

Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with proper numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge. Write with a pencil; do not scratch out, erase..

1. (15 points) Consider a sample of air, which is a mixture of O<sub>2</sub> and N<sub>2</sub> with a molar percentage of 79% N<sub>2</sub>, at 298.15 K.

(a) What is the average kinetic energy of a nitrogen molecule in this sample?

The average kinetic energy of any molecule at a temperature depends only on the temperature:

$$\langle E \rangle = \frac{3}{2}kT = \frac{3}{2} \left( 1.3806505 \times 10^{-23} \frac{J}{K} \right) (298.15 K) = 6.1746 \times 10^{-21} J$$

(b) What is the average kinetic energy of an oxygen molecule in this sample?

The average kinetic energy of an oxygen molecule in this mixture is the same as the average kinetic energy of a nitrogen molecule.

$$\langle E \rangle = \frac{3}{2}kT = 6.1746 \times 10^{-21} J$$

(c) What is the root-mean-square speed of a nitrogen molecule in this sample?

The root-mean-square speed can be calculated from kinetic theory, or one may use the average energy because

$$\langle E \rangle = \frac{1}{2}m \langle v^2 \rangle$$

Therefore,

$$\begin{aligned} \langle v^2 \rangle &= \frac{2 \langle E \rangle}{m} = \frac{2N_0 \langle E \rangle}{M} = \frac{2(6.02211415 \times 10^{23} \text{ mol}^{-1})(6.1746 \times 10^{-21} J)}{2(0.0140067 \text{ kg})} \\ &= 2.6547 \times 10^5 \text{ m}^2 \text{ s}^{-2} \end{aligned}$$

The root mean square speed is just the square root of this number:  $u = \sqrt{\langle v^2 \rangle} = 515.24 \text{ m s}^{-1}$

DO NOT WRITE  
IN THIS SPACE

p. 1 \_\_\_\_\_ /15

p. 2 \_\_\_\_\_ /10

p. 3 \_\_\_\_\_ /10

p. 4 \_\_\_\_\_ /10

p. 5 \_\_\_\_\_ /15

p. 6 \_\_\_\_\_ /15

p. 7 \_\_\_\_\_ /12

p. 8 \_\_\_\_\_ /13

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p. 9 \_\_\_\_\_ /5  
(Extra credit)

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TOTAL PTS

/100

**2. (10 points) The self-diffusion coefficient of pure water at 298.15 K is determined in an experiment using NMR spectroscopy to be  $2.25 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ . Under these conditions, determine the “size” of a water molecule, assuming it is a sphere, by giving the diameter of the water molecule.**

This problem is solved by using the Stokes-Einstein equation to calculate the radius of a spherical molecule that has the diffusion coefficient and viscosity of water. The viscosity of water is given in Table 9.4 in the handbook and the Stokes-Einstein formula is given below that table. Although the Stokes-Einstein theory technically applies only to microscopically large but macroscopically small spheres, it has been found that it often gives reasonable estimates of molecular parameters.

Rearranging the Stokes-Einstein equation to a different form gives this for the radius of the sphere:

$$r = \frac{kT}{6\pi D \eta}$$

To make all of the units come out right, one must remember to convert the viscosity, usually given in poise, to the appropriate SI unit.

$$r = \frac{(1.3806505 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}{6\pi(2.25 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})(8.937 \times 10^{-3} \text{ poise})(0.1 \text{ kg m}^{-1} \text{ s}^{-1} \text{ poise}^{-1})} = 1.0906 \times 10^{-10} \text{ m}$$

The diameter is twice the radius, so the answer is

$$d = 2r = 2.1812 \times 10^{-10} \text{ m} = 0.21812 \text{ nm} = 2.1812 \text{ Angstrom units}$$

3. (10 points) From the statements in column B, select the best match for each phrase in column A and put its letter in the adjacent blank. There is only one best match for each phrase.

Column A	Column B
<p>1. The variation in particle velocities in a material is described by the __p__.</p> <p>2. The process by which a gas passes through an aperture in a container is known as __e__.</p> <p>3. The Stokes-Einstein equation describes diffusion of a __k__ object.</p> <p>4. The general proportionality between the gradient of a material property (such as mass or heat content) and the flux of that property is expressed by a __m__.</p> <p>5. The viscosity of a solution is generally experimentally determined by application of __i__.</p>	<p>a) coefficient of viscous force</p> <p>b) concentration</p> <p>c) density coefficient</p> <p>d) diffusion</p> <p>e) effusion</p> <p>f) elongated</p> <p>g) gravitational sedimentation</p> <p>h) larger</p> <p>i) Poiseuille;s law</p> <p>j) Raoult's law</p> <p>k) spherical</p> <p>l) saturation centrifugation</p> <p>m) transport coefficient</p> <p>n) ultra-gravitational sedimentation</p> <p>o) ultracenturation</p> <p>p) velocity distribution function</p> <p>q) water mass</p>

4. (10 points) One mechanism of ozone destruction involves reaction with  $\text{HO}_2\cdot$  radicals to create oxygen and a hydroxyl radical, by this gas-phase reaction  $\text{HO}_2\cdot(g) + \text{O}_3(g) \rightarrow \text{OH}\cdot(g) + 2\text{O}_2(g)$ . The initial rate of this reaction has been determined in several experiments, as shown in the table.

$[\text{HO}_2]$ (molecules $\text{cm}^{-3}$ )	$[\text{O}_3]$ (molecules $\text{cm}^{-3}$ )	Rate (molecules $\text{cm}^{-3} \text{s}^{-1}$ )
$1.0 \times 10^{11}$	$1.0 \times 10^{12}$	$1.9 \times 10^8$
$1.0 \times 10^{11}$	$5.0 \times 10^{12}$	$9.5 \times 10^8$
$3.0 \times 10^{11}$	$1.0 \times 10^{12}$	$5.7 \times 10^8$

(a) Give the initial orders of reaction with respect to the two reactants, and explain how you got those values.

The initial orders may be obtained from the rates. For example, in the first and second reactions the concentration of  $\text{O}_3$  is changed, so may show that the ratio of the rates of these reactions must be a power of the ratio of the concentrations of  $\text{O}_3$ :

$$\frac{R_1}{R_2} = \frac{\{[\text{O}_3]_1\}^a}{\{[\text{O}_3]_2\}^a} \Rightarrow \frac{1.9 \times 10^8}{9.5 \times 10^8} = \frac{\{1.0 \times 10^{12}\}^a}{\{5 \times 10^{12}\}^a} \Rightarrow \frac{1}{5} = \left\{\frac{1}{5}\right\}^a$$

By solution,  $a = 1$ .

Similarly, from the first and third reactions, one can determine the order with respect to  $\text{HO}_2$ :

$$\frac{R_1}{R_3} = \frac{\{[\text{HO}_2]_1\}^b}{\{[\text{HO}_2]_2\}^b} \Rightarrow \frac{1.9 \times 10^8}{5.7 \times 10^8} = \frac{\{1.0 \times 10^{11}\}^b}{\{3.0 \times 10^{11}\}^b} \Rightarrow \frac{1}{3} = \left\{\frac{1}{3}\right\}^b$$

So, the order with respect to  $\text{HO}_2$  is also 1. Thus, the reaction rate equation is of the form:

$$v = k [\text{O}_3][\text{HO}_2]$$

(b) What is the rate constant for this reaction under the quoted conditions?

With the known rate, one can calculate the rate constant by rearrangement.

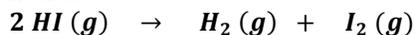
$$k = \frac{v}{[\text{O}_3][\text{HO}_2]}$$

Let's do this for the first reaction:

$$k = \frac{1.9 \times 10^8 \text{ molecules cm}^{-3} \text{s}^{-1}}{(1.0 \times 10^{12} \text{ molecules cm}^{-3})(1.0 \times 10^{11} \text{ molecules cm}^{-3})} = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$$

Similar calculations for the other two cases give the same number.

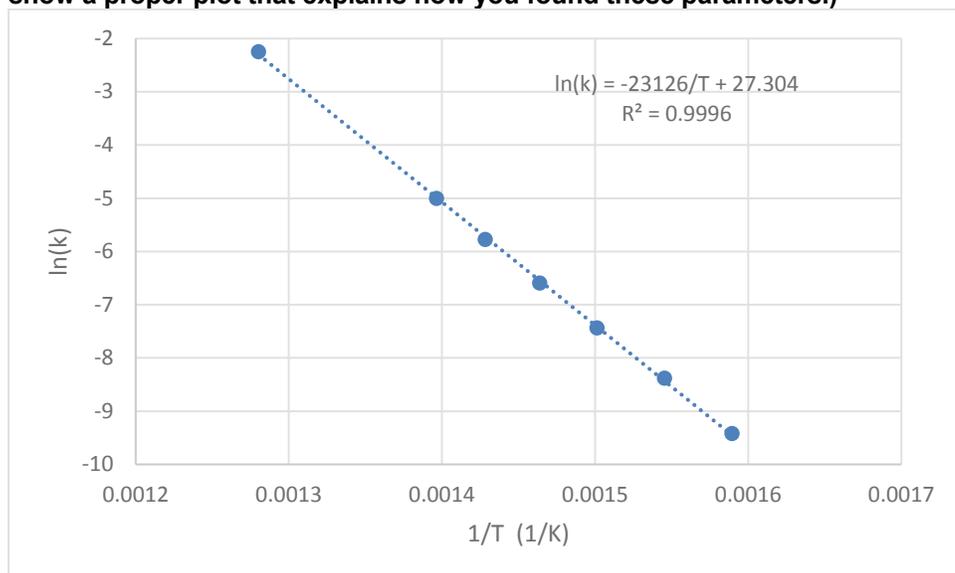
5. (15 points) The reactions of hydrogen iodide, hydrogen, and iodine were studied extensively by Max Bodenstein in the 1890s. One of the reactions he studied is



In particular, he found the following values for the rate constant at various temperatures, as shown in the table.

T (°C)	508	443	427	410	393	374	356
k / liter mol <sup>-1</sup> s <sup>-1</sup>	0.1059	6.70 × 10 <sup>-3</sup>	3.10 × 10 <sup>-3</sup>	1.370 × 10 <sup>-3</sup>	5.88 × 10 <sup>-4</sup>	2.30 × 10 <sup>-4</sup>	8.09 × 10 <sup>-5</sup>

Using all of these data, determine the activation energy and pre-exponential factor for this reaction. (You must show a proper plot that explains how you found these parameters.)



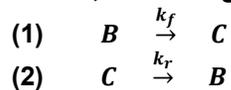
The graph shows a plot of the natural logarithm of k versus the inverse of the temperature (in kelvins), and the best-fit line through all of the points is quite linear. According to the Arrhenius theory, the slope is related to the activation energy:

$$E_a = -R(\text{slope}) = (8.3144349 \text{ J K}^{-1} \text{ mol}^{-1})(2.31 \times 10^4 \text{ K}^{-1}) = 192.3 \text{ kJ mol}^{-1}$$

Similarly, one finds that the intercept of this plot is related to the pre-exponential factor.

$$A = \exp(\text{intercept}) = \exp(27.30) = 7.182 \times 10^{11} \text{ liter mol}^{-1} \text{ s}^{-1}$$

6. (15 points) The exchange between conformations of cyclohexane (the boat (B) and chair (C)) has been studied in many experiments. Consider the simple mechanism, consisting of two steps.



(a) For each of these two elementary steps, write the velocity equation.

$$v_1 = k_f C_B$$

$$v_2 = k_r C_C$$

(b) Write an equation for the derivative of the concentration of the boat form.

$$\frac{dC_B}{dt} = -v_1 + v_2 = -k_f C_B + k_r C_C$$

(c) Assuming the initial concentration of B is  $C_B(0)$  and that  $C_C(0) = 0$ , solve for an equation for the time-dependent concentration of B,  $C_B(t)$ .

One may show that at any time,  $C_B(t) = C_B(0) - x$  and  $C_C(t) = x$  by conservation of matter. Substitution into the equation in part (b) gives, at any time,

$$-\frac{dx}{dt} = -k_f(C_B(0) - x) + k_r x = -k_f C_B(0) + (k_f + k_r)x$$

Or

$$\frac{dx}{dt} = k_f C_B(0) - (k_f + k_r)x$$

This equation is reminiscent of an exponential, so let's try a function of the sort

$$x(t) = f(t) \exp(-(k_f + k_r)t)$$

Substitution gives an equation for  $f(t)$

$$\frac{df}{dt} = \{k_f C_B(0)\} \exp[(k_f + k_r)t]$$

Integration of this form gives

$$f(t) = \frac{k_f C_B(0)}{k_f + k_r} \{ \exp((k_f + k_r)t) - 1 \}$$

Hence,

$$x(t) = \frac{k_f C_B(0)}{k_f + k_r} \{ 1 - \exp(-(k_f + k_r)t) \}$$

And

$$C_B(t) = C_B(0) - \frac{k_f C_B(0)}{k_f + k_r} \{ 1 - \exp(-(k_f + k_r)t) \}$$

Or

$$C_B(t) = C_B(0) \left[ 1 - \frac{k_f}{k_f + k_r} \{ 1 - \exp(-(k_f + k_r)t) \} \right]$$

Or

$$C_B(t) = C_B(0) \left[ \frac{k_r + k_f \exp(-(k_f + k_r)t)}{k_f + k_r} \right]$$

7. (12 points) (a) The rate of formation of HBr from dihydrogen and dibromine has the following rate law:

$$\frac{d[\text{HBr}]}{dt} = k \frac{[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k' \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

i) What are the initial orders with respect to H<sub>2</sub>, Br<sub>2</sub>, and HBr, and what is the overall initial order?

H<sub>2</sub> \_\_\_ 1 \_\_\_

Br<sub>2</sub> \_\_\_ 1/2 \_\_\_

HBr \_\_\_ 0 \_\_\_

Overall \_\_\_ 3/2 \_\_\_

ii) Near the end of the reaction, what are the orders with respect to H<sub>2</sub>, Br<sub>2</sub>, HBr, and the overall order?

H<sub>2</sub> \_\_\_ 1 \_\_\_

Br<sub>2</sub> \_\_\_ 3/2 \_\_\_

HBr \_\_\_ -1 \_\_\_

Overall \_\_\_ 3/2 \_\_\_

(b) Suppose that H<sub>2</sub> is present in great excess. What are the orders with respect to these components under those conditions at the end of the reaction.

H<sub>2</sub> \_\_\_ 1 \_\_\_

Br<sub>2</sub> \_\_\_ 3/2 \_\_\_

HBr \_\_\_ -1 \_\_\_

Overall \_\_\_ 3/2 \_\_\_

8. (13 points) Fill in each blank with a word or phrase.

- a) The collection of individual kinetic processes or steps involved in the transformation of reactants into products is the reaction mechanism.
- b) The Michaelis constant is generally found from a Lineweaver-Burk plot.
- c) For a reaction mechanism to be considered valid, the mechanism must be consistent with the experimentally determined rate law.
- d) Another name for an activated complex is the transition state.
- e) A radioactive decay is a classic example of a first order process.
- f) The determination of the rate constant for the dissociation of water has been carried out by the relaxation (perturbation) method.
- g) The process in which particles adsorb to a surface without changing their internal bonding is referred to as physisorption.
- h) Radical-chain reactions occur by steps that are classified as either initiation, propagation, or termination.
- i) Generally, nowadays, measurements in chemical kinetics are carried out by chemical or physical methods.
- j) The sedimentation coefficient is reported in svedbergs.

**9. (5 points, extra credit) Consider a random walk in one dimension, for example the movement of a drunken sailor back from a bar to his ship docked at the end of the street on which the bar is found. The bar is about 20 steps from the ship in one direction. (a) If he takes a random step every 30 seconds, what is the minimum time for the sailor to return to his ship?**

The minimum time to reach the ship occurs for the process in which every step is in the direction of the ship. There is only one way to do that. That would be  $20(30 \text{ seconds}) = 600 \text{ seconds} = 10 \text{ minutes}$ .

**(b) What is the probability that he will actually make it back to the ship in the time in part (a)?**

This is a single unique sequence, so the probability of that happening is  $P(20; 20) = \left(\frac{1}{2}\right)^{20} = \frac{1}{1,048,576} = 9.5367 \times 10^{-7}$ , a very small chance, indeed.

**(c) Because he is drunk, it probably takes more time to get to the ship. What is the likelihood he will reach the ship in exactly 40 steps, 30 which are toward the ship and 10 of which are away from the ship?**

It is not indicated that this a particular sequence, so we assume it will include all possible sequence of steps toward the ship and away from the ship. Thus, we count the possible different sequences, and the probability is

$$P(q, m) = \left(\frac{1}{2}\right)^{40} \frac{40!}{(30!)(10!)} = \left(\frac{1}{2}\right)^{40} \frac{40 \times 39 \times 38 \times 37 \times 36 \times 35 \times 34 \times 33 \times 32 \times 31}{10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1} = \left(\frac{1}{2}\right)^{40} 37 \times 34 \times 31 \times 19 \times 13 \times 11 \times 8 = 0.0008$$

So there is a probability of 8 parts in 10000 that he will make it to the ship in 40 steps, 30 of which are in the right direction. That is not a very high chance of making it to the ship.