Key

Name (please print)

CHEMISTRY 128
HOUR TEST 1
June 13, 2003

USEFUL INFORMATION:

$N = 6.022 \times 10^{23}$ $\quad R = 0.08206 \frac{L \cdot atm}{mol \cdot K} = 0.0083145 \frac{kJ}{mol \cdot K}$

$[A] = -kt + [A]_0$ $\quad t_{1/2} = \frac{0.693}{k}$ $\quad \frac{1}{[A]} = kt + \frac{1}{[A]_0}$ $\quad k = Ae^{-Ea/RT}$ $\quad t_{1/2} = \frac{[A]_0}{2k}$

$T(K) = T(C°) + 273.15$ $\quad \ln[A] = -kt + \ln[A]_0$ $\quad t_{1/2} = \frac{1}{k[A]_0}$ $\quad \ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$

$K = °C + 273.15$ $\quad K_p = K_c (RT)^{\Delta n}$ $\quad y = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

1 IA																	18 VIIIA
1 H 1.008	2 IIA											13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 ⌐	9 VIIIB	10 ¬	11 IB	12 IIB	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.30
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po 210	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226.03	103 Lr 262.1	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 146.92	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04
89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 239.05	95 Am 241.06	96 Cm 247.07	97 Bk 249.08	98 Cf 251.08	99 Es 254.09	100 Fm 257.10	101 Md 258.10	102 No 255

There Are <u>6</u> Pages On This Test Including This Cover Page.
The Test Contains <u>100</u> Points.

I. (41 points) Short Answers

1. (4 points) The following reaction is (**zero, first , second, third**) order overall and (**zero, first, second , third**)with respect to [NO].

$$2\ NO\ (g) + Br_2\ (g) \rightarrow 2\ NOBr\ (g) \qquad Rate = k[NO_2]^2[Br_2]$$

2. (4 points) Using the equation from problem 1, give the relative rate of appearance of NOBr to the relative rate of disappearance of NO.

$$Rate = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NOBr]}{\Delta t}$$

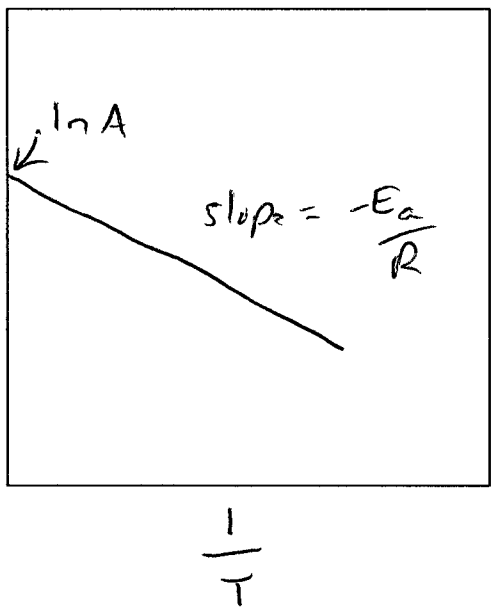
3. (4 points) Given the following rate law, write an equation for the rate-determining step of this reaction's mechanism assuming that the slow step is the first step of the mechanism.

$$Rate = k[A]^0[B]^2$$

$$B + B \rightarrow C$$

4. (8 points) For a first order reaction, a plot of time (x-axis) vs. ln [A] (y-axis) would yield a straight line with the slope equal to $-k$ and the y-intercept equal to $\ln[A]_0$.

5. (8 points) Using the space provided, sketch what must be plotted in order to determine E_a, the energy of activation, for a reaction. Be sure to label the axes and to supply a line on the graph showing appropriate slope. What is the slope equal to?



6. (4 points)Write the K_c for the following reaction.

$$SnO_2\,(s) + 2\,CO\,(g) \leftrightarrow Sn\,(s) + 2\,CO_2\,(g)$$

$$K_c = \frac{[CO_2]^2}{[CO]^2}$$

7. (9 points) Indicate, by circling the correct answer, the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left, no change, or right).

$$N_2O_4\,(g) \leftrightarrow 2\,NO_2\,(g) \qquad \Delta H = +58\ kJ$$

a. Addition of more NO_2 (g) (**left,** **no change, right**)

b. Increasing the volume of the container (**left, no change,** **right**)

c. Cooling the reaction (**left,** **no change, right**)

II. Calculations. **Show clear, complete setup for full credit.**

8. (11 points) Cobalt-60 has a half-life of 5.26 yr. The cobalt-60 source in a radiotherapy unit must be replaced when its radioactivity falls to 75% of the original sample. If a sample was purchased on June 1, 2003, in what month and year will it be necessary to replace the cobalt-60?

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \qquad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.26\,hr} = 0.132\,yr^{-1}$$

$$\ln(0.75) = -(0.132\,yr^{-1})(t)$$

$$2.18\,yr = t$$

Therefore, 2.18 yr will elapse. Therefore, it must be replaced 2 yrs, 65 days later or August 4, 2005.

9. (15 points) The following reaction was studied at -10°C and the following data were collected

$$2\ ClO_2\ (aq) + 2\ OH^-\ (aq) \rightarrow ClO_2^-\ (aq) + ClO_3^-\ (aq) + H_2O\ (l)$$

experiment	$[ClO_2]_o$ (mol*L^{-1})	$[OH^-]_o$ (mol*L^{-1})	initial rate (mol*L^{-1}*s^{-1})
1	0.0500	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.0500	1.15×10^{-1}

a. Determine the order of the reaction with respect to ClO_2.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{2.30 \times 10^{-1}}{5.75 \times 10^{-2}} = \frac{k[0.100]^m[0.100]^n}{k[0.0500]^m[0.100]^n}$$

$$4.00 = (2.00)^m \qquad m = 2$$

b. Determine the order of the reaction with respect to OH^-.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{2.30 \times 10^{-1}}{1.15 \times 10^{-1}} = \frac{k[0.100]^m[0.100]^n}{k[0.100]^m[0.0500]^n}$$

$$2.00 = (2.00)^n \qquad n = 1$$

c. Write the rate law expression for this reaction.

$$\text{Rate} = k[ClO_2]^m[OH^-]^n = k[ClO_2]^2[OH^-]$$

d. What is the overall order of this reaction?

$$\text{Overall order} = m + n = 2 + 1 = 3$$

e. Determine the value of the rate constant, k, including the units.

$$k = \frac{\text{Rate}}{[ClO_2]^2[OH^-]^1} = \frac{5.75 \times 10^{-2}\ \frac{\text{mol}}{\text{L}\cdot\text{s}}}{\left(0.0500\ \frac{\text{mol}}{\text{L}}\right)^2\left(0.100\ \frac{\text{mol}}{\text{L}}\right)^1} = 230\ \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}$$

10. (9 points) At a particular temperature, the equilibrium constant, K, is 1.0×10^2 for the following reaction.

$$H_2\,(g) + I_2\,(g) \leftrightarrow 2\,HI\,(g)$$

In the lab, it was observed that a 0.500 L contained 1.00 mol H_2, 1.00 mol I_2, and 1.00 mol HI.

a. (5 points) Is the system in equilibrium? (Prove either yes or no mathematically and show your work)

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{1.000\ mol}{0.500\ L}\right)^2}{\left(\frac{1.00\ mol}{0.500\ L}\right)\left(\frac{1.00\ mol}{0.500\ L}\right)} = 1$$

Since $Q < K$, the equilibrium has not been reached.

b. (2 points) If the system in not in equilibrium, will the concentration of I_2 increase or decrease as it continues towards equilibrium? ~~If~~ the system is in equilibrium, simply state "at equilibrium."

Decrease

c. (2 points) If a catalyst is added to the system once it reached equilibrium, what direction will the equilibrium shift?

It won't shift. Catalysts don't shift equilibria.

11. (9 points) A sample of solid ammonium chloride was placed in an evacuated container and then heated so that it decomposed to NH_3 (g) and HCl (g). After heating, the total pressure in the flask was 4.4 atm. Calculate K_p (including units, if any) at this temperature for the decomposition reaction

$$NH_4Cl\,(s) \leftrightarrow NH_3\,(g) + HCl\,(g)$$

Initial	P	0	0
Change	P	+2.2	+2.2
Equil	P	2.2	2.2

$P_{Total} = P_{NH_3} + P_{HCl}$

$4.4 = x + x$

$4.4 = 2x$

$2.2 = x$

$$K_p = (P_{NH_3})(P_{HCl})$$

$$K_p = (2.2\ atm)(2.2\ atm)$$

$$K_p = 4.8\ atm^2$$

12. (15 points) When a certain partial pressure of NH_3 (g) was put into an empty vessel at 25°C, equilibrium was achieved when 50% of the original NH_3 had decomposed according to the following equation.

$$N_2\,(g) + 3\,H_2\,(g) \leftrightarrow 2\,NH_3\,(g) \qquad K_p = 5.3 \times 10^5$$

Calculate the original partial pressure of NH_3 (in atm) before any decomposition occurred.

	N_2	+	$3H_2$	⇌	$2NH_3$
Initial	0		0		y
Change	$+\frac{1}{4}y$		$+\frac{3}{4}y$		$-\frac{1}{2}y$
Equil	$\frac{1}{4}y$		$\frac{3}{4}y$		$\frac{1}{2}y$

50% Decomposition

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = 5.3 \times 10^5 = \frac{(\frac{1}{2}y)^2}{(\frac{1}{4}y)(\frac{3}{4}y)^3}$$

$$5.3 \times 10^5 = \frac{0.25y^2}{(0.25y)(0.4219y^3)}$$

$$5.3 \times 10^5 = \frac{1}{0.4219y^2}$$

$$y^2 = \frac{1}{(0.4219)(5.3 \times 10^5)}$$

$$y = \sqrt{4.472 \times 10^{-6}} = 2.1 \times 10^{-3}\ atm$$