THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM: Version 01

CHEMISTRY 209

Date: Wednesday October 19th, 2016 Time: 7:00pm – 9:00pm

First Name: ______________________ Last Name: ______________________

When you start the test, please **fill in your ID# on the next page**.

Please circle your lecture section:

L01 Dr. Musgrove-Richer
TR 2:00 pm

L02 Dr. Mozol
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, smartwatches, 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.

All questions must be answered to obtain full marks. The answers to the multiple-choice section must be entered on the optical score sheet **within** the 2 hour exam time. The answers to the long answer questions must be written in the space provided on the question sheets **AND** written in **non-erasable ink** to be eligible for re-grading. Work on page backs will not be graded unless it is clearly indicated to do so within the space provided for answering each question.

This test consists of **13 multiple choice** questions worth 2 marks each (total 26 marks) and **5 long answer** questions (total 27 marks). The total value for the test is 51 marks. The exam has **11 pages** (including this one), so please make sure you have all 11 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 number and lecture section will result in the loss of two points.

Write your ID# here:	**Sec II - Q1**	**Sec II - Q2**	**Sec II - Q3**	**Sec II - Q4**	**Sec II – Q5**
	Do not write in the shaded part. For marking only.				

SECTION I – Machine-graded section (Total value 26)
To be answered on Optical Score Sheet

1. What value correctly expresses the answer to this density calculation with the correct units and significant figures?

$$\frac{(82.631\ g - 18.39\ g)}{(52.87\ mL - 47.43\ mL)}$$

   a. 11.809 g/mL
   b. 11.8 kg/L
   c. 11.809 kg/L
   d. 12 g/mL
   e. 11.81 g/mL

2. Which sample below contains the greatest number of carbon atoms?
   a. 12.01 g of C (s)
   b. 20.79 g of oleic acid ($C_{18}H_{34}O_2$)
   c. 24.21 g of benzene (C_6H_6)
   d. 31.05 g of ethane (C_2H_6)
   e. 42.89 g of carbon tetrachloride (CCl_4)

3. Which of the following statements about reaction kinetics is **true**?
   a. If the activation energy of a reaction is decreased, the speed of the reactant particles in the sample has been decreased.
   b. For a 0^{th} order reaction, rate constant will decrease as reactant concentration is decreased because the number of effective collisions will be lower.
   c. The effect of temperature on the value of the rate constant (*k*) depends on the activation energy of the reaction.
   d. Adding a catalyst increases the yield of reaction products by increasing *K*.
   e. The rate of a 1 M gaseous reaction will be faster in a 1 L container than a 2 L container.

4. The gas-phase decomposition of acetaldehyde (CH_3CHO) produces methane and carbon monoxide:

$$CH_3CHO\ (g) \longrightarrow CH_4\ (g) + CO\ (g) \qquad \text{rate} = k[CH_3CHO]^2$$

If the concentration of acetaldehyde is halved, the rate will:

a. not change.

b. be quartered.

c. be halved.

d. double.

e. quadruple.

5. Consider the reaction: $P_4 + 6\,H_2 \rightarrow 4\,PH_3$. A rate study of this reaction was conducted at 298 K. The data that were obtained are shown in the table below.

$[P_4]$ (mol/L)	$[H_2]$ (mol/L)	Initial Rate ($M^{-1}s^{-1}$)
0.0110	0.0075	3.20×10^{-4}
0.0110	0.0150	6.40×10^{-4}
0.0220	0.0150	6.39×10^{-4}

Which statement about the kinetics of this reaction is true?

a. The order with respect to $[H_2]$ is 0, and the overall order is 1.

b. The order with respect to $[H_2]$ is 1, and the overall order is 1.

c. The order with respect to $[H_2]$ is 2, and the overall order is 2.

d. The order with respect to $[H_2]$ is 1, and the overall order is 2.

6. A proposed mechanism for the reaction of NO_2 with CO is shown below. Which of the given rate laws would accurately describe a reaction with this mechanism?

$$\begin{array}{ll} NO_2\ (g) + NO_2\ (g) \longrightarrow NO_3\ (g) + NO\ (g) & slow \\ NO_3\ (g) + CO\ (g) \longrightarrow NO_2\ (g) + CO_2\ (g) & fast \\ \hline NO_2\ (g) + CO\ (g) \longrightarrow NO\ (g) + CO_2\ (g) & overall \end{array}$$

a. Rate = k $[NO]^2$

b. Rate = k $[NO_2]$ [CO]

c. Rate = k $[NO_2]^x [CO_2]^y$

d. Rate = k $[NO_3]$ [CO]

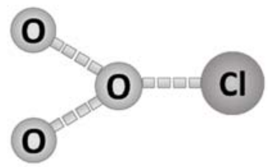
e. Unable to be determined using the given information.

7. The decomposition of ozone to oxygen gas can also occur in the presence of chlorine atoms. A proposed mechanism for this exothermic reaction is as follows:

$$Cl\ (g) + O_3\ (g) \longrightarrow ClO\ (g) + O_2\ (g) \qquad slow$$
$$O_3\ (g) \longrightarrow O\ (g) + O_2\ (g) \qquad fast$$
$$ClO\ (g) + O\ (g) \longrightarrow Cl\ (g) + O_2\ (g) \qquad fast$$

Which of these statements about this reaction is **true**?

a. A reasonable transition state for the formation of the intermediate ClO is:



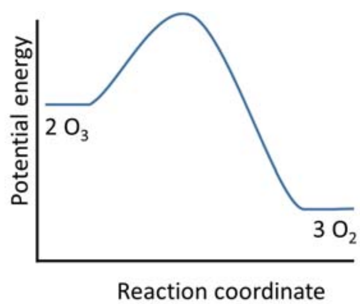
b. The presence of chlorine does not affect the rate for the overall reaction

$$2\ O_3\ (g) \longrightarrow 3\ O_2\ (g)$$

c. For this mechanism, the reaction does not depend on the chlorine concentration.

d. Chlorine is a catalyst in this mechanism.

e. The reaction coordinate diagram describing the overall reaction is:



8. Silver chloride will react with acetic acid to form the complex ion silver acetate. A reaction mixture is prepared by adding 0.25 g of AgCl to a 1.25 L solution that already contains 4.6×10^{-6} M $Ag(CH_3COO)$ (aq), 2.3×10^{-3} M Cl^-, 1.1×10^{-8} M H^+, and 0.010 M CH_3COOH.

Based on this information, which of the statements below is **true**?

$$AgCl\ (s) + CH_3COOH\ (aq) \rightleftharpoons Ag(CH_3COO)(aq) + Cl^-(aq) + H^+(aq) \qquad K = 5.87 \times 10^{-16}$$

After allowing this solution to rest for some time:

a. Nearly all of the AgCl added will be consumed by the reaction.

b. More products will be present than initially because a reactant was added.

c. The concentration of Cl^- will be lower than the initial value.

d. There will be no change in the concentrations, since solids do not affect equilibrium.

e. The pH of the solution will decrease, compared to the initial value.

9. The reaction of calcium hydroxide to form calcium carbonate is a key reaction in the hardening of lime mortar, and is an exothermic process. If this reaction was studied at room temperature (298 K) and compared to the reaction at 325 K, which statement below is true?

$$Ca(OH)_2(s) + CO_2\ (aq) \longrightarrow CaCO_3\ (aq) + H_2O\ (l)$$

a. More calcium carbonate will be produced at 325 K, and *K* will increase.
b. Less calcium carbonate will be produced at 325 K, and *K* will decrease.
c. More calcium carbonate will be produced at 325 K, because heat is a product.
d. Less calcium carbonate will be produced at 325 K, because heat is a reactant.

10. For the reaction of barium carbonate shown here, which of these changes suggested below will result in a decrease in pH at equilibrium? Assume that the reaction is at equilibrium before making any change, and that there is excess $BaCO_3$ and H_2O present.

$$BaCO_3\ (s) +\ 2\ H^+\ (aq) \rightleftharpoons Ba^{2+}\ (aq) +\ CO_2\ (g) +\ H_2O\ (l)$$

a. Increase the volume of the reaction container
b. Remove half of the $BaCO_3$ from the mixture
c. Allow CO_2 to escape the reaction container
d. Add a few mL of barium chloride solution

11. Carbon disulfide, CS_2, and chlorine gas react according to the following equation:

$$CS_2(g) + 3\ Cl_2\ (g)\ \rightleftharpoons S_2Cl_2\ (g) + CCl_4\ (g)$$

When 1.00 mol of CS_2 and 3.00 mol of Cl_2 are placed in a 2.00 L container and allowed to come to equilibrium, the mixture is found to contain 0.250 mol of CCl_4. What is the amount of Cl_2 at equilibrium?

a. 2.75 mol
b. 2.25 mol
c. 0.75 mol
d. 0.50 mol
e. 0.25 mol

12. The reaction for the decomposition of $COBr_2$ gas is shown below. What is the K_P for this reaction, expressed using standard units?

$$COBr_2\ (g) \rightleftharpoons CO\ (g) + Br_2\ (g) \qquad K_C = 0.190\ at\ 73°C$$

a. 0.190

b. 1.153

c. 5.468

d. 15.74

e. 539.6

13. Which of the solutions below would have the HIGHEST pH value?

a. 1.0 M of acetic acid (K_a = $1.75x10^{-5}$)

b. 0.1 M of acetic acid (K_a = $1.75x10^{-5}$)

c. 0.1 M of butanoic acid (K_a = $1.52x10^{-5}$)

d. 1.0 M of cyanoacetic acid (K_a = $3.37x10^{-3}$)

<u>END OF MULTIPLE CHOICE SECTION</u>

Make sure you have “bubbled in” on the Optical Scoring Sheet:

- **Answers for all 13 questions**
- **Your name and ID number**
- **The Version Number (on the exam cover page)**

SECTION II: Long Answers: To be graded manually (Total value 27)

Answers must be written in non-erasable ink to be considered for re-grading.

For full marks, show all your work.

Question 1 [Total value: 4 points]

Hydrazine can be synthesized by reacting ammonia gas (NH_3) with an aqueous solution of hydrogen peroxide (H_2O_2) according to the reaction:

$$2\ NH_3\ (g) + H_2O_2\ (aq) \longrightarrow N_2H_4\ (aq) + 2\ H_2O\ (l)$$

To perform a given experiment, a technician connects a gas cylinder containing an excess of ammonia gas to a reaction flask containing 5.00 L of a 9.77 M hydrogen peroxide solution. After the reaction is complete, the H_2O_2 concentration has decreased to 2.53 M and the chemist is able to isolate 33.3 g of hydrazine (N_2H_4). Determine the % yield for this experiment.

Question 2 [Total value: 4 points]

5.51×10^{-4} mol of trimethylammonium chloride ($(CH_3)_3NH^+$, a weak acid) is diluted to a total volume of 500. mL. The pH of this solution was found to be 6.529. What is the K_a of trimethylammonium chloride?
Hint: Start by writing the balanced equation.

Question 3 [Total value: 5 points]

Ammonia gas (NH_3) can decompose into hydrogen (H_2) and nitrogen (N_2) gases when it is heated in the presence of a metal surface. The rate constant for the decomposition of ammonia at 873°C is 1.5×10^{-3} M/s.

a. Write the balanced reaction for the decomposition of ammonia, including phases. [1 point]

b. The decomposition of ammonia is a ____________________ order reaction. [0.5 point]

0th | 1st | 2nd

c. Write the generic rate law and integrated rate law that describe this reaction: [1 point]

GENERAL RATE LAW	INTEGRATED RATE LAW

d. If 1.00 g of ammonia is placed in a 1.00 L flask, how long will it take for the reaction to reach ½ of the initial ammonia concentration? [2.5 point]

Question 4 [Total value: 7 points]

a. Nitrogen dioxide (NO_2) can decompose to form N_2 and O_2 gases. Given the reaction conditions and kinetic data below, determine the activation energy for this reaction. [3 points]

$$2\ N_2O\ (g) \longrightarrow 2\ N_2\ (g) + O_2\ (g) \qquad \Delta H = -67.6\ \mathrm{kJ/mol}$$

Rate constant *k*	Temperature
$1.3 \times 10^{-11}\ s^{-1}$	270 K
$4.5 \times 10^{-10}\ s^{-1}$	350 K

b. The decomposition of nitrogen dioxide described above is proposed to occur with the following mechanism: (Note – the *k* values above are unrelated to this proposed mechanism). [4 points]

$$N_2O\ (g) \longrightarrow N_2\ (g) + O\ (g) \qquad slow$$
$$N_2O\ (g) + O\ (g) \longrightarrow N_2\ (g) + O_2\ (g) \qquad fast$$

Based on this information, sketch the reaction coordinate diagram (reaction energy diagram) for the mechanism above. Be sure to label on the diagram (if present): [

- *x* and *y* axis labels
- Reactants and products
- Activation energy (value not required)
- Transition state(s)
- Intermediate (s)

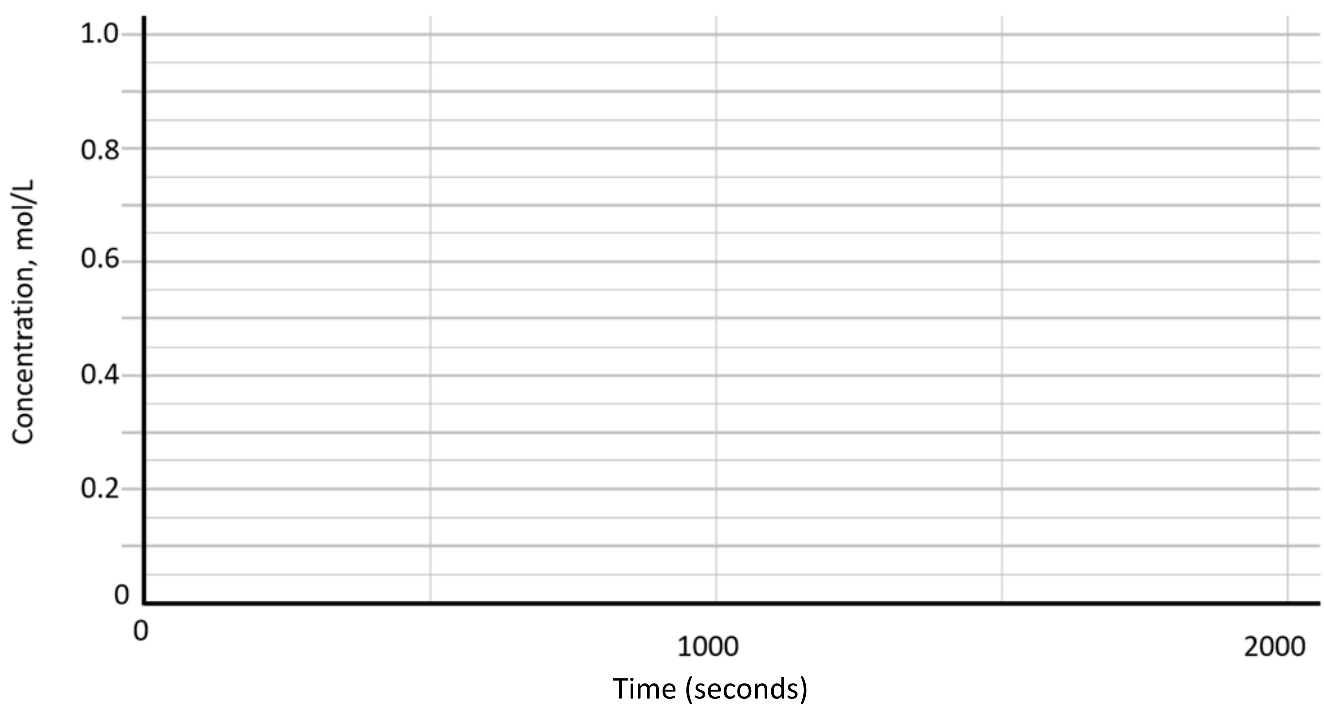
Question 5 [Total value: 7 points]

a. The endothermic decomposition of $COBr_2$ proceeds as follows:

$$COBr_2\ (g) \rightleftharpoons CO\ (g) + Br_2\ (g) \qquad K_C = 0.190 \text{ at } 73°\text{C}$$

A reaction vessel was prepared by filling a 1.0 L container with 0.500 mol $CoBr_2$. After 1000 sec at 73°C, the reaction has reached equilibrium. Determine the concentrations of $COBr_2$, CO, and Br_2 at 1000 sec. [4 points]

b. Below is space to make a concentration vs. time plot for the reaction. Based on your values, sketch the concentration with time of all 3 species for t=0 to 1000 sec. Be sure to label the lines. [2 points]



c. At 1001 sec, the temperature of the reaction vessel is increased to 125°C. Add to the plot above a sketch (*approximately* – no numerical values required) of how the concentrations of all reagents will change from t= 1001 until 2000 sec, where the reaction is once again at equilibrium. [1 point]

END OF LONG ANSWER SECTION.

Data Sheet – CHEM 209

Periodic Table

Legend: 1 / H / 1.008 — ← Atomic number (Z) ← Atomic symbol ← Atomic mass (amu)

1 1A	2 2A	3	4	5	6	7	8	9	10	11	12	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	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)

Strong Acids: HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$

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

Constants:	**Conversion Factors:**
Gas Constant: R = 0.08205 L·atm·mol^{-1}·K^{-1}	1 J = 1 kg·m^2·s^{-2}
= 8.314 L·kPa·mol^{-1}·K^{-1} = 8.314 J·mol^{-1}·K^{-1}	T (K) = T (°C) + 273.15
= 0.08314 L·bar·mol^{-1}·K^{-1}	1 Pa = 1 kg·m^{-1}·s^{-2} = 10^{-5} bar
Avogadro's number: N_A = 6.022×10^{23} mol^{-1}	1 L·atm = 101.3 J
Faraday's Constant: F = 96 485 C/mol electrons	1 atm = 760.0 torr = 101.3 kPa = 760.0 mm Hg = 1.013 bar
Planck's Constant: h = 6.626×10^{-34} J·s	1 L = 10^{-3} m^3
Speed of Light: c = 2.998×10^8 m·s^{-1}	1 C = 1 J/V 1 A = 1 C/s
Rydberg Constant: R = 1.096776×10^7 m^{-1}	STP conditions: 0°C, 100 kPa
Factoring Rydberg Constant: R_H = R·h·c = 2.18×10^{-18} J	Electrochemical standard state: 100 kPa, 1 M, (25°C unless stated otherwise)

$$[A]_t = -kt + [A]_0 \qquad \ln[A]_t = -kt + \ln[A]_0 \qquad PV = nRT \qquad E^\circ = E^\circ_{cathode} - E^\circ_{anode} \qquad c = \lambda\nu$$

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt \qquad \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \qquad K = K_C(RT)^{\Delta n} \qquad E = E^\circ - \frac{0.0592}{n_e}\log Q \qquad E = h\nu$$

$$pH = -\log[H^+] \qquad E = mc^2$$

$$t_{1/2} = \frac{[A]_0}{2k} \qquad t_{1/2} = \frac{0.693}{k} \qquad K_w = K_a \cdot K_b \qquad E^\circ = \frac{RT}{nF}\ln K \qquad \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$ax^2 + bx + c = 0$$

$$t_{1/2} = \frac{1}{k[A]_0} \qquad k = Ae^{(-E_a/RT)} \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad E^\circ = \frac{0.0592}{n_e}\log K \qquad \Delta E = -R_H\left(\frac{Z^2}{n_f^2} - \frac{Z^2}{n_i^2}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad pH = pK_a + \log\left(\frac{[conj.base]}{[conj.acid]}\right) \qquad nFE^\circ = RT\ln K$$