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) ____________

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

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

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

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

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

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

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

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

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

$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

the currently accepted mechanism is:

$N_2O_5 \rightleftharpoons NO_2 + NO_3$	fast, at equilibrium (k_1, k_{-1})
$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$	slow (k_2)
$NO + NO_3 \rightarrow 2\ NO_2$	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 $[NO_3]$.

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

$$2\ H_2O_2\ (aq) \rightarrow 2\ H_2O\ (l) + O_2\ (g)$$

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 MnO_2 (*s*) to the peroxide solution accelerates the rate by a factor of 1.0×10^{10}. What is the corresponding value of E_a?

C) The uncatalyzed reaction follows first order kinetics with respect to H_2O_2 with $k = 0.0410$ 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

$$2\,NO_2 \rightarrow 2\,NO + O_2$$

at 500 K. Take the average diameter of an NO_2 molecule to be 2.6×10^{-10} m and the steric factor as 5.0×10^{-2}.

5. **(10 points)** The rate for the reaction

$$OH^- \, (aq) + NH_4^+ \, (aq) \rightarrow H_2O \, (l) + NH_3 \, (aq)$$

is the first order in both OH^- and NH_4^+ concentrations and the rate constant k at 20°C is 3.4×10^{10} L mol^{-1} s^{-1}. Suppose 1.00 L of a 0.0010 M NaOH solution is rapidly mixed with the same volume of 0.0010 M NH_4Cl solution. Calculate the time (in seconds) required for the OH^- concentration to decrease to a value of 1.0×10^{-5} 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):

	T (°C)	t (sec)
1	17.5	26
2	10.5	34