THE UNIVERSITY OF CALGARY FACULTY OF SCIENCE FINAL EXAMINATION CHEMISTRY 209 Version A

Date: Tuesday,	April 22 nd , 2014	Time: 12:00 noon – 3:00 pm
FIRST NAME: _		LAST NAME:
	ID #	
Please circle your	electure section number below.	
	Lec. 01 Dr. M. Parvez (Tu/Th 12:30 pm)	Lec. 02 Dr. E. Sullivan (Tu/Th 8:00 am)

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 <u>not</u> be allowed. Only non-programmable 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 using a pencil within the 3 hour exam. 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.

This test consists of 22 multiple choice questions worth 2 marks each (total 44 marks) and 4 long answer questions (total 34 marks). The total value for the test is 78 marks. The exam has 15 pages make sure you have all 15 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, Exam Version (A or B), ID and Lecture Section, will result in the loss of two marks

DO NOT WRITE IN THIS BOX, FOR GRADING PURPOSES ONLY!

Q 23	Q 24	Q25	Q26

<u>SECTION I - Machine graded section (**Total value 44**)</u> <u>To be answered on provided Optical Score Sheet</u>

1. Morphine reacts in a 1:1 mole ratio with acetic anhydride to form Heroin, as shown below:

If we had 14.00 g of Morphine ($C_{17}H_{19}NO_3$, 285.34 g/mol) and 5.00 mL of acetic anhydride ($C_4H_6O_3$, 102.09 g/mol, d = 1.082 g/mL), which reagent would **limit** the amount of Heroin ($C_{21}H_{23}NO_5$, 369.45 g/mol) that forms?

- A) Morphine
- B) Acetic anhydride
- C) Heroin
- D) We would have exactly the same amount of the product since the reaction involves a 1:1 mole ratio of the reactants.
- E) Insufficient information given
- 2. Tetrafluoroethylene, C_2F_4 , can be converted to octafluorocyclobutane which can be used as a refrigerant or an aerosol propellant. A plot of $1 / [C_2F_4]$ vs. time gives a straight line with a slope of $0.0448 \text{ L mol}^{-1} \text{ s}^{-1}$. What is the **rate law** for this reaction?
 - A) Rate = $0.0448 \text{ L mol}^{-1} \text{ s}^{-1} [\text{C}_2\text{F}_4]$
 - B) Rate = 22.3 mol L^{-1} s $[C_2F_4]$
 - C) Rate = $0.0448 \text{ L mol}^{-1} \text{ s}^{-1} [C_2 F_4]^2$
 - D) Rate = 22.3 mol L^{-1} s $[C_2F_4]^2$
 - E) Rate = $0.0448 \text{ s}^{-1} [C_2F_4]$

- 3. The decomposition of dimethylether at 504 °C is first order with a half-life of 1570. seconds. What fraction of dimethylether ($[A]_t/[A]_o$) remains after 4710. seconds?
 - A) 1/3
 - B) 1/6
 - C) 1/8
 - D) 1/16
 - E) 1/32

4. Carbon monoxide and chlorine combine in an equilibrium reaction to produce the highly toxic product, phosgene (COCl₂).

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

If the equilibrium constant for this reaction is $K_c = 248$, predict, if possible, what will happen when the reactants and product are combined with the concentrations shown below:

$$[CO] = [Cl_2] = 0.010 \ mol \ L^{-1}; \ [COCl_2] = 0.070 \ mol \ L^{-1}$$

- A) The reaction will proceed to the right.
- B) The reaction will proceed to the left.
- C) The reaction is at equilibrium, and no change in concentrations will occur.
- D) The container volume needs to be specified before a prediction can be made.
- E) The temperature needs to be specified before a prediction can be made.

5. Nitric oxide is formed in automobile exhaust when nitrogen and oxygen in air react at high temperatures.

$$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$$

The equilibrium constant K_p for the reaction is 0.0025 at 2127 °C. If a container is charged with 8.00 bar of nitrogen and 5.00 bar of oxygen and the mixture is allowed to reach equilibrium, what will be the equilibrium partial pressure of nitrogen?

- A) 0.16 bar
- B) 0.31 bar
- C) 3.1 bar
- D) 7.7 bar
- E) 7.8 bar

6. The acid dissociation constant K_a equals 1.26×10^{-2} for HSO_4^- and is 5.6×10^{-10} for NH_4^+ . Which statement about the following equilibrium is **correct**?

$$\mathrm{HSO_4}^-(aq) + \mathrm{NH_3}(aq) \rightleftharpoons \mathrm{SO_4}^{2-}(aq) + \mathrm{NH_4}^+(aq)$$

- A) The reactants will be favored because ammonia is a stronger base than the sulfate anion.
- B) The products will be favored because the hydrogen sulfate ion is a stronger acid than the ammonium ion.
- C) Neither reactants nor products will be favored because all of the species are weak acids or bases.
- D) The initial concentrations of the hydrogen sulfate ion and ammonia must be known before any prediction can be made.
- E) This reaction is impossible to predict, since the strong acid and the weak base appear on the same side of the equation.

- 7. What is the pH of a 1.0 L aqueous solution containing 1.0×10^{-8} mol of HNO₃?
 - A) 8.00
 - B) 7.02
 - C) 7.00
 - D) 6.98
 - E) 6.00

- 8. Exactly 100 mL 0f 0.10 M HNO₂ are titrated with 100 mL of a 0.10 M KOH solution. What is the pH at the equivalence point? $(K_a \text{ for HNO}_2 = 7.1 \times 10^{-4})$
 - A) 2.22
 - B) 7.00
 - C) 7.92
 - D) 8.07
 - E) 11.9

- 9. Buffer solutions with the component concentrations shown below were prepared. Which of them should have the **lowest** pH?
 - A) $[CH_3COOH] = 0.25 \text{ mol } L^{-1}, [CH_3COO^-] = 0.25 \text{ mol } L^{-1}$
 - B) $[CH_3COOH] = 0.75 \text{ mol } L^{-1}, [CH_3COO^-] = 0.75 \text{ mol } L^{-1}$
 - C) $[CH_3COOH] = 0.75 \text{ mol } L^{-1}, [CH_3COO^-] = 0.25 \text{ mol } L^{-1}$
 - D) $[CH_3COOH] = 0.25 \text{ mol } L^{-1}, [CH_3COO^-] = 0.75 \text{ mol } L^{-1}$
 - E) $[CH_3COOH] = 1.00 \text{ mol } L^{-1}, [CH_3COO^-] = 1.00 \text{ mol } L^{-1}$

- 10. Barium sulfate (BaSO₄) is a slightly soluble salt, with $K_{\rm sp} = 1.1 \times 10^{-10}$. What mass of Ba²⁺ ions will be present in 1.0 L of a saturated solution of barium sulfate?
 - A) $< 10^{-7} \text{ g}$
 - B) 1.0×10^{-5} g
 - C) 0.0014 g
 - D) 0.0024 g
 - E) > 0.05 g
- 11. Balance the following redox equation using the smallest integers possible and select the correct coefficient for the hydrogen sulfite ion, HSO₃⁻.

$$MnO_4^-(aq) + HSO_3^-(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2O(l)$$

- A) 1
- B) 2
- C) 3
- D) 5
- E) 10
- 12. Calculate E°_{cell} and indicate whether the overall reaction shown is spontaneous or nonspontaneous:

$$\operatorname{Co}^{3+}(aq) + \operatorname{e}^{-} \rightleftharpoons \operatorname{Co}^{2+}(aq)$$
 $E^{\circ} = 1.82 \text{ V}$

$$MnO_4^-(aq) + 2 H_2O(l) + 3e^- \Rightarrow MnO_2(s) + 4 OH^-(aq)$$
 $E^\circ = 0.59 V$

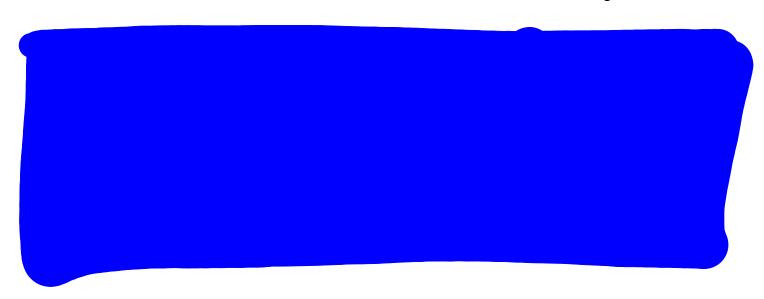
Overall reaction:

$$MnO_4^-(aq) + 2 H_2O(l) + 3 Co^{2+}(aq) \rightarrow MnO_2(s) + 3 Co^{3+}(aq) + 4 OH^-(aq)$$

- A) $E^{\circ}_{\text{cell}} = -1.23 \text{ V}$, spontaneous
- B) $E^{\circ}_{\text{cell}} = -1.23 \text{ V}$, nonspontaneous
- C) $E^{\circ}_{\text{cell}} = 1.23 \text{ V}$, spontaneous
- D) $E^{\circ}_{\text{cell}} = 1.23 \text{ V}, \text{ nonspontaneous}$
- E) $E^{\circ}_{\text{cell}} = -0.05 \text{ V}$, nonspontaneous

Material in this question was not covered this year.





- 17. Which of the following would represent **diamagnetic** species?
 - i. Ca
 - ii. Ge
 - iii. Se
 - A) i only
 - B) ii only
 - C) iii only
 - D) ii & iii only
 - E) None of the above

- 19. Which of the following are organized in an incorrect order?
 - A) Increasing Ionic Size: $Mg^{2+} < F^- < N^{3-}$
 - B) Decreasing first ionization energy: F > Br > K
 - C) Increasing electronegativity: N < O < F
 - D) Decreasing Atomic size: Se > S > Si
 - E) They are all in correct orders
- 20. Which of the following structures will have a single lone pair of electrons on the central atom?
 - i. SbF₃
 - ii. BrCl₃
 - iii. PCl₅
 - A) i only
 - B) ii only
 - C) iii only
 - D) i & ii only
 - E) All of them will
- 21. Which of the following compound(s) has(have) bent molecular shape(s)?
 - i. SO_2
 - ii. NOCl
 - iii. CO₂
 - A) i only
 - B) ii only
 - C) iii only
 - D) i & ii only
 - E) i & iii only

22. In the following Lewis structure for phosphate, phosphorus has a formal charge of _____ and an oxidation state of _____.

- A) 0, -3
- B) 0, 5
- C) 5, -3
- D) 5, 5
- E) 3, 5

****** END OF MULITIPLE CHOICE QUESTIONS SECTION **********

SECTION II: To be graded manually (**Total value 34**) For full marks show all your work.

Using methane (CH₄) and steam (H₂O(g)) as a source of hydrogen (H₂) for ammonia (NH₃) synthesis requires high temperatures. Rather than burning CH₄ separately to heat the mixture, it is more efficient to inject some O₂ into the reaction mixture. All the H₂ is, thus, released for the synthesis, and the heat of reaction for the combustion of CH₄ helps to maintain the required temperature. Imagine the reaction, occurring in two steps, as follows:

Marks

6

(1) $2 \text{ CH}_4(g) + O_2(g) \rightleftharpoons 2 \text{ CO}(g) + 4 \text{ H}_2(g)$ $K_p = 9.34 \times 10^{28} \text{ at } 1000 \text{ K}$

(2) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $K_p = 1.374 \text{ at } 1000 \text{ K}$

- (a) Write the overall equation for the reaction of methane, steam, and oxygen to form just carbon dioxide and hydrogen.
- (b) What is K_p for the overall reaction?
- (c) What is *K*c for the overall reaction?

(d) A mixture of 2.0 mol of CH₄, 1.0 mol of O₂, and 2.0 mol of steam (H₂O(g)), with a total pressure of 30. bar, reacts at 1000. K at a constant volume. Assuming that the reaction has gone to completion and the ideal gas law is a valid assumption, what is the final total pressure?

A voltaic cell has one half-cell with a Cu bar in a 1.00 mol/L Cu²⁺ salt, and the other half-cell with a 24.

Cd bar in the same volume of a 1.00 mol/L Cd²⁺ salt.

Marks 8

$$\operatorname{Cu}^{2+}(aq) + 2e^{-} \rightleftharpoons \operatorname{Cu}(s) \quad E^{\circ} = 0.34 \text{ V} \qquad \operatorname{Cd}^{2+}(aq) + 2e^{-} \rightleftharpoons \operatorname{Cd}(s) \quad E^{\circ} = -0.40 \text{ V}$$

$$Cd^{2+}(aq) + 2e^{-} \Rightarrow Cd(s) \quad E^{\circ} = -0.40 \text{ V}$$

Find E°_{cell} and K. a.

As the cell operates, $[Cd^{2+}]$ increases. Find E_{cell} when $[Cd^{2+}]$ is 1.95 mol/L. b.

c. Write a balanced chemical equation for the reaction, keeping in mind the value of K, setup an ICE Table, and find E_{cell} , and $[Cu^{2+}]$ at equilibrium.

Every diagram drawn in the table below was drawn by a person just learning about chemistry. Help this person out by associating each diagram with one of the statements A. through G. below to explain why a given structure is incorrect or correct. Each statement can only be used once, choose the statement that best matches the structures given below.

Marks

6

- A. The formal charges are not minimized.
- B. The central atom cannot have an expanded octet.
- C. The dipoles are drawn incorrectly.
- D. The formal charge(s) have not been included.
- E. Lone pairs are missing.
- F. The bond angles and thus geometry are incorrect.
- G. The structure is correct.

			, , , , , , , , , , , , , , , , , , , ,
Lewis Diagram	Letter for the	VSEPR Diagram	Letter for
	error	_	the error
H H		-io: 	
H C = O = C H		$ \begin{array}{c c} CI^{\delta^{+}} \\ \delta^{+} \\ CI & P \\ CI & \delta^{+} \end{array} $ $ \begin{array}{c c} CI & \delta^{-} \\ CI & \delta^{+} \end{array} $ $ \begin{array}{c c} CI & \delta^{+} \\ \delta^{+} & CI \\ \delta^{+} & CI \end{array} $	
:F: :F: :Br :Br :F: :F:		F //////S —— F	

26. For the species given below, draw Lewis (2D) and VSEPR (3D) structures and identify electron pair geometries, molecular geometries, bond angles around the central atom, net polarity and hybridization. Enter your answers in the appropriate boxes. **Note: Lewis structures need to show all electron groups and all non-zero formal charges.**

Marks 14

Molecule	COBrF	SiF ₄	SeCl ₃	I_3^-
Lewis structure (2D)				
VSEPR structure (3D)				
Electron pair geometry				
Mole- cular geometry				
Bond angles				
Net Polarity				
Hybridi- zation				

Data Sheet - CHEM 209

1							F	Period	ic Tat	ole							18
1A	1																8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
3	4											5	6	7	8	9	10
Li	Be											В	C	N	O	F	Ne
6.941	9.012											10.81	12.01	14.01	16.00	19.00	20.18
11	12											13	14	15	16	17	18
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
22.99	24.31											26.98	28.09	30.97	32.07	35.45	39.95
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
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	78.96	79.90	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	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	56	57*	72	73	74	75	76	77	78	79	80	81	82 D1	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.9	137.3	138.9 89**	178.5	180.9	183.9	186.2	190.2	192.2	195.1	197.0	200.6	204.4	207.2	209.0	(209)	(210)	(222)
87 E.:	88 D -		104 D.C	105	106	107	108	109	110	111							
Fr	Ra	Ac	Rf	Ha	Sg	Ns	Hs	Mt	Uun	Uuu							
(223)	226.0	(227)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)							

Lanthanides *	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthamacs	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
	140.1	140.9	144.2	(145)	150.4	152.0	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0
Actinides **	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
	232.0	231.0	238.0	237.0	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

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

Strong Bases: Hydroxides of Group 1A (Li to Cs) and Group 2A (Ca, Sr, Ba)	
Constants:	Conversion factors:
Gas constant, $R = 0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1}$	$1 J = 1 kg m^2 s^{-2}$ $1 Pa = 1 kg m s^{-2}$
$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \text{ or } 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$	$T K = T^{\circ}C + 273.15$
Avogadro's number: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$	1 L atm = 101.3 J
Faraday: $F = 96,485 \text{ C} / \text{mol electrons}$	1atm = 760.0 torr = 101.3 kPa = 760.0 mm Hg = 1.013 bar
Planck's constant $h = 6.626 \times 10^{-34} \text{Js}$	$1 L = 10^{-3} m^3$
Speed of light, $c = 2.998 \times 10^8 \text{m/s}$	$1 \text{ C} = 1 \text{ J/V}$ $1 \text{ A} = 1 \text{ C s}^{-1}$
Rydberg constant, $R = 1.09678 \times 10^{-7} \text{ m}^{-1}$	STP conditions: 0 °C, 1 atm
Factoring constant $R_{IJ} = Rhc = 2.18 \times 10^{-18} I$	Electrochemical standard state: 1 atm 1M 25 °C

$$\begin{split} & [AJ_{t} = -kt + [AJ_{0}] & \ln[AJ_{t} = -kt + \ln[AJ_{0}] & \frac{1}{[AJ_{t}]} = kt + \frac{1}{[AJ_{0}]} & \ln\left(\frac{[AJ_{0}]}{[AJ_{t}]}\right) = kt \\ & t_{1/2} = \frac{[AJ_{0}]}{2k} & t_{1/2} = \frac{0.693}{k} & t_{1/2} = \frac{1}{k[AJ_{0}]} & k = Ae^{\frac{-E_{a}}{RT}} & \ln\left(\frac{K_{2}}{K_{t}}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_{t}} - \frac{1}{T_{2}}\right) \\ & \ln\left(\frac{k_{2}}{k_{t}}\right) = \frac{E_{a}}{R} \left(\frac{1}{T_{t}} - \frac{1}{T_{2}}\right) & PV = nRT & K_{p} = K_{c}(RT)^{\Delta n} & ax^{2} + bx + c = 0 \\ & pH = -\log[H^{+}] & K_{w} = K_{a}K_{b} & pH = pK_{a} + \log\left(\frac{[\text{cong.base}]}{[\text{cong.acid}]}\right) & x = \frac{-b \pm \sqrt{b^{2} - 4ac}}{2a} \\ & E^{\circ} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} & E = E^{\circ} - \frac{0.0592}{n_{e}} \log Q & E^{\circ} = \frac{0.0592}{n_{e}} \log K & \text{or } nFE^{\circ} = RTlnK \\ & c = \lambda v & E = hv & E = mc^{2} & \frac{1}{\lambda} = R\left(\frac{1}{n_{1}^{2}} - \frac{1}{n_{2}^{2}}\right) & \Delta E = -R_{H}\left(\frac{Z^{2}}{n_{f}^{2}} - \frac{Z^{2}}{n_{i}^{2}}\right) \end{split}$$