

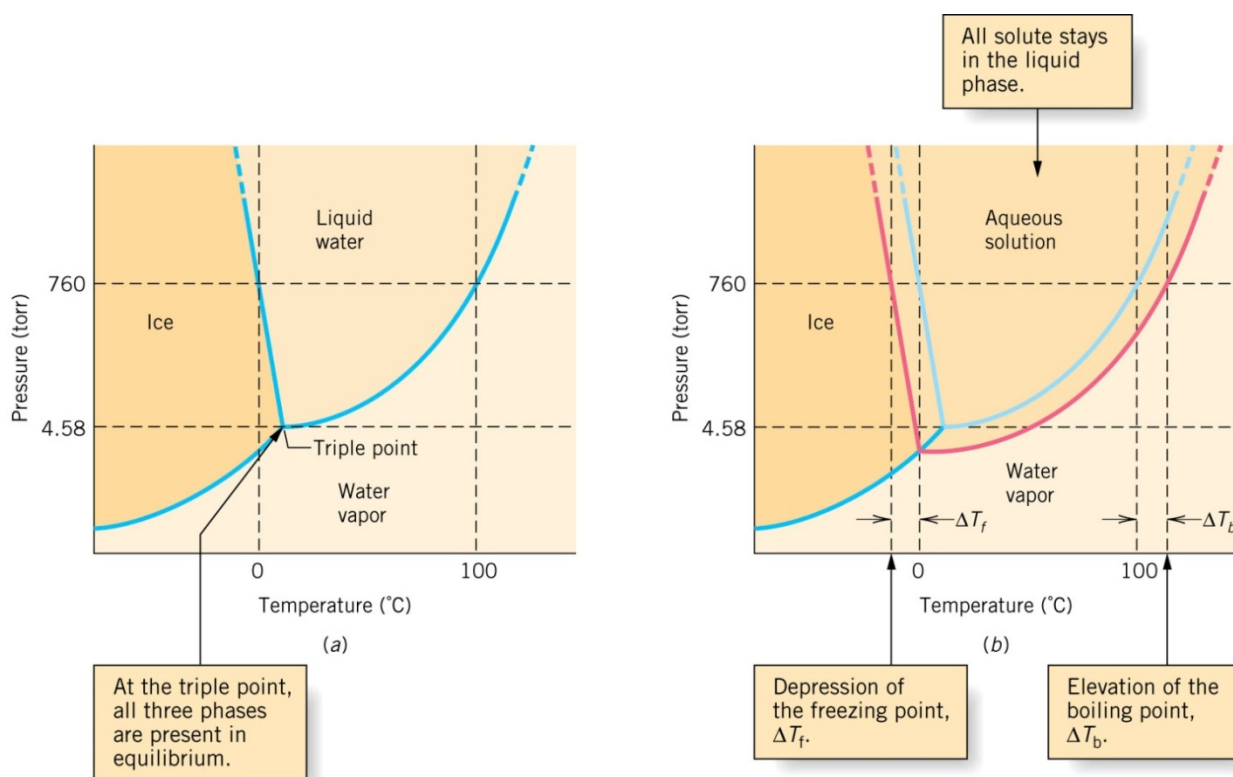
## ACTIVITIES FROM FREEZING POINT LOWERING AND FROM EMF MEASUREMENTS

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**This experiment consists of two independent measurement techniques to determine the mean ionic activity coefficient of an ionic salt at various molal concentrations. The mean ionic activity coefficients determined from freezing point lowering measurements and from EMF measurements will be determined and compared with those calculated from the Debye-Hückel theory.**

### I. FREEZING POINT LOWERING MEASUREMENTS.

The freezing point lowering is an example of a colligative property - a property that depends on the nature of the solvent and the number of moles of solute particles dissolved in solution. The phase diagram for water is shown below for both the pure solvent (solid line) and solution (dashed line).



(Figure is from Brady, Senese, and Jespersion, *Chemistry, Matter and Its Changes*, 5<sup>th</sup> Ed (Wiley 2007) ISBN 0470120940).

The colligative properties assume that the solute does not contribute to the vapor pressure above the solution and that, when the solution freezes, only the solvent freezes out of the solution. In such a case, at equilibrium, the free energy of the pure solid solvent A equals the free energy of the solvent A in the solution. Thus

$$G_{s,A} = \mu_{s,A} = G_{l,A}^0 + RT \ln(a_A)$$

Since only solvent freezes out, the free energy of fusion is given by

$$\Delta G_{\text{fus}} = G_{l,A}^{\circ} - G_{s,A} = -RT \ln(a_A)$$

or

$$\frac{\Delta G_{\text{fus}}}{T} = -R \ln a_A$$

now the dependence of the freezing point of the solution on composition is obtained from the Gibbs-Helmholtz equation:

$$\frac{\partial \left( \frac{\Delta G}{T} \right)}{\partial T} = -R \frac{\partial \ln a_A}{\partial T} = -\frac{\Delta H_{\text{fus},A}}{T^2}$$

or

$$d \ln a_A = \frac{\Delta H_{\text{fus},A}}{RT^2} dT$$

which when integrated from  $a = 1$  at  $T = T_0$  to  $a = a_A$  at  $T = T$  assuming  $\Delta H_{\text{fus},A}$  is independent of  $T$ , gives

$$(1) \quad \ln a_A = -\frac{\Delta H_{\text{fus},A}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

Thus we can determine the activity of the solvent from freezing point measurements on the solution.

If the solution is not dilute, we must work with activities directly. However, for dilute solutions  $a_A = X_A$  and the solution behaves ideally, thus

$$\ln a_A = \ln X_A = \frac{\Delta H_{\text{fus},A}}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) = \frac{\Delta H_{\text{fus},A}}{R} \left( \frac{T - T_0}{TT_0} \right)$$

Now, for very dilute solutions,  $T \approx T_0$ , thus  $TT_0 \approx T_0^2$ . Also, for very dilute solutions,

$\ln X_A = \ln(1 - X_B) \approx -X_B$ . Thus, with the definition  $\Delta T_{\text{fp}} = T_0 - T$ , the above equation becomes

$$X_B = \frac{\Delta H_{\text{fus},A}}{RT_0^2} \Delta T_{\text{fp}} = \frac{MW_A \cdot m}{1000}$$

or

$$\Delta T_{\text{fp}} = \frac{RT_0^2 \cdot MW_A}{1000 \Delta H_{\text{fus},A}} \cdot m = K_{\text{fp}} \cdot m$$

However, for solutions more concentrated than about 0.1 m, this equation is not applicable. In such cases  $K_{\text{fp}}$  is equal to  $\Delta T_{\text{fp}}/m$  as  $m \rightarrow 0$ . Thus

$$(2) \quad K_{\text{fp}} = \lim_{m \rightarrow 0} \left( \frac{\Delta T_{\text{fp}}}{m} \right) = \frac{RT_0^2 \cdot MW_A}{1000 \Delta H_{\text{fus}}}$$

thus a plot of  $\Delta T_{fp}/m$  vs  $m$  when extrapolated to  $m = 0$  will give the value of the freezing point constant of the solvent. Once  $K_{fp}$  is obtained, the value of  $\Delta H_{fus}$  of the solvent can be found from Eq 2.

In order to obtain information about the activities of the solute we use the Gibbs-Duhem equation, which in terms of activities is  $X_A \ln a_A + X_B \ln a_B = 0$  or

$$(3) \quad d \ln a_A = -\frac{X_B}{X_A} d \ln a_B = -\frac{n_B}{n_A} d \ln a_B = -m(MW_A) d \ln a_B$$

if  $n_B$  is the moles of solute in 1 kg of solvent.

Now differentiating Eq 1 and substituting Eq. 3 above gives

$$d \ln a_B = \frac{\Delta H_{fus,A}}{RT^2} dT = -m(MW_A) d \ln a_B$$

or

$$d \ln a_B = -\frac{\Delta H_{fus,A}}{(MW_A)RT^2 m} dT$$

which can be rearranged to

$$d \ln a_B = \frac{d(\Delta T)}{K_{fp} m \left(1 - \frac{\Delta T}{T_o}\right)^2}$$

where  $K_{fp}$  is the freezing point lowering constant of the solvent,  $\Delta T = T_o - T$  is the freezing point lowering, and  $d\Delta T = -dT$ . Now, if  $\Delta T/T_o \ll 1$  we have

$$(4) \quad d \ln a_B = \frac{d\Delta T}{K_{fp} \cdot m}$$

Eq 4 is not very sensitive to deviations from ideality, thus we introduce the osmotic coefficient,  $(1-j)$ , as a measure of deviations from ideal behavior. It is defined through

$$(5) \quad \Delta T = K_{fp} \cdot m \cdot (1 - j)$$

In an ideal solution  $j = 0$ , and  $\Delta T = K_{fp}m$ . In a non-ideal solution  $j \neq 0$ . Differentiating Eq 5 gives

$$(6) \quad d(\Delta T) = K_{fp}[(1 - j)dm - mdj]$$

Now introducing the activity coefficient in terms of the molality of the solution as  $a_B = \gamma_B m_B$ , we get

$$(7) \quad d \ln a_B = d \ln \gamma_B + \frac{dm}{m}$$

Thus plugging Eq 6 and Eq 7 into Eq 4 gives

$$d \ln \gamma_B + \frac{dm}{m} = \frac{1}{m}[(1 - j)dm - mdj] = (1 - j)\frac{dm}{m} - dj$$

or

$$(8) \quad d \ln \gamma_B = -dj - \left(\frac{j}{m}\right)dm$$

Eq 8 is then integrated from  $m = 0$  to  $m = m$ . At  $m = 0$ ,  $\gamma_B = 1$  and  $j = 0$ . Thus we have

$$(9) \quad \ln \gamma_B = -j - \int_0^m \left(\frac{j}{m}\right)dm$$

Eq. 9 must be evaluated graphically. From experimental values of  $\Delta T$  and  $m$ ,  $j$  is calculated from Eq 5. To obtain  $\gamma_B$ ,  $j/m$  is plotted vs  $m$  and the area under the curve is  $\ln \gamma_B$ . The activity can then be calculated from  $a_B = \gamma_B m$ .

If the solute is an electrolyte, then it puts more particles into solution due to dissociation. Thus for electrolytes:

$$(10) \quad a = a_{\pm}^v = \gamma_{\pm}^v \cdot m_{\pm}^v = \gamma_{\pm}^v \left( v_+^{v_+} \cdot v_-^{v_-} \right) m^v$$

where  $\gamma_{\pm}$  is the mean ionic activity coefficient of the salt and the  $v$  represent the number of each type of ion put into solution. Due to the extra particles in an electrolytic solution, the freezing point constant of the solvent is found from

$$(11) \quad K_{fp} = \lim_{m \rightarrow 0} \left( \frac{\Delta T_{fp}}{vm} \right) = \frac{RT_0^2 \cdot MW_A}{1000 \Delta H_{fus}}$$

and the osmotic coefficient is now defined as

$$(12) \quad \Delta T = vK_{fp}m(1 - j)$$

where  $v$  is the number of ions from the dissociating salt.

Thus, in terms of the mean ionic activity coefficient, Eq 9 becomes

$$(13) \quad \ln \gamma_{\pm} = -j - \int_0^m \left( \frac{j}{m} \right) dm$$

Thus a plot of  $j/m$  vs.  $m$  along with the calculated value of  $j$  from Eq 12 will allow the determination of the mean ionic activity coefficient of your salt.

### Experimental

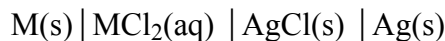
1. Prepare solutions of your salt with concentrations of 0.80 m, 0.40 m, 0.20 m, 0.10 m, 0.050 m, and 0.025 m. Prepare about 100 ml of each solution. These solutions will be used in both the freezing point part and the EMF part of this lab.
2. Using the MicroLab Interface with the thermistor probe, obtain time-temperature cooling curves to:
  - a. Determine the freezing point of the water used to make up your solutions.
  - b. Determine the freezing point of each solution.

You may use the factory calibration of the thermistor. If you choose to do your own calibration, you will need an accurate thermometer and at least 4 reliable temperature points from 0 to -10 °C.

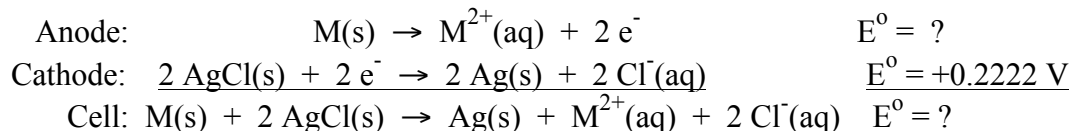
Set up a small beaker with a salt/ice slush slurry (its temperature will be about -10 to -15°C) and place it on a magnetic stirring device. Pour one of your solutions into a test tube and add a stirring magnet. Place the temperature probe in the center of the test tube and put the test tube into the low temperature bath. Record the temperature for about 10 minutes or until you get a good cooling curve. **Be sure to save the data file. Repeat the run** and then repeat the freezing point measurements for each solution, saving each run on your disk.

## II. EMF MEASUREMENTS

The object of this part of this lab is to determine the mean ionic activity coefficient of your salt solutions from EMF measurements. You will do this by determining the cell potential of the electrochemical cell



where the  $MCl_2(aq)$  are the solution of your salt prepared for the freezing point measurements. For the above cell the electrode reactions are:



From your vast knowledge of electrochemistry, you will immediately recognize that the Nernst Equation for this reaction is

$$\begin{aligned}
 (14) \quad E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{RT}{nF} \cdot \ln[a_{\text{M}^{2+}} \cdot a_{\text{Cl}^{-}}^2] = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \cdot \ln(a_{\pm}^3) = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \cdot \ln[(4m^3)(\gamma_{\pm}^3)] \\
 &= E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \cdot \log(4m^3) - \frac{(2.303)(3)RT}{nF} \cdot \log(\gamma_{\pm})
 \end{aligned}$$

which can be rearranged to give

$$(15) \quad E' = E_{\text{cell}} + (9.922 \times 10^{-5})T \cdot \log(4m^3) = E_{\text{cell}}^{\circ} - (2.977 \times 10^{-4})T \cdot \log(\gamma_{\pm})$$

According to the Debye-Hückel theory of dilute electrolyte solutions, the mean ionic activity coefficient is given by

$$(16) \quad \log \gamma_{\pm} = 0.5092 z^{+} z^{-} \sqrt{I} \quad \text{where} \quad I = \frac{1}{2} \sum_i m_i z_i^2$$

$I$  is called the ionic strength of the solution and the sum is over all ions in the solution. Now since  $I \propto m$ , we see that  $\log \gamma_{\pm} = (\text{const.}) \cdot \sqrt{m}$ . With this substitution, and specifying 25 °C, Eq 15 becomes

$$(17) \quad E' = E_{\text{cell}} + 0.02958 \log(4m^3) = E_{\text{cell}}^{\circ} + (\text{const.}) \cdot \sqrt{m}$$

Thus a plot of  $E'$  vs  $\sqrt{m}$  will extrapolate to  $E_{\text{cell}}^{\circ}$  as  $m \rightarrow 0$ . This happens since  $\gamma_{\pm} \rightarrow 1$  when  $m \rightarrow 0$ . Once  $E_{\text{cell}}^{\circ}$  is known, Eq 15 can be used to calculate  $\gamma_{\pm}$  for each solution from the measured EMF.

## **Experimental**

1. Prepare a silver electrode as described in class. Convert the silver electrode to a  $\text{Ag(s)} | \text{AgCl(s)}$  electrode by anodizing the silver electrode in concentrated HCl solution. Connect the silver electrode to the positive terminal of two dry cells connected in series. A copper wire connected to the negative terminal makes a good cathode. Electrolyze the HCl solution until a deposit of  $\text{AgCl(s)}$  is formed on the silver electrode.
2. Calibrate the  $\text{Ag(s)} | \text{AgCl(s)}$  electrode in saturated KCl against the saturated calomel electrode.
3. Place the metal electrode for your system and the calibrated silver/silver chloride electrode into each of your solutions and measure the EMF using the MicroLab interface. Make sure the electrodes do not touch. Record the EMF at each molality.

## **Calculations**

- I. Freezing Point Lowering Measurements.

1. Determine  $\Delta T_{\text{fp}}$  for each solution.
2. Plot  $\frac{\Delta T_{\text{fp}}}{\nu m}$  vs  $m$  and extrapolate to  $m = 0$  to obtain  $K_{\text{fp}}$  for water. See equation 11.
3. Using Eq. 11, determine the heat of fusion of water.
4. Using Equation 1, determine the activity of water in each solution.
5. Using Eq. 12, determine the osmotic coefficient  $j$  of your salt for each solution.
6. Make a plot of  $j/m$  vs  $m$ .
7. Determine  $\ln \gamma_{\pm}$  and then  $\gamma_{\pm}$  of your salt for each solution.
8. Determine  $a_{\pm}$  of your salt for each solution.

## II. EMF Measurements.

1. Calculate the empirical correction to be added to or subtracted from the measured EMF's to compensate for the fact that, due to the method of preparation, the  $\text{Ag(s)} | \text{AgCl(s)}$  electrode will probably not have the exact standard potential.
2. From a plot of  $E'$  vs  $\sqrt{m}$ , determine  $E^{\circ}$  of your electrochemical cell.
3. Determine  $E^{\circ}$  of your metal electrode and compare with the accepted value.
4. From your measured cell potential, determine  $\gamma_{\pm}$  for each of your solutions.
5. Using the Debye-Hückel theory, calculate the mean ionic activity coefficient of each of your solutions.

## Discussion

Your discussion should include comparisons of activity coefficients from both EMF and the freezing point measurements. Also, you should compare your activity coefficients with those calculated from the Debye-Hückel theory. Comment on any differences. Are there any trends in behavior? Get with other groups and compare your results with theirs. Were your freezing point measurements about what you expected? Why or why not? Based on your results, comment on any trends in solution behavior such as ideal behavior, etc..