Properties of gases – problem sheet

1. Calculate the most probable speed, the mean speed, and the root-mean-square speed for carbon dioxide molecules at 298 K.

2. Calculate:

   (a) the mean free path of molecules in air at 1 bar pressure and 25 °C (take the average collision cross section, σ, to be 0.43 nm^2);

   (b) the pressure at which the mean free path in air becomes equal to 10 cm;

   (c) the number of collisions *per cm*^{3} in one second between oxygen and nitrogen molecules in air at 25 °C and 1 bar pressure (take the radii to be equal to 178 and 185 pm, respectively).

3. Graham's law of effusion states that the rate at which gas is lost from a vessel into a vacuum through a small hole is proportional to $M^{1/2}$, where M is the molecular mass.

   (a) By considering the number of molecules, N, striking a hole of area A_0, show that the rate of effusion is given by

$$\frac{dN}{dt} = \frac{pA_0N_A}{(2\pi MRT)^{1/2}}$$

   (b) Show that the rate of change of pressure in a vessel of volume V is given by

$$\frac{d\ln p}{dt} = -\left(\frac{RT}{2\pi M}\right)^{1/2}\frac{A_0}{V}$$

   (c) Hence calculate how long it would take the pressure of potassium vapour in a vessel to drop to 1/e of its original value, given that V = 5 cm^3, T = 1100 K, and the hole has a diameter of 10 μm. Would the vapour pressure of sodium decrease more or less rapidly?

   (d) Graham's law of effusion only holds if the diameter of the hole is small compared with the mean free path of the molecules. Estimate the maximum pressure of potassium vapour at which Graham's law applies (take the radius of a K atom to be 0.2 nm).

4. Calculate the diffusion coefficient of oxygen molecules at 290 K and 1 bar pressure, and at 200 K and 1 Pa pressure (conditions one might find in the earth's stratosphere). How long would it take a molecule to diffuse 1 m in each case? Take σ = 0.43 nm^2.

5. The frequency of light emitted by a molecule is shifted if the molecule is moving towards or away from the observer with velocity v (this known as the Doppler effect, and is explained further in Atkins). Provided v is much less than the speed of light, c, the observed frequency, ν, is related to the true frequency, ν_0, by

$$\frac{\nu - \nu_0}{\nu} = \frac{v}{c}$$

   (a) Using the appropriate form of the Maxwell-Boltzmann distribution, argue that the emitted light has a Gaussian lineshape with a width at half height of

$$\delta\nu = \frac{2\nu}{c}\left(\frac{2k_BT\ln 2}{m}\right)^{1/2}$$

   (b) Calculate $\delta\nu$ (in s^{-1}) for emission from an excited state of NO_2 at 530 nm, at room temperature. You may neglect any other mechanisms that contribute to the linewidth.