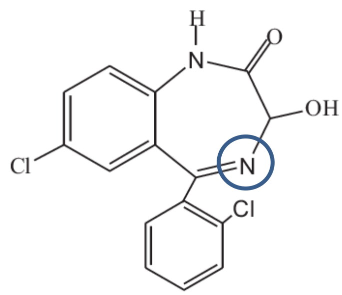
EXAM IV – November 25, 2019

You will have 75 minutes to complete this exam. Please show all work in the space provided or on the attached scratch page. Remember to report your final answers with the correct units and significant figures, as appropriate. A Periodic Table and a sheet of helpful constants, conversion factors, and equations are provided for your use. GOOD LUCK!!

1. (14 pts) Lorazepam, $C_{15}H_{10}Cl_2N_2O_2$, belongs to a class of molecules called benzodiazepines (or sometimes "benzos"). It is marketed under the brand name Ativan and commonly prescribed as a sedative and anti-anxiety medication.



a. Lorazepam is a weak base. Abbreviating its formula as $R_1{=}\ddot{N}{-}R_2$ (where the N is the atom circled at left), **complete the equation** below for its ionization in water. On the product side, label the **conjugate acid and conjugate base**.

$R_1\ddot{N}R_2\ (aq) \quad + \quad H_2O\ (l)$

b. There are many benzodiazepine drugs. (For example, oxazepam is structurally identical to lorazepam, except that it has a hydrogen in place of one of the Cl atoms.) Suppose that you wanted to compare the basicity of a series of benzodiazepines. Briefly, **what values** would you look up, and **how would you choose the strongest base**?

2. (16 pts) Sulfuric acid, H_2SO_4, is arguably the most commonly used chemical in the world, with myriad applications. Among them, you may know that it is the "battery acid" in most car batteries.

Suppose that a mechanic keeps a solution of lye (more formally known as sodium hydroxide, NaOH) on hand to neutralize any H_2SO_4 that happens to leak from used car batteries.

a. What is the pH of a 6.0 M solution of NaOH?

Question 2, continued: Note that you can answer part (b) without answering part (a).

b. **Complete and balance** the "molecular" equation below for the neutralization reaction between NaOH and H_2SO_4 in aqueous solution.

NaOH (*aq*) + H_2SO_4 (*aq*)

3. (18 pts) Phosgene, $COCl_2$, is used in manufacturing bulletproof glass. (A poisonous gas, it was used as a chemical warfare agent during World War I.) $COCl_2$ is produced by reacting carbon monoxide and chlorine gas in an exothermic process:

$$CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g) \qquad \Delta H < 0$$

a. Write an expression for the equilibrium constant, K_P.

b. Under typical conditions, $K_P = 0.10$. Do reactants or products dominate at equilibrium? How do you know?

<u>For parts (c) through (e): Suppose that you wish to shift the position of this equilibrium as far to the left as possible</u>, in order to minimize health risks of phosgene exposure.

c. Should you **compress or expand** the reaction vessel? Explain briefly.

d. Should you **raise or lower the temperature?** Explain briefly.

(Extra space here…)

4. (18 pts) Radioactive iodine, ^{131}I, is used to treat hyperthyroidism (overactive thyroid) by shrinking the thyroid gland. It decays according to first-order kinetics. $ln\frac{[A]_t}{[A]_0} = -kt$

a. Suppose you monitored the concentration of ^{131}I after it was administered. Clearly **label the axes** below to show what you would graph to confirm that the reaction is first order in ^{131}I. Then explain specifically **how you would determine the rate constant** from your graph.

How to determine k (be specific):

b. The half-life of ^{131}I is 8.021 days. Calculate the rate constant for its decay.

c. How much time must pass after administration of ^{131}I before its concentration has decayed to 5.0% of its initial value?

5. (12 pts) The hemoglobin in our blood (abbreviated Hb) readily binds to carbon monoxide. (This is a key factor in CO poisoning, as the CO displaces oxygen.) The rate of this binding reaction was studied at 20 °C. [1 μM = 1 × 10^{-6} M = 1 μmol/L]

$$Hb + CO \rightarrow Hb\text{—}CO$$

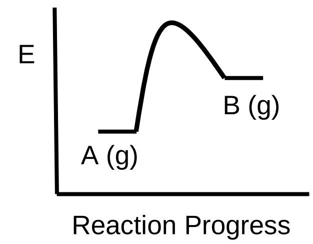
$[Hb]_0$ (μM)	$[CO]_0$ (μM)	Initial Rate (μM/s)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

a. Determine the rate law for the reaction, clearly specifying the order with respect to each reactant.

b. Calculate the rate constant.

6. (10 pts) Suppose that the energy profile below represents the following reaction: A (g) $\rightarrow$ B (g)

a. Is the reaction spontaneous? How do you know?



b. On the plot above, **draw a double-headed arrow** corresponding to the activation energy of the reaction. (Make sure your understanding is clear.)

c. Suppose that a catalyst is added to the reaction. Draw a **new profile on the same plot above** to show how this would affect the reaction.

d. Briefly list **one other step** you could take to speed up the reaction.

7. (17 pts) Uric acid ($C_5H_4N_4O_3$, $K_a = 1.29 \times 10^{-4}$) can collect in joints, giving rise to a medical condition known as gout. What is the pH of a 0.0650 M solution of uric acid? [**Hint:** Find the equilibrium concentration of H_3O^+.]

$$C_5H_4N_4O_3\ (aq) + H_2O\ (l) \rightleftharpoons C_5H_3N_4O_3^-\ (aq) + H_3O^+\ (aq) \qquad K_a = 1.29 \times 10^{-4}$$

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If there is material to be graded here, make sure that it is clearly labeled, and that your name is written on top of this page.

Constants, Conversion Factors and Equations

Constants and Conversion Factors:

$h = 6.626 \times 10^{-34}$ J·s

$c = 2.9979 \times 10^{8} \frac{\text{m}}{\text{s}}$

$1 \text{ J} = 1 \frac{\text{kg} * \text{m}^2}{\text{s}^2}$

$N_A = 6.022 \times 10^{23}$

$R = 0.08206 \frac{L \cdot atm}{mol \cdot K} = 8.31451 \frac{J}{mol \cdot K}$

1 cal = 4.184 J = 1×10^{-3} Cal

1 atm = 760 Torr = 101.3 kPa = 1.013 bar

Equations:

$d = \frac{m}{\text{V}}$

$\nu = \frac{c}{\lambda}$

$E_{\text{photon}} = h\nu$

E_K (ejected electron) = $E_{\text{photon}} - \phi$

$E_K = \frac{1}{2} m\text{v}^2$

$\Delta E = -2.18 \times 10^{-18} \text{J} \left(\frac{1}{\text{n}_\text{f}^2} - \frac{1}{\text{n}_\text{i}^2} \right)$

$E_{\text{photon}} = |\Delta E|$

$\lambda_{\text{matter}} = \frac{h}{m\text{v}}$

$\text{M}_\text{i}\text{V}_\text{i} = \text{M}_\text{f}\text{V}_\text{f}$

$PV = nRT$

$PM = dRT$

$P_A = \chi_A P_{total}$

$\chi_A = \frac{n_A}{n_{total}}$

$E_K = \frac{1}{2} mv^2$

$\overline{E}_K = \frac{3}{2} RT$

$v_{rms} = \sqrt{\frac{3\,RT}{M}}$

$q = mC_s\Delta T$

$q_{rxn} = -q_{soln}$

$\Delta H = q_P$

$\Delta G = \Delta H - T\Delta S$

$\Delta S^\circ_{rxn} = \Sigma[nS^\circ_m \text{ (products)}] - \Sigma[nS^\circ_m \text{ (reactants)}]$ (similar for ΔG°, ΔH°)

$\Delta G = \Delta G^\circ + RT(\ln Q)$

$\Delta G^\circ = -RT(\ln K)$

$k = Ae^{\frac{-E_a}{RT}}$

First order: $\ln[A]_t = -kt + \ln[A]_0$

$t_{1/2} = \frac{0.693}{k}$

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

$pH = -\log[H_3O^+]$

$pH + pOH = pK_w$ ($pK_w = 14.00$ at 25 °C)

$K_a \times K_b = K_w$

Main groups | Transition metals | Main groups

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.998403	10 Ne 20.1797
11 Na 22.98977	12 Mg 24.305											13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.41	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.33	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0254	89 †Ac 227.0278	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun	111 Uuu	112 Uub		114 Uuq		116 Uuh		

*Lanthanide series	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)