Columbia University in the City of New York
New York, N.Y. 10027

Chemistry C2407x **2002**
First Exam **George Flynn**
September 26, 2002 **Total Points: 150** **75 Minutes**

All questions are NOT weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided and sign where indicated. Tear off this sheet and pass it to the right for the proctors to pick up.

Print your last name:
Print your first name:

Signature:____

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Do not write anything else on this page. Answer the questions in the spaces provided on the following pages.

1a	**2a**	**3a**	**4a**
1b	**2b**	**3b**	**4b**
1c		**3c**	**4c**
1d		**3d**	**4d**
		3e	
		3f	

Print your name here:

Problem 1: (35 points) [Oxtoby Problems 4.41-4.43]

a)(10 points) Compute the root-mean-square speed of H_2 molecules in hydrogen gas at a temperature of 300 °K. The molecular weight of H_2 is 2 gm/mole. Show all reasoning clearly.

b)(10 points) Compute the root-mean-square speed of SF_6 molecules in sulfur hexafluoride gas at a temperature of 300 °K. The molecular weight of SF_6 is 146 gm/mole. Show all reasoning clearly.

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c)(10 points) Compute the root-mean-square speed of 500 Na atoms contained in an optical trap of volume 1.0×10^{-15} m^3, at a temperature of 0.00024 °K. The atomic weight of Na is 23 gm/mole. Show all reasoning clearly.

d)(5 points) Compute the ratio of the root-mean-square speed of He at the surface of the sun, where the temperature is 6000 °K, to the root-mean-square speed of He in interstellar space, where the temperature is 100 °K. The atomic weight of He is 4 gm/mole. Show all reasoning clearly.

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Problem 2: (20 points) 2.00 moles of diatomic N_2 gas and 1.00 moles of monatomic He gas are confined to a rigid container of fixed volume V.
a)(10 points) Calculate the heat absorbed by this gas mixture in the vessel of fixed volume, if the temperature is raised from 250 °K to 350 °K. Show all reasoning clearly.

b)(10 points) Imagine now that the sample of 2.00 moles of N_2 gas and 1.00 moles of He gas is transferred to a cylindrical container with a moveable, frictionless piston that holds the gas at a constant pressure of 2.00 atm. Determine the heat absorbed by this sample if its temperature is raised from 350 to 400 °K at constant pressure. Show all reasoning clearly.

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Problem 3: (50 Points) A 1.0 liter bulb is evacuated until the pressure of gas inside the bulb is negligible. Unfortunately, there is a hole in the bulb that allows air to leak into the bulb and the pressure to rise to 1.00×10^{-6} Atm after 1.00 hour. In what follows, use exact kinetic theory formulas from the free formula sheet. You may assume that the surrounding atmosphere of gas is pure N_2 (MW=28 gm/mole) at one atmosphere pressure and that the temperature is constant at 275 °K. The pressure of the gas surrounding the bulb never changes because the volume of the surroundings is infinite compared to the volume of the bulb.

a) (5 points) Determine the **average** speed of N_2 molecules in this problem. Show all reasoning clearly!

b) (10 points) What is the number density ρ_s (number of molecules/cm^3), of N_2 molecules in the surrounding atmosphere? Show all reasoning clearly.

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c) (5 points) What is the number density ρ_b (number of molecules/cm^3), of N_2 molecules in the bulb at the end of one hour? Show all reasoning clearly.

d) (10 points) To be exact, N_2 molecules effuse into the bulb and once inside can effuse out again. By considering the ratio of (the constant rate of effusion in) to (the **maximum** rate of effusion out) during the one hour leak time, show that effusion out of the bulb can be safely neglected. Show all reasoning clearly.

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e)(10 points) Determine the rate (molecules/sec) at which molecules leak into the bulb over the 1 hour period from the data given. Show all reasoning clearly.

f) (10 points) What is the area of the hole in the bulb through which the gas leaks? Show reasoning clearly.

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Problem 4 (45 points) In the binary collision theory of chemical reactions, the energy needed to "climb the barrier" E_A to the transition state comes from the kinetic energy of relative motion of the reactants, A and B. Suppose instead that this form of energy is **completely useless** in promoting the reaction between A and B. (This often turns out to be true for reactions with large E_A because the number of energetic molecules in the high energy tail of the Boltzmann Distribution at low to moderate temperatures is very small.)

However, "internal" energy added to **either** of the molecules by the absorption of light can be effective in promoting chemical reaction. Suppose that **only** molecule A is capable of absorbing light and let the energy added to molecule A by light absorption be E_L. A mixture of A and B is subjected to continuous irradiation by a laser beam producing a constant fraction f_A of excited A molecules with energy E_L. We designate the excited A molecules as A*. You may assume that the speed distribution for A* is identical to that for A before excitation with light. In what follows, you may wish to consult the Free Formula Sheet for definitions of the "All or Nothing" and Arrhenius models.

a)(10 points) If $P(E_L)$ is the reaction probability when an A molecule of energy E_L (i.e. an A* molecule) encounters any B molecule, write an expression for the reaction rate using concepts from the binary collision model. Show all reasoning clearly.

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b)(10 points) Using the "All or Nothing" model, write an expression for the reaction rate between A and B when $E_L = E_A/2$ and when $E_L = 2E_A$. Show all reasoning clearly.

c)(10 points) Using the "Arrhenius" model, write an expression for the reaction rate between A and B when $E_L = E_A/2$ and when $E_L = 2E_A$. Show all reasoning clearly.

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d)(15 points) A more realistic picture for light absorption is that both A and B molecules can absorb light. Suppose that **both** A and B molecules absorb light of energy $E_L=2E_A$, with the fraction of A molecules excited being f_A and the fraction of B molecules excited being f_B. Using the Arrhenius model, write an expression for the reaction rate. (Note that, if N_A is the total number of A molecules, the number of excited A's is f_AN_A while the number of unexcited A's is $(1-f_A)N_A$. A similar comment applies to B molecules.).

Show all reasoning clearly. (Be careful, this question is more subtle than it may appear! There are three different "kinds" of collisions.)

The End