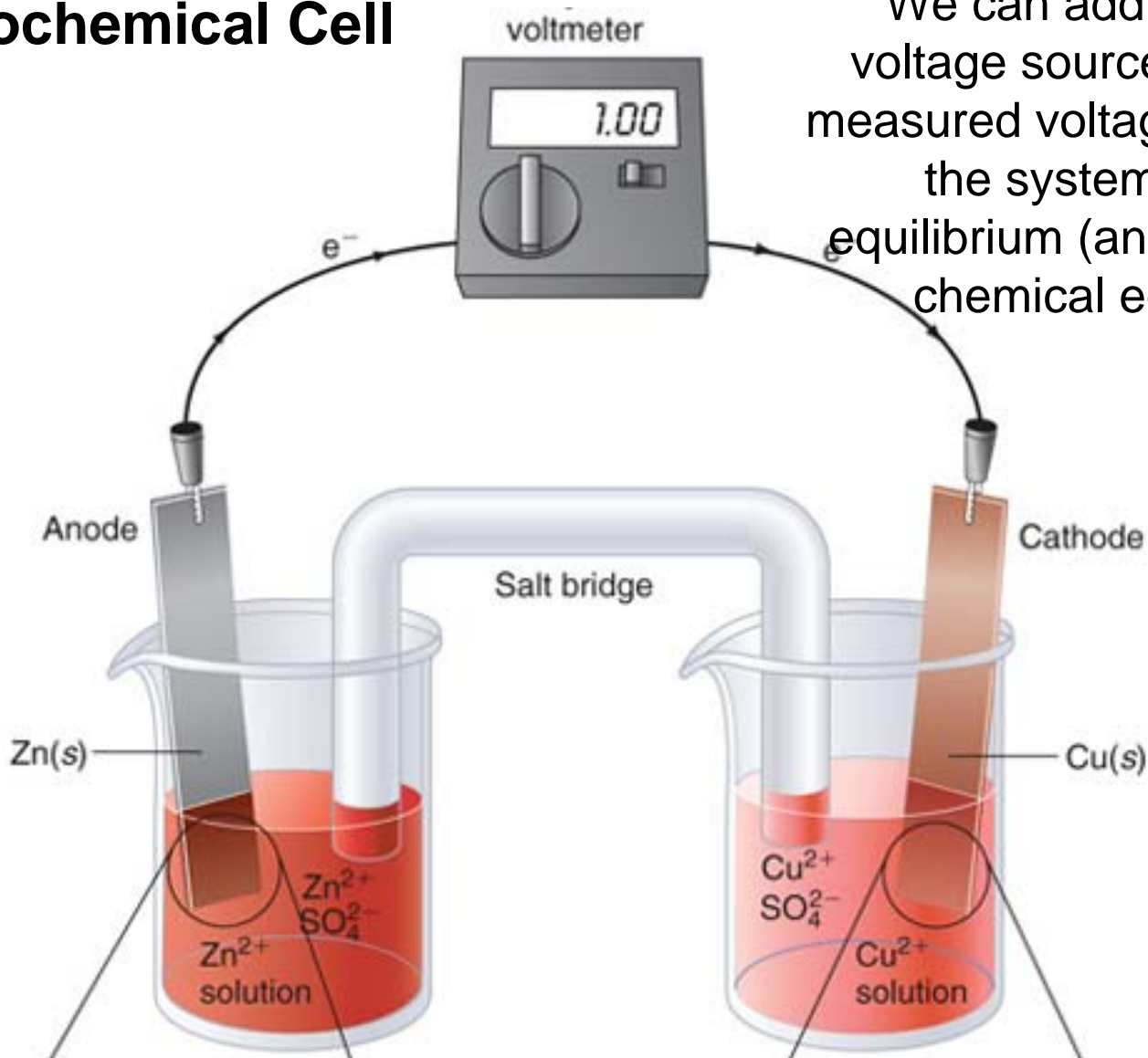


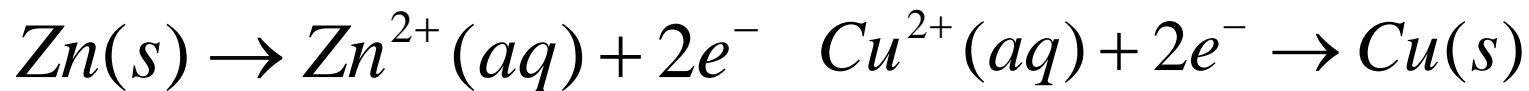
Effects of charges in solutions and chemistry

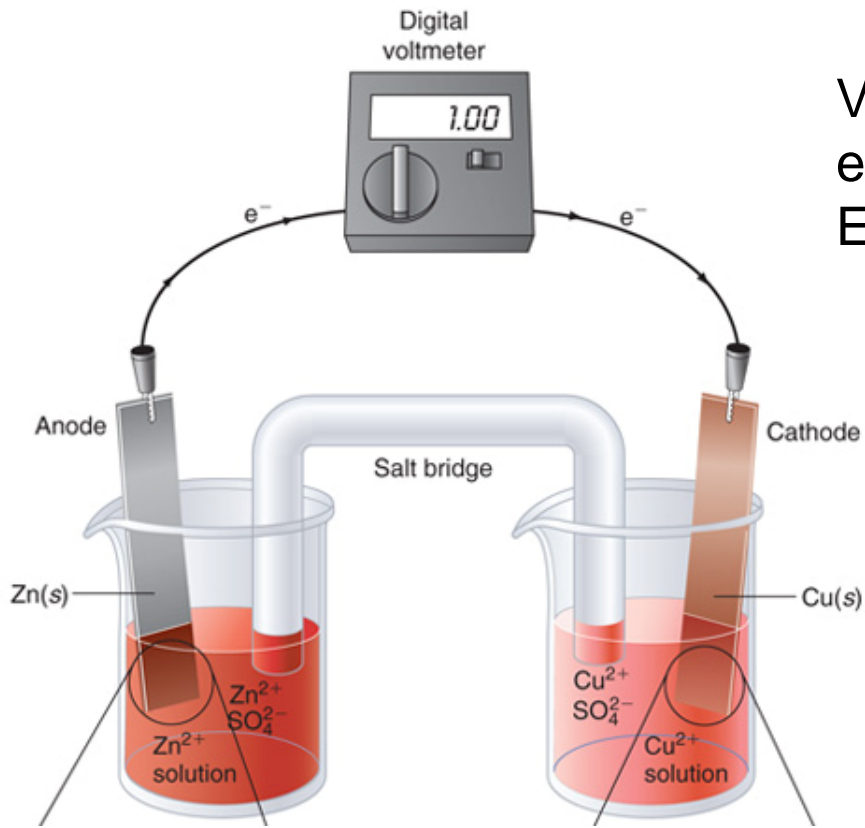
- **Current from moving ions**
 - **Batteries (9.1, 9.3, 9.6-9.11)**
- **Effects of electrical potentials on concentration**
 - **Donnan Potential (9.13)**
- **Activity (“effective concentration”) of ions in water**
 - **Debye Huckel Theory of ionic strength. (9.3-9.5)**
- **Effective Charge on a Polyion**
 - **Counterion Condensation or Manning Theory**

Electrochemical Cell



We can add an external voltage source to offset the measured voltage; At that point the system will be in equilibrium (an electrical plus chemical equilibrium)





Voltage difference between the electrodes is called electromotive force or EMF, E . (in Volts)

What is the electrical work done by this cell?

$$W_{\text{electrical}} = -QV = -QE$$

$$= -(total\ charge)(voltage)$$

The arrangement separates what would be a spontaneous reaction of Cu ions displacing Zn metal to make Cu metal and Zn ions.

$$Q = (n_e)(e)(N_A)(n)$$

$$= \left(\frac{\# e}{rxn}\right) \left(\frac{charge}{e}\right) \left(\frac{rxn}{mole}\right) (moles)$$

If one coulomb of charge moves through a potential of one volt, that releases one joule of energy: A volt is a Joule/Coulomb. The Faraday tells us how many coulombs are in one mole of electrons.

$$F = \text{Faraday's constant} = eN_A = 96485 \text{ C/mole of electrons}$$

$$W_{\text{electrical}} = -QE = -nFE$$

$$Q = nF = (n_e)xF$$

For a chemical reaction $n = (n_e)x = \left(\frac{\# e}{\text{rxn}}\right)(\text{moles rxn})$

Say an electrochemical cell (i.e. a battery) runs at constant pressure and temperature. What is $w_{\text{electrical}} = ?$

$$W_{\text{electrical}} = W_{\text{nonPV}} = \Delta G_{T,P} = \Delta G_{\text{rxn}}x = -nFE$$

$$\Delta G_{\text{rxn}} \equiv \Delta \bar{G} = -n_e FE$$

The molar free energy for the (spontaneous) chemical reaction then is related to the voltage generated (without the need to actually have the reaction proceed).

The external E is adjustable so the reaction can be at equilibrium if the external E just balances the E generated by the reaction.

Therefore, $\overline{\Delta G} = -n_e F E$

And for a chemical reaction at constant T and P:

$$\overline{\Delta G} = \overline{\Delta G}^0 + RT \ln Q \quad Q \equiv \left(\frac{\prod_{products} (a_i)^{v_i}}{\prod_{reactants} (a_i)^{v_i}} \right)$$

Now for a little bit of algebraic Rearrangement:

$$E = -\frac{\overline{\Delta G}^0}{n_e F} - \frac{RT}{n_e F} \ln \left(\frac{\prod_{products} (a_i)^{v_i}}{\prod_{reactants} (a_i)^{v_i}} \right)$$

The external E is adjustable so the reaction can be at equilibrium if the external E just balances the E generated by the reaction.

By setting the external voltage the cell can be at equilibrium at any set of concentrations; this is the electro-chemical equilibrium

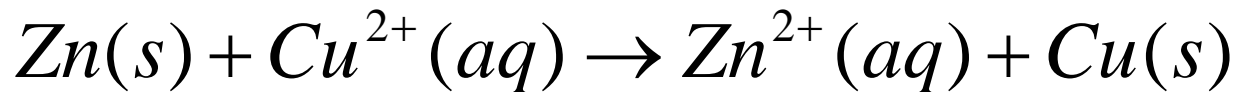
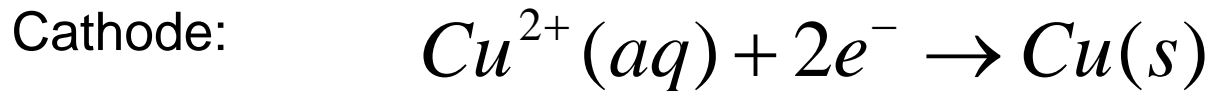
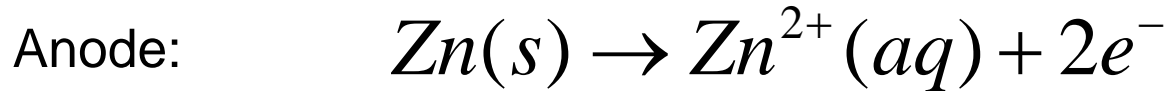
We can define a standard state for electrochemical cells, which give the voltage when each species is at unit activity:

$$E^0 = -\frac{\overline{\Delta G}^0}{n_e F}$$

Now we can write:

$$E = E^0 - \frac{RT}{n_e F} \ln \left(\frac{\prod_{products} (a_i)^{\nu_i}}{\prod_{reactants} (a_i)^{\nu_i}} \right)$$

Let's go back to the electrochemical cell we started with:



$$\overline{\Delta G}^0 = -2.1 \times 10^5 \text{ J mole}^{-1} \quad n_e = 2 \text{ e}'s / rxn$$

Suppose that $[Zn^{2+}] = 10^{-8} \text{ M}$ and $[Cu^{2+}] = 0.1 \text{ M}$. What is the voltage drop across the electrodes at $T = 298 \text{ K}$?

$$E = E^0 - \frac{RT}{n_e F} \ln \left(\frac{\prod_{products} (a_i)^{v_i}}{\prod_{reactants} (a_i)^{v_i}} \right) \quad \frac{RT}{F} = \frac{(8.314 \text{ JK}^{-1} \text{ mole}^{-1}) 298 \text{ K}}{(96485 \text{ C mole}^{-1})} = 0.02569 \text{ J/C} = 25 \text{ mV}$$

$$E = -\frac{\overline{\Delta G^0}}{n_e F} - \frac{RT}{n_e F} \ln \left(\frac{\prod_{products} (a_i)^{v_i}}{\prod_{reactants} (a_i)^{v_i}} \right)$$

$$E = \frac{2.1 \times 10^5 \text{ J mole}^{-1}}{2(96485 \text{ C mole}^{-1})} - \frac{25}{2} \cdot 10^{-3} \ln \left(\frac{10^{-8} \text{ M}}{10^{-1} \text{ M}} \right)$$

$$E = 1.1 \text{ V} + 0.2 \text{ V} = 1.3 \text{ V}$$

The metals have unit activity. There are very little products so the reaction is far from equilibrium, the concentrations term is very small. Q can be formed as though the reaction were all together in a single beaker.

Electrochemical Equilibrium

At equilibrium,

$$Q = K \quad \Delta G = 0$$

$$E = -\frac{\overline{\Delta G}}{n_e F} = 0$$

At standard state

$$Q = 1 \quad \overline{\Delta G} = \overline{\Delta G}^0$$

$$E = E^0$$

$$E^0 = \frac{RT}{n_e F} \ln \left(\frac{\prod_{products} (a_i)^{\nu_i}}{\prod_{reactants} (a_i)^{\nu_i}} \right)_{eq}$$

$$E^0 = \frac{RT}{n_e F} \ln K_{eq}$$

Calculating thermodynamic quantities in electrochemical reactions

$$\overline{\Delta G} = -n_e F E$$

$$dG = -SdT + VdP$$

$$d\overline{\Delta G} = -\Delta SdT + \Delta\overline{V}dP$$

$$\overline{S} = -\left(\frac{\partial\overline{G}}{\partial T}\right)_P$$

$$\Delta\overline{S} = -\left(\frac{\partial\overline{\Delta G}}{\partial T}\right)_P = \left(\frac{\partial(n_e F E)}{\partial T}\right)_P = n_e F \left(\frac{\partial E}{\partial T}\right)_P$$

How can we find ΔH ?

At constant P and T:

$$\overline{\Delta H} = \overline{\Delta G} + T \overline{\Delta S}$$

Combining above:

$$\overline{\Delta H} = -n_e F E + n_e F T \left(\frac{\partial E}{\partial T} \right)_P$$

Also from the van't Hoff type expression

$$G = H - TS$$

$$\left(\frac{\partial G/T}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{H}{T^2} + \frac{S}{T}$$

$$H = -T^2 \left(\frac{\partial G/T}{\partial T} \right)_P = \left(\frac{\partial G/T}{\partial 1/T} \right)_P$$

$$\Delta \bar{H} = -T^2 \left(\frac{\partial \Delta \bar{G}/T}{\partial T} \right)_P = n_e F T^2 \left(\frac{\partial E/T}{\partial T} \right)_P$$

Example: If I measure the voltage drop across an electrochemical cell in my lab, I find that it has the following form:

$$E(T) = A + BT + CT^2$$

Find the change in Gibbs Free Energy, entropy and enthalpy for the chemical reaction in my cell at 298 K.

$$\overline{\Delta H} = -n_e F E + n_e F T \left(\frac{\partial E}{\partial T} \right)_P = n_e F T^2 \left(\frac{\partial E/T}{\partial T} \right)_P$$

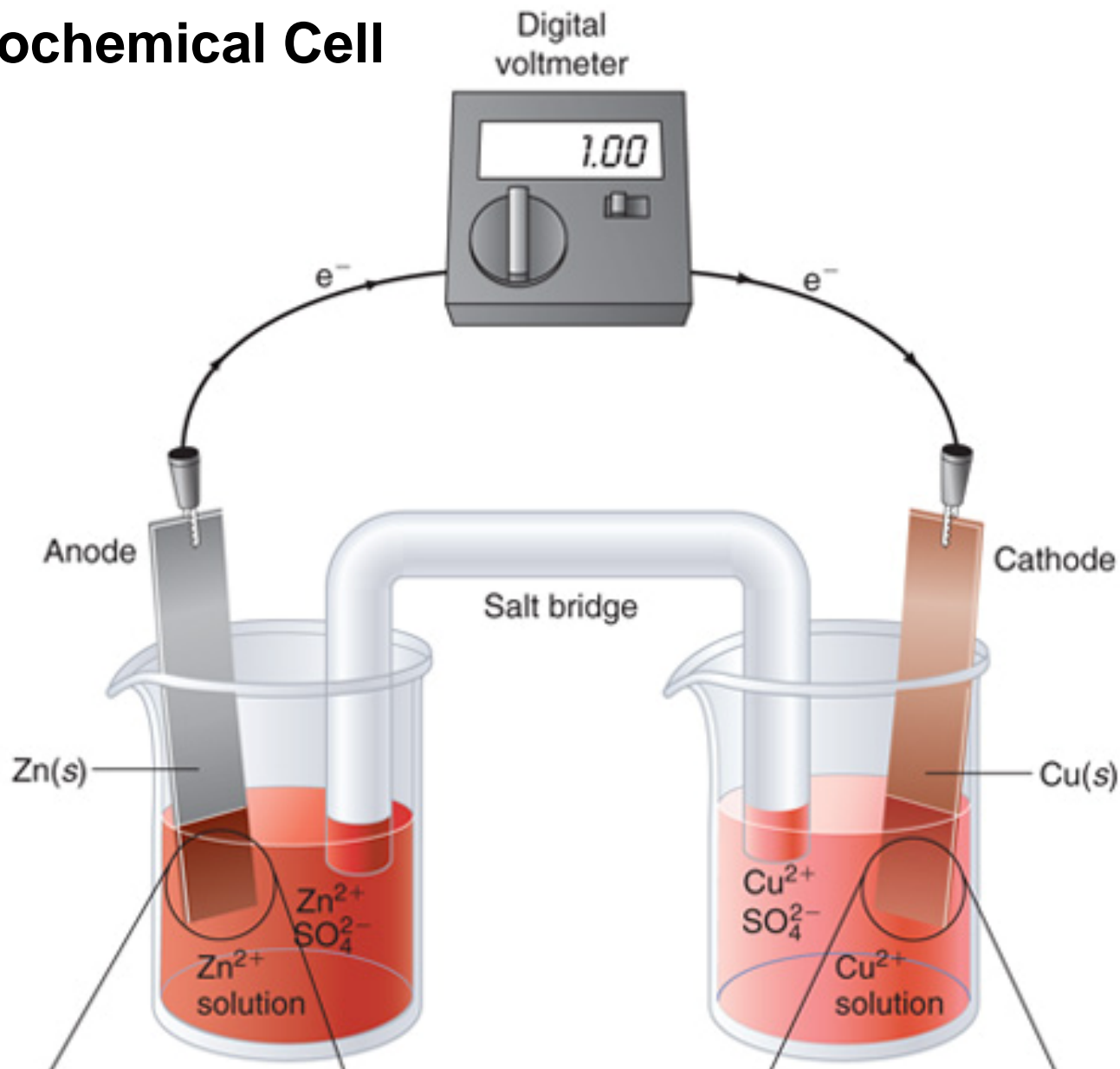
$$\Delta \overline{S} = n_e F \left(\frac{\partial E}{\partial T} \right)_P$$

The temperature dependence of the voltage then directly gives the enthalpy, entropy, and Gibbs energy for the chemical reaction at T,P

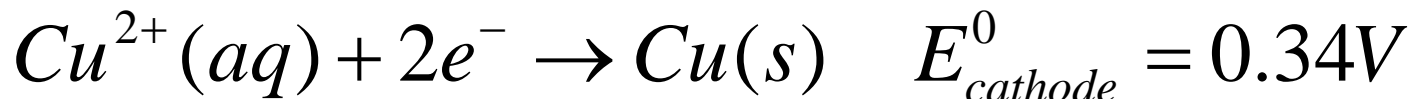
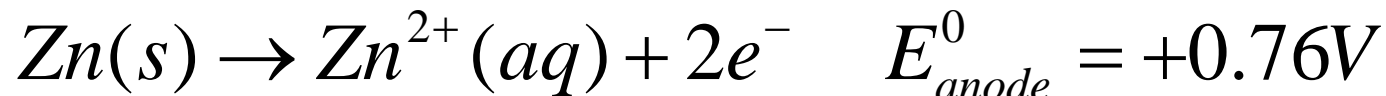
Using the temperature dependence of E, the A term goes with the enthalpy, and the B term goes with the entropy and the C term goes partly to each of the two.

Why does a battery “work harder” in cold weather?

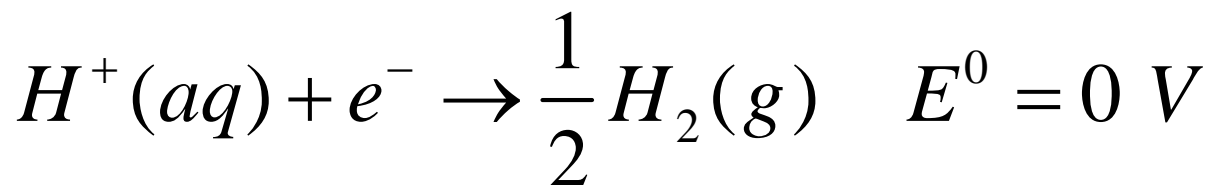
Electrochemical Cell



Standard Reduction Potentials: Half-cell Potentials



E^0 of each half cell is called the standard electrode potential and defined relative to a standard hydrogen electrode



Tables of Standard Gibbs Free Energy Tables (at T,P), the molar heats of formation, so there are Standard Half Cell Potential Tables, referenced to the Standard Hydrogen Electrode.

Overall Cell Potential

$$E_{cell}^0 = E_{reduction}^0 + E_{oxidation}^0$$

For our cell:

$$\begin{aligned} E_{cell}^0 &= E_{Cu^{2+}}^0 + E_{Zn^{2+}}^0 \\ &= 0.34V + (+0.76V) = 1.1V \end{aligned}$$

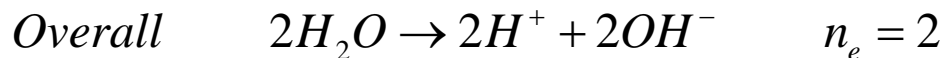
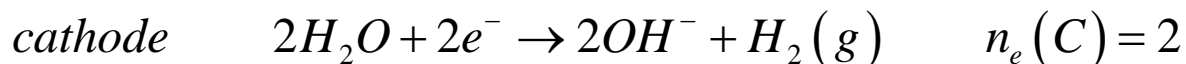
Is this spontaneous under standard conditions (Q=1)?

$$E^0 = -\frac{\overline{\Delta G}^0}{n_e F} \quad \longrightarrow \quad \text{Yes!}$$

Galvanic Cells (Batteries) can be used to measure equilibrium constants

- Water dissociates very poorly ($K_w = 10^{-14}$)
- This constant is the basis of acid base chemistry.
- How to measure it?
- Use a Battery (this was indeed how K_w was measured)
- Anode has 0.1M HCl solution (H_2 gas bubbled in on Pt electrodes)
- Cathode has 0.1 M NaOH solution.

$$E = E^0 - \frac{RT}{n_e F} \ln \left\{ [H^+] [OH^-] \right\}^2$$



Measure the voltage $E = -0.708V$, Solve for E^0 and K_w

$$E^0 = E + \frac{.025}{2} \ln \left\{ [H^+] [OH^-] \right\}^2 = -0.708 + .025 \ln \{0.1\}^2 = -0.826V$$

$$\Delta G^0 = -n_e F E^0 = 160 \text{ kJ/mole}$$

A concentration cell: Measuring concentrations of ions.

- Measure Chloride ion concentration
- Have a reference solution at 0.1M Cl ion and terminals that connect chloride to metal chloride (like AgCl) to metal (Ag)
- Then the reaction at anode and cathode



- Reactions do not have to proceed very far; and are driven only by the concentration imbalance.

$$E = E^0 - \frac{RT}{n_e F} \ln \left\{ \frac{[Cl^- (Ref)]}{[Cl^- (U)]} \right\} = 0 - 0.025 \ln \frac{0.1}{X}$$

For example, measure -0.288V, then the concentration is 1 micromolar

There is never a charge imbalance in either beaker; but there is a voltage generated by the concentration difference (of the Cl in this case) between the two beakers.

- The equilibrium constant in terms of activity:

$$K = Q(X_{\text{equilibrium}})$$

$$K_a = \prod_i (a_i^{eq})^{v_i} = \prod_i \left(\gamma_i^{eq} \frac{c_i^{eq}}{c_o} \right)^{v_i} = \prod_i (\gamma_i^{eq})^{v_i} \prod_i \left(\frac{c_i^{eq}}{c_o} \right)^{v_i}$$

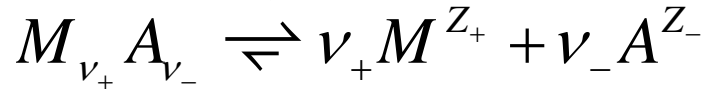
$$Q = Q(X) = \Gamma(X) \prod_i \left(\frac{c_i(X)}{c_o} \right)^{v_i}$$

$$\Gamma(X) = \prod_i (\gamma_i(X))^{v_i}$$

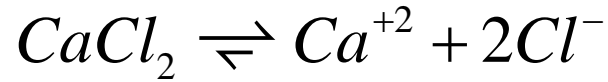
Consider the solubility of a salt in water. Neglect the activity coefficient for now, soon we will define it for electrolytes.

If the K_a is known for a salt what is the solubility, S ?

Solubility of a general binary salt and K_{sp}



- A salt dissociates:



$$0 = \nu_+ Z_+ + \nu_- Z_-$$

- The concentration is: $c_+ = \nu_+ X$

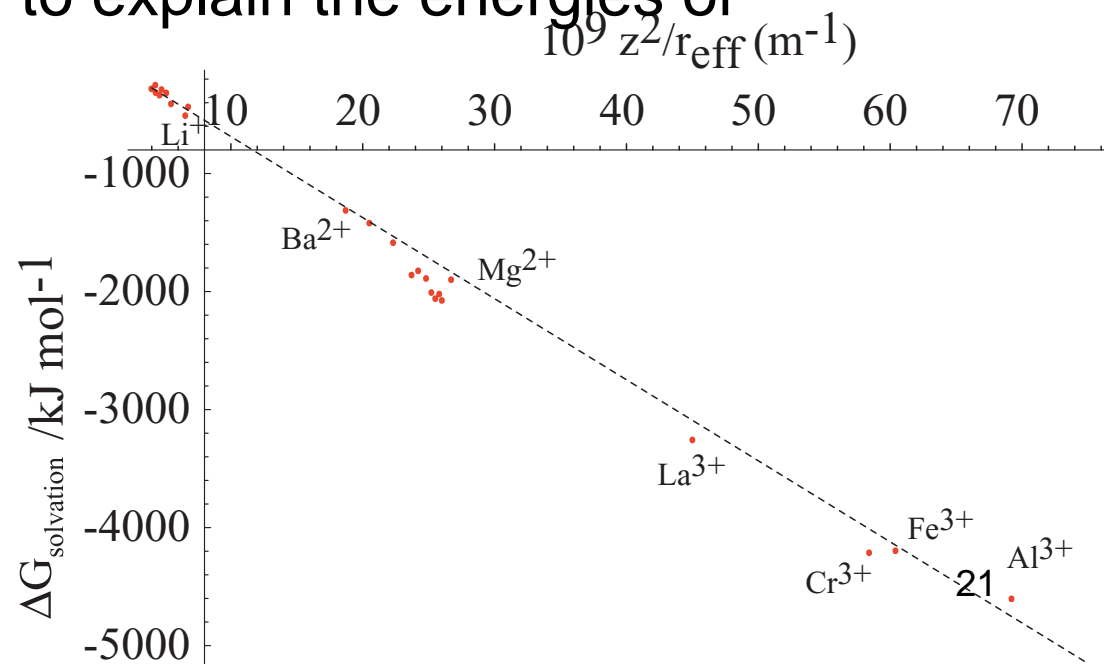
- X is the solubility $c_- = \nu_- X$

- The Equilibrium K is: $K_{sp} = \left(\frac{c_+}{c_o}\right)^{\nu_+} \left(\frac{c_-}{c_o}\right)^{\nu_-}$
Set Activity coefficients to 1

The solubility is X, and is related to the equilibrium constant or the solubility product. The activity of the solvent and the solid salt (before dissociation) are taken to be unity.

$$K_{sp} = \left(\frac{c_+}{c_o}\right)^{\nu_+} \left(\frac{c_-}{c_o}\right)^{\nu_-} = \left(\frac{X}{c_o}\right)^{(\nu_+ + \nu_-)} (\nu_+)^{\nu_+} (\nu_-)^{\nu_-}$$

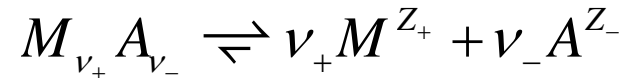
- The solvation energy is negative, so solvation of charges is spontaneous, because the dielectric polarizes to accommodate the ion. Charges like to go into solvents with large dielectrics: Organic solvents are typically 2-4 (dimensionless), while water is 78.
- One question is: What is the size of the ion? The text discusses this and the upshot is that the radius of the ion ought to be roughly the radius from the crystal structure plus 1 Angstrom to account for the size of water. This seems to work pretty well to explain the energies of solvation.



Charge and activity

- We can estimate the extra energy for solvation: determine what happens to the activity (via and activity coefficient) for the effect of charged ions in solution.
- Consider the dissociation of a binary salt that produces ions.
- M is the Molarity, m is the molality of the salt, they are almost the same thing.

- The ionic strength is defined as (see the reaction for a binary salt into solution):



$$I_{1:1} = \frac{1}{2}(c_+ + c_-) = m \quad \text{e.g. } NaCl$$



$$I = \frac{1}{2}(m\nu_+z_+^2 + m\nu_-z_-^2) = m \left\{ \frac{1}{2}(\nu_+z_+^2 + \nu_-z_-^2) \right\}$$

$$0 = \nu_+Z_+ + \nu_-Z_-$$

- E.G. $CaSO_4$ has 4 times the ionic strength of $NaCl$ at the same Molarity.

- Want to correct the reaction quotient for the fact that the solutes are charged. Both Q and K are written in terms of activities, which is the product of the concentration (either molarity or molality) and the activity coefficient.
- Debye-Huckel theory tells us how to estimate (compute) the activity coefficient for the ions, through the ionic strength of the salt (or acid or base).
- Apply the description of Q to the dissociation of a binary salt:

$$Q_a(X) = \Gamma(X) \prod_i \left(\frac{c_i(X)}{c_o} \right)^{v_i} = \Gamma \left(\frac{c_+}{c_o} \right)^{v_+} \left(\frac{c_-}{c_o} \right)^{v_-}$$

$$\Gamma(X) = \prod_i \left(\gamma_i(X) \right)^{v_i} = \gamma_+^{v_+} \gamma_-^{v_-}$$

$$\gamma_{\pm}^v = \gamma_+^{v_+} \gamma_-^{v_-} \quad \text{where } v = v_+ + v_-$$

$$K_a = Q_a \quad @ \text{ Equilibrium}$$

Debye Huckel Theory

- They reasoned (from the Poisson-Boltzmann Equation) that the charges will arrange themselves in a statistical way about each other and screen each other.
- We would expect the activity coefficients to be lower, or less than 1 as the ionic strength increases because there are more charges in the solution, stabilized by the solvent and each other. So the smaller gamma is (as a number less than 1) the more stable the solution is, and the lower the activity hence lower the free energy is.
- Normally charges interact by the coulomb potential. For ions free to move in solution they see each other by a screened coulomb interaction. The greater the screening the more stable the solution.

$$V(r) = \frac{z_1 z_2}{r} e^{-\kappa r}$$

$$\kappa = 3.3\sqrt{I} \text{ (nm)}^{-1}$$

$$\lambda = \frac{1}{\kappa}$$

To correct K for the activity compute the correction:

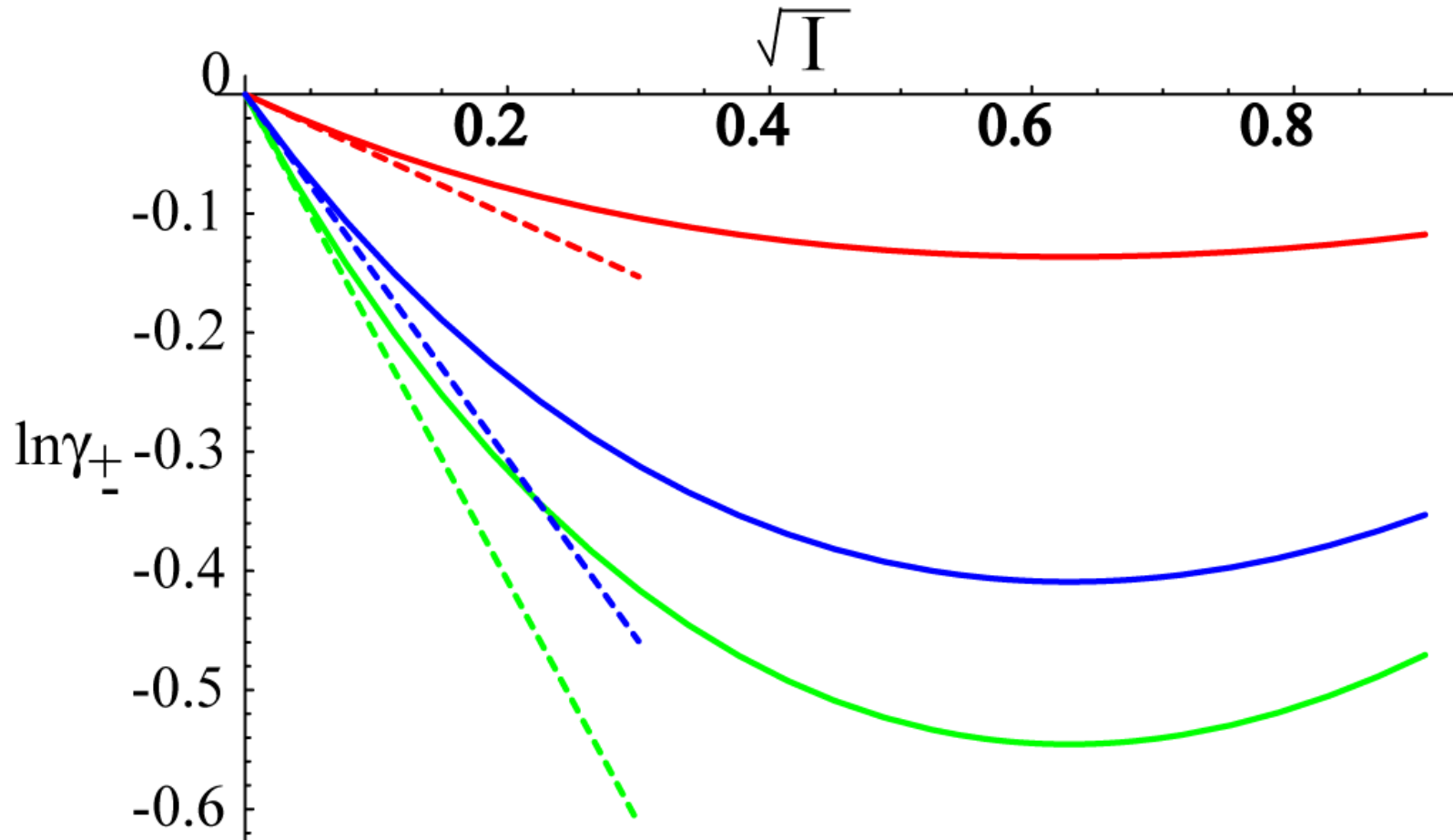
$$\ln \Gamma = \nu \ln \gamma_{\pm} = 2.303\nu \log_{10} \gamma_{\pm}$$

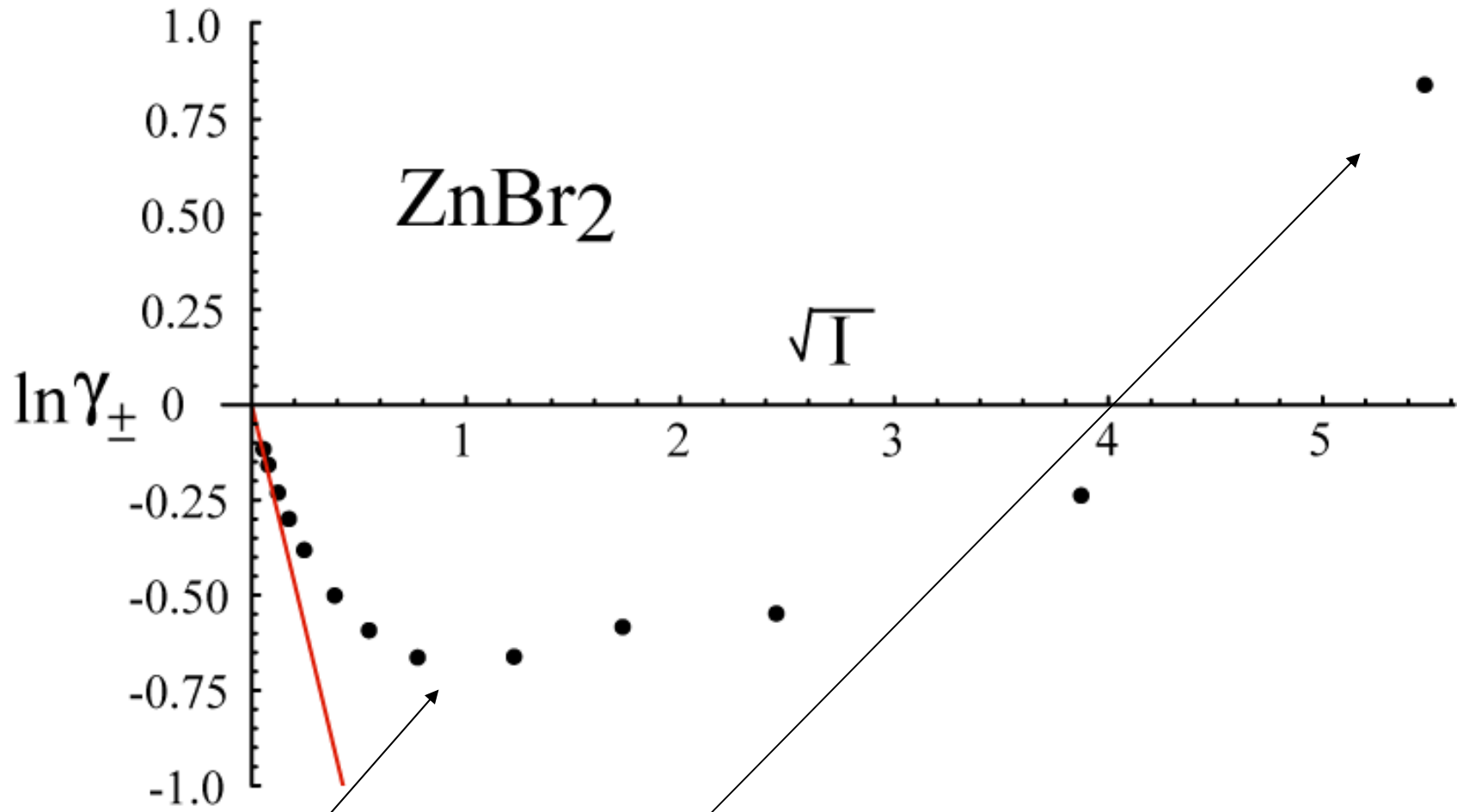
$$\ln \gamma_{\pm} = -1.174 |z_+ z_-| \left\{ \frac{\left(\frac{I}{m_o}\right)^{\frac{1}{2}}}{1 + \left(\frac{I}{m_o}\right)^{\frac{1}{2}}} - 0.2 \left(\frac{I}{m_o}\right)^{\frac{1}{2}} \right\} \approx -1.174 |z_+ z_-| \left(\frac{I}{m_o}\right)^{\frac{1}{2}}$$

The full equation is the Modified-Davies equation, which is empirical, the simplified version is the Debye-Huckel limiting law. This is for binary salts in water. m_o is the reference concentration of 1 M or 1m. Other texts report the correction is -0.3 not -0.2 , but say the formula is limited to $I < 0.5$, in any event. The modification (I added) seems to work quite well to Molar amounts. I raised I to the $\frac{1}{2}$ power; Davies has it to the 1 power.

Empirical modification of the Debye- Hückel limiting law

Dashed lines are DH for 1:1, 1:2 and 1:3 electrolytes, solid lines, which pretty well fit the data, are the Davies equation.

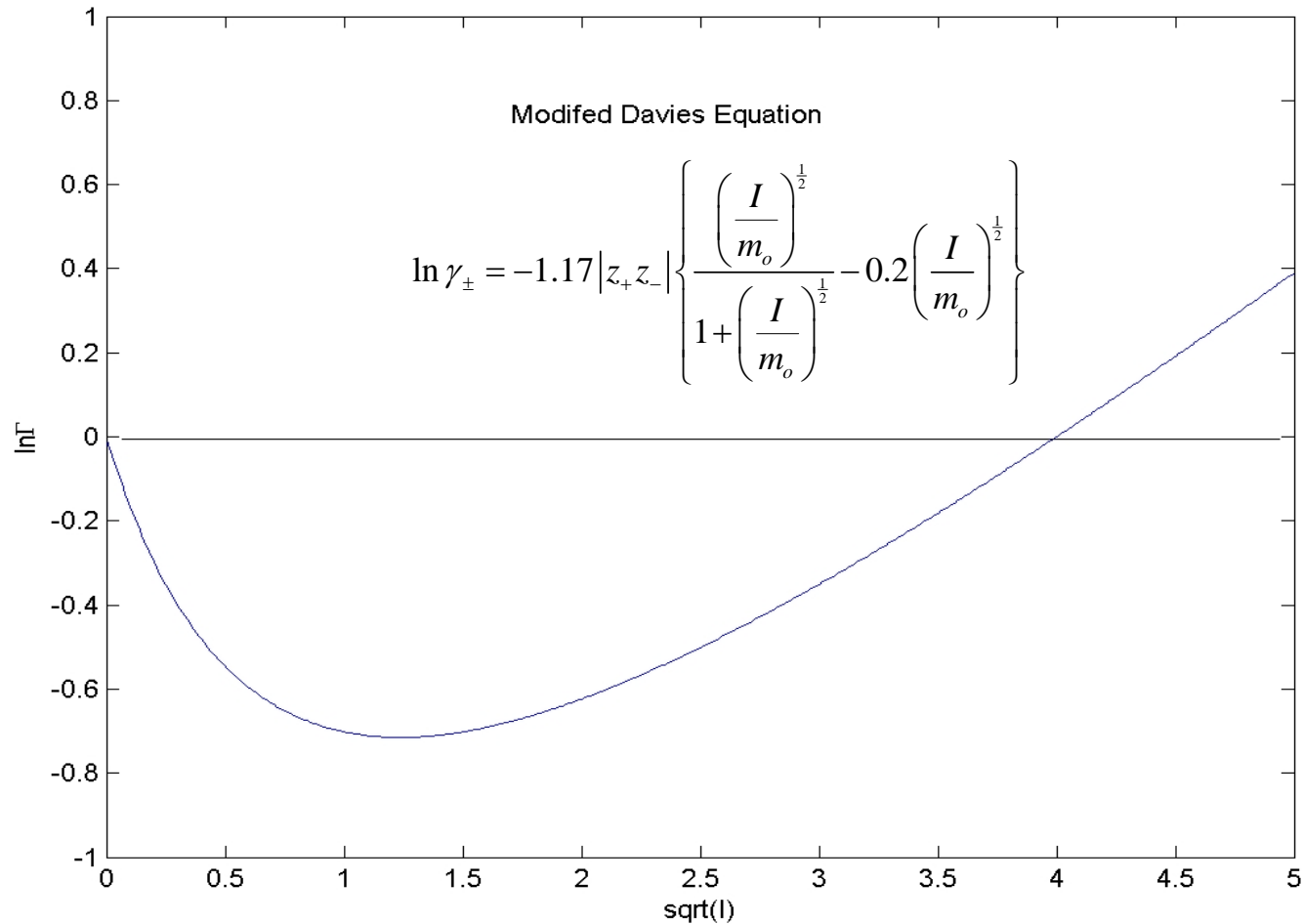




For high values of the ionic strength, $\gamma_{\pm} > 1$ and the solubility is less than at low values of I . This effect is known as salting out.

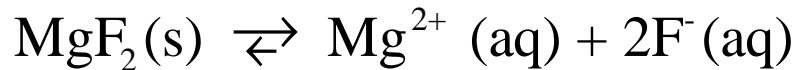
Salting in and salting out are frequently encountered in studies of the solubility of proteins in aqueous electrolyte solutions.

I modified the Davies equation, and compared to the previous slide, this looks pretty good to me. There seems to be a lot of discussion on line that there aren't any good empirical equations, but hey this works for me.



Chemical Equilibrium in Electrolyte Solutions

$$\boxed{K_a = \prod_i (a_i^{eq})^{v_j}} \quad a_i = \gamma_i \frac{c_i}{c^\circ}$$



$$\boxed{K_{sp} = a_{\text{Mg}^{2+}} a_{\text{F}^{-}}^2 = \left(\frac{c_{\text{Mg}^{2+}}}{c^\circ} \right) \left(\frac{c_{\text{F}^{-}}}{c^\circ} \right)^2 \gamma_{\pm}^3 = 6.4 \times 10^{-9}}$$

We solve for γ_{\pm} and $c_{\text{F}^{-}}$ iteratively.

We first assume that $\gamma_{\pm} = 1$ and solve equation 9.38 for $c_{\text{F}^{-}}$, giving

$c_{\text{Mg}^{2+}} = 1.17 \cdot 10^{-3} \text{ mol/L}$. We next calculate the ionic strength from

$$I = \frac{1}{2} (z_+^2 m_+ + z_-^2 m_-) = 3m = 3.4 \cdot 10^{-3} \text{ mol/L}.$$

Iterate on the coefficient

$$\gamma_{\pm} = 0.87$$

Use this value of Γ to correct the concs. $\Gamma = \gamma_{\pm}^3 = 0.66$

After two iterations the concentration is increased by 15%. It is expected that there would be an increase, as the screening interactions stabilize ions, so more go into solution. (An example of how ions can go into solution in higher concentrations because the interaction with the solvent reduces the activity.)

Donnan potential (9.13) A model for moving charges across membranes:

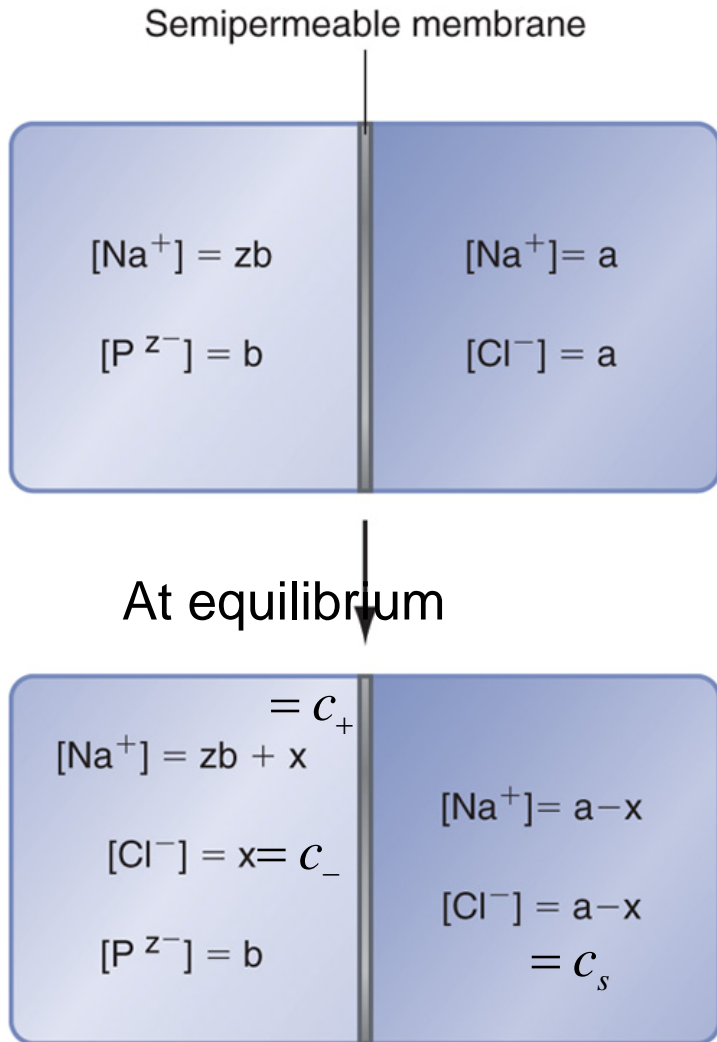


Figure: 09-16

Left side: A polymer that cannot get across the membrane and its dissociated counter ions, Na.

Right side: A large volume of a NaCl solution.

Without the polymer both sides would come to the same concentration.

Because of polymer the concentration of Cl ions on the left will be less than that on the right, at equilibrium.

In coming to equilibrium, cannot bring more Cl ions to the left than Na ions; this would cause a charge buildup on different sides; this does not happen.

Chemical balance is achieved when chemical potentials for the ions on both sides balance.

What are the chemical potentials.

- As charged ions flowing from one side to the other there might be an electrostatic potential difference that is present $\Phi = \Phi_L - \Phi_R$

- Because these are charged ions they experience that potential and the energy (as Joules/mole) is $zF\Phi$

- Therefore the complete chemical potential for each ion (on the left) is

$$\mu_{\pm} = \mu_{\pm}^0 + RT \ln a_{\pm} + z_{\pm} F \Phi \quad \textit{Left}$$

$$\mu_{\pm} = \mu_{\pm}^0 + RT \ln a_{\pm} \quad \textit{Right}$$

- The potential drops out for the sum of the Na and Cl Chem. Pots.

$$\mu_{+} + \mu_{-} = \mu_{\pm}^0 + RT \ln a_{+} + RT \ln a_{-} + z_{+} F \Phi + z_{-} F \Phi = \mu_{\pm}^0 + RT \ln (a_{+} a_{-})$$

Donnan potential (Section 9.13)

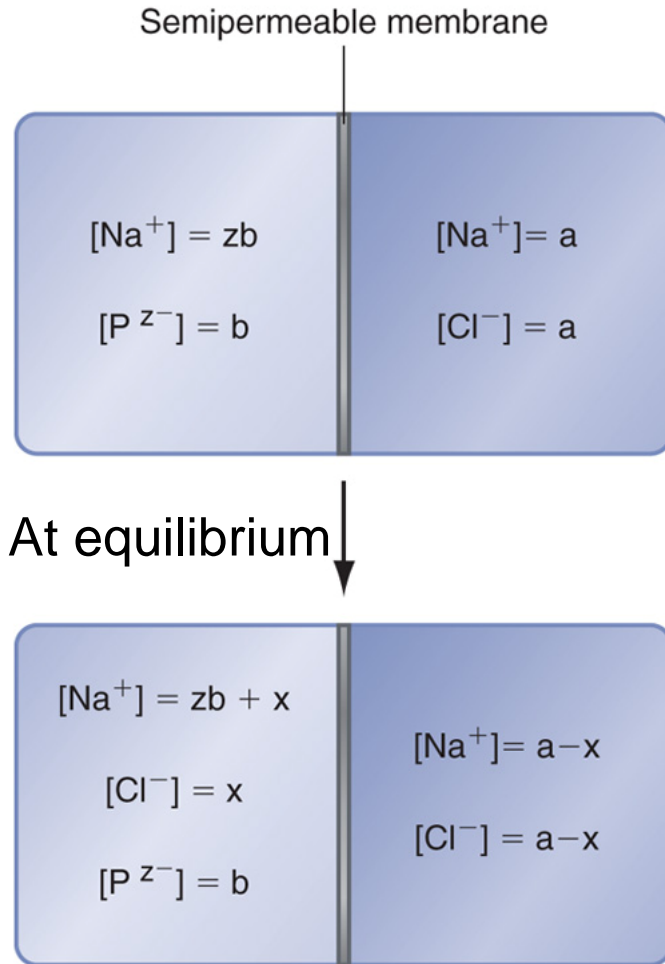


Figure: 09-16

At equilibrium, we know that

$$\mu_L^+ + \mu_L^- = \mu_R^+ + \mu_R^-$$

This reduces to:

$$a_L^+ a_L^- = a_R^+ a_R^- = a_s^2$$

In the limit of ideal dilute solutions:

$$c_L^+ c_L^- = c_R^+ c_R^- = c_s^2$$

If we only had permeable species:

$$\frac{c_{L,eq}^+}{c_{R,eq}^+} = \frac{c_{R,eq}^-}{c_{L,eq}^-} = 1$$

In the presence of impermeable species we have the Donnan effect:

$$\frac{c_{L,eq}^+}{c_{R,eq}^+} = \frac{c_{R,eq}^-}{c_{L,eq}^-} = r_D > 1$$

- The additional constraint is that the number of charges should sum to zero in each side of the container. (There is no actual potential to measure, but this affects the chemical concentrations.) So the Na ions come from polymer and NaCl:

$$c_+ = zb + c_- \quad c_s^2 = c_+ c_- = (zb + c_-) c_-$$

- Gives a quadratic equation for how many Cl ions come into the left hand side and how it depends on the concentration of the polymer (zb).

$$c_-^2 + c_- zb - c_s^2 = 0$$

- As the polymer concentration vanishes the Cl ion concentration on the left equals that on the right.

$$c_- = \frac{\sqrt{(zb)^2 + 4c_s^2} - zb}{2}$$

The polymer (because it cannot pass through the membrane) excludes salt from the left. As the polymer concentration gets large the amount of chloride entering goes to zero.

$$r_D = \frac{c_s}{c_-} = \frac{2c_s}{\sqrt{(zb)^2 + 4c_s^2} - zb} > 1$$

We neglected the electrostatic part of the chemical potentials; the electrically neutral forms cancel out. Membrane pressure also neglected, it is small.³⁴

The electro-chemical potential for ions

- Because the ions are charged, moving from the right to the left might change the nature of the environment, because the potential might be different on both sides.
- At equilibrium the chemical potentials for each of the ions must be balanced across the membrane.

• Take Cl⁻ ions for example:

• Because the [Cl⁻] is not the same on both sides; the concentration must be balanced by an effective electrostatic potential (due to some other ions, the polymer)

• However the potential drops out for the sum of the ions.

• Approximately, the Donnan Ratio goes as the ratio of polymer to salt concentration.

$$\mu_L = \mu_R \quad z_- = -1$$

$$\mu_-^0 + RT \ln c_- + z_- F \Phi = \mu_-^0 + RT \ln c_s$$

$$\Phi = -\frac{RT}{z_- F} \ln \left(\frac{c_-}{c_s} \right) = \frac{RT}{z_- F} \ln (r_D)$$

$$r_D \sim 1 + \frac{zb}{c_s}$$

Examples of the Donnan Potential

- Assume polymer concentration (as charges) is 0.01M inside a dialysis bag; and the salt is same, $c_s=0.01M$. What is the Donnan Potential and how much chloride is pulled in at equilibrium?

$$r_D \sim 2$$

$$c_- = \frac{c_s}{r_D} \sim .005M$$

$$\Phi = \frac{RT}{z_- F} \ln(r_D) \sim \frac{25}{-1} \ln 2 = -17mV$$

- Same problem as above but $c_s=0.1M$ and polymer 1mM in ions. In this case the Donnan potential is virtually gone.
- What is the pH difference across the membrane for above problems?

$$\mu_{H^+L} = \mu_{H^+}^0 + RT \ln[H^+]_L + z_{H^+} F \Phi = \mu_{H^+R} = \mu_{H^+}^0 + RT \ln[H^+]_R$$

$$\left\{ \ln[H^+]_R - RT \ln[H^+]_L \right\} = \Phi \frac{z_{H^+} F}{RT}$$

$$\Delta pH = pH_L - pH_R = \Phi \frac{z_{H^+} F}{2.303RT} \sim -\frac{17}{2.2 \cdot 25} = -0.3$$

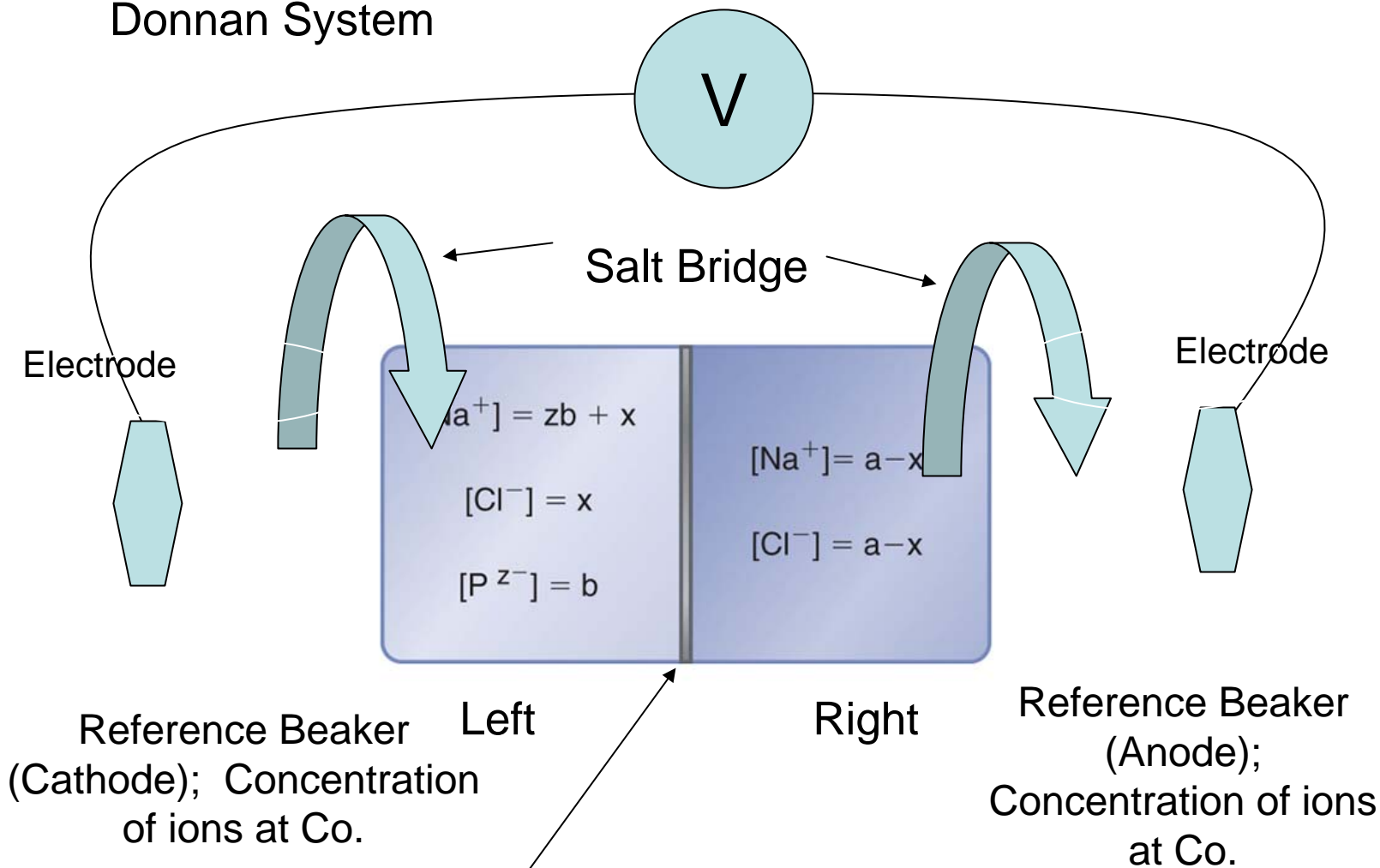
Protons, as positive ions, are drawn into the left (like Na), left is more acidic.

Measuring the Donnan Potential

- Can't directly measure by putting electrodes into the two sides. The potential must be there because the chloride concentrations on the two sides are different; and if chloride were not charged then the concentrations would be the same. Direct contact on both side of membrane will read zero voltage
- System is at equilibrium so no net potential difference across the membrane.
- However, we can measure the Donnan potential with a voltmeter by a somewhat indirect method.
- Use two silver/silver chloride (or calomel) electrodes
- Need to connect through salt bridges on each side to the two reference beakers with the same Chloride concentration. (Need electrical balance; but concentration imbalance.)
- The difference in potential between these two is the Donnan Potential.

Measure Donnan Potential

- Put two reference beakers with Electrodes attached to each side of Donnan System



$$\Delta G = \mu_{Cathode}(Cl) - \mu_{Anode}(Cl) = zF\Phi_{Cat} - zF\Phi_{An} = zF\Delta\Phi$$

Membrane; Barrier

$$E = -\frac{\Delta G}{F} = \Delta\Phi$$

How a pH electrode works

- Almost the same as a Donnan potential.
- A glass membrane is permeable to protons only.
- Inside glass (a sphere) is a 0.1M HCl solution, and the Chloride cannot migrate. So chloride acts like the polymer.
- Chemical potential for protons is balanced across glass.

$$\mu_{Inside} (H^+) = \mu_{Outside} (H^+)$$

$$\mu^0 + RT \ln c_o + F\Phi = \mu^0 + RT \ln c$$

$$\Phi = \frac{RT}{F} \ln \left(\frac{c}{c_o} \right) \Rightarrow \Phi = -50 \cdot pH (mV)$$

Have one electrode inside the glass and one outside. But, like the Donnan potential you measure against a reference, don't put the other electrode in the unknown solution, put it in a cell with 0.1 M HCl (a reference) measure the potential between the inside of the glass and the reference.

Measuring the effective charge on an ionic polymer (DNA/RNA)

- For highly charge polyions (like DNA and RNA) the effective charge is much less than what one might expect from just dissociation.
- DNA double helix has 3.4Å between base pairs and two phosphate groups that each has a -1 charge. The neutral form has 2 Na ions per base pair.
- Charge released then could be up to 2 electrons per base pair. (But it turns out to be much less.)
- We can use the Donnan potential to measure the effective charge on the polymer.

Why counter ions condense on DNA

- The idea is that because the polymer has such a large (negative) charge and the ions are so close together that the counter ions (sodium) are strongly attracted and do not leave but “condense” on the DNA and reduce the effective charge.
- Coulomb’s law, the potential between two charges is:

$$\frac{V}{kT} = z_1 z_2 \cdot \frac{e_0^2}{\epsilon k T r_{ij}} \quad k = \frac{R}{N_A}$$

- A length scale based on this dimensionless ratio is (the Bjerrum length)
$$L_B = \frac{e_0^2}{\epsilon k T} = 7.1 \text{ \AA} \quad (\text{for charges in water at } 25\text{C})$$

- Manning connected this length to the distance between charges (r) on the polymer divided by the charge (z_2) on the polymer:

$$b = \frac{r}{z_2} \quad \text{and} \quad \frac{V}{kT} \Rightarrow \zeta = z_1 \frac{L_B}{b}$$

Counterion Condensation

- If the length (per charge) between charges on the polymer is large, then none (or little) condensation happens $b > L_B$
- If the length is small, meaning a very high charge density on the polymer then, $b < L_B$ and $\zeta = z_1 \frac{L_B}{b} > 1$
- The reciprocal is the fraction of charge not condensed.

$$f_{\text{condensed}} = 1 - \frac{1}{\zeta}$$

- For DNA

$$(L_B = 7.1 \text{ \AA} \text{ and}) \quad b = \frac{3.4}{2} = 1.7 \text{ \AA} \quad z_1 = 1 \text{ for Na}$$

$$\zeta = z_1 \frac{L_B}{b} = \frac{7.1}{1.7} = 4.2$$

75% of sodium ions are condensed on the DNA. The greater the charge density of the polymer, the more ions condense. This is measured directly by the Donnan Potential; which is 25% of what would be predicted in the absence of counter ion condensation.