Thermal Expansivity

In this experiment, thermal expansivity is determined from (1) measurements of volume (V) as a function of T for fixed mass (dilatometry), and (2) measurements of density as a function of T for fixed V (pycnometry). In both cases a KNOWN substance (water) is used to calibrate the measurement device, which is then used to measure an UNKNOWN.

Dilatometry Analysis

In the dilatometry measurements, mass is needed ONLY in the calibration phase. The mass of water is determined by difference weighing. Then use the results you obtained in Problem Set 3, where you fitted the precise volume/g data for water to a polynomial in T(˚C), to compute the V of the water in your dilatometer at each T. (This is easily done spreadsheet style, using, for example, Formula Entry in KG.) Your capillary h scale starts at something other than 0.0 (due to lack of appropriate materials in the glass shop when these devices were made). Subtract the lowest value (h_0) to put your h values on a scale that runs 0.00-15.00. Then plot V *vs.* h' ($= h - h_0$). You should observe a linear or nearly linear relation. A fit of these data to a straight line will yield intercept V_b (*i.e.*, the volume at the lowest mark, $h' = 0$, or $h = h_0$); the term linear in h' gives the volume V_c. (Recall that the total volume is partitioned as $V = V_b + V_c$; see eq 5 in the Class Pak.) HOWEVER, you should experiment with higher-order fits of $V(h')$ to ensure that the linear relation is suitable.

[The Class Pak notes that the bulb volume V_b is slightly T-dependent. However, you can verify that increasing T from 10˚C to 40˚C results in an increase of V_b by only ~0.01 mL. This is small enough to be of no significance in all but the most precise measurements, so you may ignore the corrections for this T dependence in eq 6 and just assume a fixed (T-independent) V_b.]

The "unknowns" we use in this experiment (alcohols) have larger thermal expansivity than water in the 10˚-40˚C range. Thus, to span this full T range, you will have had to record data for several different masses, since full scale on the capillary corresponds to only ~5˚. You should have recorded at least 5 h values for each fixed-mass data set. Use your water calibration results to convert these h readings to V values. Then fit EACH of these data sets SEPARATELY to eq 4 (since this equation assumes fixed mass). In this fit, you specify T_r; this can be any T that you like, but to obtain sensible results, it should be some T in the middle of the range of the data set in question. (For example, if the data span the range 16.4˚-20.7˚C, then T_r = 19.0˚C is a reasonable choice.) V_r, a, b, ... are then adjustable parameters in such a fit and will have to be specified as such in your fit function. Note that V_r is the volume at $T = T_r$. Also, if you fit to the suggested polynomial in $(T - T_r)$ given after eq 4, the coefficient (a) of the linear term is α at $T = T_r$. You should experiment with different orders of $(T - T_r)$ to see how many terms are warranted. [For small T ranges, a single term $a\,(T - T_r)$ will likely suffice.]

If for some reason you do not have enough h *vs.* T measurements in each fixed-mass data set to fit to eq 4, you may still be able to obtain good estimates of α from your data. For example, even two values will suffice to estimate α from the fundamental definition of the derivative, $(\partial V/\partial T)_P \approx (\Delta V/\Delta T)_P$.

The ultimate goal of the measurements is α as a function of T. Your different fixed-mass data sets will have provided α values and their uncertainties. Plot these (with error bars) vs. T. If the results exhibit a smooth dependence, carry out a weighted fit to obtain a mathematical expression for $\alpha = \alpha(T)$.

Pycnometry Analysis

The fundamental determined property here is density = mass/V, so mass IS needed. For our modified pycnometers, V is not quite constant but is still known for each measurement. This is because we know V for the calibration mass of H_2O and can calculate V for any other h value, since we know the diameter of the capillary. (Note: Check the h scale against a ruler; there are several in the lab.) We are trying to obtain precise AND accurate ρ values here, so correction for the buoyancy of air is needed, as described in the Class Pak.

In comparing your two calibrations of the bulb V, it is necessary to choose a common reference. This could be taken as any mark on the capillary, but the lowest mark is a particularly convenient choice for defining the bulb volume V_b. Then, for any measurement of h, the total V is the sum of V_b and the extra volume contained in the capillary extension up to level h.

Equation 2 can be integrated to yield a result similar to that given in eq 3 for integration of eq 1. Alternatively, in analogy to eq 4, we can assume that ρ can be expressed as

$$\rho = \rho_r \exp[-g(T, T_r)] ,$$

where ρ_r is the density at $T = T_r$, and the function g is defined to go to zero when $T = T_r$. α is thus obtained as dg/dT.

Plot your density values *vs*. T. Then fit these to the equation given just above, taking g as $a(T - T_r) + b(T - T_r)^2 + \ldots$. Experiment with different fit orders. The coefficient a of the linear term can again be shown to be α at $T = T_r$. Then refit your data for different T_r values, taking T_r as your actual T values for the different density determinations. In this way you will obtain α and its uncertainty at each T_r. Plot these (with error bars) *vs*. T for comparison with your dilatometry results. Obtain an expression for α as a function of T from the results of one of your fits to the equation given above.