

Final Exam**5.111**

Write your name and your TA's name below. **Do not open the exam until the start of the exam is announced.** 1) Read each part of a problem thoroughly. Many of a problem's latter parts can be solved without having solved earlier parts. If you need a numerical result that you were not successful in obtaining for the execution of a latter part, make a physically reasonable approximation for that quantity. 2) Significant figure usage and units must be correct. 3) If you don't understand what the problem is requesting, raise your hand. 4) Physical constants, formulas and a periodic table are given on the last 2 pages. You may detach these pages **once the exam has started.**

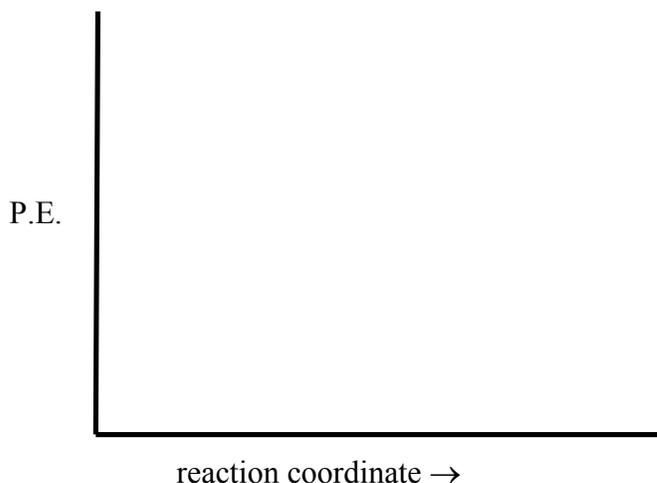
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	TOTAL	(200 points) _____

TA _____ Name _____

1. KINETICS AND EQUILIBRIUM (29 points total)

For a reversible, one step reaction $2A \rightleftharpoons B + C$, the rate constant for the forward reaction is $406 \text{ M}^{-1} \text{ min}^{-1}$ and the rate constant for the reverse reaction is $244 \text{ M}^{-1} \text{ min}^{-1}$. The activation energy for the forward reaction is 26.2 kJ mol^{-1} and that for the reverse reaction is 42.4 kJ mol^{-1} .

(a) (5 points) On the axes below, draw a reaction coordinate diagram for this reaction, showing the curve, and labeling (i) ΔE , (ii) $E_{a,f}$, and (iii) $E_{a,r}$. State whether the reaction is endothermic or exothermic.



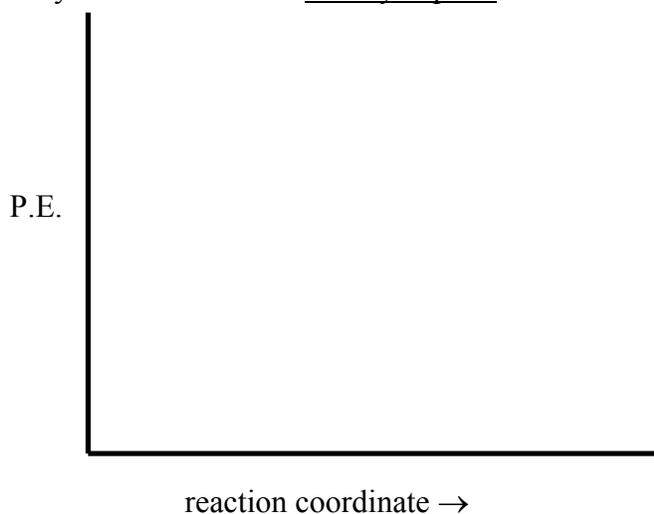
(b) (4 points) Calculate ΔE for this reaction ($2A \rightleftharpoons B + C$). Show your work.

(c) (4 points) Calculate the equilibrium constant (K) for this reaction ($2A \rightleftharpoons B + C$). Show your work.

(d) (6 points) (i) Predict the effect of raising the temperature on the forward **rate constant (k_1)**, and (ii) compare it to the effect of raising the temperature on the **reverse rate constant (k_{-1})**. Explain your answer.

(e) (4 points) Predict the effect of raising the temperature on the **equilibrium constant** (K). Explain your answer.

(f) (6 points) On the axes below, draw a single reaction coordinate diagram, that includes both a catalyzed (**dashed line**) and a noncatalyzed (**solid line**) reaction curve, indicating the effect of adding a catalyst to the reaction. Briefly explain what a catalyst does.



2. ENZYME KINETICS (7 points total)

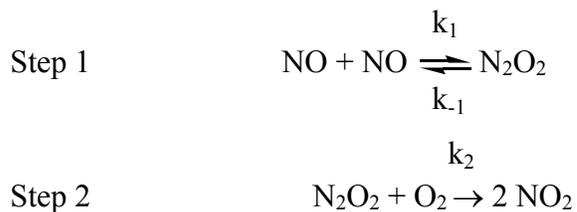
The enzyme penicillinase degrades the antibiotic penicillin, leading to bacterial resistance. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 5 \times 10^{-5} \text{ mol/L}$ and $k_2 = 2 \times 10^3 \text{ s}^{-1}$.

(a) (4 points) Calculate the maximum rate of this reaction if the total enzyme concentration is $7 \times 10^{-5} \text{ M}$.

(b) (3 points) Find the substrate concentration for which the rate will be half of that calculated in part (a). No need to show work.

3. REACTION MECHANISMS (8 points total)

For the reaction $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$, write the rate law for the formation of NO_2 using the following mechanistic proposal and the steady state approximation. Be sure to eliminate intermediates from the rate expression. **Do not** make any assumptions about fast or slow steps (i.e. do not simplify your expression by assuming anything about the relative magnitude of k_{-1} and k_2). Show all work for full credit.



4. TRANSITION METALS (16 points total)

Ni^{2+} in a coordination complex is paramagnetic. (a) Draw the crystal field splitting diagrams showing relative splitting energies for an octahedral crystal field and a tetrahedral crystal field, labeling the diagrams with the (b) names of the d-orbitals, and (c) and symbols for octahedral and tetrahedral field splitting energy. (e) Fill both diagrams with the proper number of electrons and state below each diagram whether the geometry is consistent with a paramagnetic species.

OCTAHEDRAL DIAGRAM

TETRAHEDRAL DIAGRAM

5. OXIDATION-REDUCTION (8 points total)

When a ruthenium chloride solution was electrolyzed for 32 minutes with a 60-mA current, 40. mg of ruthenium was deposited. Calculate the oxidation number of Ru in the ruthenium chloride solution.

6. REDOX AND THERMODYNAMICS (12 points total)

Given that the standard reduction potentials for vitamin B₁₂ and the protein flavodoxin are

$$\text{Vitamin B}_{12} \ E^\circ = -0.526 \text{ V}$$

$$\text{Flavodoxin} \ E^\circ = -0.230 \text{ V}$$

(a) (8 points) Calculate ΔG° in kJ for the one-electron reduction of vitamin B₁₂ by flavodoxin.

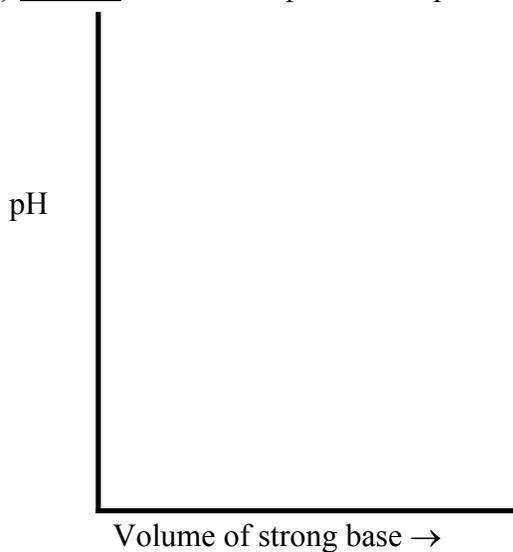
(b) (4 points) State whether vitamin B₁₂ or flavodoxin is the better reducing agent. Explain your answer.

7. ACID-BASE EQUILIBRIA (10 points total)

Ketoacidosis is a serious medical condition caused by a build-up of ketone bodies. A 0.50 M solution of one of those ketone bodies, acetoacetic acid, is found to have a pH of 1.95. Determine the K_a of acetoacetic acid. Show all work.

8. ACID-BASE TITRATION CURVES (5 points total)

On the axes below, draw a titration curve for a weak acid/strong base titration. **(a)** Mark the equivalence point, **(b)** mark the half-equivalence point, **(c)** mark the buffering region with a double headed arrow, and **(d)** indicate whether the pH at the equivalence point should be < 7 , 7 , or > 7 .

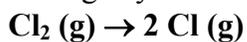


9. BUFFERS (10 points total)

Your UROP supervisor wants you to make a buffer solution with an equal number of moles of acetic acid (CH_3COOH) and acetate (CH_3COO^-). Calculate to **one significant figure** the minimum number of **moles** of each that you must use to prevent a change in the pH of more than 0.20 pH units after the addition of 1.0 mL of 5.00 M HCl (aq) to 100.0 mL of the buffer solution, generating 101.0 mL of solution. The K_a of acetic acid is 1.8×10^{-5} .

10. THERMODYNAMICS (12 points total)

Without doing any calculations, predict the answers to the following questions for this reaction:



(a) (4 points) Predict if ΔH° for this reaction is endothermic, exothermic, or zero. Explain your answer.

(b) (4 points) Predict if ΔS° is positive, negative, or zero. Explain your answer.

(c) (4 points) Predict whether this reaction is spontaneous at all temperatures. Explain your answer.

11. MOLECULAR ORBITAL THEORY (26 points total)

(a) (4 points) (i) Briefly compare in words or pictures the probability density (ψ^2) between two nuclei for a σ orbital with that of a σ^* orbital. (ii) Explain how this difference in probability density relates to the relative energies of electrons in these two types of molecular orbitals.

(b) (10 points) **(i)** Draw the MO diagram for the **valence electrons of N₂**. Label the **(ii)** atomic and **(iii)** molecular orbitals, including the x, y, and z designations where appropriate. **(iii)** Fill both the atomic and molecular orbitals with the proper number of electrons. **(iv)** Draw and label the Energy axis. Use the full space available to spread out your energy levels.

(c) (3 points) Write the valence electron configuration for N₂ from the MO diagram above.

(d) (3 points) Calculate the bond order for N₂ based on the MO diagram above.

(e) (6 points) **(i)** Arrange the following from lowest to highest ionization energy: N, N₂, N₂⁻

Lowest IE _____ Highest IE

(ii) Explain your order:

12. LEWIS STRUCTURES, VSEPR, and HYDRIBIZATION (25 points total)**(a) For SF₄ (11 points)**

(i) (4 points) Draw the most stable Lewis structure for SF₄ including lone pairs. Indicate any non-zero formal charge(s) and draw any resonance structures if appropriate.

(ii) (3 points) SN is _____.

(iii) (2 points) The geometry of the molecule is _____ (example: linear).

(iv) (2 points) Circle the expected F-S-F angle or angles

<90; 90°; >90; <109.5°; 109.5°; >109.5°; <120°; 120°; >120°

(b) For NH₃ (14 points)

(i) (4 points) Draw the most stable Lewis structure for NH₃ including lone pairs. Indicate any non-zero formal charge(s) and draw any resonance structures if appropriate.

(ii) (2 points) The geometry of the molecule is _____ (example: linear)

(iii) (2 points) Circle the expected H-N-H angle or angles:

<90; 90°; >90; <109.5°; 109.5°; >109.5°; <120°; 120°; >120°

(iv) (6 points) Write the symmetry of an N-H bond (example σ), give the hybrid or atomic orbital (with their principle quantum numbers) that overlap to form each bond. Where appropriate, include the x,y,z designations.

13. ORBITALS AND PERIODIC TRENDS (12 points total)

Circle the correct italicized answer and briefly explain your choice.

(a) A 1s orbital of a multi-electron atom is *lower* *higher* in energy than the 1s orbital of hydrogen.

Explanation:

(b) In general, ionization energy *increases* *decreases* down a column of the periodic table.

Explanation:

(c) Low electronegativity is associated with low electron affinity and *high* *low* ionization energy.

Explanation:

14. PHOTOELECTRIC EFFECT (12 points total)

Explain the following observations.

(a) (4 points) Classical physics predicted that the number of electrons ejected from a metal surface would be unaffected by increasing the intensity of the light. However, experiment showed that an increased number of electrons were ejected as the intensity of light was increased. Explain this experimental observation.

(b) (4 points) Classical physics predicted that the kinetic energy of electrons ejected from a metal surface would increase as the intensity of light increased. However, experiment showed that the kinetic energy of the electrons did not change as the intensity of light was increased. **(i)** Identify a property of light that was found by experiment to affect the kinetic energy of the ejected electrons and **(ii)** briefly explain why this property has such an effect.

(c) (4 points) Explain what threshold frequency is and why the value is dependent on the metal in question.

15. PHOTON EMISSION (8 points total)

A new prototype UV light source emits photons at a wavelength of 388.65 nm.

(a) (4 points) Calculate the energy per photon in **Joules** to **four significant figures**.

(b) (4 points) Calculate the total energy (in **kJ** to **three significant figures**) associated with the emission of 0.0166 moles of photons at this wavelength.

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

$$h = 6.6261 \times 10^{-34} \text{ J s}$$

$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$$

$$m_e = 9.10939 \times 10^{-31} \text{ kg}$$

$$R = 8.314 \text{ J/(K mol)} \quad R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$R_H = 2.17987 \times 10^{-18} \text{ J}$$

$$e = 1.60218 \times 10^{-19} \text{ C} \quad 1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$$

$$\epsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

$$K_w = 1.00 \times 10^{-14} \quad \& \quad 14.00 = \text{pH} + \text{pOH at } 25.0^\circ\text{C}$$

$$\mathfrak{F} \text{ (Faraday's constant)} = 96,485 \text{ C mol}^{-1}$$

Electromagnetic Spectrum:
Violet ~ 400-430 nm
Blue ~ 431-490 nm
Green ~ 491-560 nm
Yellow ~ 561-580 nm
Orange ~ 581-620 nm
Red ~ 621-700 nm

Complementary Colors: red/green,
blue/orange, yellow/violet

$\Gamma < \text{Br}^- < \text{Cl}^-$ (weak field ligands)

$< \text{F}^- < \text{OH}^- < \text{H}_2\text{O}$ (intermediate)

$< \text{NH}_3 < \text{CO} < \text{CN}^-$ (strong field ligands)

$$1 \text{ C} \cdot \text{V} = 1 \text{ J} \quad 1 \text{ J} = 1 \text{ kgm}^2 \text{ s}^{-2}$$

$$1 \text{ A} = 1 \text{ C/s} \quad 1 \text{ W} = 1 \text{ J/s}$$

$$\ln = 2.3025851 \log$$

$$1 \text{ Bq} = 1 \text{ nuclei/sec}$$

$$x = [-b \pm (b^2 - 4ac)^{1/2}] / 2a \quad ax^2 + bx + c = 0$$

$$\text{K.E.} = \frac{1}{2} mv^2 \quad p = mv \quad \lambda = \frac{h}{p}$$

$$E = hv = hc/\lambda \quad c = v\lambda$$

$$E_n = -\frac{Z^2 R_H}{n^2} \quad E_{n_l} = -\frac{Z_{\text{eff}}^2 R_H}{n^2}$$

for $n_f < n_i \dots \dots$ for $n_f > n_i \dots \dots$

$$v = \frac{Z^2 R_H}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad v = \frac{Z^2 R_H}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$U(r) = (z_1 z_2 e^2) / (4\pi\epsilon_0 r)$$

$$\text{Electronegativity} = (\text{IE} + \text{EA}) / 2$$

$$\Delta H_r^\circ = \Sigma \Delta H_B(\text{reactants}) - \Sigma \Delta H_B(\text{products})$$

$$\Delta H_r^\circ = \Sigma \Delta H_f^\circ (\text{products}) - \Sigma \Delta H_f^\circ (\text{reactants})$$

$$\Delta S_r^\circ = \Sigma S^\circ (\text{products}) - \Sigma S^\circ (\text{reactants})$$

$$\Delta G_r^\circ = \Sigma \Delta G_f^\circ (\text{products}) - \Sigma \Delta G_f^\circ (\text{reactants})$$

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

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

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

$$\Delta G = RT \ln Q/K$$

$$\ln (K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$$

$$PV = nRT$$

$$s = k_H P$$

$$\text{pH} \approx \text{pK}_a - \log ([\text{HA}]/[\text{A}^-])$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{pOH} = -\log [\text{OH}^-]$$

$$K_w = K_a K_b \quad \text{pK} = -\log K$$

$$Q = It$$

$$\Delta G^\circ_{\text{cell}} = -(n)(\mathfrak{F}) \Delta E^\circ_{\text{cell}}$$

$$\Delta E^\circ(\text{cell}) = E^\circ(\text{cathode}) - E^\circ(\text{anode})$$

$$\Delta E^\circ = E^\circ(\text{reduction}) - E^\circ(\text{oxidation})$$

$$\Delta E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/n\mathfrak{F}) \ln Q$$

$$\Delta E_{\text{cell}} = E^\circ_{\text{cell}} - [(0.025693 \text{ V})(\ln Q)/n] \text{ at } 25.0^\circ\text{C}$$

$$\ln K = (n\mathfrak{F}/RT) \Delta E^\circ$$

$$A = A_0 e^{-kt} \quad N = N_0 e^{-kt} \quad A = kN$$

$$[A] = [A]_0 e^{-kt} \quad t_{1/2} = \ln 2 / k$$

$$1/[A] = 1/[A]_0 + kt \quad t_{1/2} = 1 / k[A]_0$$

$$\ln(k) = \ln(A) - E_a/RT \quad k = A e^{-(E_a/RT)}$$

$$\ln(k_2/k_1) = -(E_a/R) (1/T_2 - 1/T_1)$$

$$d[\text{P}]/dt = (k_2[\text{E}]_0[\text{S}]) / ([\text{S}] + K_m)$$

$$V_{\text{max}} = k_2[\text{E}]_0$$

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18 ^a
IA	IIA	IIIB	IVB	VB	VIB	VIIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA _b

The Active Metals

1	2	3	4
H	Li	Na	Be
1.008	6.941		9.012
	11	12	
	Na	Mg	
	22.990	24.305	

Noble Gases

2	10	18
He	Ne	Ar
4.003	20.179	39.948

The Nonmetals

5	6	7	8	9
B	C	N	O	F
10.81	12.011	14.007	15.999	18.998
13	14	15	16	17
Al	Si	P	S	Cl
26.982	28.086	30.974	32.06	35.453

Transition Elements

19	20	21	22	23	24	25	26	27	28	29	30
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
39.098	40.08	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.38
37	38	39	40	41	42	43	44	45	46	47	48
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.906	106.42	107.868	112.41
55	56	57	* 72	73	74	75	76	77	78	79	80
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
132.905	137.33	138.905	178.49	180.948	183.85	186.21	190.2	192.22	195.08	196.966	200.59
87	88	89	† 104	105	106						
Fr	Ra	Ac	Unq	Unp	Unh						
(223)	226.025	227.028	(261)	(262)	(263)						

Inner Transition Metals

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.908	144.24	(145)	150.36	151.96	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	231.036	238.029	237.048	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

* Lanthanides

† Actinides

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5.111 Principles of Chemical Science
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