## Chemistry 240 Semester 01-2009 Homework for Submission #2

Answer the following question and submit them for marking on or before Thursday 5th February in class. If any answers show evidence of copying, the whole exercise will attract zero marks. Please note that presentation of your answer (not neatness as such!) is extremely important.

1) Radon is a radioactive noble gas. It is produced in granitic rocks by the radioactive decay of uranium. It has a short half-life, but apart from that would not be expected to present a significant threat at altitude. Demonstrate the truth of this statement by applying the barometric formula to show that if the gas is expelled at sea level the number of radon atoms at 100 m is expected to be considerably diminished. Take the temperature as  $27^{\circ}\text{C}$ . (Hint: calculate  $N_1/N_0$ .)

The Barometric formula may be stated as

$$\frac{p_1}{p_0} = e^{-Mg(h_1 - h_0)/RT}$$
 where P<sub>1</sub> is the pressure at height h<sub>1</sub> and P<sub>0</sub> is the pressure at

height  $h_0$ , M is the molar mass of the gas in kg mol<sup>-1</sup>, g the acceleration due to gravity and T the temperature.

But since PV=nRT and n = N/L, where N is the number of molecules and L is Avogadro's number,

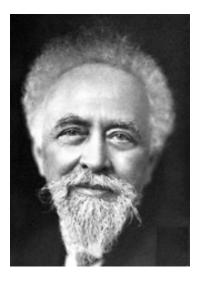
$$\frac{P_1}{P_0} = \frac{N_1}{N_0} = e^{-Mg(h_1 - h_0)/RT} = e^{-222 \times 10^{-3} \times 9.81 \times (100 - 0)/\{8.31 \times (273 + 27)\}} = \underline{0.916} \text{ to 3 sig. figs.}$$

(This compares with a figure of 0.989 at 100 m for nitrogen, showing that the concentration of radon drops much more rapidly than that of a lighter gas.)

2) Jean Perrin, a Frenchman (shown on the right), was awarded the Noble prize in 1922. In 1909 he conducted a beautiful series of experiments on sedimentation equilibria. These are governed by the Boltzmann distribution as shown below:

$$\frac{N_1}{N_0} = e^{-mg(h_1 - h_0)/kt}$$

He examined a suspension of fine gamboge particles of radius  $0.212 \, \mu \text{m}$  in water. These have a density of  $1.207 \times 10^{-3} \, \text{kg m}^3$  as compared with that of water of  $1.00 \times 10^3 \, \text{kg m}^{-3}$ . This gives each of the particles an effective mass of  $\frac{4}{3} \pi r^3 (\rho_g - \rho_w)$  where  $\rho_g$  represents the



density of the gamboge and  $\rho_w$  the density of the water.

Derive the expression

$$\ln(N) = \frac{-4\pi r^{3}(\rho_{g} - \rho_{w})gh}{3kT} + \ln(N_{0})$$

for the relative numbers of gamboge particles at height h (N) as compared with the number at height  $h_0 = 0$  ( $N_0$ ) from the Boltzmann distribution.

## Answer

$$\frac{N_1}{N_0} = e^{-mg(h_1 - h_0)/kt}$$

But  $m = \frac{4}{3}\pi r^3(\rho_g - \rho_w)$ ,  $N_1$  becomes N,  $h_1$ becomes h and  $h_0 = 0$ 

$$\therefore \frac{N}{N_0} = e^{-\frac{4}{3}\pi r^3(\rho_g - \rho_w)g(h-0)/kt} = e^{\left(\frac{-4\pi r^3(\rho_g - \rho_w)gh}{3kt}\right)}$$

:. Taking natural logarithms of both sides, we have:

$$\ln\left(\frac{N}{N_0}\right) = \left(\frac{-4\pi r^3(\rho_g - \rho_w)gh}{3kt}\right)$$

$$\therefore \ln N - \ln N_0 = \left(\frac{-4\pi r^3(\rho_g - \rho_w)gh}{3kt}\right)$$

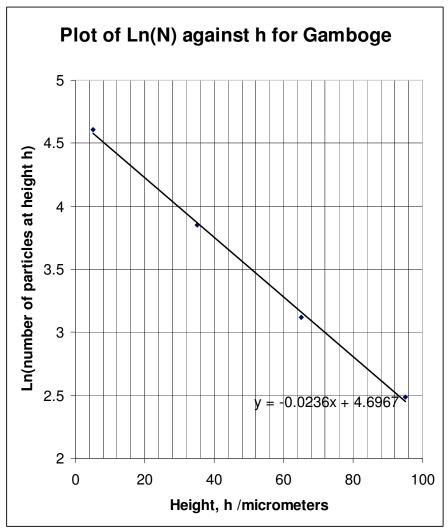
$$\therefore \ln N = \left(\frac{-4\pi r^3(\rho_g - \rho_w)gh}{3kt}\right) + \ln N_0$$

The following data are taken from one of Perrin's experiments:

Height h / μm	5	35	65	95
N (relative units)	100	47	22.6	12

Plot ln(N) against h and from the slope of the straight-line graph determine k. Given that  $R = 8.31 \text{ JK}^{-1} \text{mol}^{-1}$ ,  $g = 9.81 \text{ ms}^{-2}$  and  $T = 20^{\circ}\text{C}$ , calculate L (Avogadro's number). (This was an early experiment, and only gives a rather rough estimate of L.)

## **Answer**



Slope of graph is  $-0.0236(\mu \text{m})^{-1} = -0.0236 \times (10^{-6} \text{ m})^{-1} = -0.0236 \times 10^{6} \text{ m}^{-1}$ .

$$\therefore -0.0236 \times 10^6 = \frac{-4\pi r^3 (\rho_g - \rho_w)g}{3kT}$$

$$\therefore k = \frac{4\pi r^3 (\rho_g - \rho_w)g}{3 \times 0.0236 \times 10^6 T} = \frac{4 \times 3.142 \times (0.212 \times 10^{-6})^3 \times (1.207 - 1.00) \times 10^3 \times 9.81}{3 \times 0.0236 \times 10^6 \times (20 + 273)} = 1.172 \times 10^{-23}$$

$$\therefore L = \frac{R}{k} = \frac{8.31}{1.172 \times 10^{-23}} = \frac{7.089 \times 10^{23}}{1.000 \times 10^{23}} \text{mol}^{-1}$$

(Of course, we now know that the value of L is  $6.02...\times10^{23}$ , but at that time the value above was a reasonable estimate.)