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

Name KEY

TA ____________________

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

TOTAL EXAM SCORE (100) ______

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·L^{-1} to 0.080 mol·L^{-1}, given that k = 0.015 L·mol^{-1}·min^{-1} for the rate law expressed in terms of the loss of A.

$2\,A \rightarrow B + C$

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

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = \int_0^t -k\,dt$$

$$-\frac{1}{[A]}\Big|_{[A]_0}^{[A]_t} = -kt\Big|_0^t$$

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

$$\boxed{t = 166.67 \text{ min}}$$

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** $NO_2 + NO_2 \rightarrow NO_2 + NO_3$ (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.

(a) one step ∴ Rate $\propto k[NO_2][CO]$

(b) Step 1 slow ∴ Rate $\propto k[NO_2]^2$

(c) Step 2 slow ∴ Rate $\propto k[NO_3][CO]$

$$k_1[NO_2]^2 = k_{-1}[NO][NO_3]$$

$$[NO_3] = \frac{k_1[NO_2]^2}{k_{-1}[NO]}$$

$$\text{Rate} \propto \frac{k k_1 [NO_2]^2[CO]}{k_{-1}[NO]}$$

mechanism (b) agrees w/ the rate law.

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.

$T_1 = 45°C = 318\ K$ $\quad k_1 = 5.1 \cdot 10^{-4}\ s^{-1}$ $\quad E_a = 103\ \frac{kJ}{mol} = 103000\ \frac{J}{mol}$

$T_2 = 50°C = 323\ K$ $\quad k_2 = ?$

$$k = Ae^{-E_a/RT}$$

$$\frac{k_1}{k_2} = \frac{Ae^{-E_a/RT_1}}{Ae^{-E_a/RT_2}}$$

$$\frac{k_1}{k_2} = e^{\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$k_2 = k_1 e^{-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$\boxed{k_2 = 9.32 \cdot 10^{-4}\ s^{-1}}$$

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

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

$$\Delta H° = -5470\ kJ$$

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 gallon = 3.785 L $\quad$ MW $C_8H_{18} = 8(12.01\ g/mol) + 1.0079(18) = 114.22\ g/mol$

$$3.785\ L \cdot \frac{1000\ mL}{1\ L} \cdot \frac{0.70\ g}{mL} \cdot \frac{1\ mol}{114.22\ g} = 23.2\ mol\ C_8H_{18}$$

$$\Delta H = -\frac{5470\ kJ}{mol} \cdot 23.2\ mol = -126904 = \boxed{-1.3 \cdot 10^5\ kJ}$$

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).

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

K : 39.1 g/mol ⇒ M_1 = 0.0391 kg/mol

Br_2 : 159.8 g/mol ⇒ M_2 = 0.1598 kg/mol

$$\mu = \frac{0.006248\ kg^2/mol^2}{0.1989\ kg/mol}$$

$$\boxed{\mu = 0.0314\ kg/mol}$$

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

$$\bar{c}_{rel} = \left(\frac{8RT}{\pi\mu}\right)^{\frac{1}{2}}$$

$$= \left(\frac{8(8.314\ J/mol\cdot K)(273\ K)}{\pi \cdot 0.0314\ kg/mol}\right)^{\frac{1}{2}}$$

$$= (184070\ J/kg)^{\frac{1}{2}} \qquad 1J = 1kg\cdot m^2/s^2$$

$$= (184070\ m^2/s^2)^{\frac{1}{2}}$$

$$\boxed{\bar{c}_{rel} = 429\ m/s}$$

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

$$A = \sigma \cdot \bar{c}_{rel} \cdot N_o$$

$$= 3.0 \cdot 10^{-19} \cdot 429 \cdot 6.022 \cdot 10^{23}$$

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

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.

$$P = \frac{A_{exp}}{A_{theory}}$$

$$P = \frac{1.2 \cdot 10^8}{7.75 \cdot 10^7}$$

$$\boxed{P = 1.55}$$

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]:

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

t(sec)	T(°K)
33	280
12	355

Calculate the activation energy for this reaction.

$$\text{Rate} \propto \frac{1}{t}$$

$$\frac{t_2}{t_1} = \frac{A e^{-E_a/RT_1}}{A e^{-E_a/RT_2}}$$

$$\frac{t_2}{t_1} = e^{-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$E_a = \frac{-\ln\left(\frac{t_2}{t_1}\right) \cdot R}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\boxed{E_a = 11147 \text{ J/mol}}$$

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.

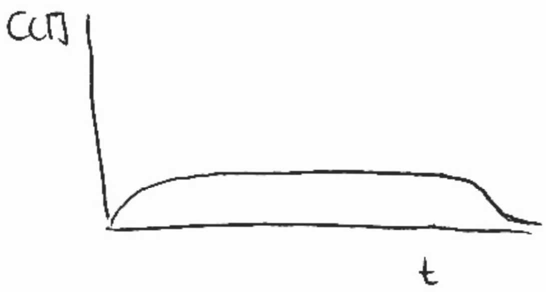
$$\frac{d[Cl]}{dt} = k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl] = 0$$

$$[Cl] = \frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

$$\text{Rate} \propto k_2[Cl][NO_2Cl]$$

$$\text{Rate} \propto \frac{k_2 k_1 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

B. Graph the concentration of Cl vs. time.



C. Find the rate law and graph $\frac{d\,[Cl_2]}{dt}$ vs. $[NO_2Cl]$ as expected for high NO_2 concentrations.

From part (a)

$$\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

for high $[NO_2]$, $k_{-1}[NO_2] \gg k_2[NO_2Cl]$

$$\frac{d[Cl_2]}{dt} = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2]}$$

$$\approx k'[NO_2Cl]^2$$