quad \geq \quad 0 \quad \text{or} \quad < \quad 0 \quad ?
    \]

  o 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 \( G(T,P,N) \):

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

      \[
      \left( \frac{\partial G}{\partial T} \right)_{P,N} = -S \quad \text{since} \quad S \geq 0 \quad \text{for stability,}
      \]

      ...thus, the slope of the curve is \(-S\). THEN SLOPE \( \leq 0 \)

  o 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:

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

- The heat capacity and the absolute temperature must always be \( \geq 0 \), 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 multivariate function $f(x,y)$ as:

\[
\frac{\partial f (x,y)}{\partial x} \frac{\partial y}{\partial y} = \frac{\partial f (x,y)}{\partial y} \frac{\partial x}{\partial x} 
\]

**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 $U(S,V,N)$:

\[
\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}
\]

\[
\frac{\partial^2 U}{\partial V \partial S} = \left[ \frac{\partial}{\partial S} \left[ \frac{\partial U}{\partial V} \right] \right]_{S,n} = \frac{\partial P}{\partial S} v_n
\]

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

\[
\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S}
\]

\[
\frac{\partial^2 H}{\partial S \partial P} = \left( \frac{\partial T}{\partial P} \right)_{S,n}
\]

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

<table>
<thead>
<tr>
<th>Function</th>
<th>Maxwell Relations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U$</td>
<td>$\frac{\partial P}{\partial V} = \frac{\partial T}{\partial S}$</td>
</tr>
<tr>
<td>$H$</td>
<td>$\frac{\partial V}{\partial S} = \frac{\partial P}{\partial T}$</td>
</tr>
<tr>
<td>$G$</td>
<td>$\frac{\partial S}{\partial P} = \frac{\partial V}{\partial T}$</td>
</tr>
<tr>
<td>$F$</td>
<td>$\frac{\partial T}{\partial V} = \frac{\partial S}{\partial P}$</td>
</tr>
</tbody>
</table>
References

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Year: 2005
Title: Physical Chemistry
City: New York
Publisher: John Wiley
Number of Pages: 944
Edition: 4th

Reference Type: Electronic Source
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Year: 2002
Title: 3.00 Thermodynamics of Materials Lecture Notes
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