Temperature Calibration and Correction.

We use two temperature-measuring devices in the laboratory — thermometers and thermistors — and they both require calibration. For the thermometers, which are mostly mercury-filled, calibration is simple: Allow the thermometer to equilibrate in an ice/water bath and record the apparent T. The error may be assumed constant at all T. Thus, if the thermometer reads 0.7°C in the ice bath, you can assume that all recorded Ts will be high by 0.7°C and correct them accordingly. The only possible hitch here is incomplete equilibrium in the ice bath — between the ice and water or between the thermometer and the bath. To ensure that ice, water, and thermometer are all in thermal equilibrium, place the ice and DI water in an insulated Dewar and keep stirring while observing the Hg level on the thermometer, until it is clear that it is not changing.

Thermistors are used in the Bomb Calorimetry, Triple Point, and Freezing Point Depression experiments. They are very PRECISE devices (~0.001 K) and very rapid in their response to changing Ts. Unfortunately, they are not very ACCURATE, so they need to be calibrated against reliable standards. We have used very accurate Hg thermometers to calibrate the Freezing Point and Bomb Calorimetry thermistors. The Triple Point thermistors record temperatures down to –40°C, where Hg thermometers cannot be used (since Hg freezes). Thus we have used an electronic thermometer stated to be accurate within 0.1°C to calibrate the two Triple Point thermistors. The calibration procedure involves placing the standard reference thermometer and the thermistor probe in a stirred liquid bath contained in an insulated Dewar. The readings of both devices are observed long enough to ensure that both are in thermal equilibrium with the bath. Then both readings are recorded. The procedure is repeated at a number of different temperatures, by warming or cooling the bath.

The two Triple Point thermistors (cyclohexane = "Cyc"; water = "wat") were calibrated simultaneously, yielding the results contained in the data file TripCal-01.txt, which is available on the web site. The first column is the "true" value, as obtained from the electronic device. (Its precision is only 0.1°, but that is commensurate with its accuracy.) The 2nd & 4th columns are the apparent Ts, as recorded on the two thermistors. The 3rd and 5th columns are the corresponding corrections. Note that the corrections are obtained as "true-apparent" for a range of apparent temperatures (T_{app}) on each thermistor. Thus we correct our apparent values (*i.e.*, our recorded thermistor values) by ADDING the correction. (I.e., if corr = true – app, true = app + corr.) We can assume that the thermistors will behave the same way each time they are used (though in the experiment we check a few points to be sure). Then we can use these calibration data to correct our apparent temperatures as recorded in the T & P *vs.* time data files. For example, if an apparent temperature of –21.37°C is recorded in the data file for the cyclohexane measurements, and if the correction at that thermistor T is –0.32 K, the corrected ("true") temperature is –21.69°C. All temperatures in the data file are similarly corrected, but the correction is now a <u>function</u> of the apparent T, not just a single additive constant, as in the Hg thermometer calibration.

The first figure given below is a plot of the calibration correction (true – apparent) vs. T_{app} (the thermistor reading) for both Triple Point thermistors. The calibration data exhibit some "noise" (as do all experimental data). For reliability and convenience, we should express the correction for each thermistor as a smooth function of the apparent T — *e.g.* a polynomial in T_{app}. Then the correction can be easily computed at any T_{app}. In this way, all of the thermistor temperatures in a column of a data sheet can be corrected in a single keystroke, using a program like KaleidaGraph. (You employed a similar procedure in Problem Set 3, where you fitted the specific volume data for water to a polynomial in T and then used that function to compute the volume for another set of temperatures.)

Why not just plot "true" T *vs*. T_{app}, and fit that relationship? Such a plot is illustrated in the lower figure given below. This procedure <u>can</u> work, but it requires some care. At first glance the data in this representation look like a nearly perfect straight line, and you may be lulled into assuming that a linear relationship is adequate. But, just as in your work fitting the H_2O density data in Problem Set 3, residuals inspection will show systematic deviations, indicating that a higher-order fit is required. The plot of the T correction *vs*. T_{app} is, in effect, such a residuals plot; it is immediately more informative about the relationship between the true and apparent temperatures.

The same correction techniques apply to the data you record in the Bomb Calorimetry and Freezing Point Depression experiments. Calibration data for the FPD experiment have already been placed on the web site, as the file THERMIST.DAT; those for BombCal will be put there soon, under the name BombTCal-01.txt. All of these files are located in the /Chem236 directory, *e.g.*,

http://www.vanderbilt.edu/AnS/Chemistry/Tellinghuisen/Chem236/TripCal-01.txt

new Trip. T calib. (9/30/01)

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