Chemistry 1B, Exam I
February 8, 2007
Professor R.J. Saykally

Name [redacted]

TA Ashley

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1.	(15)	15
2.	(10)	10
3.	(10)	10
4.	(10)	10
5.	(20)	19
6.	(15)	5
7.	(20)	18

TOTAL EXAM SCORE (100) 92

Rules:
- Work all problems to 2 significant figures
- No lecture notes or books permitted
- No word processing calculators
- Time: 90 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, and Conversion Factors included

1. (15 points) Given the elementary reaction, determine the time required for the concentration of A to decrease from 0.10 $mol \cdot L^{-1}$ to 0.080 $mol \cdot L^{-1}$, given that $k = 0.015\ L \cdot mol^{-1} \cdot min^{-1}$ for the rate law expressed in terms of the loss of A.

$2\ A \rightarrow B + C$

2nd order

$-\frac{d[A]}{dt} = k[A]^2$

$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$

$\frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k} = t = \frac{\frac{1}{0.080M} - \frac{1}{0.10M}}{0.015\ L/mol/min} = \boxed{166.67\ min}$

15

2. (10 points) Three mechanisms for the reaction $NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$ have been proposed:

a) **Step 1** $NO_2 + CO \rightarrow CO_2 + NO$

b) **Step 1** $NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)
Step 2 $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

c) **Step 1** $NO_2 + NO_2 \rightarrow NO + NO_3$ and its reverse (both fast, equilibrium)
Step 2 $NO_3 + CO \rightarrow NO_2 + CO_2$ (slow)

Which mechanism agrees with the following rate law: $rate = k[NO_2]^2$? Explain your reasoning.

$k[NO_2]^2$ → want 2nd ord wRT NO_2

a) $R = k[NO_2][CO]$ → does not agree

b) $R = k[NO_2]^2$ → agrees

10

c) $R = k[NO_3][CO]$

$k[NO_2][NO_2] = k[NO][NO_3]$

$\frac{k_1[NO_2][NO_2]}{k_2} = [NO_3]$ does not agree

3. (10 points) The rate constant for the decomposition of N_2O_5 at 45°C is $k = 5.1 \times 10^{-4}\ s^{-1}$. The activation energy for the reaction is 103 kJ·mol–1. Determine the value of the rate constant at 50.°C.

a) $T_1 = 45°C = 318\ K$ 1st order

$K = 5.1 \times 10^{-4}\ s^{-1}$

$E_a = 103\ KJ/mol$

$T_2 = 50°C = 323\ K$

$K_1 = A e^{-E_a/RT_1}$

$K_2 = A e^{-E_a/RT_2}$

$$\frac{K_2}{K_1} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}}$$

$K_2 = K_1 e^{-E_a/RT_2 + E_a/RT_1}$

$= 5.1 \times 10^{-4} e^{(-103\times10^3/8.3145/323 + 103\times10^3/8.3145/318)}$

$K_2 = 9.32 \times 10^{-4}\ s^{-1}$

4. (10 points) The combustion of octane is expressed by the thermochemical equation

$$C_8H_{18}(1) + \frac{25}{2} O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(1)$$

$\Delta H° = -5470$ kJ

How much heat will be evolved from the combustion of 1.0 gal of gasoline (assumed to be exclusively octane)? The density of octane is 0.70 g·mL^{-1}.

$$1\ \text{gal octane} \times \frac{3.78541\ L}{1\ \text{gal}} \times \frac{1000\ mL}{1\ L} \times \frac{0.70\ g\ \text{octane}}{mL} \times \frac{1\ \text{mol octane}}{114.26\ g} \times \frac{5470\ KJ\ \text{released}}{mol}$$

$= 126854\ KJ$ of heat evolved

20

5. **(5 points each)** Consider the collision theory result for the bimolecular reaction of K with Br_2 at 273 K.

a) Calculate the reduced molar mass (in kg).

$$\frac{M_{m_1} \times M_{m_2}}{M_{m_1} + M_{m_2}} = \frac{(39.1\ g/mol)(79.9 \times 2\ g/mol)}{39.1\ g/mol + 79.9 \times 2\ g/mol} = \frac{6248.18\ g^2}{198.9\ g}$$

$$= 31.4\ g = \boxed{0.0314\ kg}$$

5

b) Calculate the average relative speed $(8RT/\pi\mu)^{1/2}$.

$$\bar{v} = \sqrt{\frac{8(8.3145)(273)}{\pi(0.0314)}} = \boxed{429\ m/s}$$

5

c) Calculate A ($A = \sigma \bar{C}_{rel} N_0$) given that the collision cross section is $3.0 \times 10^{-19}\ m^2$.

$$A = (3 \times 10^{-19})(6.02 \times 10^{23})(429)$$

$$\boxed{A = 7.75 \times 10^7}$$

units

4

d) The measured value of A is 1.2×10^8 and E_a is 180 kJ/mol. Compute the steric factor for the reaction.

$P = \frac{\text{value observed}}{\text{value theoretical}} = \frac{1.2 \times 10^8}{7.75 \times 10^7} = 1.55 = P$

5

6. (15 points) The following results were obtained for the rate of the iodine clock reaction in a lecture demonstration [t ≡ time for blue color to appear]:

blue color appears when all I^- is used up

$6I^-(aq) + BrO_3(aq) + 6H^+(aq) \rightarrow 3I_2 + Br^- + 3H_2O$

	t(sec)	T(°K)
1)	33	280
2)	12	355

Calculate the activation energy for this reaction.

$R = K[I^-]^x[BrO_3]^y[H^+]^z$

$R_1 = KAe^{-E_a/RT_1}$

$R_2 = KAe^{-E_a/RT_2}$

$Rate = \frac{d[I]}{dt}$; $\frac{Rate\,2}{Rate\,1} = \frac{\frac{d[I]}{12\,s}}{\frac{d[I]}{33\,s}} = \frac{33}{12} = 2.75$

Rate 2 = 2.75 Rate 1

→ only the $\sqrt{T}$ terms are left from "A"

$\frac{Rate\,2}{Rate\,1} = 2.75 = \frac{K\sqrt{T_2}}{K\sqrt{T_1}} e^{\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$

$\ln\left(2.75\sqrt{T_1/T_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\frac{R\ln\left(2.75\sqrt{\frac{T_1}{T_2}}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = E_a = \frac{8.3145\ln\left(2.75\sqrt{\frac{280}{355}}\right)}{\left(\frac{1}{280} - \frac{1}{355}\right)} = 9839.7\ \frac{J}{mol} = E_a$

~~5~~ 10

7. (10+5+5 points) The mechanism for the gas phase decomposition of NO_2Cl is:

$$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

A. By making a steady-state approximation for [Cl], express the rate of appearance of Cl_2 in terms of the concentrations of NO_2Cl and NO_2.

$R = K_2[NO_2Cl][Cl]$

S.S.A

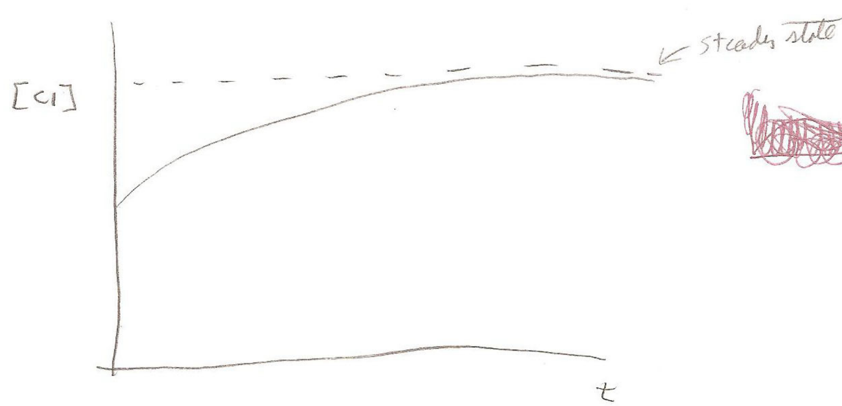
$\frac{d[Cl]}{dt} = 0 = K_1[NO_2Cl] - K_{-1}[NO_2][Cl] + K_2[NO_2Cl][Cl]$

$0 = K_1[NO_2Cl] + [Cl](-K_{-1}[NO_2] + K_2[NO_2Cl])$

$\frac{-K_1[NO_2Cl]}{K_2[NO_2Cl] - K_{-1}[NO_2]} = [Cl] \Rightarrow [Cl] = \frac{K_1[NO_2Cl]}{K_{-1}[NO_2] - K_2[NO_2Cl]}$

$R = \frac{K_2[NO_2Cl]K_1[NO_2Cl]}{K_{-1}[NO_2] - K_2[NO_2Cl]} = \boxed{\frac{K_1K_2[NO_2Cl]^2}{K_{-1}[NO_2] - K_2[NO_2Cl]} = R}$ Rate of appearance of Cl_2

B. Graph the concentration of Cl vs. time.



+13