

Chemistry 4B, Exam I

February 9, 2018

Professor Saykally

Name \_\_\_\_\_

SID \_\_\_\_\_

TA \_\_\_\_\_

1. (20) \_\_\_\_\_

2. (30) \_\_\_\_\_

3. (10) \_\_\_\_\_

4. (15) \_\_\_\_\_

5. (10) \_\_\_\_\_

6. (15) \_\_\_\_\_

TOTAL EXAM SCORE (100) \_\_\_\_\_

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

$$c = c_0 e^{-kt}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k}$$

$$\frac{1}{c} = \frac{1}{c_0} + 2kt$$

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E]_0[S]}{[S] + K_m}$$

$$A = 2d^2 N_A \sqrt{\frac{\pi RT}{\mu}} P$$

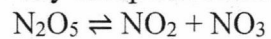
**Rules:**

- Work all problems to 2 significant figures
- No lecture notes or books permitted
- No word processing calculators or cell phones
- Time: 50 minutes
- Show all work to get partial credit; do not write outside the boxes.
- Periodic Table, Tables of Physical Constants, Equations, and Conversion Factors included

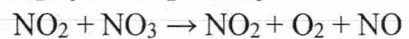
1. (10+10 points) For the reaction



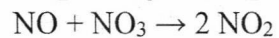
the currently accepted mechanism is:



fast, at equilibrium ( $k_1, k_{-1}$ )



slow ( $k_2$ )

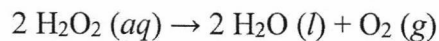


fast ( $k_3$ )

a) Write the differential rate law for this reaction.

b) Suppose that the  $k_1$ ,  $k_{-1}$  and  $k_2$  reactions are all slow. Solve for the steady-state value of  $[\text{NO}_3]$ .

2. (10 +10 +10 points) In class, we demonstrated the disproportionation reaction of hydrogen peroxide:



- A) The activation energy for this reaction is 76 kJ/mol. What fraction of collisions can lead to reaction at 25°C?

- B) Addition of the electron transfer catalyst  $\text{MnO}_2 (s)$  to the peroxide solution accelerates the rate by a factor of  $1.0 \times 10^{10}$ . What is the corresponding value of  $E_a$ ?

- C) The uncatalyzed reaction follows first order kinetics with respect to  $\text{H}_2\text{O}_2$  with  $k = 0.0410 \text{ min}^{-1}$ . If the initial concentration is 0.35 moles/L, what is the concentration after 10 min?

3. (10 points) Certain bacteria use the enzyme penicillinase to decompose penicillin and render it inactive. The Michaelis–Menten constants for this enzyme and substrate are

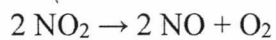
$$K_m = 5.3 \times 10^{-5} \text{ mol L}^{-1}$$

$$k_2 = 2.6 \times 10^3 \text{ s}^{-1}$$

At what substrate concentration will the rate of decomposition be half of the maximum rate?



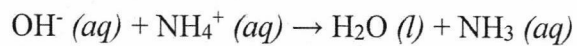
4. (15 points) Use collision theory to estimate the pre-exponential factor in the rate constant for the elementary reaction



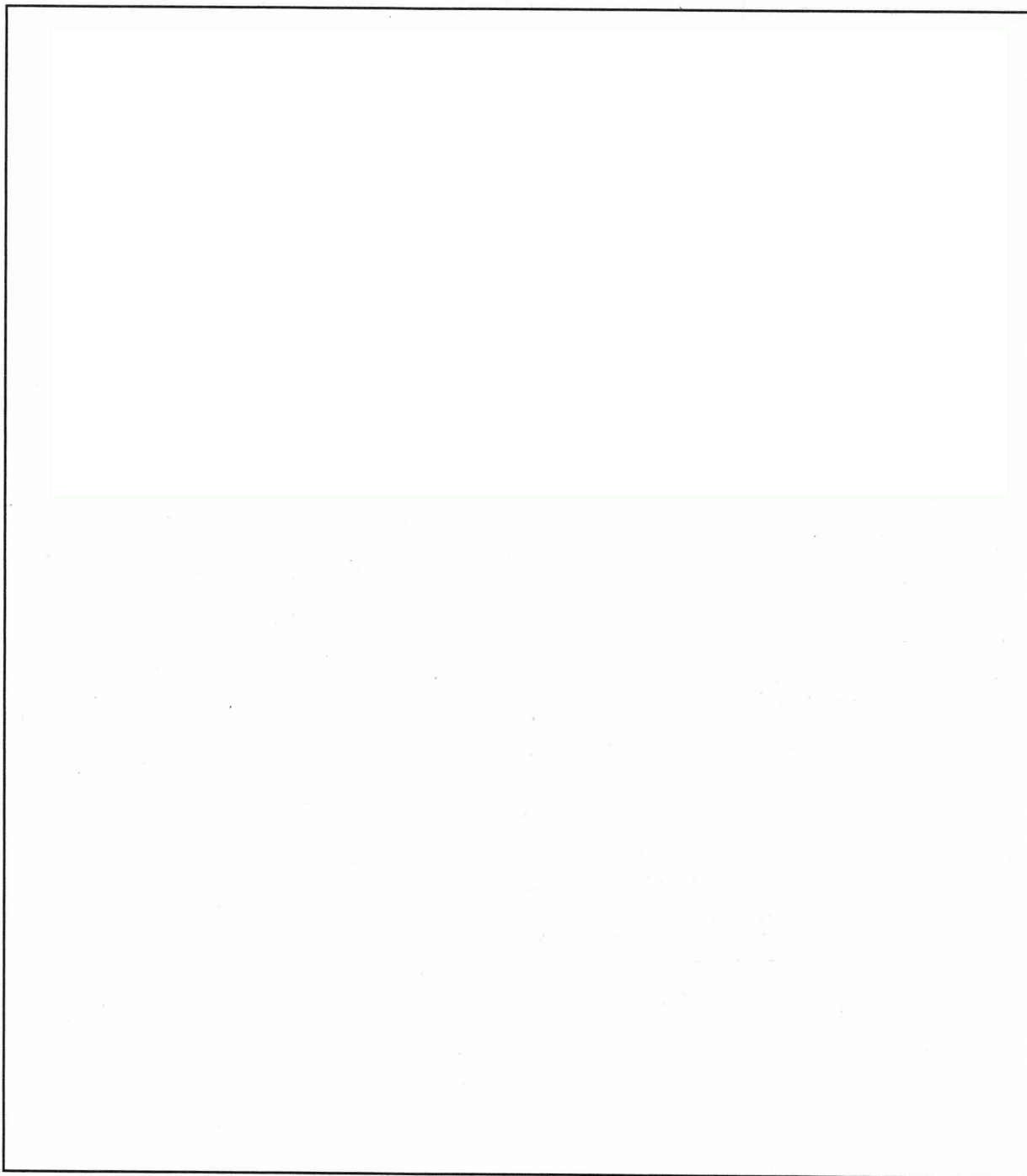
at 500 K. Take the average diameter of an  $\text{NO}_2$  molecule to be  $2.6 \times 10^{-10}$  m and the steric factor as  $5.0 \times 10^{-2}$ .



5. (10 points) The rate for the reaction



is the first order in both  $\text{OH}^-$  and  $\text{NH}_4^+$  concentrations and the rate constant  $k$  at  $20^\circ\text{C}$  is  $3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . Suppose 1.00 L of a 0.0010 M NaOH solution is rapidly mixed with the same volume of 0.0010 M  $\text{NH}_4\text{Cl}$  solution. Calculate the time (in seconds) required for the  $\text{OH}^-$  concentration to decrease to a value of  $1.0 \times 10^{-5} \text{ M}$ .



6. (15 points) In class, we measured the rate of the “iodine clock” reaction at several temperatures. Use the following data to calculate  $E_a$  for this reaction ( $t$  is the time required for blue color to appear):

	<u>T (°C)</u>	<u>t (sec)</u>
1	17.5	26
2	10.5	34

