Dec. 11 2002: Lecture 34: _____________

Equilibrium Conditions for Charged Species

Last Time

Reactions with Condensed Phases

Ellingham Diagrams: Oxidation

Electrochemistry

Background:
Consider the maximum work that can be obtained when 1 mole of oxygen combines with half a mole of hydrogen to form water vapor at 25°C.

\[
\begin{align*}
\text{H}_2(\text{gas}) + \frac{1}{2}\text{O}_2(\text{gas}) &\rightleftharpoons \text{H}_2\text{O}(\text{gas}) \\
\Delta H_{\text{rx}}(T = 300^\circ\text{K}, P = 1\text{atm}) &= 286\text{(KJ)/(moleH}_2) \\
\Delta S_{\text{rx}}(T = 300^\circ\text{K}, P = 1\text{atm}) &= [70 - (130.5 + \frac{1}{2}205)] = -163\text{(J)/(moleH}_2^\circ\text{K}) \\
\end{align*}
\]

The entropy of the thermal surroundings of the reaction increase by

\[
\Delta S_{\text{surround}}(T = 300^\circ\text{K}, P = 1\text{atm}) = \frac{286 \times 10^3}{300} = 953\text{J/(moleH}_2^\circ\text{K))}
\]

So the total entropy of the universe increases\(^{34}\) by 953 - 163 = 790 J/mole K. **WHAT a WASTE!** In order not to violate the second law, only only \(q_{\text{min}}\) amount of heat needs to be transferred.

\(^{34}\)It had better increase because we know this is spontaneous reaction.
\[
\Delta S_{\text{surround.}} + \Delta S_{R_x} = 0 \quad \text{ reversible}
\]
\[
\frac{q_{\text{min}}}{T_{\text{surround.}}} = \frac{q_{\text{min}}}{300} = -\Delta S_{R_x} = 163 \text{J}/(\text{moleH}_2 \cdot \text{K})
\]

which leaves
\[
\Delta H - q_{\text{min}} = w_{\text{max}}
\]
\[
w_{\text{max}} = \Delta H - (-\Delta S)T = \Delta G
\]
\[
= 286 \times 10^3 - (163)(300) = 237 \text{J}/(\text{moleH}_2)
\]

Apparently, \( \Delta G^{re} \) represents the maximum work that can be extracted from a system.

How can this work be extracted? In principle it could be harnessed to drive an electric motor. To do this, a source of electrons is needed and those can be generated those by the reactions:

\[
\text{H}_2(\text{gas}) \leftrightarrow 2\text{H}^+(\text{Aq.}) + 2e^- \quad \text{(generates electrons)}
\]
\[
\frac{1}{2}\text{O}_2(\text{gas}) + 2\text{H}^+(\text{Aq.}) + 2e^- \leftrightarrow \text{H}_2\text{O}(\text{liq.}) \quad \text{(consumes electrons)}
\]

The work done by the electric motor is the potential drop between the source and sink of the electrons, multiplied by the net charge that they carry:
\[
w_{\text{max}} \text{ (done by system)} = \Delta \phi(2\text{Navag.} \cdot e) = \Delta \phi_{\text{max}} 2F
\]
\[
\quad -\Delta G_{R_x} = \Delta \phi_{\text{max}} 2F
\]

or

\[
\Delta \phi_{\text{max}} = \frac{-\Delta G_{R_x}}{nF}
\]

The maximum potential is related to the molar Gibbs free energy of the reaction.

--- Systematic Treatment of the Electrochemical Potential ---

Recall how the the internal degrees of freedom were extended to include work terms associated with the transfer of charged particles from one electrostatic potential to another:

\[
dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i + \sum_{i=1}^{C} \Delta \phi_i Z_i F dn_i
\]

(Note: \( dn_i \) represents the change in the number of moles of species \( i \) if \( \mu_i \) is the chemical potential of a mole of species \( i \). This is done so that the Faraday constant \( F \) appears in the equation from the start—the Faraday constant is the charge on a mole of electrons.)
Equation 34-8 can be rewritten as

$$dU = TdS - PdV + \sum_{i=1}^{C} (\mu_i + \Delta \phi_i Z_i F) dn_i$$

(34-9)

$$dU = TdS - PdV + \sum_{i=1}^{C} \eta_i dn_i$$

where

$$\eta_i dn_i \equiv \mu_i + \Delta \phi_i Z_i F$$

(34-10)

$\eta_i$ is called the "electrochemical potential".

The conditions for equilibrium are analogous to all other reactions:

$$\sum_{i=1}^{C} \eta_i dn_i = 0 \quad \text{subject to} \quad \sum_{i=1}^{C} dn_i = 0$$

(34-11)

and when, in addition, the system is closed ($\sum dN_i = 0$)

$$\eta_i^\alpha = \eta_i^\beta \quad \text{or} \quad (\mu_i^\alpha + \phi_i^\alpha Z_i F) + (\mu_i^\beta + \phi_i^\beta Z_i F)$$

(34-12)

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**An Example**

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Figure 34-1: Example Battery
Writing out the the equilibrium equations between each of the phases:

At I/II

\[ \eta_{\text{Cu}^{++}}^{I} = \eta_{\text{Cu}^{++}}^{II} \]
\[ \mu_{\text{Cu}^{++}}^{I} + 2\mathcal{F}\phi^{I} = \mu_{\text{Cu}^{++}}^{II} + 2\mathcal{F}\phi^{II} \] (34-13)

At II/III

\[ \mu_{\text{SO}_{4}^{--}}^{II} - 2\mathcal{F}\phi^{II} = \mu_{\text{SO}_{4}^{--}}^{III} - 2\mathcal{F}\phi^{III} \] (34-14)

At III/IV

\[ \mu_{\text{Zn}^{++}}^{III} + 2\mathcal{F}\phi^{III} = \mu_{\text{Zn}^{++}}^{IV} + 2\mathcal{F}\phi^{IV} \] (34-15)

At Electrodes

\[ \text{Cu} \rightleftharpoons \text{Cu}^{++} \text{(Aq.)} + 2e^{-} \quad \text{and} \quad \text{Zn} \rightleftharpoons \text{Zn}^{++} \text{(Aq.)} + 2e^{-} \] (34-16)

or\(^{35}\)

\[ \mu_{\text{Cu}}^{I} = \mu_{\text{Cu}^{++}}^{I} + 2\mu_{\text{e}^{-}}^{I} \quad \text{and} \quad \mu_{\text{Zn}}^{II} = \mu_{\text{Zn}^{++}}^{II} + 2\mu_{\text{e}^{-}}^{II} \] (34-17)

Combining all the equilibrium equations and solving:

\[ \phi^{I} - \phi^{IV} = \frac{1}{2\mathcal{F}}[(\mu_{\text{Zn}}^{IV} - \mu_{\text{Zn}^{++}}^{III}) - (\mu_{\text{Cu}}^{I} - \mu_{\text{Cu}^{++}}^{II}) + (\mu_{\text{SO}_{4}^{--}}^{III} - \mu_{\text{SO}_{4}^{--}}^{II})] \] (34-18)

If the membrane is perfect: \( \mu_{\text{SO}_{4}^{--}}^{II} = \mu_{\text{SO}_{4}^{--}}^{III} \), then:

\[ \Delta \phi = \frac{1}{n\mathcal{F}} \left[ \frac{G_{R_{x}^{I}}}{G_{R_{x}^{II}}} - \frac{G_{R_{x}^{II}}}{G_{R_{x}^{I}}} + RT \log \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} \right] \] (34-19)

Which is known as the Nernst Equation.

\(^{35}\)The difference in chemical potentials of electrons in two different materials at the same voltage is the difference in Fermi levels.