Chemistry 1B, Exam I
February 18, 2009
Professor R.J. Saykally

Name KEY

TA ________________

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

TOTAL EXAM SCORE (100) ______

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

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

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

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

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

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

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

Rules:

- Work all problems to 3 significant figures
- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, and Conversion Factors included

1. (20 points) The mechanism for the decomposition of gaseous NO_2Cl is

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

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

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.

rate of appearance: $\frac{d[Cl_2]}{dt} = k_2[NO_2Cl][Cl]$

steady state approx.: $\frac{d[Cl]}{dt} = k_1[NO_2Cl] - k_{-1}[NO_2][Cl] - k_2[NO_2Cl][Cl] = 0$

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

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

$$\frac{d[Cl_2]}{dt} = \frac{k_1k_2[NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

2. (15 points) A certain first-order reaction has an activation energy of 53 kJ mol^{-1}. It is run twice, first at 298 K and then at 308 K (10°C higher). All other conditions are identical. Show that, in the second run, the reaction occurs at double its rate in the first run.

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

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

$$\ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$= -\frac{53\ kJ \cdot mol^{-1} \times 10^3\ J \cdot kJ^{-1}}{mol \cdot 8.314\ J \cdot mol^{-1} \cdot K^{-1} \cdot 308\ K} + \frac{53\ kJ \cdot mol^{-1} \cdot 10^3\ J \cdot kJ^{-1}}{mol \cdot 8.314\ J \cdot mol^{-1} \cdot K^{-1} \cdot 298\ K}$$

$$\ln\left(\frac{k_2}{k_1}\right) = -20.697 + 21.392 = 0.695$$

$$\frac{k_2}{k_1} = 2.00$$

3. (10 points each) Certain bacteria use the enzyme penicillinase to decompose penicillin and render it inactive. The Michaelis–Menten constants for this enzyme and substrate are $K_m = 5 \times 10^{-5}$ mol L^{-1} and $k_2 = 2 \times 10^3$ s^{-1}.

A) What is the maximum rate of decomposition of penicillin if the enzyme concentration is 6×10^{-7} M?

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

maximum rate requires high substrate concentration

$$[S] >> K_m$$

$$\left(\frac{d[P]}{dt}\right)_{max} = \frac{k_2[E]_0[S]}{[S]+K_m} = k_2[E]_0$$

$$= (2.00 \times 10^{3}\ s^{-1})(6.00 \times 10^{-7}\ M)$$

$$= 1.20 \times 10^{-3}\ mol \cdot L^{-1} \cdot s^{-1}$$

B) At what substrate concentration will the rate of decomposition be half that calculated in part (A)?

$$\frac{rate}{max.\ rate} = \frac{1}{2} = \frac{\frac{k_2[E]_0[S]}{[S]+K_m}}{k_2[E]_0}$$

$$\frac{1}{2} = \frac{k_2[E]_0[S]}{k_2[E]_0([S]+K_m)}$$

$$\frac{1}{2} = \frac{[S]}{[S]+K_m}$$

$$2[S] = [S] + K_m$$

$$[S] = K_m = 5.00 \times 10^{-5}\ mol \cdot L^{-1}$$

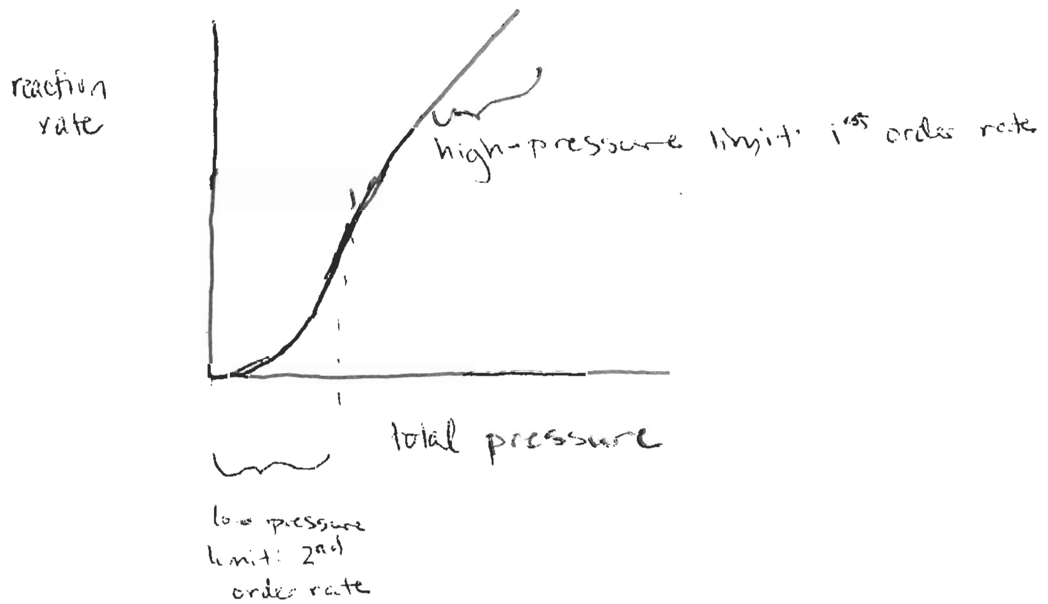
4. **(5 points each)** In class, we described the Lindemann mechanism for the "unimolecular" decomposition of a gaseous molecule, e.g. $N_2O_5 + M \rightarrow 2N_2O + \frac{1}{2} O_2 + M$

A) Write the differential rate law appropriate for the reaction found at low pressure?

At low pressure, this reaction is second-order (low [M] allows collisional excitation step)

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5]^2$$

B) Sketch and label a plot of the reaction rate vs. total pressure.



5. (5 points each) Manganate ions, MnO_4^{2-}, react at 2.0 mol·L^{-1}·min^{-1} in acidic solution to form permanganate ions and manganese(IV) oxide:

$$3\ MnO_4^{2-}(aq) + 4\ H^+(aq) \rightarrow 2\ MnO_4^-(aq) + MnO_2(s) + 2\ H_2O(l)$$

A) What is the rate of formation of permanganate ions?

$$\frac{1}{2}\frac{d[MnO_4^-]}{dt} = -\frac{1}{3}\frac{d[MnO_4^{2-}]}{dt}$$

$$\frac{d[MnO_4^-]}{dt} = \frac{2}{3}(2.0\ mol\cdot L^{-1}\ min^{-1})$$

$$= 1.3\ mol\cdot L^{-1}\cdot min^{-1}$$

B) What is the rate of reaction of H^+(aq):

$$-\frac{1}{4}\frac{d[H^+]}{dt} = -\frac{1}{3}\frac{d[MnO_4^{2-}]}{dt}$$

$$\frac{d[H^+]}{dt} = \frac{4}{3}(2.0\ mol\cdot L^{-1}\cdot min^{-1})$$

$$= 2.7\ mol\cdot L^{-1}\cdot min^{-1}$$

6. (10 points) The rate of a particular reaction is found to decrease as the temperature increases by 10°C. What does this imply? Explain.

The reaction has more than one elementary step: it is not an elementary reaction. For any elementary reaction, rate is related to temperature by the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad \left(\text{or } \ln k = \ln A - \frac{E_a}{RT}\right)$$

This means the rate of an elementary reaction must increase with increasing temperature. (A, E_a, R, & T are all always positive)

7. (3 points each) Short Answer

A) The total world energy consumption is currently about 13–15 Terawatts, and about 90 % of this energy is currently produced from chemical reactions.

B) Two types of chemical explosions were demonstrated in class. Specify these types and give an example of each.

Chain reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ OR hydrocarbon combustion

thermal: $CS_2 + NO$

C) Rates for chemical reactions with low activation energies that occur in liquids are diffusion limited.