

Adding Fields to μ

10.1

To see what happens to the chemical pot. in the presence of an external field, let's look at gravity:

The gravitational field is the derivative of Φ_g , grav. pot. and $\Phi_g = gh$ where g is the field strength (9.8 m/s^2)

The chemical potential will now be a function of height:

$$\mu_i(h) = \mu_i(h=0) - \overset{\substack{\text{part that} \\ \text{responds to} \\ \Phi_g}}{M_i} \overset{\Phi_g}{gh} \quad (M_i \text{ is molar mass})$$

this equation can give us (problem 10.1) the barometric formula:

$$p_i(h) = p_i(h=0) e^{-\frac{M_i g h}{RT}}$$

which gives us the pressure as a function of height.

A more useful field for chemical reactions is the Electric field, E , which is the derivative of Φ_E , the electric potential, with respect to position: $E = -\frac{\partial \Phi_E}{\partial x}$

the chemical potential will now be a function of position:

$$\tilde{\mu}_i = \mu_i(E=0) + \overset{\substack{\text{charge (part that} \\ \text{responds to } \Phi_E)}{F z_i} \Phi_E(x) \quad \Phi_E(x) \text{ is a function of position}$$

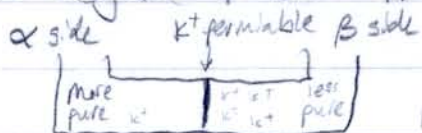
$\tilde{\mu}_i$ is called the electrochemical potential, which we will use to show how the ΔG_{rxn} changes in an electric field

recall how we derived $\Pi V = N_B RT$ (osmosis):

We set $\mu_{\text{pure H}_2\text{O}} = \mu_{\text{sugar sol'n}}$ at equilibrium, noting $\nabla \mu = RT \ln x_A$

that: $\mu_{\text{sugar sol'n}} = \mu_{\text{pure H}_2\text{O}} + (\text{correction for pressure}) + (\text{corr. for mixture})$

Now we'll note again that if we had the following situation:



in which there are initially more K^+ ions

on the right (β), the K^+ are going to cross the K^+ permeable membrane barrier. This will leave behind negative counterions (e.g. Cl^-) that couldn't cross the membrane. So we note:

$$\tilde{\mu}_{K^+}^{\alpha} = \tilde{\mu}_{K^+}^{\beta} \quad \text{at equilibrium}$$

and: $\tilde{\mu}_{K^+} = \mu_{K^+}^{\circ} + (\text{corr. for Electric field}) + (\text{corr. for mixture})$

(This time Φ_E^{α} and Φ_E^{β} are constants, not functions of x)

$$\text{so: } \tilde{\mu}_{K^+}^{\beta} - \tilde{\mu}_{K^+}^{\alpha} = 0 = \mu_{K^+}^{\circ} - \mu_{K^+}^{\circ} + Fz_{K^+}(\Phi_E^{\beta} - \Phi_E^{\alpha}) + RT \ln \frac{a_{K^+}^{\beta}}{a_{K^+}^{\alpha}}$$

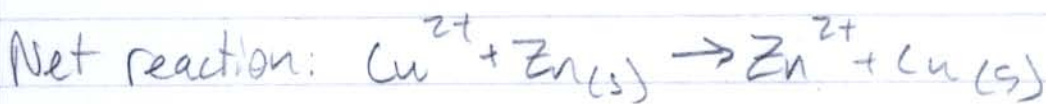
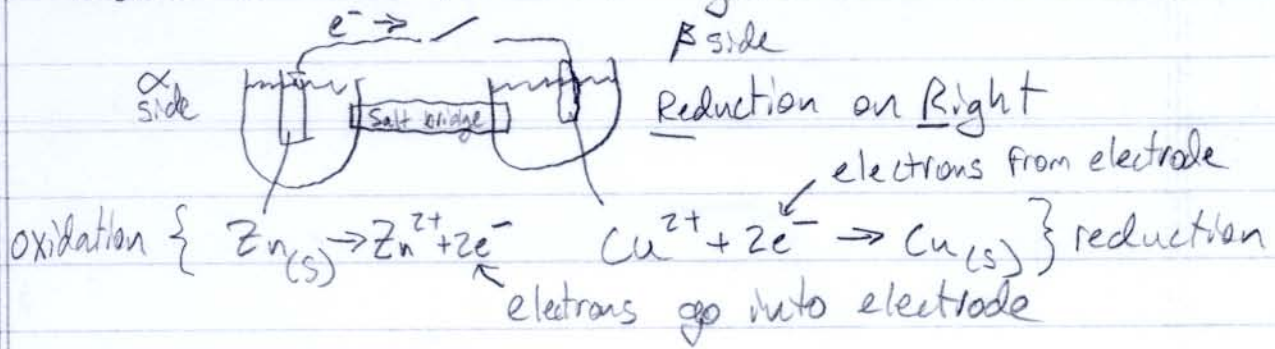
$$\text{moving the } \Phi\text{'s to the left: } \Phi_E^{\alpha} - \Phi_E^{\beta} = \frac{RT}{F} \ln \frac{a_{K^+}^{\beta}}{a_{K^+}^{\alpha}} \quad (z_{K^+} = 1)$$

But in this example we didn't have a chemical reaction so ΔG_{rxn} didn't enter in.

Next we'll look at Electrochemical cells...

Basics of electrochemistry: "LEO says GER"

Lose $e^- \rightarrow$ oxidation gain $e^- \rightarrow$ reduction



Once again why the analogy to osmotic pressure
 What is the e^- "pressure" (i.e. voltage) that
 would keep this reaction from going forward?

this occurs when $\tilde{A} = 0 = \mu_{Cu^{2+}} + \mu_{Zn} - \mu_{Zn^{2+}} - \mu_{Cu} - nF(\phi_E^{\beta} - \phi_E^{\alpha})$

$n=2$ (moles of e^-)

since $\phi_E^{\beta} - \phi_E^{\alpha} = V_{cell}$ the terminal voltage, and since $\mu_i = \mu_i^0 + RT \ln a_i$

and since $V_0 = \frac{\sum \mu_i^0}{nF} = \frac{-\Delta G_{rxn}^0}{nF}$, $V_{cell} = V_0 - \frac{RT}{nF} \ln \left(\frac{a_{Zn^{2+}} \cdot a_{Cu}}{a_{Cu^{2+}} \cdot a_{Zn}} \right)$

K_{eq}

This is the Nernst Equation, which would yield

$V_0 = E_{Cu}^0 - E_{Zn}^0 = 0.339 V - (-0.763 V) = 1.10 V = \frac{RT}{nF} \ln K_{eq}$

standard electrode potentials

This K_{eq} is for the reaction $Cu^{2+} + Zn \rightleftharpoons Zn^{2+} + Cu$ and
 is > 1 since $\frac{RT}{nF} \ln K_{eq}$ is a positive number (1.1)

This also says that a voltage of 1.1 V stops the rxn

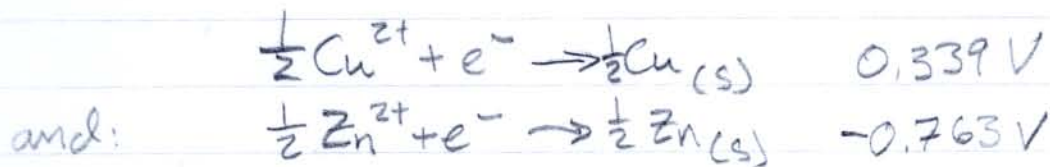
Can we make a battery from a concentration gradient?
 Our results from the K^+ cell say, "yes we can!"

These batteries are called concentration cells

According to Nernst: $V_{cell} = V_0^{\circ} - \frac{RT}{nF} \ln \frac{a_{K^+}^R}{a_{K^+}^L}$, which
 was what we had before ($n=1$)

since $E_{K^+}^{\circ} - E_{K^+}^{\circ} = 0$

In the previous example with Cu + Zn
 we used the standard electrode potentials:



These standard potentials allow us to calculate
 the EMF