The following topics are covered in this set of problems:

1. A brief introduction to interatomic/intermolecular forces and potentials. (This largely involved a revision of topics covered in the Autumn semester Modelling module – approximate form of a function near a minimum, finding equilibrium separation…) [Lecture 1];
2. Very gentle introduction to changes of phase, latent heats etc.. (Phase changes will be revisited in the last few lectures of the module) [Lectures 1 and 2];
3. Distribution functions [Lecture 3];
4. Derivation and simple applications of the ideal gas law [Lectures 3 and 4];
5. Boltzmann distribution and Boltzmann factors [Lectures 4 and 5].

Q1. One mole of an ideal gas is held in a container (volume: 0.1 m^3) at a pressure of 5 kPa. Determine the temperature of the gas. If the temperature is changed to 373K and the volume of the container is kept constant, calculate the change in gas pressure. In an isothermal expansion where the volume of gas is doubled, what is the change in the internal energy of the gas?
[From 2003 F31ST1 resit paper].

Q2. A block of steel of 1 kg mass and at a temperature of 250°C is placed into an insulated container that holds 100 grams of water at 10°C. The container is made of aluminium and weighs 20 grams. Calculate the mass of the fraction of water that is converted into steam. [Specific heat of steel = 448 J kg^{-1} K^{-1}; specific heat of water = 4186 J kg^{-1} K^{-1}; specific heat of aluminium = 660 J kg^{-1} K^{-1}; latent heat of vaporisation of water = 2.26×10^6 J kg^{-1}]

Q3. Suppose we have a large collection of N molecules with total energy E. The individual energies available to each molecule are such so that there are N_i molecules with energy ε_i (hence, $E = \sum N_i \varepsilon_i$). Boltzmann's distribution law states that:

$$N_i = N_0 e^{-\frac{\Delta E}{kT}}$$

where N_0 is the number of molecules found in the energy state ε_0, $\Delta E = \varepsilon_i - \varepsilon_0$, and k is Boltzmann's constant. If we increase the temperature of the system, which of the following statements is/are true?

(a) All of the energy levels will become more populated;
(b) All of the energy levels will become less populated;
(c) All of the energy levels will be more closely spaced together;
(d) All of the energy levels will be spaced further apart;
(e) Some of the energy levels will be more closely spaced, others will be spaced further apart;
(f) Some of the energy levels will become more populated, some less populated.

Q4. In 1910, Perrin and Dabrowski determined Avgadro's number by examining the distribution of particles in a colloidal suspension (a mixture of spherical mastic particles in water). The particles had a radius of 0.52 μm and a density ρ of 1.063 g cm^{-3}. Perrin and Dabrowski determined the number of particles in layers separated by a distance of 6 μm to be 305, 530, 940, and 1880. Calculate the value of Avogadro's constant using these data and the expression for Boltzmann's distribution law given in Q3.

[Take the density of the suspending fluid to be 1.00 g cm^{-3} and the temperature to be 15° C. Furthermore, note that the gravitational force on a particle suspended in a liquid is reduced by the buoyancy of the liquid and is given by: $\dfrac{4\pi r^3 g(\rho - \rho_1)}{3}$, where r is the radius of the particle, and ρ and ρ_1 are the densities of the particles and the surrounding liquid respectively].

Q5. The probability distribution ($P(v_x)\,dv_x$) associated with the x component of velocity, v_x, of the molecules of an ideal gas is given by:

$$P(v_x)dv_x = \sqrt{\frac{m}{2\pi kT}}\exp(-\frac{mv_x^2}{2kT})dv_x$$

Sketch the form of the velocity distribution curve for two temperatures T_1 and T_2 ($T_1 > T_2$) and write down the value of $<v_x>$ for the distribution in each case. Show that the mean square value of v_x (i.e. $<v_x^2>$) is kT/m.

Solutions

Q1.

$PV = RT$. Plug numbers in: $T = 60.2$ K

$$\frac{T_1}{P_1} = \frac{T_2}{P_2} \Rightarrow P_2 = 5000\left(\frac{373}{60.2}\right) = 30.98 kPa$$

$\Delta P = 25.98$ kPa

Isothermal expansion. For an ideal gas U is a function of T only so change in internal energy = 0.

[*Note to tutors*: the idea that the internal energy of an ideal gas is a function only of temperature is introduced in Lecture 4. The students will therefore probably struggle to answer the final part of the question so you may need to spend some time explaining the answer (and the question!)].

Q2.

The first thing to realise is that as not all the water has been converted to steam, the heat input from the block drives the phase transition at 100°C rather than raising the temperature above 100°C.

Heat lost by the steel = heat gained by the container and water

$Q_{steel} = m_{steel}\, c_{steel}\,(\Delta T) = 448\,(100 - 250) = 6.72$ x 10^4 J (Heat *lost* by steel)

$Q_{water} = 0.1$ x 4186 x $(100 - 10) = 3.77$ x 10^4 J (Heat gained by water to get to 100°C)

$Q_{steam} = m_{steam}\,(2.26$ x $10^6)$ J. (Heat gained by a mass m_{steam} of water in conversion to steam).

$Q_{container} = 0.02\,[660]\,[90]$ J $= 1188$ J

Thus, 6.72 x 10^4 J $= 3.77$ x $10^4 + 1188$ J $+ m_{steam}\,(2.26$ x $10^6)$ J

Therefore, 12.5 grams of water are converted to steam.

Q3.

The correct answer is (f).

Solutions (contd.)

Q4.

In Lecture 5, the students have seen the derivation of the Boltzmann distribution for a 'column' of gas (see Set 2a of the lecture notes available on the website). In the case of the colloidal suspension described above we can write:

$$\frac{N}{N_0} = \exp(-\frac{4\pi r^3 g(\rho - \rho_1)h}{3kT})$$

$$\Rightarrow \ln N = -\frac{4\pi r^3 g(\rho - \rho_1)h}{3kT} + \ln N_0$$

Thus, a graph of *ln N* vs *h* (from Perrin and Dabrowski's data) yields a slope of $-\frac{4\pi r^3 g(\rho - \rho_1)}{3kT}$. The slope of the graph is approximately -1×10^5 m^{-1} and hence k can be estimated as 1.26×10^{-23} J K^{-1}. Avogadro's number $= R/k = 6.60 \times 10^{23}$ mol^{-1}.

Q5.

Students get confused between the *velocity* and *speed* distributions. The velocity distribution given above is Gaussian with mean, $<v_x> = 0$ and standard deviation of $\sqrt{\frac{kT}{m}}$.

[*Note to tutors*: In Lecture 3, a little time is spent revisiting concepts related to Gaussian-distributed variables. The students have previously encountered these in the 1st year lab. module (and in the associated errors manual) and in the autumn semester *Analytical Skills and Modelling* module.]

To evaluate $<v_x^2>$:

$$<v_x^2> = \sqrt{\frac{m}{2\pi kT}}\int_{-\infty}^{+\infty} v_x^2 e^{-\frac{mv_x^2}{2kT}} dx$$

$$\Rightarrow <v_x^2> = 2\sqrt{\frac{m}{2\pi kT}}\int_0^\infty v_x^2 e^{-\frac{mv_x^2}{2kT}} dx$$

Using the standard integrals given in the Appendix to Set 2b of the F31ST1 notes:

$$\Rightarrow <v_x^2> = 2\sqrt{\frac{m}{2\pi kT}}\frac{\sqrt{\pi}}{4}\left(\frac{m}{2kT}\right)^{-3/2}$$

$$\Rightarrow <v_x^2> = 2\sqrt{\frac{m}{2\pi kT}}\frac{\sqrt{\pi}}{4}\left(\frac{m}{2kT}\right)^{-3/2}$$

$$\Rightarrow <v_x^2> = \frac{kT}{m}$$

[Note that in Set 2 of the coursework, the students will evaluate $<v^2>$ from the Maxwell-Boltzmann distribution and (hopefully) find that it is *3kT/m*. The result above follows from $<v_x^2> = \frac{1}{3}<v^2>$.]