Chemistry 4A, Exam III
October 27, 1999
Professor R.J. Saykally

Name ______ ____________

TA ______ ____________

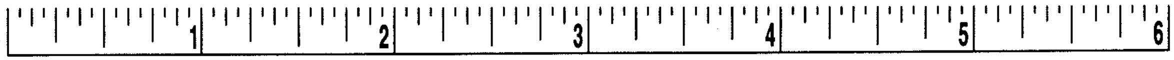
I.	(20)	4+4+4 + 8 → 20
II.	(10)	9
III.	(25)	25
IV.	(10)	10
V.	(15)	15
VI.	(10)	9
VII.	(10)	Ø

TOTAL EXAM SCORE (100) 88

Rules:

- Work all problems to 2 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, Conversion Factors included

Inches



Periodic Table of the Elements

Atomic number → 27; Atomic mass → 58.93; symbol: **Co**; name: Cobalt

symbol: Black — naturally occurring; White — synthetically prepared; *most stable isotope*

- Metals
- Metalloids
- Nonmetals
- Noble gases

[illegible]																	2 4.003 He Helium
3 6.94 Li Lithium	4 9.01 Be Beryllium											[illegible]	C	N	O	F	10 20.18 Ne Neon
11 22.99 Na Sodium	12 24.31 Mg Magnesium											13 26.98 Al Aluminum	[illegible]	P	S	Cl	18 39.95 Ar Argon
19 39.10 K Potassium	20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.90 Ti Titanium	23 50.94 V Vanadium	24 51.996 Cr Chromium	25 54.94 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.70 Ni Nickel	29 63.55 Cu Copper	30 65.37 Zn Zinc	31 69.72 Ga Gallium	[illegible]	[illegible]	Se	Br	36 83.80 Kr Krypton
37 85.47 Rb Rubidium	38 87.62 Sr Strontium	39 88.91 Y Yttrium	40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 (98) Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.40 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.69 Sn Tin	[illegible]	[illegible]	[illegible]	54 131.30 Xe Xenon
55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 180.95 Ta Tantalum	74 183.85 W Tungsten	75 186.21 Re Rhenium	76 190.20 Os Osmium	77 192.22 Ir Iridium	78 195.09 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.37 Tl Thallium	82 207.19 Pb Lead	83 208.98 Bi Bismuth	[illegible]	[illegible]	86 (222) Rn Radon
87 (223) Fr Francium	88 226.03 Ra Radium	89 227.03 Ac Actinium	104 (261) Rf Rutherfordium	105 (262) Ha Hahnium	106 (266) Sg Seaborgium	107 (262) Ns Nielsbohrium	108 (265) Hs Hassium	109 (266) Mt Meitnerium	110 (271)	111 (272)	112 (277)	(113)	(114)	(115)	(116)	(117)	(118)

Lanthanide series	58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 (145) Pm Promethium	62 150.40 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium
Actinide series	90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Americium	96 (247) Cm Curium	97 (247) Bk Berkelium	98 (251) Cf Californium	99 (252) Es Einsteinium	100 (257) Fm Fermium	101 (260) Md Mendelevium	102 (259) No Nobelium	103 (262) Lr Lawrencium

Note: Atomic masses shown here are the 1983 IUPAC values (maximum of six significant figures).

Physical Constants

Standard acceleration of terrestrial gravity	$g = 9.80665$ m s^{-2} (exactly)
Avogadro's number	$N_0 = 6.022137 \times 10^{23}$
Bohr radius	$a_0 = 0.52917725$ Å$=5.2917725 \times 10^{-11}$ m
Boltzmann's constant	$k_B = 1.38066 \times 10^{-23}$ J K^{-1}
Electron charge	$e = 1.6021773 \times 10^{-19}$ C
Faraday constant	$\mathcal{F} = 96{,}485.31$ C mol^{-1}
Masses of fundamental particles:	
Electron	$m_e = 9.109390 \times 10^{-31}$ kg
Proton	$m_p = 1.672623 \times 10^{-27}$ kg
Neutron	$m_n = 1.674929 \times 10^{-27}$ kg
Ratio of proton mass to electron mass	$m_p/m_e = 1836.15270$
Permittivity of vacuum	$\epsilon_0 = 8.8541878 \times 10^{-12}$ C^2 J^{-1} m^{-1}
Planck's constant	$h = 6.626076 \times 10^{-34}$ J s
Speed of light in a vacuum	$c = 2.99792458 \times 10^8$ m s^{-1} (exactly)
Universal gas constant	$R = 8.31451$ J mol^{-1} K^{-1}
	$= 0.0820578$ L atm mol^{-1} K^{-1}

'alues are taken from "Quantities, Units and Symbols in Physical Chemistry," International Union of Pure and Applied Chemistry, Blackwell Scientific ublications, 1988.

Conversion Factors

Standard atmosphere	1 atm = 1.01325×10^5 Pa = 1.01325×10^5 kg m^{-1} s^{-2} (exactly)
Atomic mass unit	1 u = 1.660540×10^{-27} kg
	1 u = 1.492419×10^{-10} J = 931.4943 MeV (energy equivalent from $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = $1.6021773 \times 10^{-19}$ J = 96.48531 kJ mol^{-1}
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U.S.)	1 gallon = 4 quarts = 3.78541 L (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 metric ton = 1000 kg (exactly)
Pound	1 lb = 16 oz = 0.45359237 kg (exactly)

I. (4 points each)

A) Professor Ahmed Zewail won the 1999 Nobel Prize in Chemistry. Briefly describe the work for which he was recognized.

using fentospectroscopy in observing transition rates in chemical reactions (... ...) one such rxn was the dissociation of NaI_2

4

B) The chemical formula for the Strongest (measured) Acid in the World is $HSO_3F \cdot SbF_5$,

4

(HF · SbF5 is currently being measured, supposed to be higher than)

but the strongest theoretically predicted acid is H^+.

C) The rigorous definition of pH is $-\log\left(\gamma_{H^+}\frac{[H]}{[H_0]}\right)$, and the pH range of water is

4

0-14.

D) Define the Hammett acidity function.

$$\underbrace{-\log\left(a_{H^+}\frac{\gamma_B}{\gamma_{BH^+}}\right)}_{H_0} : -\log K_{BH^+} + \log\frac{[B]}{[BH^+]}$$

$B + H^+ \rightarrow BH^+$

4

E) State the Principle of Detailed Balance (or microscopic reversibility).

At equilibrium of a reaction, the rate of formation of products equals the rate of formation of reactants (forward rate = reverse rate)

4

II. (10 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)
k_2 17.5	29
k_1 10.5	36

$k = A e^{-Ea/RT}$

$\ln k_1 = \ln A - \frac{Ea}{R}\left(\frac{1}{T_1}\right)$

$-\left(\ln k_2 = \ln A - \frac{Ea}{R}\left(\frac{1}{T_2}\right)\right)$

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

$\ln \frac{k_1}{k_2} = \frac{Ea}{8.3145 \frac{J}{K\,mol}}\left(\frac{1}{290.5} - \frac{1}{283.5}\right)$

$\ln \frac{k_2}{k_1} = \frac{Ea}{8.3145 \frac{J}{K\,mol}}\left(8.50 \times 10^{-5} K^{-1}\right)$

$Ea = \ln\left(\frac{k_2}{k_1}\right) \div 1.02 \times 10^{-5}$

$= \ln\left(\frac{k_2}{k_1}\right)(97822)$

$= \ln\left(\frac{25.0}{20.1}\right)(97822)$

$= 21340 \frac{J}{mol} = 21.3 \frac{kJ}{mol}$

$\ln \frac{C}{C_0} = -kt$

$(29s) \ln 2 = k_1 = 20.1$

$(36s) \ln 2 = k_2 = 25.0$

−1 sf

9

III. (5 points each) Let's examine the collision theory result for the bimolecular reaction of H_2 with C_2H_4 at 273 K.

A) Calculate the reduced molar mass (in kg)

$$\mu = \left(\frac{M_x + M_y}{M_x M_y}\right) : \left(\frac{M_x M_y}{M_x + M_y}\right)$$

$$= \frac{(.002016 \frac{kg}{mol} \cdot .02803 \, kg/mol)}{(.002016 + .02803) \frac{kg}{mol}}$$

$$= .00188 \, \frac{kg}{mol}$$

5

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

$$\bar{u} = \sqrt{\frac{8RT}{\pi \mu}}$$

$$= \sqrt{\frac{8(8.3145 \frac{J}{mol \cdot K})(273 K)}{\pi \, (.00188 \frac{kg}{mol})}}$$

$$= 1750 \sqrt{\frac{J}{kg}} = 1750 \, m/s$$

5

C) Calculate A ($A = \sigma \overline{C}_{rel} N_o$) given that the collision cross section is 4.6×10^{-19} m^2

$\sigma = \pi d^2 = 4.6 \times 10^{-19}$ m^2

$A = (4.6 \times 10^{-19}$ m$^2)(1750 \frac{m}{s})(6.022 \times 10^{23}$ mol$^{-1})$

$4.86 \times 10^{8} \frac{m^3}{s\ mol}$

5

D) The measured value of A is 1.24×10^6. Compute the steric factor for the reaction.

$\frac{m^3}{mol \cdot s}$

$P \cdot A_o = A$

$(P) \; 4.86 \times 10^{8} \frac{m^3}{mol \cdot s} = 1.24 \times 10^{6} \frac{m^3}{mol \cdot s}$

$P = .00255$

5

E) Describe the effects that the steric factor corrects for.

The steric factor corrects for the necessity for two colliding particles to be oriented correctly in order to react (which means fewer molecules react than collide)

5

IV. (10 points) The mechanism for the decomposition of NO_2Cl is

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

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

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.

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

$= 0$ (after time)

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

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

$$\frac{d[Cl_2]}{dt} \text{ Rate} = k_2[NO_2Cl][Cl]$$

$$= k_2[NO_2Cl]\left(\frac{k_1[NO_2Cl]}{k_{-1}[NO_2] + k_2[NO_2Cl]}\right)$$

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

10

V. (5+5+5 points) The Lindeman mechanism accounts for the decomposition of N_2O_5 with apparent first order kinetics at high pressure. One can construct a mechanism and apply the steady state approximation to produce a differential rate law that gives this behavior.

A) Write out the Lindeman mechanism for this process. → thermally excited state

$$N_2O_5 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_5^* + M$$

$$N_2O_5^* \xrightarrow{k_2} NO_2 + NO_3$$

$$2NO_3 \xrightarrow{k_3} 2NO_2 + O_2$$

+5

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

B) Apply the steady-state approximation to obtain the differential rate law in terms of stable reactants.

$$\frac{d[N_2O_5^*]}{dt} = k_1[N_2O_5][M] - k_{-1}[N_2O_5^*][M] - k_2[N_2O_5^*] = 0$$

$$[N_2O_5^*] = \frac{k_1[N_2O_5][M]}{k_{-1}[M] + k_2}$$

+5

$$Rate = k_2[N_2O_5^*] = \frac{k_1k_2[N_2O_5][M]}{k_{-1}[M] + k_2}$$

C) Obtain the appropriate limit of the above result.

as pressure ↑, $k_{-1}[M] \gg k_2$

so $$\frac{d[N_2O_5]}{dt} = \frac{k_1k_2[N_2O_5][M]}{k_{-1}[M]} = \frac{k_1k_2[N_2O_5]}{k_{-1}}$$

+5

1st order kinetics . $K_1k_2[N_2O_5]$

$$K_1 = \frac{k_1}{k_{-1}}$$

VI. (10 points) The reaction $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ is first order, with a rate constant of $2.2 \times 10^{-5}\ s^{-1}$ at 320°C. The partial pressure of $SO_2Cl_2(g)$ in a sealed vessel at 320°C is 1.0 atm. How long will it take for the partial pressure of $SO_2Cl_2(g)$ to fall to 0.50 atm?

$\ln\left(\frac{P_o}{P}\right) = kt$

$\int_{C_o}^{C} \frac{dc}{c} = \int_0^t kt$

$\ln\frac{2P_o}{P_o} = kt$

$\ln\frac{C}{C_o} = -kt$

$\ln 2 = (2.2\times10^{-5}\,s^{-1})\,t$

~~$3.15\times10^{4}\,s = t$~~

SF

9

$-\frac{dc}{dt} = kc$

$-\int \frac{dc}{c} = \int_0^t k\,dt$ $\ln\frac{c}{C_o} = kt$

VII. (10 points) The dimerization of tetrafluoroethylene (C_2F_4) to octafluorocyclobutane (C_4F_8) is second order in the reactant C_2F_4, and at 450 K its rate constant is $k = 0.0448\ L\ mol^{-1}\ s^{-1}$. If the initial concentration of C_2F_4 is $0.100\ mol\ L^{-1}$, what will its concentration be after 205 s?

$2C_2F_4 \longrightarrow C_4F_8$

~~$\ln\left(\frac{C_o}{C}\right) = kt$~~

Not 1st order

~~$\ln .1 - \ln C$ $\ln\left(\frac{.100M}{C}\right) = .0448\frac{L}{mol\cdot s}(205\,s)$~~

~~$\ln .100 - \ln C$~~

~~$C = [C_2F_4] = .0399\ \frac{mol}{L}$~~

0

$-\frac{1}{2}\frac{dc}{dt} = kc^2$

$\int_{C_o}^{C}\frac{dc}{c^2} = \int_0^t 2k\,dt$ $-\frac{1}{c}\Big]_{C_o}^{C} = -2kt$ $\frac{1}{C} - \frac{1}{C_o} = 2kt$