

# Chemistry 240 Semester 01-2009

## Homework for Submission #3

Answer the following questions and submit them for marking on or before Monday 16<sup>th</sup> 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  $\frac{N_{\infty} - N_a}{N_{tot}} = e^{-E_a/kT}$ .

### Solution

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

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

$$\therefore \frac{1}{N_{tot}} \int_{N_a}^{\infty} dN = \frac{1}{kT} \int_{E_a}^{\infty} e^{-E/kT} dE$$

where  $N_a$  represents the number of molecules which possess energy  $\leq E_a$ . Integrating both sides we have :

$$\frac{1}{N_{tot}} [N]_{N_a}^{\infty} = \left[ \frac{1}{kT} (-kT) e^{-E/kT} \right]_{E_a}^{\infty}$$

and putting in the limits we have :

$$\frac{1}{N_{tot}} (N_{\infty} - N_a) = (0 - (-e^{-E_a/kT}))$$

$$\frac{N_{\infty} - N_a}{N_{tot}} = e^{-E_a/kT}$$

$N_{\infty}$  is in fact the same as  $N_{tot}$ , since it represents all the molecules having energy less than or equal to infinity, and  $N_{\infty} - N_a$  represents the number of molecules with energy between  $E_a$  and infinity i.e., with energy greater than  $E_a$ . Thus  $\frac{N_{\infty} - N_a}{N_{tot}}$  represents the proportion of molecules with energy greater than  $E_a$ .

- b) A typical value for the activation energy of a chemical reaction is  $100 \text{ kJ mol}^{-1}$ . Convert this value to

$\text{J mol}^{-1}$  and calculate the proportion of molecules in a sample of nitrogen which have energy greater than  $E_a$  at (i)  $25^\circ\text{C}$  and (ii)  $2000^\circ\text{C}$ .

### Solution

$100 \text{ kJ mol}^{-1}$  represents the energy of 1 mole of molecules (Avogadro's number,  $L = 6.02 \times 10^{23}$ ). When we have an equation with  $k$  (the Boltzmann constant) we are referring to a single molecule. Thus, before substituting in the equation we must divide the energy by  $L$ :

$$100 \text{ kJ mol}^{-1} = 1 \times 10^5 \text{ J mol}^{-1} = 1 \times 10^5 / 6.02 \times 10^{23} \text{ J molecule}^{-1}$$

$$\frac{N_\infty - N_a}{N_{\text{tot}}} = e^{-E_a/kT} = e^{-(10^5 / 6.02 \times 10^{23}) / kT} = e^{-(10^5 / (6.02 \times 10^{23} kT))}$$

But  $6.02 \times 10^{23} \times k = R$  and  $25^\circ\text{C} = 298 \text{ K}$

$$\therefore \frac{N_\infty - N_a}{N_{\text{tot}}} = e^{-10^5/RT} = e^{-(10^5 / 8.31 \times 298)} = \underline{\underline{2.90 \times 10^{-18}}}$$

At  $2000^\circ\text{C}$  we have  $T = 2273 \text{ K}$  and so :

$$\frac{N_\infty - N_a}{N_{\text{tot}}} = e^{-10^5/RT} = e^{-(10^5 / 8.31 \times 2273)} = \underline{\underline{5.02 \times 10^{-3}}}$$

(In other words, whilst at  $25^\circ\text{C}$ , very few molecules have sufficient energy to react, at  $2000^\circ\text{C}$ , about 0.5% of them do.)

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

### Solution

From the results given above it is clear that many more molecules have sufficient energy to react at  $2000^\circ\text{C}$  than at  $25^\circ\text{C}$  and so the reaction will be very much faster at the higher temperature.

- 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.

### Answer

Essentially the Van der Waals equation is very much more cumbersome: apart from the difficulty of calculation,  $a$  and  $b$  are different for different gases. In contrast the ideal gas equation is the same for all gases. (Also the Van der Waals equation is only slightly better than the ideal gas equation most of the time.)

- b) Calculate the molar volume of ammonia at  $27^\circ\text{C}$  and 2.00 atm pressure,  
i) assuming that the gas behaves ideally, and

### Solution

The molar volume is the volume of 1 mol, and so, since

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{RT}{P} = \frac{0.08206 \times 300.15}{2.00} = \underline{\underline{12.3 \text{ L}}} \text{ to 3 sig. figs.}$$



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

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

and since  $n = 1$ ,

$$\therefore PV - Pb + a \left( \frac{1}{V} \right)^2 V - a \left( \frac{1}{V} \right)^2 b = RT$$

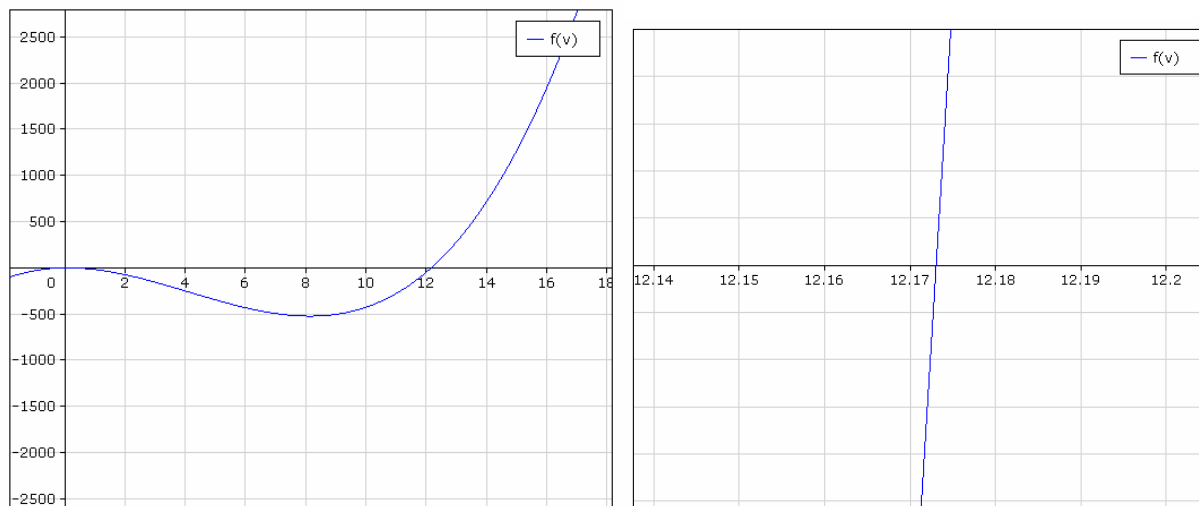
$$\therefore PV - Pb + a \left( \frac{1}{V} \right)^2 V - a \left( \frac{1}{V} \right)^2 b - RT = 0$$

and multiplying through by  $V^2$ , we have :

$$PV^3 - PbV^2 + aV - ab - RTV^2 = 0$$

$$\therefore PV^3 - (Pb + RT)V^2 + aV - ab = 0 = f(v)$$

Using SpeQ to plot  $f(v)$  against  $V$  we have on the left at low magnification and on the right at high magnification:



From the plot on the right we can see that  $V$  is 12.2 to 3 sig. figs.

Alternatively, employing SpeQ with the Newton-Raphson method, we have, first defining some values:

$$R=0.08206$$

$$R = 0.08206$$

$$P=2$$

$$P = 2$$

$$a=4.225$$

$$a = 4.225$$

$$b=3.707e-2$$

$$b = 0.03707$$

$$T=300$$

$$T = 300$$

and then defining  $f(v)$  and its first derivative with respect to  $v$ ,  $fdash(v)$ :

$$f(V) = P*V^3 - (P*b + R*T)*V^2 + a*(V - b);$$

$$fdash(v) = 3*P*V^2 - 2*(P*b + R*T)*V + a;$$

and then setting  $v$  to an initial value of 12

$$V=12;$$

we recalculate a better value of  $v$  as:

$V = V - f(V)/f'(V)$ ; - *this is the essence of the Newton-Raphson method.*

and print the answer:

$V$

**Ans = 12.173063948**

then using this new value of  $v$ , we recalculate to give:

$V = V - f(V)/f'(V)$ ;

and print the new value:

$V$

**Ans = 12.173059517**

It is clear that little further change will occur if the process is repeated, and the value is certainly correct to at least 3 sig. figs, i.e. 12.2 L.

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

**Answer**

The difference in values is slight, but the molar volume as predicted by the Van der Waals equation is a little (roughly 1%) less than that predicted by the ideal gas equation although the pressure is the same in the two cases.

The difference must arise from the attractive forces between molecules which at moderate pressures, lower the actual pressure of a gas as compared with the ideal value. A molecule leaving the body of a real gas to impact with the wall of the container is slowed slightly by these forces. It therefore impacts the wall slightly less violently, and as a result the pressure is less, than with the ideal gas.