

Freezing Point Depression of Weak Electrolytes

Robert Ichiyama

Office Hour: Thursday 9 am or by appointment

E-mail: robertichiyama@uri.edu

Office: Beupre 450

Presentation adapted and modified from original done by Cali Antolini

WARNING!

- You **must** have nitrile gloves for this experiment.
- Wear the nitrile gloves **throughout the whole experiment** – we are going to work with potentially dangerous substances.

Purpose

- To determine the degree of dissociation of a weak acid (chloroacetic acid in this experiment) using freezing point depression.

Symbols

- α – degree of dissociation
- n_0 – initial number of moles, [moles]
- n – obtained number of moles, [moles]
- m – molality, [moles of solute/kg of solvent]
- m' – total molality, [moles of solute/kg of solvent]
 - the number of non-dissociated and dissociated species per kg solvent
- T_0 – freezing point of a pure solvent, [K]
- T_f – freezing point of a solvent with a solute dissolved in it, [K]
- ΔT_f – freezing point depression, [K]
- K_f – freezing point depression constant, [K/molal]
 - **Dependent on solvent**
- k_f – freezing point depression correction coefficient, [1/K]
 - **Dependent on solvent**
- w – mass, [g] {Note that this is not the conventional notation}
- M – molarity, [mol/l]
- K_c Equilibrium constant
- MW-Molecular weight

Freezing point depression

- Freezing point depression is the process of lowering the freezing point of pure **solvent** by adding a **solute** to it.

$$\Delta T_f = T_0 - T_f$$

T_0 – freezing point of a pure **solvent**, [K]

T_f – freezing point of a solvent with a **solute** dissolved in it, [K]

ΔT_f – freezing point depression, [K]

Freezing point depression

- Freezing point depression is the process of lowering the freezing point of pure **solvent** by adding a **solute** to it.

$$\Delta T_f = T_0 - T_f$$

- It is approximately proportional to the number of moles of **solute** dissolved in a giving amount of the **solvent**.

$$\Delta T_f = K_f m'$$

m' – total molality, [moles of **solute**/kg of **solvent**]

K_f – freezing point depression constant, [K/molal]

ΔT_f – freezing point depression, [K]

Freezing point depression

- Freezing point depression is the process of lowering the freezing point of pure **solvent** by adding a **solute** to it.

$$\Delta T_f = T_0 - T_f$$

- It is approximately proportional to the number of moles of **solute** dissolved in a given amount of the **solvent**.

$$\Delta T_f = K_f m'$$

- Degree of dissociation of **solute** can be determined by freezing point depression.

Dissociation

Upon being put in a solvent, an acid dissociates:



The degree of dissociation is:

$$\alpha = \frac{\text{\# of moles of reactant dissociated}}{\text{\# of moles of reactant initially}} \quad (2)$$

If the initial number of moles of HA is represented by n_0 , then at equilibrium we obtain:

$$n_{\text{H}^+} = \alpha n_0 \quad (3)$$

$$n_{\text{A}^-} = \alpha n_0 \quad (4)$$

$$n_{\text{HA}} = (1-\alpha) n_0 \quad (5)$$

Dissociation

Then the *total number of moles of all species (dissociated and non-dissociated ones)* is the sum of the terms in the right sides of equations (3), (4), (5):

$$n_{\text{total}} = n_0(1 + \alpha) \quad (6)$$

Next, should recall the definition of *molality* (determined via titration):

$$m = \frac{\text{\# of moles solute}}{\text{mass of solvent in kg}} \quad (7)$$

Molality m is the number of moles of acid added to 1 kg of solvent.

We will have:

$$m' = m(1 + \alpha) \quad (8)$$

Total molality m' of a solution is the number of non-dissociated and dissociated species per kg solvent, and is determined by freezing point depression observation.

Total molality

We can find the *total molality* via freezing point observation:

$$\Delta T_f = K_f m' \quad (9)$$

A more accurate relation between the total molality and the freezing point depression is

$$m' = \frac{\Delta T_f}{K_f} (1 + k_f \Delta T_f) \quad (10)$$

where

$$\Delta T_f = T_0 - T_f \quad (11)$$

and

$$k_f$$

Is the freezing point depression constant

Equilibrium constant

Now that we know the degree of dissociation and *molality* we can calculate the equilibrium constant:

$$K_c = \frac{m\alpha^2}{1 - \alpha} \quad (12)$$

Using an ICE table, please show the derivation for the this equation.

Experimental Setup – Wear Gloves!



1 - Dewar



2 – Cap, probe, rod



3 - Thermometer



4 – Ice bucket



5 – Weighing bottle



6 - Buret



7 – Erlenmeyer flask

Procedure

Make sure weighing bottles are **clean and dry** prior using them.

1. Fill the burette with 0.1M NaOH solution, write down the volume.
2. Measure the mass of the weighing bottles (with cap on) on the balance.
3. Make sure you have a capped dewar, cryoscopic thermometer, and stirring rod ready to use.
4. Using a beaker measure out about 300 ml of ice, wash it with chilled distilled water. Dispose the water into sink, leave the washed ice in the beaker.
5. Load washed ice in the dewar, such that the dewar is about $\frac{1}{3}$ filled, add about **100 ml of chilled distilled water** as well.
 - The **level of liquid** should cover the bottom third of the thermometer

Procedure

6. Insert the stirring rod and cryoscopic thermometer in the cap of the dewar and cap the dewar.
7. Stir the ice-water mixture vigorously with the stirring rod, achieve the temperature of 0.00 ± 0.01 °C in the thermometer readout, this will be t_0
8. Empty the dewar, repeat steps 4 through 6 –you will be using **100 ml of 0.25 M solution of chloroacetic acid** instead of distilled water in step 4.
9. While stirring, write down the temperature every 30s for 3 minutes, until the temperature become stable– this stable temperature will be T_f for this solution.
10. Withdraw 10 ml aliquots of the liquid parts from the bottom of the dewar (avoid the ice).

Procedure

11. Transfer the aliquot in a dry and pre-weighed glass jar.
12. Measure the mass of the aliquot and glass jar on the balance **after it has warmed to room temperature**, about 45 minutes.
13. Transfer the aliquot from the weighing bottle in an Erlenmeyer flask, rinse the weighing bottle with a small amount of distilled water and pour the rinse in the Erlenmeyer flask – at this point we are not interested in the concentration of the acid solution, but are concerned with the *quantity* of the acid.
14. Add three drops of the indicator phenolphthalein in the flask.
15. Record the initial volume of the sodium hydroxide solution in the burette.

Procedure

16. Perform titration of the aliquot with a solution of sodium hydroxide by dropping drops of the basic solution from a burette into the acid solution in the flask.
17. Achieve the neutral point roughly corresponding to $\text{pH} = 7$ by seeing a stable for more than one minute faint pink color of the titrated solution.
18. Record the final volume of the sodium hydroxide solution in the burette.
19. Dispose of the waste accordingly – use specifically designated waste containers.
20. Repeat experiment with **100 ml of 0.125 M solution of chloroacetic acid** instead of 0.25 M chloroacetic acid solution.
(Titration needs **$\approx 15\text{ml}$ NaOH for 0.25M** **$\approx 7\text{ml}$ NaOH for 0.125M)**)

Calculations

- Knowing the molarity and volume of the sodium hydroxide solution gives the following relationship of the number of moles:

$$n_{NaOH} = M_{NaOH} V_{NaOH} = n_{acid} \quad (13)$$

- Then the mass of the *acid only*:

$$w_{acid} = MW_{acid} \times n_{acid} \quad (14)$$

- After you have weighed the solution of acid in water, you know the *combined* mass of the the acid and water:

$$w_{total} = w_{acid} + w_{water} \quad (15)$$

1. Use Eq. (15) and the result from Eq. (14) to find the mass of the water in the solution.

Calculations

1. Now it is possible to calculate *molality* (m) of the titrated solution.

$$m = \frac{n_{acid}}{W_{solvent}} \quad (16)$$

Note: $w_{solvent}$ needs to be in kg.

1. Calculate total molality (m') by using eq (10)

Use K_f and k_f of water (1.855 [K/molal] and 0.005 [1/K]) for all calculations.

1. Calculate the degree of dissociation (α) by using eq (8)
2. Calculate equilibrium constant (K_c) by using eq (12)

Error Analysis

- See **page 48** in syllabus.
- Assume the error in each temperature measurement is $\pm 0.01^\circ\text{C}$, the error in each mass measurement is $\pm 0.0002\text{g}$, the error in the volumes recorded from burette is $\pm 0.05\text{ml}$.
- REMEMBER TO USE THE ADDITION/SUBTRACTION FORMULA TO PROPAGATE ERRORS FOR ALL DIFFERENCES
- REMEMBER TO USE THE PRODUCTS\QUOTIENTS FORMULA TO PROPAGATE ERRORS FOR ALL PRODUCTS

Eg. $f = a + b - c$ $\epsilon(f) = ?$

$f = ab/c$ $\epsilon(f) = ?$

Error Analysis

- Error in mass of solution
- Error in volume of titrant
- Error in number of moles of acid
- Error in mass of acid
 - Use +/- 0.002 g/mol for error in MW
- Error in mass of solvent
- Error in molality
- Error in freezing point depression
- Error in total molality
 - K_f and k_f in the total molality equation as constant (error in $K_f = k_f = 0$)
- **Error in degree of dissociation**
- **Error in equilibrium constant**
- **Error in pKa**

Lab Report Requirements

- 1. Title Page:** Give the title of the experiment, the date the experiment was performed, your name and the name of your laboratory partner (my name is, my partner is format).
- 2. Abstract:** This should be a 1 paragraph summary of what is to follow including the results. It is suggested that you write the abstract after the rest of the report is complete.
- 3. Introduction:** This should be a discussion of the purpose of the experiment.
- 4. Theory:** (A) Derive the relation between the equilibrium constant, the molality and the degree of dissociation, ie. Eq (12).
(B) Explain the difference between m and m' and how they are determined experimentally. Definitions must be provided for all symbols used in this and subsequent sections.
- 5. Procedure:** Attach the outline of the procedure you brought to class and had signed by your TA.

Lab Report Requirements

6. **Original Data:** Attach the original data signed by your TA.

7. **Data Table:** Tabulate your data (for both 0.25M and 0.125M) so that it can be used in the calculations to follow. (w_{bottle} , $w_{\text{bottle+aliquot}}$, $w_{\text{aliquot}}/w_{\text{acid+solvent}}$, t_0 , t_f , V_{initial} , V_{final} , V_{NaOH} , M_{NaOH})

8. Calculations:

(A). Calculate the molality of all solutions. Recall that molality is the moles of solute per kg of solvent. The moles of solute are determined from the titration part of the experiment, and the mass of water is determined by subtracting the mass of solute from the total mass of the solution.

(B). Calculate the degree of dissociation (i.e. the fraction dissociated) for chloroacetic acid at both concentrations. Calculate the equilibrium constant for both concentrations.

(C). **Ignore question # 3 in the syllabus** asking to calculate g_1 for chloroacetic acid. *We did not discuss ideality in lab today!

Lab Report Requirements

9. **Error Analysis:** Use error propagation to determine the errors in the degree of dissociation and the equilibrium constant for chloroacetic acid.

10. **Summary of Data:** Summarize the final result with errors included. Be sure to report only the proper number of significant figures.

11. **Conclusions:** Discuss the significance of your results.

12. **Discussion:** Discussion questions on **page 49 in syllabus**

(A). For chloroacetic acid do the computed equilibrium constants obtained at the two concentrations agree within experimental error?

(B). Use the equilibrium constant of chloroacetic acid determined at the highest concentration to calculate the degree of dissociation expected at the lower concentration. Does your computed value agree with your measured degree of dissociation to within experimental error?

(C). Calculate the pK_a of chloroacetic acid (along with the error in pK_a) at both concentrations. Compare with literature values and discuss any differences you find outside your computed errors.