Quiz Solutions: S10 (Section 011, CHEM444)

27th February 2010

1 Quiz 1

1.1 Problem 1

What is the ratio of the following values for a particle of Argon and Krypton at 298K?

- $\frac{\nu_{ave}^{Ar}}{\nu_{ave}^{Kr}}$

$$\frac{\nu_{ave}^{Ar}}{\nu_{ave}^{Kr}} = \sqrt{\frac{m_{Kr}}{m_{Ar}}} = \sqrt{\frac{83.798}{39.948}} = 1.45$$

- $\frac{\nu_{most\ probable}^{Ar}}{\nu_{most\ probable}^{Kr}}$

$$\frac{\nu_{most\ probable}^{Ar}}{\nu_{most\ probable}^{Kr}} = \sqrt{\frac{m_{Kr}}{m_{Ar}}}$$

- $\frac{\nu_{rms}^{Ar}}{\nu_{rms}^{Kr}}$

$$\frac{\nu_{rms}^{Ar}}{\nu_{rms}^{Kr}} = \sqrt{\frac{m_{Kr}}{m_{Ar}}}$$

1.2 Problem 2

What is the ratio of average kinetic energy of the two systems of Problem 1?

$$\frac{< KE >_{Ar}}{< KE >_{Kr}} = 1$$

We will show this the long way.

$$\begin{aligned} < KE >_{Ar} &= \int_0^{\infty} 4\pi \left(\frac{m_{Ar}}{2\ \pi\ k_B\ T}\right)^{3/2} \left(\frac{1}{2}\ m_{Ar}\ \nu^2\right)\ e^{(-m_{Ar}\ \nu^2\ /2\ k_B\ T)}\ \nu^2\ d\nu \\ &= \frac{1}{2}\ m_{Ar}\nu_{rms}^2 = \frac{1}{2}\ m_{Ar}\ \frac{3\ k_B\ T}{m_{Ar}} = \frac{3}{2}\ k_B\ T \end{aligned}$$

$$\begin{aligned} < KE >_{Kr} &= \int_0^{\infty} 4\pi \left(\frac{m_{Kr}}{2\ \pi\ k_B\ T}\right)^{3/2} \left(\frac{1}{2}\ m_{Kr}\ \nu^2\right)\ e^{(-m_{Kr}\ \nu^2\ /2\ k_B\ T)}\ \nu^2\ d\nu \\ &= \frac{1}{2}\ m_{Kr}\nu_{rms}^2 = \frac{1}{2}\ m_{Kr}\ \frac{3\ k_B\ T}{m_{Kr}} = \frac{3}{2}\ k_B\ T \end{aligned}$$

Thus the ratio is **1**. For ideal gases, energy is a function of temperature. Note that the expression for the average kinetic energy we derived in this exercise is identically the result one would obtain from rigorous statistical mechanical treatment. The kinetic energy is related to the rms speed, not the average or the most probable.

The following information be of use:

- 3-D Maxwell Speed Distribution: $F(\nu) = \Omega(\nu) = 4\pi \left(\frac{m}{2\ \pi\ k_B\ T}\right)^{3/2} e^{-m\ \nu^2\ /2\ k_B\ T}\ \nu^2\ d\nu$
- $\nu_{ave} = \left(\frac{8\ k_B\ T}{\pi\ m}\right)^{1/2}$
- $\nu_{most\ probable} = \left(\frac{2\ k_B\ T}{m}\right)^{1/2}$
- $\nu_{rms} = \left(\frac{3\ k_B\ T}{m}\right)^{1/2}$

- $R = N_{Avogadro}\ k_B$
- $R = 8.3144349\ J\ K^{-1}\ mol^{-1}$
- $N_{Avogadro}\ = 6.022\ \text{x}\ 10^{23}\ mol^{-1}$
- $M(molar\ mass)\ of\ Argon\ =\ 39.948\ gram\ mol^{-1}$
- $M(molar\ mass)\ of\ Krypton\ =\ 83.798\ gram\ mol^{-1}$

2 Quiz 2

2.1 Problem 1

What is the order of the reaction for each species *and* the total reaction order for each rate expression given below:

$$Rate = k\ [ClO]\,[BrO]$$

$$1,\ 1,\ overall = 2$$

$$Rate = k\ [NO]^2\,[O_2]$$

$$2,\ 1,\ overall = 3$$

$$Rate = k\ \frac{[HI]^2\,[O_2]}{[H^+]^{1/2}}$$

$$2,\quad 1,\quad -1/2,\quad overall = 5/2$$

2.2 Problem 2

What is the **overall order** of the reaction corresponding to the following rate constants?

$$k = 1.63\ x\ 10^{-4}\ M^{-1}\ s^{-1} \qquad order = 2$$
$$k = 1.63\ x\ 10^{-4}\ M^{-2}\ s^{-1} \qquad order = 3$$
$$k = 1.63\ x\ 10^{-4}\ M^{-1/2}\ s^{-1} \qquad order = 3/2$$

2.3 Problem 3

Consider the following first-order reaction, the decomposition of cyclobutane at 438 C at constant volume:

$$C_4H_8\ (g) \rightarrow\ 2\ C_2H_4\ (g)$$

Express the rate of this reaction in terms of the change in total pressure as a function of time. Initially there is no product, and thus the partial pressure of product initially is 0. We will also call the initial pressure, which is due only to reactant, as P_0 in the following discussion.

The rate for this reaction is:

$$Rate \ = \ -\ \frac{d\ [C_4H_8]}{dt} = \frac{1}{2}\frac{d\ [C_2H_4]}{dt}$$

We can rewrite this in terms of the **partial pressures** of each species assuming ideal gas behavior:

$$Rate \ = \ -\ \frac{1}{RT}\frac{d\ P_{C_4H_8}}{dt} = \frac{1}{2RT}\frac{d\ P_{C_2H_4}}{dt}$$

Now let's consider the pressure issue, since we were asked to determine the rate in terms of the total pressure. Keep in mind that we are considering all gases to be ideal. For a given time, t, the total pressure is:

$$P_{total} \ = \ P_{C_4H_8} + P_{C_2H_4}$$

If x moles of C_2H_4 form, at constant volume of reaction, the pressure corresponding to that amount of product is identically $P_{C_2H_4}$. Thus, at time t, the pressures due to reactant and product are:

$$\begin{aligned} P_{C_4H_8} &= P_0 - \frac{1}{2}P_{C_2H_4} \\ P_{C_2H_4} &= P_{C_2H_4} \\ P_{total} &= P_0 + \frac{1}{2}P_{C_2H_4} \end{aligned}$$

Now, let's take the time derivative of the total pressure:

$$\frac{d\ P_{total}}{dt} \ = \frac{1}{2}\frac{d\ P_{C_2H_4}}{dt}$$

Thus the rate is:

$$Rate \ = \ \frac{1}{RT}\ \frac{d\ P_{total}}{dt}$$