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 of hydrogen combines with half a mole of of oxygen to form water vapor at 25°C.

$$\begin{aligned}
&\mathrm{H}_{2(\mathrm{gas})} + \frac{1}{2}\mathrm{O}_{2(\mathrm{gas})} + \rightleftharpoons \mathrm{H}_2\mathrm{O}_{(\mathrm{gas})} \\
&\overline{\Delta H_{Rx}}(T = 300°\mathrm{K}, P = 1\mathrm{atm}) = 286(\mathrm{KJ}/(\mathrm{mole}\mathrm{H}_2) \qquad (34\text{-}1) \\
&\overline{\Delta S_{Rx}}(T = 300°\mathrm{K}, P = 1\mathrm{atm}) = [70 - (130.5 + \frac{1}{2}205)] = -163(\mathrm{J}/(\mathrm{mole}\mathrm{H}_2°\mathrm{K}))
\end{aligned}$$

The entropy of the thermal surroundings of the reaction increase by

$$\overline{\Delta S_{\mathrm{surround.}}}(T = 300°\mathrm{K}, P = 1\mathrm{atm}) = \frac{286 \times 10^3}{300} = 953\mathrm{J}/(\mathrm{mole}\mathrm{H}_2°\mathrm{K}) \qquad (34\text{-}2)$$

So the total entropy of the universe increases[34] by $953 - 163 = 790\frac{\mathrm{J}}{\mathrm{mole}°\mathrm{K}}$

WHAT a WASTE! In order **not** to violate the second law, only only q_{min} amount of heat needs to be transfered.

[34] It had better increase because we know this is spontaneous reaction.

$$\begin{aligned} \overline{\Delta S_{\text{surround.}}} + \overline{\Delta S_{Rx}} &= 0 \quad \text{reversible} \\ \frac{q_{\text{min}}}{T_{\text{surround.}}} = \frac{q_{\text{min}}}{300} &= -\overline{\Delta S_{Rx}} = 163\text{J}/(\text{mole}\text{H}_2{}^\circ\text{K}) \end{aligned} \tag{34-3}$$

which leaves

$$\begin{aligned} \overline{\Delta H} - q_{\text{min}} &= w_{\text{max}} \\ w_{\text{max}} &= \overline{\Delta H} - (-\overline{\Delta S})T = \overline{\Delta G} \\ &= 286 \times 10^3 - (163)(300) = 237\text{J}/(\text{mole}\text{H}_2) \end{aligned} \tag{34-4}$$

Apparently, ΔG^{rx} 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:

$$\begin{aligned} \text{H}_{2(\text{gas})} &\rightleftharpoons 2\text{H}^+_{(\text{Aq.})} + 2\text{e}^- \quad \text{(generates electrons)} \\ \frac{1}{2}\text{O}_{2(\text{gas})} + 2\text{H}^+_{(\text{Aq.})} + 2\text{e}^- &\rightleftharpoons \text{H}_2\text{O}_{(\text{liq.})} \quad \text{(consumes electrons)} \end{aligned} \tag{34-5}$$

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:

$$\begin{aligned} w_{\text{max (done by system)}} &= \Delta\phi(2\text{N}_{\text{avag.}}|\text{e}|) \\ -\overline{\Delta G_{Rx}} &= \Delta\phi_{\text{max}} 2\mathcal{F} \end{aligned} \tag{34-6}$$

or

$$\Delta\phi_{\text{max}} = \frac{-\overline{\Delta G_{Rx}}}{n\mathcal{F}} \tag{34-7}$$

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:

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dn_i + \sum_{i=1}^{C} \Delta\phi_i Z_i \mathcal{F} dn_i \tag{34-8}$$

(Note: dn_i represents the change in the number of moles of species i if μ_i is the chemical potential of a mole of species i. This is done so that the Faraday constant $\mathcal{F}$ 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

$$dU = TdS - PdV + \sum_{i=1}^{C}(\mu_i + \Delta\phi_i Z_i \mathcal{F})dn_i$$
$$dU = TdS - PdV + \sum_{i=1}^{C}\eta_i dn_i \tag{34-9}$$

where

$$\eta_i dn_i \equiv \mu_i + \Delta\phi_i Z_i \mathcal{F} \tag{34-10}$$

η_i is called the "electrochemical potential".
The conditions for equilibrium are analogous to all other reactions:

$$\sum_{i=1}^{C}\eta_i dn_i = 0 \quad \text{subject to} \quad \sum_{i=1}^{C} dn_i = 0 \tag{34-11}$$

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

$$\eta_i^\alpha = \eta_i^\beta \quad \text{or} \quad (\mu_i^\alpha + \phi_i^\alpha Z_i \mathcal{F}) + (\mu_i^\beta + \phi_i^\beta Z_i \mathcal{F}) \tag{34-12}$$

An Example

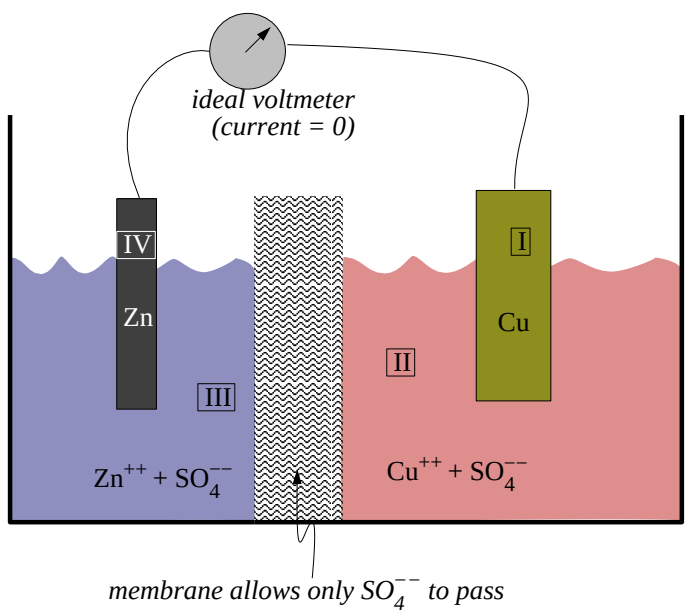

Figure 34-1: Example Battery

Writing out the the equilibrium equations between each of the phases:

At I/II

$$\begin{aligned} \eta^{\mathrm{I}}_{\mathrm{Cu}^{++}} &= \eta^{\mathrm{II}}_{\mathrm{Cu}^{++}} \\ \mu^{\mathrm{I}}_{\mathrm{Cu}^{++}} + 2\mathcal{F}\phi^{\mathrm{I}} &= \mu^{\mathrm{II}}_{\mathrm{Cu}^{++}} + 2\mathcal{F}\phi^{\mathrm{II}} \end{aligned} \tag{34-13}$$

At II/III

$$\mu^{\mathrm{II}}_{\mathrm{SO}_4^{--}} - 2\mathcal{F}\phi^{\mathrm{II}} = \mu^{\mathrm{III}}_{\mathrm{SO}_4^{--}} - 2\mathcal{F}\phi^{\mathrm{III}} \tag{34-14}$$

At III/IV

$$\mu^{\mathrm{III}}_{\mathrm{Zn}^{++}} + 2\mathcal{F}\phi^{\mathrm{III}} = \mu^{\mathrm{IV}}_{\mathrm{Zn}^{++}} + 2\mathcal{F}\phi^{\mathrm{IV}} \tag{34-15}$$

At Electrodes

$$\mathrm{Cu} \rightleftharpoons \mathrm{Cu}^{++}_{(\mathrm{Aq.})} + 2\mathrm{e}^- \quad \text{and} \quad \mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{++}_{(\mathrm{Aq.})} + 2\mathrm{e}^- \tag{34-16}$$

or[35]

$$\mu^{\mathrm{I}}_{\mathrm{Cu}} = \mu^{\mathrm{I}}_{\mathrm{Cu}^{++}} 2\mu^{\mathrm{I}}_{\mathrm{e}^-} \quad \text{and} \quad \mu^{\mathrm{II}}_{\mathrm{Zn}} = \mu^{\mathrm{II}}_{\mathrm{Zn}^{++}} 2\mu^{\mathrm{II}}_{\mathrm{e}^-} \tag{34-17}$$

Combining all the equilibrium equations and solving:

$$\phi^{\mathrm{I}} - \phi^{\mathrm{IV}} = \frac{1}{2\mathcal{F}}[(\mu^{\mathrm{IV}}_{\mathrm{Zn}} - \mu^{\mathrm{III}}_{\mathrm{Zn}^{++}}) - (\mu^{\mathrm{I}}_{\mathrm{Cu}} - \mu^{\mathrm{II}}_{\mathrm{Cu}^{++}}) + (\mu^{\mathrm{II}}_{\mathrm{SO}_4^{--}} - \mu^{\mathrm{III}}_{\mathrm{SO}_4^{--}})] \tag{34-18}$$

If the membrane is perfect: $\mu^{\mathrm{II}}_{\mathrm{SO}_4^{--}} = \mu^{\mathrm{III}}_{\mathrm{SO}_4^{--}}$, then:

$$\Delta\phi = \frac{1}{n\mathcal{F}}\left[\overline{G^{\mathrm{I}}_{Rx}} - \overline{G^{\mathrm{II}}_{Rx}} + RT\log\frac{a_{\mathrm{Zn}^{++}}}{a_{\mathrm{Cu}^{++}}}\right] \tag{34-19}$$

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