Lecture 31

Now we are going to touch briefly on the **activities and the thermodynamics of ions in solution**. This is an important area of chemistry for several reasons. One is the commercial utility of electrochemical processes. Another is the fact that many inorganic compounds or biochemical species in solution exist in the form of solvated ions. To accurately describe their equilibria we need to talk about the specifics of the solution chemistry of ions.

We'll only do a fairly limited treatment of this subject with three basic goals. The first will be a treatment of the **activities of ionic solutions**, since the activities are our road to accurate chemical potentials and accurate equilibrium constants. Next will be the **Debye-Hückel law** for the calculation of ionic activity coefficients. Finally we'll study voltaic cells and the central equation of thermochemistry of ions, the **Nernst Equation**, which links the electrochemical potential to the equilibrium constant.

Let's begin with **ionic activities.** It is actually more important to consider activities for ions than activities for nonelectrolytes, because solutions containing ions and other ionic substances are not ideal, and the deviations from ideality are large. This is because the intermolecular forces involving ions are the strongest for any chemical substance. For example, when we consider the strengths of forces, the strongest are coulomb forces, the forces between two ions. The second strongest are ion-dipole interactions. Next are ion-induced dipole interactions. Finally we have dipole-dipole interactions, which are the strongest interactions for nonionic species. So we see that three of the four strongest intermolecular forces involve ions.

This is even more obvious if we look at the equations for the **form of the potential** for each of these interactions. Each of these potentials is a function of charge and distance. There are two things we need to look for. The strongest potential is the one with the smallest power of r in the denominator, and the one with the largest numerator. For the **potential between the two ions** we use Coulomb's law,

$$\Phi^{CC} = \frac{Q_1 Q_2}{r}$$

where Q_1 and Q_2 are the charges of the ions and r is the distance between them.

For the **charge-dipole interaction** the equation is

$$\Phi^{C\mu} = \frac{-1}{3kT}\frac{Q_1^2 \mu_2^2}{r^4}$$

Here k is Boltzmann's constant, and μ is the dipole moment of the second molecule. Since the power of r is greater here and the magnitude of μ is less than that of Q, this is weaker than the coulomb interaction.

For the **charge-induced dipole interaction**, the equation is

$$\Phi^{Cind\,\mu} = \frac{Q_1^2 \alpha}{2r^4}$$

where $Q_1\alpha$ is the induced dipole moment which has much lower magnitude than the dipole moment μ and the denominator is larger than for the charge dipole interaction. Thus this force is weaker than the charge-dipole interaction.

Finally, the **dipole-dipole interaction** is given by

$$\Phi^{\mu\mu} = \frac{-2}{3kT}\frac{\mu_1^2 \mu_2^2}{r^6}$$

Since this denominator has the highest power of r, and the dipole moment, which is small, is squared, this is the weakest force of the four.

Now if you consider an aqueous solution of say, sodium chloride in water, remember that the interactions between water molecules are dipole-dipole interactions, while the interactions between the ions and the water molecules are ion-dipole interactions, which are much stronger. Small wonder that ionic solutions are far from ideal.

In order to treat the activities of ions let's begin by considering the reaction,

$$H^+\ (aq) + Cl^-\ (aq) \rightleftharpoons HCl\ (g),$$

where the H^+ and Cl^- come from dissolution of HCl (g) in H_2O. Q: WHAT IS THE FORMULA FOR K FOR THIS REACTION?

$$K = \frac{a_{HCl(g)}}{a_{H^+(aq)}a_{Cl^-(aq)}}$$

The activity of the HCl(g) is given by

$$a_{HCl(g)} = \frac{\gamma_{HCl(g)}p_{HCl(g)}}{p^0}.$$

In the limit of low pressures $\gamma_{HCl(g)} \to 1$ and we can write

$$K = \frac{p_{HCl(g)}/p^0}{a_{H^+(aq)}a_{Cl^-(aq)}}.$$

The activity coefficient for our ion in solution is defined identically to that of any other solute. For concentration written in molalities,

$$a_{ion} = \gamma_{ion}m_{ion}$$

which means

$$K = \frac{p_{HCl(g)}/p^0}{m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-}},$$

where, as before, both γ_{H+} and γ_{Cl-} approach one in the limit of low concentration, i.e., $\gamma_{H+}, \gamma_{Cl-} \to 1$ as $m \to 0$.

HCl is a strong acid. WHAT DOES IT MEAN FOR AN ACID TO BE STRONG? Since HCl will be completely dissociated in an aqueous solution, saying that we have a given concentration of HCl is the same as saying that we have the same concentrations of H^+ and Cl^-. In other words,

$$m_{H+} = m_{Cl-} = m_{HCl}$$

and therefore we can write

$$K = \frac{p_{HCl(g)}}{m_{HCl}^2 \gamma_{H^+} \gamma_{Cl^-}}$$

Note that from our earlier equation for K, we can write as well that

$$a_{HCl} = a_{H^+} a_{Cl^-} = \gamma_{H^+} \gamma_{Cl^-} m_{H^+} m_{Cl^-}$$

While we can determine the activity of the HCl, it is impossible to experimentally determine the absolute activity of either the H^+ or the Cl^-, since it is impossible to prepare a solution of either alone. This is because of the **electroneutrality condition**, which states that the number of positive charges in a solution must equal the number of negative charges in the solution.

Since we can't define an activity coefficient for the individual ions, we define a new quantity called the **mean activity coefficient**, $\gamma_\pm$. The definition of the mean activity coefficient depends on the number of ions into which a molecule dissociates when it is dissolved. So for HCl, we have

$$\gamma_\pm(HCl) = (\gamma_{H^+} \gamma_{Cl^-})^{1/2}$$

While for $CaCl_2$ we would have

$$\gamma_\pm(CaCl_2) = (\gamma_{Ca^{+2}} \gamma_{Cl^-}^2)^{1/3}.$$

From these two examples, we should be able to see that the pattern for defining mean activity coefficients is

$$\gamma_\pm = (\gamma_+^a \gamma_-^b)^{1/a+b}$$

where a is the number of positive ions the electrolyte dissociates into, b is the number of anions the electrolyte produces. Unlike the ionic activity coefficients, mean activity coefficients are measurable quantities.

If we were given a mean activity coefficient, or we looked one up, how would we relate it to activity? The relationship between the mean activity coefficient of a substance and its activity is as follows. For HCl we have

$$a_{HCl} = a_{H^+} a_{Cl^-} = m_{H^+} m_{Cl^-} \gamma_{H^+} \gamma_{Cl^-} = m_{H^+} m_{Cl^-} (\gamma_{\pm}(HCl))^2$$

Since

$$\gamma_{H^+} \gamma_{Cl^-} = (\gamma_{\pm}(HCl))^2$$

So in this case we have a molecule that dissociates into two ions and we square its mean activity coefficient.

Now for a molecule like $FeBr_2$ which dissociates according to the reaction

$$FeBr_2 \rightleftharpoons Fe^{+2} + 2Br^-,$$

$$a_{FeBr_2} = a_{Fe^{+2}} a_{Br^-}^2 = m_{Fe^{+2}} m_{Br^-}^2 \gamma_{Fe^{+2}} \gamma_{Br^-}^2 = m_{Fe^{+2}} m_{Br^-}^2 (\gamma_{\pm FeBr_2})^3$$

So we use the mean activity coefficient by raising it to a power equal to the number of ions a molecule dissociates to and using this term to replace the ionic activity coefficients in the equation.

How do we determine the mean activity coefficient? We could measure it, or we could look it up or we could calculate it. To measure it we have to turn to electrochemical measurements. The theory necessary to convert the measured quantities in the electrochemical experiment to the mean activity coefficients is described at the end of this section of lecture notes, from pages 216 to 219. To calculate it, we can use the following equation, the Debye-Hückel equation.

$$\log_{10}\gamma_{\pm} = \frac{-.511|Z^{+}Z^{-}|I^{1/2}}{1+I^{1/2}}$$

In this equation, Z^{+} is the cation charge and Z^{-} is the anion charge. Notice that we take the absolute value of the product of the charges. I is a function called the **ionic strength** of the solution and is defined as

$$I = \frac{1}{2}\sum_{i} m_i Z_i^2 ,$$

where m_i is the molality of the i^{th} ionic species, Z_i is its charge and the summation is over all the ionic species in the solution.

Note that for a 1:1 electrolyte with ionic charges of +1 and -1, like HCl,

$$I = \frac{1}{2}(m_{H^{+}}(+1)^2 + m_{Cl^{-}}(-1)^2)$$

and since

$$m_{H^{+}} = m_{Cl^{-}} = m_{HCl}$$

$$I = m_{HCl}.$$

Let's try to make sense of our equation for the mean ionic activity by taking it apart. There are two terms to consider here, the term with the ionic charges and a term involving ionic strengths. The part with the charges yields a simple interpretation - the bigger the charge, the more negative the argument for the exponential is and the farther away from the ideal value of one it is. This should make sense since larger charges cause larger forces and therefore larger deviations from ideality.

The term involving the ionic strengths can be written as

$$\frac{I^{1/2}}{1+I^{1/2}}$$

We can see that this term varies between 0 and 1. When the ionic strengths are small this term is close to 0 and the mean activity coefficient will be close to 1. As the ionic strength increases, the argument of the exponential gets more negative and the mean activity coefficient moves away from its maximum value of 1. Again this makes sense, since the larger the ionic strength is, the larger the number of ions is, and we could easily argue that the larger the number of ions, the stronger the overall interactions and the larger the deviation from ideality.

Let’s do an example of calculating the ionic strength. We'll calculate I for a solution that is .30 molal in KCl and .5 molal in $K_2Cr_2O_7$.

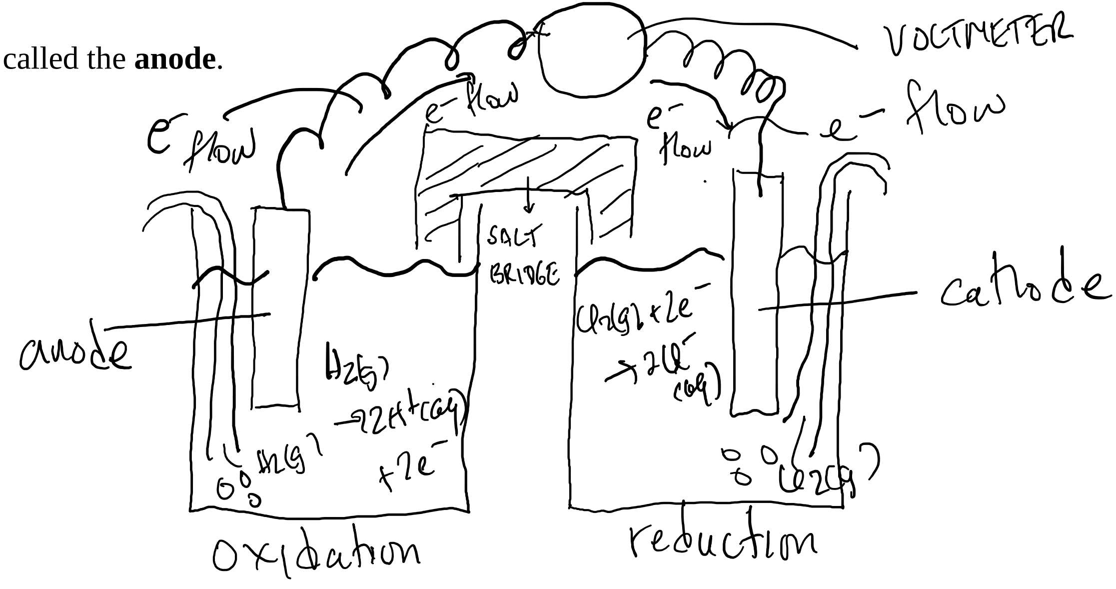
$$I = \frac{1}{2}\sum_i m_i Z_i^2 = \frac{1}{2}(m_{K^+}(1)^2 + m_{Cl^-}(-1)^2 + m_{Cr_2O_7^=}(-2)^2) = \frac{1}{2}(1.3+.3+.5x4) = 1.8$$

Now let’s use this result to calculate the mean activity coefficients for KCl and $K_2Cr_2O_7$ in this solution. Plugging into the equation with the values for KCl yields $\gamma_\pm$ (KCl) = .510. Notice even at these relatively low concentrations the strong deviation from ideality. For $K_2Cr_2O_7$, the deviation is even stronger, with $\gamma_\pm(K_2Cr_2O_7) = .253$. The effect on the overall activity is significantly larger, since for KCl, the mean activity is squared, yielding an ionic activity of $.260\, m_{K^+} m_{Cl^-}$, a full factor of 4 lower than the ideal activity. For $K_2Cr_2O_7$, the effect is even more dramatic since cubing the mean activity coefficient yields an ionic activity of $1.62x10^{-2}\, m_{K^+}^2 m_{Cr_2O_7^{-2}}$ a factor of 62 smaller than the ideal activity. So you can see here that treating ionic solutions as ideal can result in enormous errors even in simple systems like these with modest charges. Imagine the effect in a protein with multiple charges! Note that the activity of both ions depends on the ionic strength, which depends on the concentrations of all the ions present in the solution. This means that even though spectator ions are not reactants or products in an ionic reaction, they do have a role in the chemistry, since they contribute to the ionic strength of the solution, which in turn affects the mean activity coefficient.

In the limit of low ionic concentrations we can use an even simpler equation to calculate the mean activity coefficient. In the limit of small concentration $I^{1/2} << 1$ and we can write $\log_{10} \gamma_{\pm} = -.511 | Z_+ Z_- | I^{1/2}$. This simpler equation is called the **Debye-Hückel Limiting Law**. Again this only applies to cases where $I^{1/2} << 1$.

Lecture 32

The most common means of the study of ions in solution is an **electrochemical cell**. Such a cell consists of two electrolyte solutions connected by a salt bridge. Each of the electrolyte solutions has an electrode inserted into it that is connected to a potentiometer, which measures the potential generated by the oxidations and reductions carried out at the electrodes. The electrode at which reduction is carried out is called the **cathode**, while the electrode at which the oxidation occurs is called the **anode**.



A typical reaction that can take place in one of these cells is the reaction

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(aq),$$

in which the H_2 and Cl_2 are bubbled into the reservoirs. This reaction can be separated into two half reactions,

$$H_2(g) \rightleftharpoons 2H^+ + 2e^- \text{ (oxidation)}$$

and

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \text{ (reduction).}$$

It is conventional to write that oxidation occurs at the left electrode, the anode, while reduction occurs at the right electrode, the cathode.

Since the two reactions are coupled by the electrodes, the chemical reaction induces a flow of current. If we draw the circuit for this reaction, we see that for the reaction as written, electrons flow from the anode to the cathode. In order to keep the solution neutral, ions must flow. **Anions will flow from the cathode, where they are in excess, to the anode, where they are depleted**. This flow of ions is called an ion current.

It should be clear that the most important difference between electrochemical systems and the systems we have studied up to now is the presence of this electrical current and the associated voltage or **electrical potential E**. (We used the symbol Φ for electrical potential in our earlier work on electrochemical work). This electrical potential is characteristic of a given reaction and is a thermodynamic intensive variable. One immediate consequence of the presence of this new intensive variable is that **the Gibbs Phase Rule is different for electrochemical systems**. **For electrochemical systems the phase rule is f = c + 3 - p**, rather than the more usual f = c + 2 - p.

We would like to work out the thermodynamics of electrochemical systems. To do this we hark back to our equation for the change in the energy of an open system,

$$dU = dq + dw + \sum_j \mu_j \, dn_j$$

However, for this system, in addition to the pV work, we have the work associated with moving a charge against an electrical potential, and we need to specify both of these kinds of work in order to calculate our energy change. Thus the equation becomes

$$dU = dq + dw_{pV} + dw_{el} + \sum_j \mu_j \, dn_j$$

The form of the electrical work is

$$dw_{el} = -EdQ$$

where E is the cell voltage and dQ is the charge transferred. Thus for a reversible process, we have

$$dU = TdS - pdV - EdQ + \sum_j \mu_j dn_j .$$

Since G = U -TS + pV, we have for an electrochemical cell,

$$dG = -SdT + Vdp - EdQ + \sum_j \mu_j dn_j$$

At constant pressure, temperature, and composition we have

$$dG_{p,T,n_i} = -EdQ$$

Under these conditions a finite charge transfer results in a finite free energy change.

$$\Delta G_{p,T,n_i} = -EQ$$

If our cell diagram is written as we showed earlier so that oxidation is assumed to occur at the left electrode, the anode, then if the left electrode is negative , $E > 0$, $\Delta G < 0$ and the reaction is spontaneous. If the right electrode, the cathode, is negative $E<0$, $\Delta G>0$ and the reverse reaction is spontaneous.

For the occurrence of the reaction as written, the charge Q is given by Q = nF, where n is the number of moles of electrons transferred, and F is Faraday's constant (96484.6 C / mole e-). So for example in our reaction

$$H_2 + Cl_2 \rightleftharpoons 2HCl$$

n = 2, because 2 electrons are transferred from H_2 to Cl_2.

If we plug this into our equation for ΔG we get

$$\Delta G = -EnF.$$

This is a very important equation because it links ΔG, the change in free energy, directly with the potential difference of electrochemical reactions. In other words, under appropriate conditions of a constant T,p, n_i ; ΔG and -E are both measures of the driving force of an electrochemical reaction.

We can also write $\Delta G^o = -E^o nF$ where all reactants and products are in their standard states. We showed earlier that free energies are linked to the composition of the reacting mixture by $\Delta_r G = \Delta_r G^o + RT \ln Q$. Substituting our formula for ΔG and ΔG^o we get

$$-nFE = -nFE^o + RT \ln Q$$

or

$$E = E^0 - \frac{RT}{nF} lnQ$$

the Nernst Equation.

Remember that for $\Delta_r G$ is the free energy, which is a function of composition, where $\Delta_r G^0$ is a constant. Similarly in electrochemistry, E is the observed cell voltage, which changes as the composition of the cell's contents changes, while E^o, the standard cell voltage, is the voltage the cell would have if all the reactants and products were in their standard states with a = 1. Note that at $E = E^o$, Q = 1.

How do we calculate a standard cell voltage? The answer goes back to the half cell reactions we talked about earlier. Such half cell reactions are commonly tabulated. All that needs to be done to determine E^o for a reaction is to divide the reaction into two half cell reactions, look up the value of E^o for the two reactions and add them. There are only two points that need to be remembered. First, typically such tables tabulate only reduction reactions or only oxidation reactions. If a reaction you need is the reverse of the tabulated reaction, all you have to do is change the sign on the tabulated E°. Second remember the E is an intensive variable. This means that you never multiply the tabulated value by a stoichiometric coefficient. You just add the tabulated values together. In other words, the voltage for the reaction

$$Cl_2(g) + 2\,e^- \rightleftharpoons 2Cl^-$$

is exactly the same as the voltage for the reaction

$$2Cl_2(g) + 4\,e^- \rightleftharpoons 4Cl^-$$

The standard cell voltage can be simply related to the equilibrium constant K. Remember that $\Delta G^o = -RT \ln K$. For electrochemical systems we can replace this with

$$-nFE^o = -RT \ln K,$$

which can be rewritten as

$$E^0 = \frac{RT}{nF}\ln K$$

If we substitute this result into the Nernst Equation, we get

$$E = \frac{RT}{nF}\ln K - \frac{RT}{nF}\ln Q = -\frac{RT}{nF}\ln\frac{Q}{K}$$

This shows in a clear way that the cell voltage is a measure of the driving force of a reaction just as ΔG is.

Note that:

If $Q<K$, $Q/K < 1$, $E > 0$, $\Delta G < 0$ and the reaction is spontaneous.

If $Q>K$, $Q/K >1$, $E<0$, $\Delta G>0$ and the reverse reaction is spontaneous.

If $Q = K$, $E = 0$, $\Delta G = 0$ and we have equilibrium.

I stated earlier that we can use electrochemical cells to determine ionic activities. To see how this works, consider the reaction

$$H_2 + Cl_2 \rightleftharpoons 2HCl(aq)$$

If we apply the Nernst equation to this reaction we get

$$E = E^0 + \frac{RT}{2F}\ln\frac{a^2_{HCl(aq)}}{a_{H_2(g)}a_{Cl_2(g)}}$$

If we make the approximation that the gases are ideal, then their activities reduce to their pressures, and our equation becomes

$$E = E^0 + \frac{RT}{2F}\ln\frac{a^2_{HCl(aq)}}{p_{H_2(g)}p_{Cl_2(g)}}$$

Earlier we showed that

$$a_{HCl} = m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-} = m^2_{HCl}\gamma^2_{\pm HCl}$$

Inserting this into our equation yields

$$E = E^0 + \frac{RT}{2F}\ln\frac{m^4_{HCl}\gamma^4_{\pm HCl}}{p_{H_2(g)}p_{Cl_2(g)}}$$

If we plug in known values of R and F and limit ourselves for the moment to room temperature measurements, this becomes

$$E = E^0 + \frac{25.693mV}{2}\ln p_{H_2}p_{Cl_2} - 25.693mV\ln m^2_{HCl} - 25.693\ln\gamma^2_{\pm HCl}$$

In this equation, we will generally know m, p_{H2}, and p_{Cl2}, since these are variables we can control. If we put all our knowns on one side of the equation and our unknowns on the other, we get

$$E - 25.693(\ln m^2_{HCl} - \frac{1}{2}\ln p_{H_2}p_{Cl_2}) = E^0 - 25.693\ln\gamma^2_{\pm HCl}$$

What we have here is generally known in mathematical circles as one equation with two unknowns, since we don't assume that we know either E^o or $\gamma\pm$ at the beginning of our experiment. To get E^o

and γ± we use our extended Debye Huckel Law as a starting point. We have from before

$$\log_{10}\gamma_{\pm} = \frac{-.511|Z_+Z_-|I^{1/2}}{1+I^{1/2}}$$

We want to substitute this for the mean activity coefficient in our equation for E, but in that equation we have a natural log rather than a log base 10. Fortunately logs and natural logs are related by the simple equation

$$2.303 \log_{10} x = \ln x.$$

So we can rewrite our Debye Huckel Equation as

$$\ln\gamma_{\pm} = \frac{-1.177|Z_+Z_-|I^{1/2}}{1+I^{1/2}}$$

Remember that when we first introduced this equation we said that it approximates the mean activity coefficient. This equation approaches the exact value of the mean activity coefficient in the limit of low concentration. Now remember that for a 1:1 electrolyte like HCl, we have $I_{HCl} = m_{HCl}$. This means that in the limit of low concentration we have

$$\ln\gamma_{\pm HCl} = \frac{-1.177 m_{HCl}^{1/2}}{1+m_{HCl}^{1/2}}$$

For a solution of real electrolytes at moderate to high concentrations ln γ± will deviate from this simple expression so we can write

$$\ln\gamma_{\pm HCl} = \frac{-1.177 m_{HCl}^{1/2}}{1+m_{HCl}^{1/2}} + f(m_{HCl})$$

where f(m) is some as yet unspecified function of the molality. We do know one thing about f(m) though and that's its limiting behavior, i.e. its behavior as m → 0. WHAT IS THE $\lim\limits_{m \to 0} f(m)$? Now we'll put this all into our equation for the voltage of an electrochemical cell. We get

$$E - 25.693(\ln m_{HCl}^{2} - \frac{1}{2}\ln p_{H_2} p_{Cl_2}) = E^{0} - 25.693(2)(\frac{1.177m^{1/2}}{1+m^{1/2}} + f(m))$$

where we multiply by two because

$$\ln \gamma_{\pm}^{2} = 2\ln \gamma_{\pm}$$

The molality on the right side of the equation is a known so we transfer it to the left side to yield

$$E - 25.693(\frac{1}{2}\ln(\frac{m_{HCl}^{4}}{p_{H_2} p_{Cl_2}} - (2)(\frac{1.177m^{1/2}}{1+m^{1/2}}) = E^{0} + 51.386\ f(m))$$

Note that while we still have one equation with two unknowns, we can now use our equation to determine E°, since one of our terms, f(m), disappears as m→0. In effect by specifying that $\lim_{m \to 0} f(m) = 0$. a so called boundary value, we are supplying a second determining equation, effectively giving us two equations in two variables. This suggests that the procedure we should use to determine E° and ln γ± is

1) measure E as a function of m

2) plot $E' = E - 25.693(\frac{1}{2}\ln(\frac{m_{HCl}^{4}}{p_{H_2} p_{Cl_2}} \text{-} (2)(\frac{1.177m^{1/2}}{1+m^{1/2}})$ vs m

3) the y intercept is E°

4) Now use $E - 25.693(\ln m_{HCl}^{2} - \frac{1}{2}\ln p_{H_2} p_{Cl_2}) = E^{0} - 25.693\ln \gamma_{\pm HCl}^{2}$ and the E vs m data to solve for γ± at each concentration

Note that a graph of E` vs m is generally not linear, but is approximately linear at low concentrations, .1molal or less. Of course we can easily generalize this to other problems than the standard potential and activity of HCl.