

## Activities From Freezing-Point Depression Data<sup>1,2</sup>

**Purpose:** Determine the activity coefficients for a range of solutions of 2-propanol in water.

### Introduction

The freezing point of a solution is lower than that of the pure solvent. Freezing-point depression data are of considerable value in the thermodynamic study of solutions. In particular, activity coefficients of both solvent and solute can be determined as a function of concentration to a high degree of accuracy. Freezing point depression studies are useful for non-electrolytes, where electrochemical methods are difficult.

In this experiment, the activity coefficients of 2-propanol (isopropyl alcohol) in water will be determined over the range of 0.5-3.0 m. Molality is used as the concentration measure in most careful thermodynamic studies, because molality does not depend on temperature, as does molarity. The concentration of the solutions will be determined using density measurements. The density of 2-propanol solutions is almost linear over the concentration range in this experiment. Known standard solutions will be used to determine the dependence of the density on the concentration. Then a slurry of ice and an aqueous solution of 2-propanol will be made in an insulated flask. The freezing point temperature will be determined and a sample of the solution will be withdrawn. The density of the withdrawn sample will then be determined to calculate the concentration. The next sample will then be prepared by adding a small amount of water to the slurry and the process repeated.

### Theory

The activity of a substance is its "chemically effective" concentration. When water is pure, its activity is unity. In ideal solutions, the solvent activity equals its mole fraction:

$$a_1 = X_1 \quad 1$$

In real solutions, the activity of the solvent is given by

$$a_1 = \gamma_1 X_1 \quad 2$$

The activity  $a_1$  of the solvent in a solution at temperature  $T$  is defined by

$$\mu_1 = \mu_1^* + RT \ln a_1 \quad 3$$

where  $\mu_1$  is the chemical potential of the solvent at temperature  $T$ . The chemical potential is the partial molal Gibbs free energy of solvent in solution. Also,  $\mu_1^*$  is the chemical potential of pure liquid solvent at temperature  $T$ . The chemical potential of the pure solvent is the same as the molar Gibbs free energy of pure liquid solvent,  $G_1(\text{liq})$ .

When a solution of any solute in water freezes, the following equilibrium is established:



We assume the solute is insoluble in the solid phase, so the solid water is pure. Since the system is at equilibrium:

$$\mu_1^*(\text{solid}) = \mu_1 \quad 5$$

Substituting equation 5 into equation 3 gives:

$$\mu_1^*(\text{solid}) = \mu_1^* + RT \ln a_1 \quad 6$$

The Gibbs-Helmholtz equation gives the temperature dependence of the chemical potential as:

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -H/T^2 \quad 7$$

or for chemical potentials in solution for a phase transition or chemical reaction:

$$\left(\frac{\partial \Delta\mu/T}{\partial T}\right)_P = -\Delta_{\text{tr}}H_1/T^2 \quad 8$$

where  $\Delta_{\text{tr}}H_1$  is the change in the partial molal enthalpy for the process. Dividing equation 6 by T and differentiating with respect to T at constant pressure gives using equation 8:

$$\left(\frac{\partial \Delta\mu/T}{\partial T}\right)_P = \left(\frac{\partial R \ln a_1}{\partial T}\right)_P = -\frac{\Delta_m H_1}{T^2} \quad 9$$

where  $\Delta_m H_1 = H_1^*(\text{liq}) - H_1^*(\text{solid})$  is just the molar enthalpy of melting of pure water. Dividing equation 9 by R gives:

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_P = -\frac{\Delta_m H_1}{RT^2} \quad 10$$

We must take into account that the enthalpy of melting is a function of temperature and depends on the difference in heat capacities of the pure solid water and liquid water:

$$\Delta_m H_1(T) = \Delta_m H_1(T^*) + \Delta C_p (T - T^*) \quad 11$$

with  $\Delta C_p = C_{p,m}(\text{liq}) - C_{p,m}(\text{solid})$ , and  $\Delta_{\text{tr}}H_1(T^*)$  is the molar enthalpy of melting at the normal melting point of pure water,  $T^*$ . Substituting equation 11 into equation 10 gives:

$$\left(\frac{\partial \ln a_1}{\partial T}\right)_P = -\frac{\Delta_m H_1(T^*)}{RT^2} + \frac{\Delta C_p (T - T^*)}{RT^2} \quad 12$$

At  $T^*$ , the freezing point of the pure solvent,  $a_1 = 1$ , and  $\ln a_1 = 0$ . Integrating equation 12 between  $T^*$  and T gives:

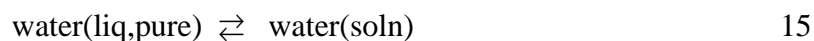
$$\int_{\ln a_1(T^*)}^{\ln a_1(T)} d \ln a_1 = \ln a_1 - \left(\frac{\Delta_m H_1(T^*) - \Delta C_p T^*}{R}\right) \left(\frac{1}{T} - \frac{1}{T^*}\right) - \frac{\Delta C_p \ln(T^*/T)}{R} \quad 13$$

For water<sup>3</sup>,  $\Delta_m H_1(T^*) = 6008 \pm 4 \text{ J mol}^{-1}$ ,  $T^* = 273.15 \text{ K}$ , and  $\Delta C_p = 38.1 \pm 0.2 \text{ J K}^{-1} \text{ mol}^{-1}$ . Substituting these values into equation 13 gives:

$$\ln a_1 = 529.16 \left( \frac{1}{T} - \frac{1}{273.15} \right) - 4.583 \ln(273.15/T) \quad 14$$

With equation 14, one can evaluate the activity of the solvent water for a solution that freezes at temperature T. Then from equation 2, the activity coefficient can be calculated.

Using equation 13, the activity and activity coefficient are calculated at the temperature of the melting solution, T. However, the activity coefficient is usually desired at the normal freezing point of the pure liquid, or even more commonly at room temperature. To convert the activities to room temperature, we consider the temperature dependence of the chemical potential from equation 3. These chemical potentials correspond to the process:



which is just the dilution of pure liquid water to the solution of interest. Luckily, the equations that give the temperature dependence follow equations 7 - 13, so we don't need to derive the equations again. In equation 13 we just need to substitute the enthalpy change that corresponds to equation 15, which is the partial molal enthalpy of solution,  $\Delta_{\text{sol}}H_1$  at the final concentration. For ideal solutions,  $\Delta_{\text{sol}}H_1 = 0$ , so for real solutions we might anticipate the enthalpy change to be small. Over the temperature and concentration ranges studied in this experiment, this anticipation is found to be true given the uncertainties in the measurements<sup>1</sup>.

One final comment is due. For dilute solutions, the freezing point depression is quite small. The  $\Delta C_p$  term is also a small correction. Under these conditions, equation 13 simplifies to the familiar form:

$$\ln a_1 = - \frac{\Delta_m H_1}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \quad 16$$

## Procedure

### Equipment.

- Vacuum bottle with cover and plastic stirrer
- thermistor, bridge, and digital voltmeter
- 200-mL Erlenmeyer flasks
- five 50-mL Erlenmeyer flasks with tight stoppers
- six 6-in. test tubes with tight stoppers
- 10-mL volumetric pipet and pipet bulb
- 25-mL graduated cylinder
- Parr density meter
- 100 ml of isopropyl alcohol (n-propyl alcohol, or acetonitrile may also be used).

### Temperature

A thermistor is a convenient and accurate device for temperature measurement. A thermistor offers definite advantages as an alternative to a mercury thermometer: The thermistor has a

relatively low time lag and, being physically smaller, does not conduct heat from the room as rapidly into the freezing solution. Thus thermal equilibration can be achieved more efficiently. The resistance of the thermistor varies as  $1/T$  over a narrow temperature range. Over a broad temperature range,

$$R = b e^{a/T} \quad \text{or} \quad \ln R = \frac{a}{T} + B$$

where  $R$  is the resistance and  $a$ ,  $b$  and  $B$  are constants. Small changes in temperature can be conveniently measured using the thermistor in a Wheatstone bridge circuit with the output of the bridge monitored by a strip chart recorder or computer. For small changes in temperature, the output of the bridge is linear with temperature. The units of the output are in milli-volts (mV).

These are strange units for temperature; the instrument must be calibrated using a separate thermometer. At the beginning of a run, the balance control is used to adjust the output voltage of the bridge. A diagram of the Wheatstone bridge circuit is shown in Figure 1. The output of the Wheatstone bridge can also be converted to a digital signal by a digital voltmeter that has a serial, RS232 communications port. This port allows the signal to be acquired by a computer.

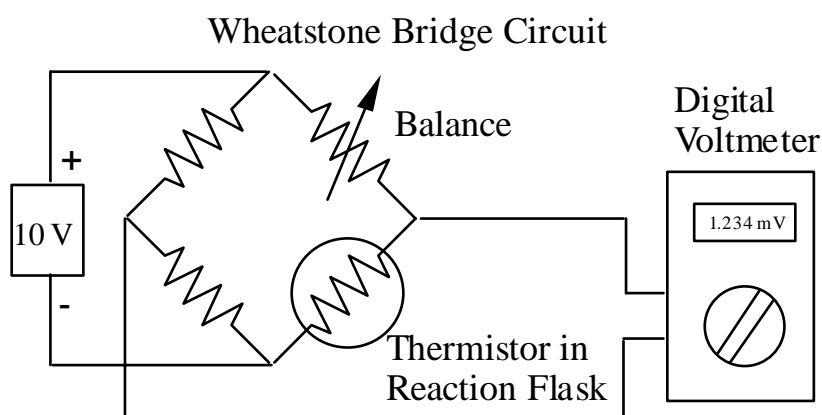


Figure 1. Wheatstone Bridge Circuit.

### Freezing Point Depression

The water used in this experiment should be pre-chilled in the freezer, to minimize the amount of impurities set free by melting of ice. So place a large plastic flask of reagent grade water in the freezer several hours before you plan to start the experiment.

Prepare 100 mL of approximately 3.0 m 2-propanol in chilled water. Make up the solution by weight on a milli-gram balance. Chill this solution in the freezer.

Add 100 mL of pre-chilled reagent grade water and an equal volume of clean crushed ice to the vacuum bottle. The freezing mixture should cover the thermistor without being too close to the cover. If the ice is not of adequate purity, the observed freezing point will slowly decrease with time as occluded impurities are freed by melting.

The ice and water are stirred vigorously until a steady temperature is attained. Adjust the thermistor bridge to produce a voltage near zero. Record the exact voltage. From this point on, do not adjust the thermistor bridge.

The water is drained off and replaced by 100-mL of the chilled 3.0 m solution of 2-propanol prepared above. The solution and ice are stirred vigorously until a constant temperature is reached, whereupon the temperature is recorded and a sample is withdrawn quickly with a 10-ml pipette; the tip of the pipette should be held near the bottom of the flask to avoid getting pieces of ice. The pipette is used here only as a matter of convenience, as the sample volume need not be accurately known. To avoid disturbance of the equilibrium system, the sample should be taken rapidly. The sample is discharged into a 6-in. test tube, which is then stoppered and placed in a 25°C constant temperature bath.

The temperature will appear to rise slightly when the stirring is interrupted for sample-taking, but this apparent rise can be ignored because it results mainly from the warming of the thermistor and does not indicate a change in temperature of the solution. After the sample has been withdrawn, vigorous stirring may be resumed and a second temperature reading taken. The temperatures recorded for the stirred system immediately before and after sampling should agree to within about 0.01°C, and these values may be averaged for the subsequent calculations.

In a similar fashion, additional samples are taken from equilibrium freezing systems with progressively more dilute solutions, obtained by adding each time a small amount of ice (to replace ice melted in the flask) and ice-cold distilled water. Some allowance should be made for dilution by melting of ice. In all, measurements should be made for about six different concentrations, ranging downward from 3 m in roughly equal steps of about 0.5 m each. Calculate the amount of added water you need for these dilutions before coming to lab [hint: try 15-20 mL for the first couple of dilutions]. [ If the thermistor bridge is calibrated to read in degrees directly, another convenient way of obtaining well-spaced points covering the desired range of molalities is to adjust the concentration each time to bring the freezing point to the desired region; a change of about 0.8°C is a good increment.]

The molalities of the samples are determined by careful measurement of density as described below. The precision required is of the order of  $\pm 0.0002 \text{ g ml}^{-1}$ .

**Measuring the Density.** The density will be measured using a density meter. The meter has a glass U-tube that is filled with the sample. The U-tube is made to vibrate and the vibration frequency is measured. The vibration frequency is a sensitive measure of the density of the solution. The more dense the solution, the smaller the vibration frequency. The meter is computer controlled, and the computer converts the vibration frequency into the measured density using a polynomial calibration equation. Density is a strong function of temperature. The meter also determines the temperature and applies a correction for the density calculation. The meter is calibrated using reagent grade water.

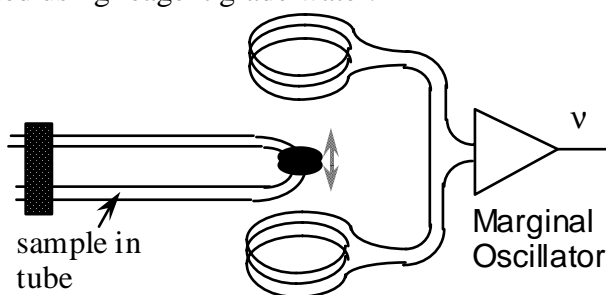


Figure 2. The operation of the density meter.

To cause the U-tube to vibrate, a small magnet is glued onto the end of the U-tube. The magnet is placed in a coil that has an oscillating current in it, Figure 2. The frequency of the oscillating current is varied until the natural vibration frequency, that is the resonance frequency, of the U-tube is found. In operation, the density meter is very similar to the speaker on a stereo.

The densities of the solutions are measured with a Parr density meter that has been calibrated by determining the density of water (see tables in the CRC or page 6 of the meter instructions) at the temperature of the measurement using the following instructions. You can calibrate the density meter while you are making the solutions, to save time. First, rinse the meter with a few portions of reagent grade water using the following steps. Rotate the sampling roller downwards to compress the sampling bellows. Fill the meter by dipping the inlet tube into the liquid and pulling the liquid into the oscillator U-tube by rotating the sampling roller upwards. Carefully examine the U-tube to ensure that there are no bubbles. Select "DENS" as the measured value by pressing the "MEAS" key and then pressing the  $\Delta$  or  $\nabla$ . Monitor the density reading for 30 sec. If the reading doesn't stabilize there is an air bubble in the measurement U-tube: empty and refill if necessary. Press the "ENTER" and "CALIB" key simultaneously. The "CALIB" symbol will be flashing and "AUTO" is displayed. The automatic calibration is at an end when "MEAS" is again displayed, which can take a minimum of one minute and a maximum of 15 minutes.

Check the calibration by emptying the measuring tube and refilling with reagent grade water. If the difference between the measured and tabulated values is greater than  $0.001 \text{ g/cm}^3$ , check to see that the measuring U-tube is clean and repeat the measurement. If the difference is less than  $0.001 \text{ g/cm}^3$ , repeat the determination two more times and use the average difference between the measured and tabulated values to correct all subsequent readings.

Exercise extreme care in filling, rinsing, cleaning, and handling the meter.

Prepare a calibration graph of molality versus density by measuring densities of pure water and five solutions of known composition made up by mixing known volumes of the two components. Make up calibration solutions at concentrations of approximately 1.0, 1.5, 2.0, 2.5, and 3.0 m by weight using a milli-gram balance. You need prepare only about 20 mL of each solution. Make sure to calculate the desired weights of solute and solvent *before* coming to lab. There won't be sufficient time to do the calculations during the lab period.

Determine the density of each of your samples in the same way as you did for calibration.

### Thermistor Calibration

The last step is to calibrate the thermistor thermometer. Once again, don't change the balance on the thermistor bridge during this process. Start with chilled water in the vacuum bottle. Place the thermistor and a  $0.1^\circ\text{C}$  mercury thermometer or an electronic  $0.1^\circ\text{C}$  platinum resistance thermometer into the vacuum bottle. Stir gently and record the two readings. Add a few mL of room temperature water and stir and take the new readings. Repeat this process several times, until you have at least five data points.

### Calculations

Assume that the thermistor bridge output is linear with temperature and do a least squares curve fit of the temperature calibration data. Use the fit coefficient for the slope, call it  $s$ , to convert the bridge voltage to degrees Kelvin for your solutions:

$$\Delta T = s (mV - mV^*) \quad 17$$

and  $T = s (mV - mV^*) + 273.15 \text{ K} \quad 18$

where  $mV^*$  is the reading for pure water and  $mV$  is the reading for the solution and  $\Delta T$  is the freezing point depression, which as defined here is less than zero.

Fit the molality versus density calibration data to a quadratic polynomial,  $m = ad^2 + bd + c$ . Use the fit coefficients to calculate the molalities for the freezing point solutions.

Convert the solute molalities to mole fractions for the solvent. To make the available number of significant figures easier to see, Equation 14 should be rearranged to give

$$\ln a_1 = -529.16 \left( \frac{\Delta T}{T \cdot 273.15} \right) - 4.583 \ln(273.15/T) \quad 19$$

The solute molalities, solvent mole fractions, freezing-point depressions, activities, and activity coefficients for the various samples are then tabulated using equation 19. Estimate the uncertainties of the activities and activity coefficients using significant figure rules and the propagation of uncertainty rule for  $\ln$ . What is the predominate error in your measurements? Discuss the chemical significance of this experiment in general and your results in particular.

### References

1. R. J. Sime, "Physical Chemistry, Methods, Techniques, and Experiments," Saunders, Philadelphia, PA., 1990. Expt. 12.
2. F. Daniels, J. W. Williams, P. Bender, R. A. Alberty, C. D. Cornwell, J. E. Harriman, "Experimental Physical Chemistry, 7th Ed.," McGraw-Hill, New York, NY, 1970. Expt. 13.
3. G. N. Lewis and M. Randall, rev. by K.S. Pitzer and L. Brewer, "Thermodynamics," 2d ed., McGraw-Hill Book Company, New York, 1961. pp. 404-409, 412-413.