

5. Freezing-Point Depression (update notes — 10/27/98)

Experimental

The procedures for conducting the measurements are spelled out in the description of Experiment 11 in the lab text. However, we are making the following deviations from those procedures:

(1) The temperature measurements will be carried out with the aid of a thermistor interfaced to a computer (see pp. 598-601 of SGN). This device will have been previously calibrated and the calibration data will be available. The procedures for operating this system are similar to those employed in the Triple Point and Bomb Calorimetry experiments.

Important Note: Be sure that the thermistor is mounted in the stopper so that it projects straight down into the center of the Dewar. If it should become mounted at an angle, it could suffer catastrophic failure from contact with the stirrer ... with similar catastrophic consequences on your results for this experiment!

(2) At the outset you should carefully measure the ice point with your thermistor (using ice and deionized water), as the value you obtain will be crucial to the correct application of the thermistor calibration function (see below).

(3) The use of the computer interface should permit students to work more efficiently, enabling each team to determine the freezing points for 6-12 different concentrations of each of the two solutes instead of just two. By monitoring the thermistor T on the computer screen you can easily discern when thermal equilibrium has been established. (Normally this should take only 2-4 min. from the time vigorous stirring is begun.) Start with a concentration of ~ 0.5 m for each solute. After withdrawing the first aliquot of solution, add some deionized water to dilute the solution; then stir vigorously again to obtain your next equilibrium point. Repeat this procedure, each time adding enough water to produce a fairly even distribution of your measurements over the range of depressed freezing points. (*E.g.*, if your first T is -1.0°C , you would like the others to be near -0.9°C , -0.8°C , ..., -0.1°C , etc. But note that while it is important to sample this range well, it is not necessary to hit these values precisely; indeed, that would be difficult!) After several such dilutions, you may find your solution volume getting too large, or your ice mostly melted, at which point you should start again with a more dilute acid solution.

(4) Each time you withdraw an aliquot of acid solution from the Dewar, note the precise time and approximate temperature on the computer screen. This information will facilitate your later retrieval of the relevant T data for each sample from the computer file.

(5) The computer program is set to record temperatures every 3 s or so. However, it stops recording when it has logged 1000 points. Therefore you should keep track of the total time and be sure to restart the program (storing your data under a new file name) before it shuts down on you in the middle of a set of measurements.

(6) Each team will probably find it effective to divide the work of measuring the freezing points, and of titrating the solutions for their acid content, operating in "parallel mode."

(7) Note that the NaOH solution will need to be standardized by titrating a weighed quantity of potassium acid phthalate (footnote on p. 191 of lab text).

Data Analysis

As was noted above, the thermistor readings need to be corrected to true. To this end there are available calibration data, in the form of a file THERMIST.DAT that can be found on the lab computer in the same directory where your data will be stored. [If you neglect to copy this file, it can also be downloaded from the course web site, at URL www.vanderbilt.edu/AnS/Chemistry/Tellinghuisen/Chem236/THERMIST.DAT.] The data in this file were obtained by simultaneously recording

temperatures on a precise low- T Hg thermometer and the thermistor; the last column contains the correction T_{COR} , defined as the quantity to be added to the thermistor reading to yield the correct T :

$$T(\text{true}, ^\circ\text{C}) = T(\text{thermistor}) + T_{\text{COR}} \quad (1)$$

Since the correction data display a lot of scatter, you should define the working correction function by means of a least-squares linear fit of the T_{COR} values, taken as a function of T (thermistor). Thus, your correction will be obtained in the following form,

$$T(\text{true}, ^\circ\text{C}) = T(\text{thermistor}) + a + b T(\text{thermistor}), \quad (2)$$

where the parameters a and b are obtained from your least-squares fit.

There is, however, one further complication. We believe that the calibration data were subject to a time lag problem, owing to the difference in response time of the Hg thermometer and the thermistor to the slowly changing temperature of the ethanol bath used to obtain those data. This problem should affect the intercept a in the correction function, but not the slope b . Here is where your precisely measured ice point comes into play: You should replace the intercept a with a new value a' , such that when you employ the apparent T , T (thermistor), in Eq. (2) at the ice point, you obtain $T(\text{true}, ^\circ\text{C}) = 0.000 ^\circ\text{C}$.

After you have corrected your thermistor temperatures as indicated above, follow the other procedures in the lab text. Be sure to compare your results with literature values. In connection with the latter you may want to check your actual measured depressions for $\text{HCl}(aq)$ against data available in the lab (*e.g.*, CRC Handbook).