Tutorial
Introduction to Physical Chemistry

Frank Schreiber
frank.schreiber@chem.ox.ac.uk
PTCL room 30.40 phone (2)-75179
Wadham staircase 13 room 2A phone (2)-77988

The tutorial work generally consists of two parts. The first part is either a series of short questions or an 'essay'. The second part is a series of problems.

Please remember that even in those cases in which the problems sheets do not explicitely mention any 'essay-type' work, I ask you to produce a two-page summary of the most important keywords, definitions, equations, etc. of a given subject. This will not only help you to organise your thoughts, but it will also be very helpful when you revise the subject later.

Please hand the work in to my pigeon hole in Wadham before dinner time two days before the day of the tutorial.

You should consider the questions marked *"Supplementary"* as those to work on *only* once you have worked on all others.

Should you have any questions, please do not hesitate to contact me by email or phone.

Literature

Atkins, Physical Chemistry

Any other general textbook on Physical Chemistry

Revision and Background

You may answer each of these items only briefly; there is no need to write long texts. The main point is that you prepare yourself for a discussion in the tutorial.

1) Describe the main phases in which matter can exist. What are the main characteristics ? How would you experimentally determine in which phase your sample is (beyond "visual inspection") ? How would you quantify the differences between the different phases ?

2) In which way do the the forces between atoms or molecules determine the phase of a given substance ?

3) What is meant by ideal (perfect) gas and what is meant by real gas ? How do real gases differ from ideal gases ? Provide an equation of state (relating temperature, pressure, and volume) for a real gas and interpret the terms which take into account the differences between a real and an ideal gas. Comment on extreme limits of the equation of state (e.g., zero temperature). What is the idea of the "virial expansion"?

4) How would you relate the pressure of a gas and the force excerted on the walls of a container to "microscopic" processes involving individual atoms or molecules ? You do not need to do a calculation (although you are welcome to try), but you should think about how to relate microscopic processes to macroscopic quantities such as pressure.

Problems

Problem 1 Ideal Gas

(a) A meteorological balloon has a radius of 1.0 m when released at sea level at 20 °C and expands to a radius of 3.0 m when it has risen to its maximum altitude, where the temperature is -20 °C. What is the pressure inside the balloon at that altitude ?

(b) A vessel of volume 22.4. L contains 2 mol H_2 and 1 mol N_2 at 273.15 K initially. All the H_2 reacted with sufficient N_2 to form NH_3. Calculate the partial pressures and the total pressures of the final mixture.

Problem 2 Freezer

Consider a freezer the door of which has been opened for a long time such that the inner walls including the air (1 m^3) inside the freezer are at room temperature (20 °C). The door (1 m^2) of the freezer is then closed, and the freezer is cooled down to -10 °C. If you assume ideal gas behaviour and no exhange of gas after closing the door, can you calculate the force needed to open the door again when the inside is at -10 °C ? Comment on your result. (Ignore complications like ice formation on the door, just use the ideal gas law.)

Problem 3 Drinking Straw

What pressure difference must be generated across the length of a 15 cm vertical drinking straw in order to drink water ?

Problem 4 Barometric Formula

The barometric formula

$$p = p_0 \, e^{-Mgh/RT}$$

relates the pressure of a gas of molar mass M at some altitude h to its pressure p_0 at sea level. Derive this relation by showing that the change in pressure dp for an infinitesimal change in altitude dh is $dp = -\rho g dh$ (where ρ is density). Remember that ρ depends on the pressure. Evaluate the pressure difference between the top and bottom of (a) a laboratory vessel of height 15 cm and (b) of a skyscraper of height 1350 ft. Ignore temperature variations.

Supplementary

Problem 5 Maxwell-Boltzmann Distribution

The Maxwell-Boltzmann distribution function of molecular speeds in a gas has the form

$$dF(c) \;=\; 4\pi\Big(\frac{m}{2\pi k_B T}\Big)^{3/2} c^2 \,\exp\Big(-\frac{mc^2}{2k_B T}\Big)\,dc$$

where $dF(c)$ is the fraction of molecules with speeds between c and $c+dc$, m is the mass of a molecule and T is the temperature.

(a) Sketch the form of this distribution and calculate the fraction of argon atoms (mass 6.64×10^{-26} kg) with speeds between 100.0 m/s and 100.5 m/s at 298 K.

(b) Derive an equation for the most probable speed of a molecule, c_p, and use this to find c_p for the same argon atoms.

(c) Derive an equation for the mean speed of a molecule, c_m. Calculate c_m for the argon atoms.
You will need the following standard integral

$$\int_0^\infty x^3 e^{-ax^3} \;=\; \frac{1}{2a^2}$$

(d) Why do the values for c_p and c_m differ ? Compare also the value of the root mean square speed, c_{rms} for argon atoms.