Problem Set 1 (due Fri Apr 21, 2017).

Show all work and use proper significant figures.

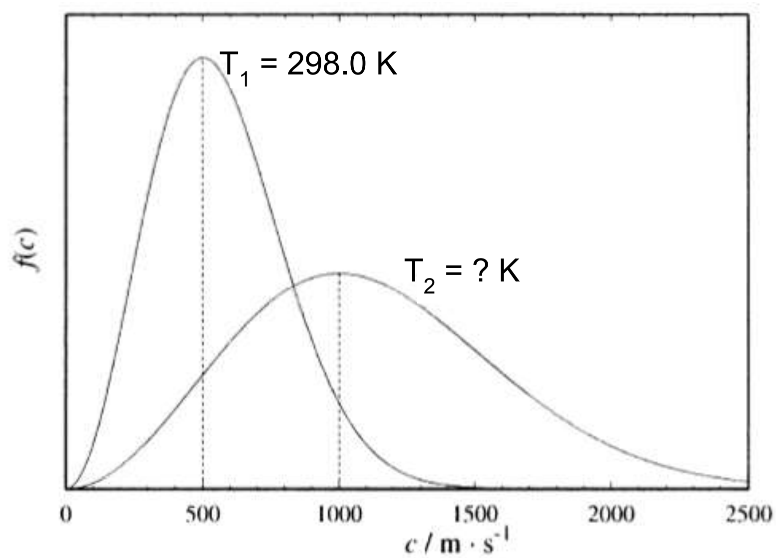
1. The diagram below shows the Maxwell speed distribution curves for an ideal gas at two different temperatures (T_1 and T_2).

   (a) What is the root mean squared speed (c_{RMS}) of the gas at 298.0 K?

   (b) Calculate the temperature at which the gas has c_{mp} = 1000 m/s.

   (c) What is the most probable speed of the gas when the temperature is lowered to 1.00 x 10^{-7} K?

   (d) What is the most probable speed of an electron gas (mass = 5.49 x 10^{-7} kg/mol) at 1.00 x 10^{-7} K?



2. The progress of a reaction (A + B → 2C) in the aqueous phase was monitored by measuring the concentration of the product (C) at various times during the reaction:

Time (s)	0	54.0	171	390	720	1400
Concentration of C (M)	0	0.200	0.340	0.414	0.449	0.473

   (a) Assuming that the initial concentration of the reactants ($[A]_0$ and $[B]_0$) are both equal to 0.250 M, calculate the concentration of both reactants ([A] and [B]) at each time point.

   (b) Assuming that $[A]_0 = [B]_0$, write an expression for $\frac{1}{[A]}$ vs time and plot $\frac{1}{[A]}$ along y-axis versus time (x-axis) to verify whether the data obey 2nd order kinetics. 6pts

   (c) What is the rate constant (k) of the reaction (include proper units)?

   (d) What is the half-life ($t_{1/2}$) of the reaction at time zero and at 720 s (include proper units)?

   (e) How long will it take the product concentration to reach 0.499 M?

3. 1.00 mole of $N_2(g)$ (molecular diameter = 3.74 x 10^{-10} m and mass = 28.0 g/mol) occupies a 22.4 liter container at 1.00 atm of pressure and at 273.15 K.

(a) Calculate the mean speed ($\langle c \rangle$) of the gas in the container.

(b) Calculate the number of collisions a single molecule makes in one second.

(c) Calculate the amount of time (in seconds) that occurs in between each collision.

(d) Calculate the average mean free path of the gas.

(e) Calculate the distance that a molecule will travel along a zigzag path during a random walk in 2 seconds (hint: the total number of steps during a random walk in t seconds is equal to the Z_1*t).

(f) Calculate how far a molecule will be displaced from its starting point in 2 seconds and after 1 minute (hint: root mean squared displacement is $\sqrt{\langle d^2 \rangle} = \sqrt{\langle c \rangle \lambda t}$).

(g) Calculate the binary collision frequency in units of Molar per second (M/s) and comment on how the binary collision frequency can be used to calculate an upper limit for the rate of a gas phase reaction at this temperature and pressure. 4 pts

4. Imidazole (Im) can react with H_3O^+ or H_2O to form positively charged imidazole (ImH^+) by the following mechanisms:

$$\mathrm{Im} + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Im}H^+ + H_2O$$

$$\mathrm{Im} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Im}H^+ + OH^-$$

The rate constants in aqueous solution are $k_1 = 1.5 \times 10^{10}\ M^{-1}\ s^{-1}$, $k_{-1} = 1.5 \times 10^3\ s^{-1}$, $k_2 = 2.5 \times 10^3\ s^{-1}$, $k_{-2} = 2.5 \times 10^{10}\ M^{-1}\ s^{-1}$.

(a) What is the value of the dissociation constant of ImH^+ ($ImH^+ + H_2O \leftrightarrow Im + H_3O^+$).

(b) What percentage of imidazole molecules are positively charged (ImH^+) at pH 7.0?

(c) Write a differential equation for the net rate of formation of ImH^+ ($\frac{d[\mathrm{Im}H^+]}{dt}$).

(d) For a 0.10 M imidazole solution at pH 7.0, what is the value of $\frac{d[\mathrm{Im}H^+]}{dt}$ at equilibrium? (hint: assume the activity of H_2O (i.e. $a_{H2O} = [H_2O]$) is equal to one).

(e) If the pH of the solution in part (d) is suddenly changed to pH = 4, what is the initial rate of formation of ImH^+ ($\left.\frac{d[\mathrm{Im}H^+]}{dt}\right|_{t=0}$) at pH = 4.0? (hint: at t = 0, [Im] = [ImH^+] = 0.05 M).

(f) The rate constants k_1 and k_{-1} both depend on temperature. Would you expect them to decrease or increase with increasing temperature? Which would you expect to change most with temperature and why?

5. The mechanism for a reaction is assumed to be: $A + B \xrightarrow{k} P$ (k = 1.0 x 10^5 M^{-1} s^{-1} at 27 °C).

a. Calculate the initial rate of formation of P ($\left.\frac{d[P]}{dt}\right|_{t=0}$) if the initial concentration of P ($[P]_0$) is equal to 0, and initial concentration of A ($[A]_0$)and B ($[B]_0$) are both equal to 0.10 M at 27 °C.

b. Calculate the initial rate of formation of P if $[P]_0$ =0, and A and B both have an initial concentration of 1.00×10^{-4} M at 27 °C.

c. How long will it take (in seconds) to form 0.040 M product using the conditions above in part "a" ($[A]_0 = [B]_0 = 0.10$ M and $[P]_0 = 0$)?