THE UNIVERSITY OF CALGARY FACULTY OF SCIENCE FINAL EXAMINATION CHEMISTRY 209

Date: Saturday, December 19th, 2015 Time: 7:00pm – 10:00pm

First Name:	Last Name:
ID:	
Please circle your lecture section:	

L01 Dr. Musgrove-Richer TR 2:00 pm L02 Dr. Sandblom TR 12:30 pm

This is a closed-book examination. The use of camera devices, MP3 Players and headphones, or wireless access devices such as cell phones, Blackberries, etc., during the examination will not be allowed. Only non-programmable Schulich-approved calculators are permitted. A Chemical Data Sheet is provided at the end of the exam and can be removed for quick reference.

Instructions:

All questions must be answered to obtain full points. The answers to the multiple-choice section must be entered on the optical score sheet **within** the 3 hour exam time. The answers to the long answer questions must be written in the space provided on the question sheets.

This test consists of **24 multiple choice** questions worth 2 points each (total 48 points) and **4 long answer** questions (total 42 points). The total value for the test is 90 points. The exam has **14 pages** (including this one), so please make sure you have all 14 pages.

AT THE END OF THE EXAMINATION, HAND IN THE OPTICAL SCORE SHEET AND THE ENTIRE EXAM PAPER.

Failing to encode this Exam Booklet or your Optical Score Sheet correctly for your name, ID, version letter and lecture section will result in the loss of two points.

Sec II - Q1	Sec II - Q2	Sec II - Q3	Sec II - Q4
Do not write in the shaded part. For marking only.			

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<u>SECTION I – Machine-graded section (Total value 48)</u> <u>To be answered on Optical Score Sheet</u>

- 1. Two reactions both follow the form $A + B \rightarrow products$. Reaction 1 has rate constant $k = 25.6 \text{ mol L}^{-1} \text{ s}^{-1}$, while Reaction 2 has a rate constant $k = 65.2 \text{ mol L}^{-1} \text{ s}^{-1}$. If [A] and [B] are the same for both reactions, which one will have the fastest rate of disappearance of A?
 - a. Reaction 1 will have the largest rate
 - b. Reaction 2 will have the largest rate
 - c. Both reactions will have the same rate
 - d. Not enough information is given to determine the rate
- 2. Tetrafluoroethylene can be converted to octafluorocyclobutane and the rate constant for this process is 0.0448 L mol⁻¹ s⁻¹. If the starting concentration of tetrafluoroethylene is 1.0 M, how much will remain after 3.7 minutes?
 - a. 4.6 x 10⁻¹ M
 - b. 1.1 x 10⁻¹ M
 - c. 9.1 x 10⁻² M
 - d. $4.8 \times 10^{-5} M$
- 3. A student in the CHEM 209 lab performed 5 replicates of a titration during class, but when they got home they realized that one of their measurements was noticeably larger than the other 4. What is the **best** way that the student should handle this measurement while writing up their lab report?
 - a. Keep the data point because no known experimental error was made.
 - b. Discard the data point if it is obviously different from the rest.
 - c. Discard the data point only if it is more than one standard deviation from the average value.
 - d. Discard the data point only if $G_{calc} > G_{table}$ in the Grubbs test.

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Use this information to answer questions 4-6.

Ammonium hydrogen sulfide decomposes according to this endothermic reaction ($\Delta H = 93 \text{ kJ mol}^{-1}$):

$$NH_4HS(s) \rightleftharpoons H_2S(g) + NH_3(g)$$
 $K = 0.11$ at 250. ${}^{0}C$

$$K_a$$
 of H_2S is 1.0×10^{-7}

- 4. Predict, if possible, what will happen if a mixture contains 1.0 bar of each of hydrogen sulfide (H₂S) and ammonia (NH₃).
 - a. Ammonium hydrogen sulfide will be formed.
 - b. Ammonium hydrogen sulfide will be consumed.
 - c. The amount of ammonium hydrogen sulfide needs to be specified.
 - d. The volume of the container needs to be specified.
- 5. Determine K at 512 °C.
 - a. 1.1 x 10⁻¹
 - b. 2.3 x 10⁻¹
 - c. 1.4×10^2
 - d. 9.7×10^8
- 6. Calculate K_c for the reaction:

$$NH_4^+(aq) + HS^-(aq) \rightleftharpoons H_2S(aq) + NH_3(aq)$$

- a. 1.8×10^{-12}
- b. 5.5×10^{-3}
- c. 1.8 x 10⁻⁵
- d. 5.5×10^{11}

- 7. Calculate K_a for an unknown acid if a 0.0100 M solution has a measured pH of 2.60.
 - a. 2.5×10^{-1}
 - b. 6.3 x 10⁻⁴
 - c. 8.4 x 10⁻⁴
 - d. 6.3 x 10⁻⁶
- 8. The rate law for the overall reaction $A + 2B \rightarrow E$ was experimentally determined to be:

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

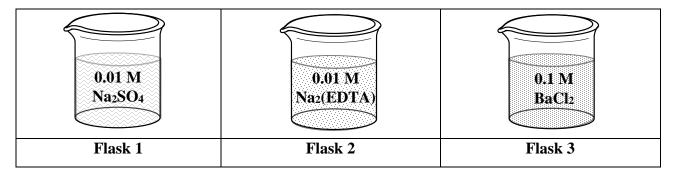
Which of these proposed mechanisms could explain this observed rate law?

- a. Step 1 (slow): $A_2 + B \rightarrow C$
 - Step 2 (fast): $C + B \rightarrow E$
- b. Step 1 (slow): $2A + B \rightarrow C$
 - Step 2 (fast): $C + B \rightarrow E$
- c. Step 1 (slow): $A + B \rightarrow C$
 - Step 2 (fast): $C + B \rightarrow E$
- d. Step 1 (slow): $2A + B \rightarrow C$
 - Step 2 (fast): $C + B \rightarrow E + A$
- 9. The potentiometric endpoint for the titration of 25.00 mL of acetic acid is 23.03 mL. If K_a of acetic acid is 1.8 x 10^{-5} and the base used in the titration is 0.012 M NaOH, calculate the acid concentration.
 - a. 8.3 x 10⁻⁵ M
 - b. 1.1 x 10⁻² M
 - c. 1.2 x 10⁻² M
 - d. 1.1 x 10¹ M

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10. Copper(II) chromate (CuCrO₄) is partially soluble in water. A solution of 0.030 M CuBr₂ is titrated with 0.10 M Na₂CrO₄ until the chromate concentration in solution is 1.2×10^{-4} M, at which point a precipitate appears. What is the K_{sp} for copper chromate?

- a. 3.6×10^{-6}
- b. 9.0×10^{-6}
- c. 3.0×10^{-4}
- d. 1.4×10^{-8}
- 11. A student adds some BaSO₄ to each of the three flasks shown here.



Given that BaSO₄ has $K_{sp} = 1.3 \times 10^{-10}$ and Ba(EDTA)²⁼ has $K_f = 7.2 \times 10^7$, which choice below correctly ranks the solubility of BaSO₄ in these flasks?

Highest BaSO₄ Solubility Lowest Solubility Flask 1 Flask 2 Flask 3 a. b. Flask 3 Flask 2 Flask 1 Flask 2 Flask 3 c. Flask 1 d. Flask 2 Flask 3 Flask 1

12. The standard potentials for two half-reactions are shown below. Based on this information, which species is the **stronger oxidizing agent**?

$$\text{Cl}_2(g) + e^- \rightarrow 2 \text{ Cl}^-(aq)$$

$$E^{\circ} = +1.4 \text{ V}$$

$$H_2O_2$$
 (aq) + 2 H⁺ (aq) + 2 e⁻ \rightarrow 2 H₂O (ℓ)

$$E^{\circ} = +1.8 \text{ V}$$

- a. Cl₂ (g)
- b. Cl⁻ (aq)
- c. H_2O_2 (aq)
- d. $H_2O(\ell)$

13. Which of the choices below correctly shows the balanced equation for the reaction of Zn and vanadium oxide (VO_2^+) in acidic solution, forming Zn^{2+} and VO^{2+} ?

a.
$$Zn(s) + 2H^{+}(aq) + VO_{2}^{+}(aq) \rightarrow Zn^{2+}(aq) + VO^{2+}(aq) + H_{2}O(\ell)$$

b.
$$Zn(s) + 4H^{+}(aq) + 2VO_{2}^{+}(aq) \rightarrow Zn^{2+}(aq) + 2VO^{2+}(aq) + 2H_{2}O(\ell)$$

c.
$$Zn(s) + 2 H_2O(\ell) + 2 VO_2^+(aq) \rightarrow Zn^{2+}(aq) + 2 VO^{2+}(aq) + 4 OH^-(aq)$$

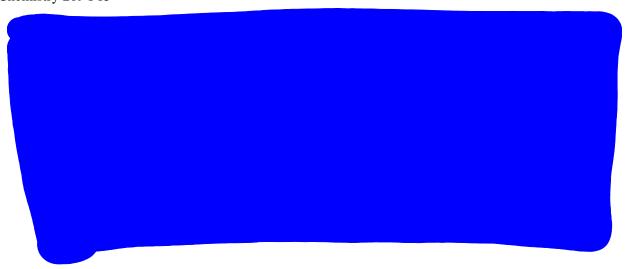
$$d. \ \ Zn\left(s \right) + H^{^{+}}\left(aq \right) \ + VO_{2}^{^{+}}\left(aq \right) \to Zn^{2^{+}}\left(aq \right) + VO^{2^{+}}\left(aq \right) + OH^{^{-}}\left(aq \right)$$

- 14. The E° for the reaction of Cu/Cu^{2+} and Sn/Sn^{2+} is + 0.19 V. What is the value of the equilibrium constant K for this reaction at 298 K?
 - a. 3.7×10^{-7}
 - b. 1.6×10^4
 - c. 2.7×10^6
 - d. 6.2×10^{14}

This question's content was not covered this year.

16.Select the **true** statement.

- a. The d subshell has 10 orbitals.
- b. The 4s orbital has 4 nodes.
- c. The 6p orbitals have 6 possible orientations.
- d. The 5f orbitals are degenerate.
- 17. Which of these elements should have the largest **first** ionization energy?
 - a. O
 - b. F
 - c. Na
 - d. Cl



19. Which of the following orbital diagrams correctly shows the ground-state valence electron configuration for a S atom?

a.
$$\frac{1}{3s} \quad \frac{1}{3p} \quad \frac{1}{3p}$$

b.
$$\frac{1}{3s} \quad \frac{1}{3p} \quad \frac{1}{3p}$$

c.
$$\frac{1}{2s} \quad \frac{1}{2p} \quad \frac{1}{2p}$$

d.
$$\frac{1}{2s}$$
 $\frac{1}{2p}$ $\frac{1}{2p}$

20. Consider the atomic and ionic radii shown in the table below. Which atomic property **best** explains the trend in these radii?

Species	Kadius
	(pm)
Br ⁻	182
Rb^+	166

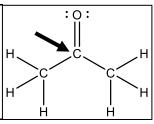
- a. Principal quantum number n
- b. Effective nuclear charge
- c. Partially filled subshells
- d. Atomic mass

- 21. Which of the following answers correctly shows the ground-state electron configuration for an As⁺ ion?
 - a. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
 - b. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
 - c. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{14} 4p^2$
 - d. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^3$
- 22. How many chemical species in this list are diamagnetic in their ground state?

F	Ar	O^{2-}	Al ³⁺	Cl ₂

- a. One
- b. Two
- c. Three
- d. Four

Acetone is a powerful solvent used in the lab, and occasionally in the household as a nail polish remover. Use the chemical structure of acetone, shown here, to help you answer the following two questions.



- 23. What is the hybridization on the carbon atom marked with an arrow?
 - a. sp
 - b. sp^2
 - c. sp^3
 - d. unhybridized
- 24. Which statement below is **true** with regards to the bonding in the acetone molecule?
 - a. There are two pi bonds in the molecule.
 - b. There are ten sigma bonds in the molecule.
 - c. All of the bonds on the atom indicated with an arrow on the structure above are nonpolar bonds.
 - d. The atom indicated with an arrow in the structure above has one pi bond and three sigma bonds.

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SECTION II: Long Answers: To be graded manually (Total value 42) For full marks show all your work.

[Total: 8 points] **Question 1**

Ozone reacts with oxygen atoms to make oxygen gas as an exelementary step:	othermic process that occurs as a single
$O_3(g) + O(g) \rightarrow 2$	$O_2(g)$
This reaction can also be catalyzed by chlorine atoms, as described $O_3(g) + Cl(g) \rightarrow ClO(g) + O_2(g)$) slow
$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$) fast
a. [1 point] Write the rate law for the uncatalyzed reaction.	
b. [1 point] Write the rate law for the catalyzed reaction.	
c. [1 point] How many transition states would you expect for the catalyzed reaction?	
d. [1 point] How would you describe the chlorine atoms? (Check one box)	☐ Homogeneous catalyst ☐ Heterogeneous catalyst
 e. [3 points] Draw a potential energy diagram for the uncatalyzed reaction, including labels for: Reactants ("R") Products ("P") For the forward reaction: Activation Energy (E_a^{Uncat}) for the rate determining step ΔΗ 	Potential Energy
	Reaction Progress

f. The bond length is 128 pm in O₃ and 110 pm in O₂. Which bond would be stronger? Explain your answer in 1-3 grammatically correct sentences. [1 mark]

Quest	Question 2 [Total: 10 Points]		
	You prepare a 0.50 M solution of bromous acid (HBrO ₂). Bromous acid has $pK_a = 3.43$		
a.	[3 points] What is the pH of this solution?		
I.	[2] nointel How many L. of 0.49 M NoOH would you need to add to 50.0 L. of this soid to make a hyffen		
b.	[3 points] How many L of 0.48 M NaOH would you need to add to 50.0 L of this acid to make a buffer with pH = 4.00?		
c.	[2 points] Draw one Lewis diagram for the conjugate base, BrO ₂ -, and show formal change calculations for each atom to prove that it is the best Lewis structure for this compound.		
	Lewis structure:		
d.	[2 points] Based on your conjugate base Lewis diagram, draw the VSEPR structure for the acid, HBrO ₂ .		
	Lewis structure:		

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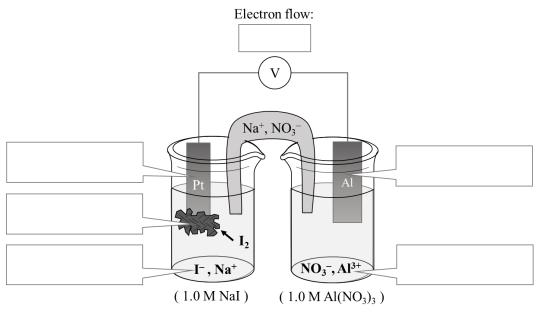
Question 3 [Total: 10 points]

The cell below is a voltaic cell based on the reaction between Al/Al^{3+} and I_2/I^- . Use this diagram and the standard reduction potentials given to answer Question 3.

Al
$$^{3+}$$
 (aq) + 3 e^{-} \rightarrow Al (s) $E^{\circ} = -1.66 \text{ V}$

$$I_2(s) + 2e^- \rightarrow 2I^-(aq)$$
 $E^\circ = +0.535 V$

a. [2 points] Label the indicated cell parts using the following terms: **Cathode, Species Being Reduced,** and **Species Being Oxidized.** As well, use the space provided to indicate the **direction of electron flow**.



b. [1 point] Write the balanced redox equation for the reaction of aluminum and iodine (as seen in this cell), in acidic solution.		
c. [1 point] Assuming that the voltmeter is connected		
correctly, what reading should it display?		
d. [1 point] Write the full electron configuration for		
the neutral aluminum atom:		

e. [1 point] Arrange the redox-active atoms & ions from this reaction (Al, Al ³⁺ and I ⁻) in order of INCREASING	SMALLEST	LARGEST
size Write your answers in the unshaded boxes.		

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f. [4 points] If the solution in the two cell compartments was replaced with the solutions described in the table below, what reading would the voltmeter then display?

	Components
In left-hand beaker (I_2 / I^-):	10.2 g of KI in 250. mL of water
In right-hand beaker (Al / Al ³⁺):	23.1 g of Al(NO ₃) ₃ in 250. mL of water

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Question 4 [Total: 14 points]

For the species given below, draw Lewis (2D) and VSEPR (3D) structures and identify electron pair arrangement, molecular shape, and net polarity. Enter your answers in the appropriate boxes.

1	BF ₃	KrF ₄	$\mathrm{IF_4}^+$	SnH ₄
Lewis structure (2D) [1 point each]				
Show all electron groups and all non-zero formal charges.				
VSEPR structure (3D)				
[1 point each]				
Electron pair arrangement [0.5 point each]				
Molecular shape [0.5 point each]				
Check one box [0.5 point each]	☐ Polar ☐ Non-polar	☐ Polar ☐ Non-polar	☐ Polar ☐ Non-polar	☐ Polar ☐ Non-polar

Data Sheet - CHEM 209

Periodic Table 1 18 1A 8A Legend: ← Atomic number (Z) 14 15 16 17 H ← Atomic symbol He 2A 4A ← Atomic mass (amu) 1.008 4.003 10 3 \mathbf{C} В N \mathbf{F} Li Be 0 Ne 16.00 6 941 9.012 10.81 12.01 14.01 20.18 12 13 14 15 18 Na Mg 5 7 8 9 10 11 12 Al Si P S Cl Ar 3 6 22.99 26.98 28.09 30.97 32.07 35.45 39.95 24.31 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 K Sc Ti \mathbf{V} Cr Mn Fe Co Ni Zn Ge Se Kr Ca Cu Ga Br As 39.10 40.08 44.96 47.88 50.94 52.00 54.94 55.85 58.93 58.69 63.55 65.38 69.72 72.59 74.92 79.90 83.80 37 51 54 \mathbf{Y} Sb Rb Sr Zr Nb Tc Ru Rh Pd Cd Te Ι Mo Ag In Sn Xe 85.47 87.62 88.91 91.22 92.91 95.94 (98) 101.1 102.9 106.4 107.9 112.4 114.8 118.7 121.8 127.6 126.9 131.3 55 82 83 86 81 Cs Hf W Pt TI Pb Bi At Ba La Ta Re Os Ir Au Hg Po Rn 183.9 132.9 137.3 138.9 178.5 180.9 186.2 190.2 192.2 195.1 197.0 200.6 204.4 207.2 209.0 (209)(210)(222)88 104 105 106 107 108 109 110 111 87 Fr Ra Ac Rf Ha Sg Ns Hs Mt Uun Uuu (223)226.0 (227)(261) (262)(263) (262)(265)(266) (269)(272) Lanthanides * Tb Pr Nd Pm Sm Gd Ho Er Tm Yb Lu Ce Eu Dv 140.1 140.9 150.4 152.0 158.9 162.5 164.9 167.3 168.9 173.0 175.0 144 2 (145)157.3 92 93 99 101 90 91 94 95 97 98 100 102 103 **Actinides** ** IJ Cf Th Pa Np Pu Cm Bk Es Fm Md No Lr Am 238.0 232.0 231.0 237.0 (244)(243)(247)(247)(251)(252)(257)(258)(260)

Strong Acids: HCl, HBr, HI, HNO3, H2SO4, HClO4

Strong Bases: Hydroxides of Group 1 (Li to Cs) and Group 2 (Ca, Sr, Ba)

Co	nstants	:

Gas Constant: $R = 0.08205 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

 $= 8.314 \ L \cdot kPa \cdot mol^{-1} \cdot K^{-1} \\ = 8.314 \ J \cdot mol^{-1} \cdot K^{-1}$

 $= 0.08314 \text{ L} \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

Avogadro's number: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Faraday's Constant: F = 96 485 C/mol electrons

Planck's Constant: $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$

Speed of Light: $c = 2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}$

Rydberg Constant: $R = 1.096776 \times 10^7 \text{ m}^{-1}$

Factoring Rydberg Constant: $R_H = R \cdot h \cdot c = 2.18 \times 10^{-18} \text{ J}$

Conversion Factors:

 $1~J=1~kg\!\cdot\! m^2\!\cdot\! s^2$

 $T(K) = T(^{\circ}C) + 273.15$

 $1 \text{ Pa} = 1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} = 10^{-5} \text{ bar}$

 $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$

1 atm = 760.0 torr = 101.3 kPa = 760.0 mm Hg = 1.013 bar

 $1 L = 10^{-3} m^3$

1 C = 1 J/V 1 A = 1 C/s

STP conditions: 0°C, 100 kPa

Electrochemical standard state: 100 kPa, 1 M, 25°C

$$[A]_{t} = -kt + [A]_{0} \qquad \ln[A]_{t} = -kt + \ln[A]_{0} \qquad PV = nRT \qquad E^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} \qquad c = \lambda v$$

$$\ln\left(\frac{[A]_{0}}{[A]_{t}}\right) = kt \qquad \frac{1}{[A]_{t}} = kt + \frac{1}{[A]_{0}} \qquad pH = -\log[H^{+}] \qquad E = E^{\circ} - \frac{0.0592}{n_{e}} \log Q \qquad E = mc^{2}$$

$$t_{1/2} = \frac{[A]_{0}}{2k} \qquad t_{1/2} = \frac{0.693}{k} \qquad K_{w} = K_{a} \cdot K_{b} \qquad E^{\circ} = \frac{RT}{zF} \ln K \qquad \frac{1}{\lambda} = R\left(\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}}\right)$$

$$t_{1/2} = \frac{1}{k[A]_{0}} \qquad k = Ae^{(-E_{a}/RT)} \qquad x = \frac{-b \pm \sqrt{b^{2} - 4ac}}{2a} \qquad E^{\circ} = \frac{0.0592}{n_{e}} \log K \qquad \Delta E = -R_{H}\left(\frac{Z^{2}}{n_{f}^{2}} - \frac{Z^{2}}{n_{t}^{2}}\right)$$

$$\ln\left(\frac{k_{2}}{k_{1}}\right) = \frac{E_{a}}{R}\left(\frac{1}{T_{1}} - \frac{1}{T_{2}}\right) \qquad nFE^{\circ} = RT \ln K$$