Chemistry 240 Semester 01-2009
Homework for Submission #3

Answer the following questions and submit them for marking on or before Monday 16th February in the chemistry drop box. If any answers show evidence of copying, the whole exercise will attract zero marks. Please note that clear and concise setting out of answers is essential for full marks.

1) According to the collision theory of reaction rates, for particles to collide with sufficient energy to react, they must have more than a certain minimum kinetic energy, the activation energy, E_a. Since they must be on a collision course, the component of energy along their common axis is the important factor. In such a situation the correct expression for the Boltzmann distribution for molecular translational energies becomes:

$$\frac{1}{N_{tot}}\frac{dN}{dE} = \frac{1}{kT}e^{-E/\,kT}$$

where N_{tot} shows the total number of molecules present and $\frac{1}{N_{tot}}\frac{dN}{dE}$ shows the fraction of molecules per unit energy interval.

a) Given that $\int_{N_a}^{\infty} dN$ gives the total number of molecules possessing energy greater than or equal to E_a, show that the proportion of molecules with energy greater than E_a (in terms of Joules per molecule) is given by $\frac{N_\infty - N_a}{N_{tot}} = e^{-E_a/\,kT}$.

b) A typical value for the activation energy of a chemical reaction is 100 kJ mol^{-1}. Convert this value to J mol^{-1} and calculate the proportion of molecules in a sample of nitrogen which have energy greater than E_a at (i) 25°C and (ii) 2000°C.

c) Suggest the implications of your results for the rate of any reaction of nitrogen having a similar value of E_a.

2) Johannes Van der Waals (shown on the right) was the first person to derive an *equation of state* for a non-ideal gas. (PV=nRT is the *equation of state* for an ideal gas.) His equation may be written as:

$$\left[(P + a\left(\frac{n}{V}\right)^2\right](V - nb) = nRT$$

a) Although this equation gives more accurate results than the ideal gas equation, the latter is very often used in preference. Suggest why this is so.

b) Calculate the molar volume of ammonia at 27°C and 2.00 atm pressure,

i) assuming that the gas behaves ideally, and

ii) employing the Van der Waals equation with a = 4.225 L^{2}atm mol^{-2} and b = 3.707×10^{-2} L mol^{-1}, R = 0.08206.

There are various ways of solving this equation for V. Whichever one is used it is best to convert the Van der Waals equation to polynomial[1] in V ($f(V) = pV^3 + qV^2 + rV + s$) and find the value of V which makes f(V) = 0. This can be done by plotting f(V) against V in the region of the ideal value of V as calculated in part (i).

[1] The polynomial is in fact a cubic. Whilst cubic equations can be solved analytically, the solutions are very messy and not straightforward – not like the solution for a quadratic. Generally it is better to use a *numerical* method, though Maple can solve cubics analytically.

Another method is to apply an *iterative* method such as the Newton-Raphson technique: http://www.en.wikipedia.org/wiki/Newton's_method A third method (also *iterative*) is to rearrange the equation as V = f(V). In the latter two methods one guesses a value for V, substitutes this into the right hand side of the equation and arrives at a better estimate of V as a result. The process is then repeated until no further change in the value of V is observed. That is why they are called *iterative* methods.

These processes are greatly eased by use of a spread sheet or a mathematics program such as Maple (probably available in the Math Lab), or a freebee you can download yourselves from http://www.speqmath.com/index.php?id=1. It is called SpeqQ maths. With Maple you can solve the equation directly, but with SpeQ you have to plot the graph and find the intercept, or use one of the iterative methods. By zooming out on the plot, you can solve to any desired number of figures.

iii) Explain any difference between the two values calculated in (i) and (ii) above in terms of theory.