

# Adding Fields to $\mu$

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  $\Phi_g$ , grav. pot. and  $\Phi_g = gh$  where  $g$  is the field strength ( $9.8 \text{ m/s}^2$ )

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  $\Phi_E$ , the electric potential, with respect to position:  $E = -\frac{\partial \Phi_E}{\partial x}$

the chemical potential will now be a function of position:

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

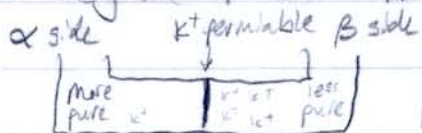
$\tilde{\mu}_i$  is called the electrochemical potential, which we will use to show how the  $\Delta G_{rxn}$  changes in an electric field

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 ( $\beta$ ), 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  $\Phi_E^{\alpha}$  and  $\Phi_E^{\beta}$  are constants, not functions of  $x$ )

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

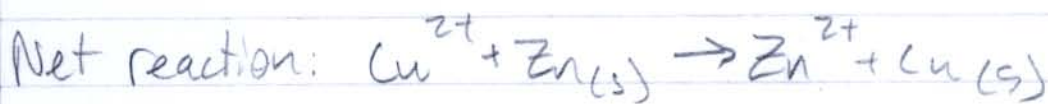
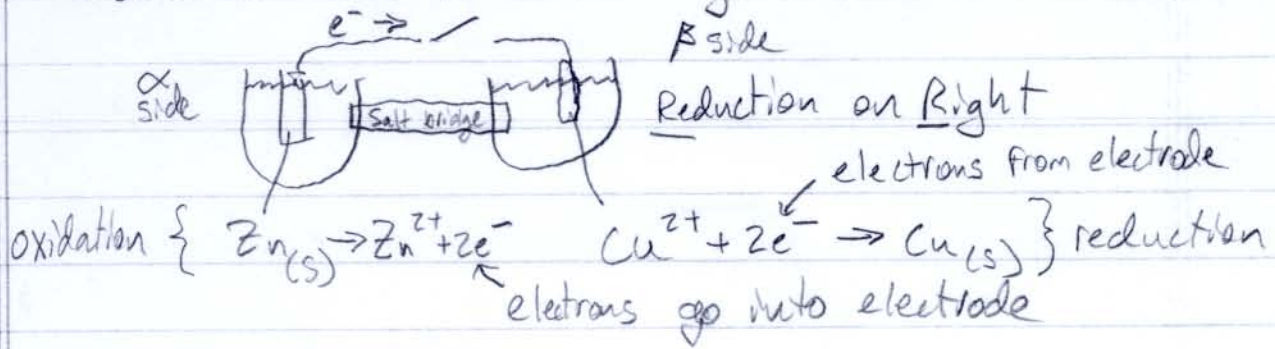
$$\text{moving the } \Phi\text{'s to the left: } \Phi_E^{\alpha} - \Phi_E^{\beta} = \frac{RT}{F} \ln \frac{a_{K^+}^{\beta}}{a_{K^+}^{\alpha}} \quad (z_{K^+} = 1)$$

But in this example we didn't have a chemical reaction so  $\Delta G_{rxn}$  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  $\tilde{A} = 0 = \mu_{Cu^{2+}} + \mu_{Zn} - \mu_{Zn^{2+}} - \mu_{Cu} - nF(\phi_E^B - \phi_E^A)$   $n=2$  (moles of  $e^-$ )

since  $\phi_E^B - \phi_E^A = V_{cell}$  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