

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) Show all steps of a calculation and indicate all values used to obtain your quantitative result. Significant figure usage 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	(300 points) _____

TA _____ Name _____

1. TRANSITION METALS (35 points total)

(a) (3 points) Calculate the d-count for Fe^{2+}

(b) (14 points) Draw the octahedral crystal field splitting diagrams for Fe^{2+} with both weak and strong octahedral fields. Label the diagrams weak and strong field, high spin and low spin, give the names of the d-orbitals, and label the appropriate orbital sets e_g and t_{2g} .

(c) (4 points) Calculate the crystal field stabilization energy (CFSE) for **high spin** Fe^{2+} . Do not include pairing energy.

(d) (4 points) Calculate the crystal field stabilization energy (CFSE) for **low spin** Fe^{2+} . Do not include pairing energy.

(e) (4 points) If the Fe^{2+} coordination complex is $[\text{Fe}(\text{CN})_6]^{4-}$, state whether you expect the complex to be high spin or low spin? Explain your answer.

(f) (6 points) Calculate the octahedral crystal field splitting energy in **kJ/mol** for $[\text{Fe}(\text{CN})_6]^{4-}$, if the wavelength of the most intensely absorbed light is 305 nm.

2. TRANSITION METALS (10 points total)

(i) Draw d-orbitals, d_z^2 and d_{yz} on top of the diagrams below, and (ii) predict the relative energies of just these two d-orbitals for the linear molecule drawn along the Z-axis. Explain your reasoning.

3. TRANSITION METALS (16 points total)

Ni^{2+} in a coordination complex is paramagnetic. Draw the crystal field splitting diagrams for an octahedral crystal field and a tetrahedral crystal field, labeling the d-orbitals. State below each diagram whether the geometry is consistent with a paramagnetic species.

4. CHEMICAL KINETICS (18 points total)

The following data were obtained for the reaction $A + B + C \rightarrow \text{products}$.

Experiments	Initial concentrations, mol•L ⁻¹			Initial rates, mol•L ⁻¹ •s ⁻¹
	[A] ₀	[B] ₀	[C] ₀	
1	0.10	0.10	0.10	1.2×10^{-3}
2	0.20	0.10	0.10	2.4×10^{-3}
3	0.10	0.30	0.10	3.5×10^{-3}
4	0.20	0.10	0.15	5.5×10^{-3}

(a) (3 points) Determine the order of the reaction with respect to A

(b) (3 points) Determine the order of the reaction with respect to B

(c) (3 points) Determine the order of the reaction with respect to C

(d) (3 points) Write the rate law for the overall reaction.

(e) (3 points) Determine the order of the overall reaction.

(f) (3 points) Calculate the rate constant k

5. CHEMICAL KINETICS AND CHEMICAL EQUILIBRIUM (32 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 direction is 42.4 kJ mol^{-1} .

(a) (5 points) Draw a reaction coordinate diagram (Potential energy versus Reaction coordinate) for this reaction and state whether the reaction is endothermic or exothermic. Label (i) ΔE , (ii) $E_{a,f}$, (iii) $E_{a,r}$.

(b) (5 points) Calculate ΔE for this reaction ($2A \rightleftharpoons B + C$). Show your work.

(c) (5 points) Calculate the equilibrium constant for this reaction ($2A \rightleftharpoons B + C$). Show your work.

(d) (6 points) Predict the effect of raising the temperature on the forward rate constant, and compare it to the effect of raising the temperature on the reverse rate constant. Explain your answer.

(e) (5 points) Predict the effect of raising the temperature on the equilibrium constant. Explain your answer.

(f) (6 points) Draw a single reaction coordinate diagram (Potential energy versus Reaction coordinate), that includes both a catalyzed and a noncatalyzed reaction trace, indicating the effect of adding a catalyst to the reaction. Briefly explain how a catalyst works.

6. ENZYME KINETICS (7 points)

Enzyme penicillinase degrades 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).

7. CHEMICAL KINETICS (12 points total)

Consider the formation of a DNA double helix from strands A and B. In the first step, strands A and B form an unstable helix (UH), and in step 2, the unstable helix (UH) converts to a stable helix (SH).



(a) (2 points) Indicate the molecularity of the first step.

(b) (2 points) Indicate the molecularity of the second step.

(c) (8 points) Write the rate law for the formation of the stable helix (SH) assuming the equilibrium between A+B and UH is fast. Be sure to eliminate intermediates from the rate expression. Show all work for full credit.

8. NUCLEAR CHEMISTRY (10 points)

The activity of a strontium-90 source is 3.0×10^{14} Bq and its half-life is 28.1 years. Calculate the activity after 75.0 years have passed. Show all work.

9. ACID-BASE EQUILIBRIA (10 points)

A 0.250 M aqueous solution of $\text{HC}_4\text{H}_7\text{O}_2$ is found to have a pH of 2.72. Determine K_a for butyric acid to two significant figures. Show all work.

10. ACID-BASE EQUILIBRIA (25 points)

Answer parts a-c for the titration of 100.00 mL of weak acid HCOOH ($K_a = 1.8 \times 10^{-4}$) with 0.0750 M strong base NaOH at 25.0°C.

(a) (5 points) Calculate the number of moles of HCOOH in 100.00 mL of an aqueous solution if it requires 15.90 mL of 0.0750 M NaOH to titrate it to the equivalence (stoichiometric) point.

(b) (12 points) Calculate the pH at the equivalence (stoichiometric) point. Show all work. Check any assumption you make for full credit.

(c) (8 points) Calculate the pH **past** the equivalence (stoichiometric) point when 1.0 mL of extra NaOH has been added. Show all work.

11. ACID-BASE EQUILIBRIA (5 points)

Draw a titration curve for a weak acid/strong base titration. (a) Label the axes, (b) mark the equivalence point, (c) mark the half-equivalence point, (d) mark the buffering region, and (e) indicate whether the pH at the equivalence point should be < 7 , 7 , or > 7

12. OXIDATION-REDUCTION (10 points)

For the following reagents under standard conditions:

$\text{Au} (s)$, $\text{Cl}_2 (g)$, $\text{Pb} (s)$, $\text{Sn} (s)$, $\text{Ni} (s)$, $\text{Cd} (s)$, $\text{Zn} (s)$, $\text{Au}^+ (aq)$, $\text{Cl}^- (aq)$, $\text{Pb}^{2+} (aq)$, $\text{Sn}^{2+} (aq)$, $\text{Ni}^{2+} (aq)$, $\text{Zn}^{2+} (aq)$

Standard Reduction Potentials at 25°C

Half-Reactions	E° (volts)
$\text{Au}^+ (aq) + e^- \Rightarrow \text{Au} (s)$	1.69
$\text{Cl}_2 (g) + 2e^- \rightarrow 2\text{Cl}^- (aq)$	0.14
$2\text{H}^+ (aq) + 2e^- \Rightarrow \text{H}_2 (g)$	0
$\text{Pb}^{2+} (aq) + 2e^- \Rightarrow \text{Pb} (s)$	-0.13
$\text{Sn}^{2+} (aq) + 2e^- \Rightarrow \text{Sn} (s)$	-0.14
$\text{Ni}^{2+} (aq) + 2e^- \Rightarrow \text{Ni} (s)$	-0.23
$\text{Cd}^{2+} (aq) + 2e^- \Rightarrow \text{Cd} (s)$	-0.40
$\text{Zn}^{2+} (aq) + 2e^- \Rightarrow \text{Zn} (s)$	-0.76

(a) (3 points) State which reagent is the strongest oxidizing agent.

(b) (3 points) State which reagent is the strongest reducing agent.

(c) (4 points) State which reagent(s) will reduce $\text{Pb}^{2+} (aq)$ while leaving $\text{Cd}^{2+} (aq)$ unreacted.

13. OXIDATION/REDUCTION REACTIONS (10 points)

A tin electrode in 0.015 M $\text{Sn}(\text{NO}_3)_2$ (aq) is connected to a hydrogen electrode in which the pressure of H_2 is 1.0 bar. If ΔE is 0.061 V at 25°C, calculate the pH at 25°C of the electrolyte at the hydrogen electrode to one decimal place for this galvanic cell. Show all work.

Standard Reduction Potentials at 25°C

Half-Reactions	E° (volts)
$2\text{H}^+ (\text{aq}) + 2\text{e}^- \Rightarrow \text{H}_2 (\text{g})$	0
$\text{Sn}^{2+} (\text{aq}) + 2\text{e}^- \Rightarrow \text{Sn} (\text{s})$	-0.140

14. ELECTRONS AND TRENDS (35 points)

Answers questions a-g below.

- (a) (5 points) Circle the statement about the photoelectric effect that is incorrect.
- 1) A plot of the kinetic energy of the ejected electrons versus the frequency of the incident radiation has a slope that is equal to the value of the work function.
 - 2) All metals have a unique work function.
 - 3) The kinetic energy of the ejected electrons does not increase with the intensity of the incident radiation.
 - 4) A plot of the kinetic energy of the ejected electrons versus the frequency of the incident radiation is linear.
- (b) (4 points) Indicate the number of nodes (both radial and angular) that are present in a 3p orbital and a 3d orbital.
- 3p: Radial: Angular:
- 3d: Radial: Angular:
- (c) (4 points) Circle the set of quantum numbers that could correspond to a 5f-orbital.
- 1) $n = 5, l = 4, m = +3$
 - 2) $n = 5, l = 3, m = +4$
 - 3) $n = 5, l = 3, m = -3$
 - 4) $n = 4, l = 3, m = +1$
 - 5) $n = 4, l = 2, m = 0$

(d) (6 points) Calculate the longest-wavelength line in the series for emission into the $n = 3$ level of the hydrogen atom. Give your answers in units of nm to four significant figures.

(e) (6 points) Consider the following ground-state electronic configurations. Circle the electronic configuration that has both the highest first ionization energy and the highest electron affinity. Write the name of the corresponding atom.



(f) (5 points) Circle the ion or element that has the largest atomic radius.

- 1) S^{2-}
- 2) Cl
- 3) Cl^-
- 4) K^+
- 5) S

(g) (5 points) Circle the compound that has the bond with the most ionic character.

- 1) AgI
- 2) AgCl
- 3) AgF
- 4) KCl
- 5) KF

15. MOLECULAR STRUCTURE AND BONDING (25 points)

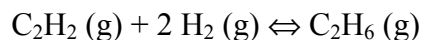
The following questions pertain to the dinitrogen monoxide molecule whose arrangement of atoms is N-N-O.

(a) (15 points) Draw at least two possible Lewis structures and indicate any nonzero formal charges. State which structure you believe is most plausible and explain (in a few words) why.

(b) (10 points) For your most plausible N-N-O Lewis structure, indicate for each bond **(i)** the bond symmetry and **(ii)** the atomic or hybrid orbitals from each of the atoms that overlap to form the bond. Where appropriate, include the x, y, or z designations with the orbitals. To describe the N-N bond, label the terminal atom N₁ and the middle atom N₂. Finally, indicate the geometry around the central atom.

16. THERMOCHEMISTRY (40 points)

Consider the following reaction:



The following may be useful.

	ΔH_f° (298K)	S° (298K)
$\text{C}_2\text{H}_6(\text{g})$	-84.68 kJ/mol	229.60 J/(K mol)
$\text{C}_2\text{H}_2(\text{g})$	226.73 kJ/mol	200.94 J/(K mol)
$\text{H}_2(\text{g})$		130.68 J/(K mol)

Throughout this problem you may make the usual assumption that ΔH° and ΔS° are independent of temperature.

(a) (8 points) Calculate the heat of reaction ($\Delta H_{\text{rx}}^\circ$). State whether the reaction is exothermic or endothermic.

(b) (8 points) Calculate ΔS° for the reaction. Explain briefly why the sign of your answer makes sense.

(c) (6 points) Calculate the equilibrium constant K at 298. K to **one** significant figure. Show all work.

(d) (6 points) Calculate the equilibrium constant K at the higher temperature of 2980 K to **one** significant figure. Show all work.

(e) (12 points) Calculate the temperature to **two** significant figures at which $K=1$, and explain briefly what is true about the spontaneity of this reaction above and below this temperature.

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 ^a VIIIA _b		
Transition Elements																			
The Active Metals																			
1 H 1.008				The Nonmetals														Noble Gases	
3 Li 6.941	4 Be 9.012																	2 He 4.003	
11 Na	12 Mg	5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar						
22.990	24.305	26.982	28.086	30.974	32.06	35.453	39.948	Transition Elements										36 Kr	83.80
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	86 Rn (222)		
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		
85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.906	106.42	107.868	112.41	114.82	118.69	121.75	127.60	126.904	131.29		
55 Cs	56 Ba	57 La	*72	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn (222)		
132.905	137.33	138.905	178.49	180.948	183.85	186.21	190.2	192.22	195.08	196.966	200.59	204.38	207.2	208.98	(209)	(210)	(222)		
87 Fr (223)	88 Ra	89 Ac	† 104 Unq (261)	105 Unp (262)	106 Unh (263)	Inner Transition Metals													
* Lanthanides																			
† Actinides																			
58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967	90 Th 232.038	91 Pa 231.036	92 U 238.029	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)				

Useful Constants And Equations

$c = 2.9979 \times 10^8 \text{ m/s}$	$\Delta G = RT \ln Q/K$
$h = 6.6261 \times 10^{-34} \text{ J s}$	$\ln (K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$
$N_a = 6.02214 \times 10^{23} \text{ mol}^{-1}$	$\text{pH} \approx \text{p}K_a - \log (\text{HA}/\text{A}^-)$
$1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$	$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad \text{pOH} = -\log [\text{OH}^-]$
$R = 8.314 \text{ J/K mol}$	$\text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ \text{C}$
$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$	$K_w = K_a K_b \quad \text{p}K = -\log K$
$m_e = 9.10939 \times 10^{-31} \text{ kg}$	$Q = It$
$R_H = 2.17987 \times 10^{-18} \text{ J}$	$\Delta G^\circ_{\text{cell}} = -(n)(\mathfrak{F}) \Delta E^\circ_{\text{cell}}$
$R_H = 13.5983 \text{ eV}$	$\Delta E^\circ(\text{cell}) = E^\circ(\text{cathode}) - E^\circ(\text{anode})$
$K_w = 1.00 \times 10^{-14} \text{ at } 25.0^\circ \text{C}$	$E_3^\circ = [n_1 E_1^\circ(\text{reduction}) - n_2 E_2^\circ(\text{oxidation})]/n_3$
$14.00 = \text{pH} + \text{pOH} \text{ at } 25.0^\circ \text{C}$	$\Delta E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/n\mathfrak{F}) \ln Q$
\mathfrak{F} (Faraday's constant) = 96,485 C mol ⁻¹	$RT/\mathfrak{F} = 0.025693 \text{ V at } 25.0^\circ \text{C}$
$1 \text{ Coulomb} \cdot \text{Volt} = 1 \text{ Joule}$	$\Delta E_{\text{cell}} = E^\circ_{\text{cell}} - [(0.025693 \text{ V})(\ln Q)/n] \text{ at } 25.0^\circ \text{C}$
$1 \text{ Bq} = 1 \text{ nuclei/sec}$	$\Delta E_{\text{cell}} = E^\circ_{\text{cell}} - [(0.0592 \text{ V})(\log Q)/n] \text{ at } 25.0^\circ \text{C}$
$[K] = 273.15 + [^\circ \text{C}]$	$\ln K = (n\mathfrak{F}/RT) \Delta E^\circ$
$1 \text{ A} = 1 \text{ C/s} \quad 1 \text{ W} = 1 \text{ J/s}$	$\mathfrak{F}/RT = 38.921 \text{ V}^{-1} \text{ at } 25.0^\circ \text{C}$
$\ln = 2.3025851 \log$	$[A] = [A]_0 e^{-kt} \quad t_{1/2} = \ln 2 / k$
$1 \text{ J} = 1 \text{ kgm}^2 \text{ s}^{-2} \quad 1 \text{ A} = 1 \text{ C/s}$	$1/[A] = 1/[A]_0 + kt \quad t_{1/2} = 1 / k[A]_0$
for $n_f < n_i \dots$	$\ln(k) = \ln(A) - E_a/RT \quad k = A e^{-(E_a/RT)}$
$v = (Z^2 R_H/h)(1/n_f^2 - 1/n_i^2)$	$\ln(k_2/k_1) = - (E_a/R) (1/T_2 - 1/T_1)$
for $n_f > n_i \dots$	$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{[S] + K_m}$
$v = (Z^2 R_H/h)(1/n_i^2 - 1/n_f^2)$	$v_{\text{max}} = k_2[E]_0$
$E = p^2/2m$	$K_m = \frac{k_{-1} + k_2}{k_1}$
$E = hv = hc/\lambda$	
$\lambda = h/p$	
$E_n = -Z^2 R_H / n^2$	
$E_{nl} = -(Z_{\text{eff}})^2 R_H / n^2$	
$x = [-b \pm (b^2 - 4ac)^{1/2}]/2a$	
$ax^2 + bx + c = 0$	
$\Delta G = \Delta H - T\Delta S$	
$s = k_H P$	
$\Delta G = \Delta G^\circ + RT \ln Q$	
$\Delta G^\circ = -RT \ln K$	