Problem Set #6 Chem 471 Fall 1999

Due Friday, 11/19/99, in class.

Show your work. Problem sets will be spot graded. Work must be shown.

R = 0.08206 liter atm K^{-1} $mole^{-1}$ = 8.314 J K^{-1} $mole^{-1}$

h = 6.626 x 10^{-34} J s c = 2.9979 x 10^{8} m s^{-1}

1. T,S,&W Ch 6 Pb 1

a) RMS velocity: $\sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314\ J\,mol^{-1}\ K^{-1})(273\ K)}{2.016x10^{-3}\ kg\,mol^{-1}}\frac{kg\ m^2\ s^{-2}}{J}} = 1.838x10^3\ m\ s^{-1}$

b) transl kin E: $\overline{U}_{tr} = \frac{3RT}{2} = \frac{3(8.314\ J\,mol^{-1}\ K^{-1})(273\ K)}{2} = 3.4\ kJ\ mol^{-1}$

c) H_2 molec/cm^3: from the ideal gas law, we have moles/volume:

$$\frac{n}{V} = \frac{P}{RT} = \frac{1\,atm}{(0.08206\ \text{liter atm K}^{-1}\ \text{mole}^{-1})(273\ K)}\frac{liter}{1000\ \text{cm}^3} = 4.46x10^{-5}\ mole\,\text{cm}^{-3}$$

$$=> 4.46x10^{-5}\ mole\,\text{cm}^{-3}\frac{6.02x10^{23}\,molecules}{mole} = 2.69x10^{19}\,molecules\,\text{mole}^{-1}$$

d) mean free path:

$$l = \frac{1}{\sqrt{2}\pi\left(\frac{n}{V}\right)\sigma^2} = \frac{1}{\sqrt{2}\pi(2.69x10^{19}molec\ cm^{-3})(2.5x10^{-8}cm)^2} = 1.34x10^{-5}\ cm$$

$$= 1.34x10^{-7}\ m = 0.134\ \mu m$$

e) collisions/sec:

$$z = 4\sqrt{\pi}\left(\frac{N}{V}\right)\sigma^2\left(\frac{RT}{M}\right)^{1/2}$$

$$= 4\sqrt{\pi}(2.69x10^{19}molec\ cm^{-3})(2.5x10^{-8}cm)^2\left(\frac{(8.314\ J\,mol^{-1}\ K^{-1})(273\ K)}{2.016x10^{-3}kg\ mol^{-1}}\frac{kg\ m^2\ s^{-2}}{J}\right)^{1/2}$$

$$= 4\sqrt{\pi}(1.68x10^4\ m^{-1})(1.126x10^6 m^2\ s^{-2})^{1/2} = 1.26x10^8\ s^{-1}$$

f) collisions/sec in a cm^3:

$$Z = \left(\frac{N}{V}\right)\left(\frac{z}{2}\right) = (2.69x10^{19}\,molec\ cm^{-3})\left(\frac{1.26x10^8\ s^{-1}}{2}\right) = 1.699x10^{27}\ \text{cm}^{-3}\ s^{-1}$$

2. T,S,&W Ch 6 Pb 1 - But substitute the gas I_2 for H_2. Assume a collisional diameter for I_2 of 30 Å.

a) RMS velocity: $\sqrt{u^2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314\ J\ mol^{-1}\ K^{-1})(273\ K)}{253.8x10^{-3}\ kg\ mol^{-1}} \frac{kg\ m^2\ s^{-2}}{J}} = 1.638x10^2\ m\ s^{-1}$

bigger molecule, slower velocity for the same kinetic energy (see next)

b) transl kin E: depends only on temperature. The same as above: $\overline{U}_{tr} = 3.4\ kJ\ mol^{-1}$

c) I_2 molec/cm^3: from the ideal gas law, we have moles/volume:

$\frac{n}{V} = \frac{P}{RT} = 2.69x10^{19} molecules\ \mathrm{mole}^{-1}$ Nothing changed from above

d) mean free path:

$$l = \frac{1}{\sqrt{2}\pi\left(\frac{n}{V}\right)\sigma^2} = \frac{1}{\sqrt{2}\pi\left(2.69x10^{19} molec\ cm^{-3}\right)\left(30x10^{-8} cm\right)^2} = 9.30x10^{-8}\ cm$$

$= 9.30x10^{-10}\ m = 9.3Å$

Heavier molecule. Velocity slower (see above), so travels a shorter distance per time. .Larger diameter works the other way,

e) collisions/sec:

$$z = 4\sqrt{\pi}\left(\frac{N}{V}\right)\sigma^2\left(\frac{RT}{M}\right)^{1/2}$$

$$= 4\sqrt{\pi}\left(2.69x10^{19} molec\ cm^{-3}\right)\left(30.0x10^{-8} cm\right)^2\left(\frac{(8.314\ J\ mol^{-1}\ K^{-1})(273\ K)}{253.8x10^{-3}\ kg\ mol^{-1}}\frac{kg\ m^2\ s^{-2}}{J}\right)^{1/2}$$

$$= 4\sqrt{\pi}\left(2.42x10^6\ m^{-1}\right)\left(8.943x10^3 m^2\ s^{-2}\right)^{1/2} = 1.62x10^9\ s^{-1}$$

Cross section bigger: more collisions. Mass larger: slower, fewer collisions.

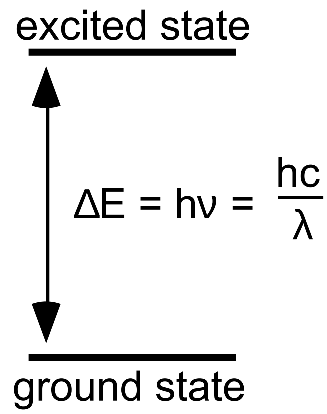
Mass term is in a square root, Molec diameter term is squared. Diameter wins this time.

f) collisions/sec in a cm^3:

$$Z = \left(\frac{N}{V}\right)\left(\frac{z}{2}\right) = \left(2.69x10^{19} molec\ cm^{-3}\right)\left(\frac{1.62x10^9\ s^{-1}}{2}\right) = 2.18x10^{28}\ cm^{-3}\ s^{-1}$$

3. The Boltzmann distribution can be used to predict the relative population of ground and excited states in various spectroscopic methods.

For each of the below, calculate at room temperature (298 K) $P_{excited\ state}$, the probability at equilibrium (in the absence of any excitation light) of finding the particle in the excited state (i.e., before any measurement is attempted).



a) In NMR spectroscopy (used to determine macromolecular structures and in medical imaging tools), the frequency (ν) of the "light" (radio wave) corresponding to the energy gap is on the order of 400 MHz.

From the Boltzmann distribution (eq 6.17):

$$E_2 - E_1 = \Delta E = h\nu = (6.626x10^{-34}\ J\ s)(400x10^{6}\ s^{-1}) = 2.65x10^{-25}\ J$$

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(E_2-E_1)/kT} = \frac{1}{1} e^{-(2.65x10^{-25}\ J)/(1.3807x10^{-23}\ J\ K^{-1})(298\ K)} = \frac{1}{1} e^{-(6.44x10^{-5})} = 0.999936$$

$$P_2 = \frac{N_2}{N_2 + N_1} = \frac{1}{1 + \frac{N_1}{N_2}} = \frac{1}{1 + \frac{1}{0.999936}} = 0.49998$$

Very small energy gap. Almost equal populations.

b) In visible spectroscopy, the wavelength of the light corresponding to the energy gap is on the order of 400 nm.

$$E_2 - E_1 = \Delta E = \frac{hc}{\lambda} = \frac{hc}{\lambda} = \frac{(6.626x10^{-34}\ J\ s)(2.9979x10^{8}\ m\ s^{-1})}{400\,nm} \frac{10^{9}nm}{m} = 4.966x10^{-19}\ J$$

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(E_2-E_1)/kT} = \frac{1}{1} e^{-(4.966x10^{-19}\ J)/(1.3807x10^{-23}\ J\ K^{-1})(298\ K)} = \frac{1}{1} e^{-(120.7)} = 3.83x10^{-53}$$

$$P_2 = \frac{N_2}{N_2 + N_1} = \frac{1}{1 + \frac{N_1}{N_2}} = \frac{1}{1 + \frac{1}{3.83x10^{-53}}} = 3.83x10^{-53}$$

Very large energy gap. Almost NOBODY is in the excited state. Far too high in energy to be populated at room temperature.

4. T,S,&W Ch 6 Pb 9

a) Neither sinks nor floats tells us that the buouyancy exactly equals the gravitational pull down. This requires:

$$\bar{\nu} = \frac{1}{\rho} = \frac{1}{1.125\ g\ cm^{-3}} = 0.8889\ cm^{3}\ g^{-1}$$

b) From discussions of centrifugation: $s = \dfrac{v}{w^2 x}$

By analogy, for the parachutist: $s = \dfrac{v}{g} = \dfrac{2\ m\ s^{-1}}{9.81\ m\ s^{-2}} = 0.204\ s^{-1}$

c) From eq. 6.65, $[\eta] = 2.5(\bar{v}_2 + \delta_1 v_1^0) = 2.5\dfrac{V_s}{m} = 2.5\dfrac{V_s\ N_o}{M}$

$$V_s = \frac{[\eta]\ M}{2.5\ N_o} = \frac{(1.5\ cm^3 g^{-1})\ (5x10^6 g\ mol^{-1})}{2.5\ (6.02x10^{23}\ mol^{-1})} = 4.98x10^{-18}\ cm^3$$

d) The charge (or more specifically, the charge/mass ratio) will increase on replacing the neutral methyl by the negatively charged carboxylate. Electrophoresis might be able to separate the two. In reality, this could be difficult. Fancier versions of electrophoresis (isoelectric focusing) might have a better chance.

e) $Z = \left(\dfrac{N}{V}\right)\left(\dfrac{z}{2}\right)$ $\quad z = 4\sqrt{\pi}\left(\dfrac{N}{V}\right)\sigma^2\left(\dfrac{RT}{M}\right)^{1/2}$ $\quad Z = 2\sqrt{\pi}\left(\dfrac{N}{V}\right)^2\sigma^2\left(\dfrac{RT}{M}\right)^{1/2}$

So double conc, rate increases 2^2 = 4-fold

collisional cross section (σ) doubles, rate increases 2^2 = 4-fold (typo in book, so 2-fold accepted as an answer…)

temperature doubles, rate increases $\sqrt{2}$ -fold

Mdoubles, rate increases $1/\sqrt{2}$ -fold

5. T,S,&W Ch 6 Pb 16

From equation 6.53, $M = \dfrac{R\ T s}{D(1-\bar{v}_2\rho)}$ So $\dfrac{s}{D} = \dfrac{M\ (1-\bar{v}_2\rho)}{R\ T}$

Measuring D before and after, and using the given values of s before and after. We can calculate the ratio s/D before and after. If the molecular weight has not changed, then the ratio should not change.(This assumes that $\bar{v}_2$ does not change, reasonable for DNA?).

6. T,S,&W Ch 6 Pb 26

$s = \dfrac{M\ (1-\bar{v}_2\rho)}{N_o\ f}$, so that

a) As the solvent temperature increases from 10° to 20° C, the density and viscosity will decrease, but the frictional coefficient can increase or decrease or not change, so we can't say what will happen to the sedimentation coefficient.

b) As the long axis of the prolate ellipsoid is reduced by 2 (everything else remaining constant), the frictional coefficient will decrease (particle becomes more spherical), so the sedimentation coefficient will increase.

c) As ^{15}N is substituted for ^{14}N, the molecular weight will increase, so the sedimentation coefficient will increase.

d) $D = \frac{kT}{f}$, so

a) T increases, hard to predict changes in *f*, so hard to know

b) more spherical, f will decrease, D will increase

c) molecular weight increases, D should not change (all else equal).

7. T,S,&W Ch 7 Pb 4

a) disappearance of A: $-\frac{dA}{dt} = k_1 A$

b) $\frac{dB}{dt} = k_1 A - k_2 B C$

c) $\frac{dD}{dt} = k_2 B C$

d) $A = A_o e^{-k_1 t}$