Exercise #1 Chem 331L

The Variation of Gas Pressure with Temperature Under Conditions of Constant Volume

Using air as the sample gas, the dependence of gas pressure upon temperature in a rigid vessel was examined using the apparatus depicted in Fig 1 below. The flask, originally open to the atmosphere at ambient conditions, was closed and connected to an open arm mercury manometer. The flask was placed in a stirred water bath fitted with a thermometer and a variable temperature thermostat. At the start the bath was at room temperature and therefore the height of mercury was the same in both arms of the manometer (difference = zero). At each of several different temperatures the equilibrium difference in heights of the two arms of the manometer was recorded. Table 1 contains the water bath temperature and the corresponding differences in the heights of the manometer columns (outside arm – inside arm).

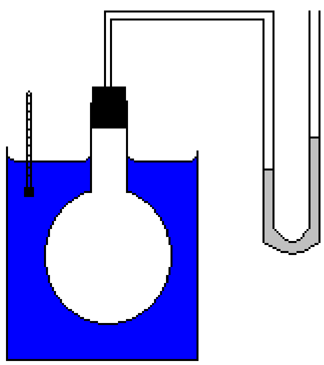

Fig 1. Apparatus used to measure the dependence of a gas pressure upon temperature.

Table 1

Temperature/ °C	**Difference/ mm Hg**
29.9	16.00
29.6	16.90
39.9	43.65
39.9	44.33
50.0	71.10
50.3	71.50
61.4	102.30

The barometric pressure in the room when the flask was initially closed was 743.00 mm Hg.

The experimental measurements can be displayed as a plot of pressure vs. temperature (on a plane of constant volume). The slope between any two adjacent points is an approximation to the slope at the midpoint between those two observations. If the plot curves, then to obtain a useful estimate of the slope one would be forced to collect data at decreased temperature intervals. If an analytic function p(T,V,n) can be found to represent the data, then the slope in general is given by the operation (âp(T,V,n)/âT)$_V$. If the data can be usefully represented by a straight line, then the partial derivative is simply the (constant) slope over the entire data range. Whether evaluated using an analytical function or as discrete stepwise approximations, the partial derivative is an important source of experimental information about the equation of state of the gas sample.

Procedure for Mathcad:

*** Please label your numbers with proper units in the worksheet! ***
*** Label all graphs appropriately! ***

1. Title your worksheet with your name and a project title.
2. Define a variable to contain the raw data in Table 1 in a matrix form.
3. Define vectors to contain the total pressure in Torr and the temperature in Kelvin.
4. Determine the intercept and slope of the (T,P) vectors and assign them to variables b_1 and b_2, respectively.
5. Define a vector p_best(Temp) as $b_1 + b_2$Temp, where Temp is the temperature.
6. Graph vectors P and p_best(Temp) over an appropriate temperature range. The experimental values of pressure must be shown as discrete symbols, while the best fit values of pressure are displayed as a line.
7. Comment on whether p_best(Temp) provides a good representation of the experimental data.
8. Create a new plot of the differences (experimental – best fit pressure) vs. the best fit pressure. Do you still think the best fit line provides a good/poor representation of the experimental data?
9. Using p_best(Temp), calculate: (a) The pressure expected in the flask if the temperature were 0 °C, (b) At 100 °C, (c) the temperature at which the pressure in the flask is predicted to be zero. How close is your answer in (c) to absolute zero?
10. If we assume that the equation of state for air under the conditions of the experiment is pV = nRT, let us now determine R from a plot of (âp/âT)$_V$ = nR/V. Approximate (âp/âT)$_V$ from our experimental data as P/T. Approximate n/V as ρ/M_{air}, where ρ is the density of air (grams/liter) as a function of the experimental pressures (torr), and experimental temperatures (°C); $\rho(t,p) = 1.293p/((1+0.00367t)760)$. Approximate M_{air} as the mass of one mole air with mole fractions, χ,: 0.78 nitrogen, 0.21 oxygen, and 0.01 argon. Determine R. What is the percent error in the experimental R relative to the accepted value of R?
11. Use the symbolic processor to find (âp/âT)$_V$ for the van der Waals and the Redlich-Kwong equations of state.
12. Suggest what might be done experimentally and analytically to obtain better values of R and absolute zero.