

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

Date: Tuesday, April 22nd, 2014

Time: 12:00 noon – 3:00 pm

FIRST NAME: _____ LAST NAME: _____

ID # _____

Please circle your lecture 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 not 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 28 marks). The total value for the test is 72 marks. The exam has 14 pages make sure you have all 14 pages.

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

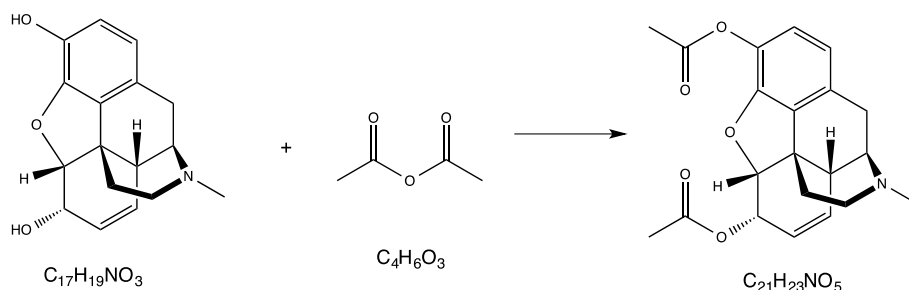
Failing to encode this Exam Booklet or your Optical Score Sheet correctly, for your name, ID and lecture section, will result in the loss of two marks

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

Q 23	Q 24	Q25	Q26

SECTION I - Machine graded section (Total value 44)
To be answered on provided Optical Score Sheet

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

Moles of morphine = $14.00 \text{ g} / 285.34 \text{ g mol}^{-1} = 0.0491 \text{ mol}$

Amount of acetic anhydride = $5.00 \text{ mL} \times 1.082 \text{ g mL}^{-1} = 5.41 \text{ g}$

Moles of acetic anhydride = $5.41 \text{ g} / 102.09 \text{ g mol}^{-1} = 0.053 \text{ mol}$

Therefore morphine is the limiting reagent!

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 = $0.0448 \text{ (L mol}^{-1} \text{ s}^{-1}) [C_2F_4]$
 B) Rate = $22.3 \text{ (mol L}^{-1} \text{ s)} [C_2F_4]$
C) Rate = $0.0448 \text{ (L mol}^{-1} \text{ s}^{-1}) [C_2F_4]^2$
 D) Rate = $22.3 \text{ (mol L}^{-1} \text{ s)} [C_2F_4]^2$
 E) Rate = $0.0448 \text{ s}^{-1} [C_2F_4]$

**From the plot and units of the constant, 2nd order is obvious.
 Therefore, C is the correct choice**

3. The decomposition of dimethylether at 504°C is first order with a half-life of 1470. seconds. What fraction of an initial amount of dimethylether remains after 4710. seconds?

- A) 1/3
 B) 1/6
C) 1/8
 D) 1/16
 E) 1/32

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{1570} = 4.414 \times 10^{-4}$$

**Initial conc. = $[A]_0 = 1$ Final conc. = $[A]_t = x$
 fraction of an initial amount = $1/x$**

$$\ln \left(\frac{[A]_0}{[A]_t} \right) = k t$$

$$\ln \left(\frac{[A]_0}{[A]_t} \right) = 4.414 \times 10^{-4} \times 4710 = 2.07899$$

$$\begin{aligned} \ln[A]_0 - \ln[A]_t &= k t \\ -\ln[A]_t &= 4.414 \times 10^{-4} \times 4710 \\ &= \mathbf{0.125 \text{ which is } = 1 / 8} \end{aligned}$$

x = 8 Therefore, Choice C is correct

4. Carbon monoxide and chlorine combine in an equilibrium reaction to produce the highly toxic product, phosgene (COCl_2). $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{COCl}_2\text{(g)}$

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.

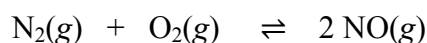
$$[\text{CO}] = [\text{Cl}_2] = 0.010 \text{ mol L}^{-1}; [\text{COCl}_2] = 0.070 \text{ mol L}^{-1}$$

- 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.

$$Q = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{[0.070]}{[0.010][0.010]} = 700$$

$Q \gg K$ Therefore, B is the correct choice

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



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

	$\text{N}_2\text{(g)}$	+	$\text{O}_2\text{(g)}$	\rightleftharpoons	2NO(g)
Before	8.00		5.00		0
Change	-x		-x		+2 x
Equilibrium	8.00 - x		5.00 - x		2 x

$$x = 0.16$$

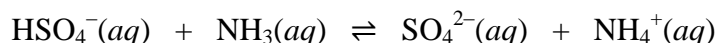
Therefore, partial pressure of nitrogen = 8.00 - 0.16 = 7.8 bar.

$$K_p = 0.0025$$

$$K_p = \frac{p_{\text{NO}}^2}{p_{\text{N}_2} p_{\text{O}_2}}$$

$$0.0025 = \frac{(2x)^2}{(8.00)(5.00)}$$

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**?



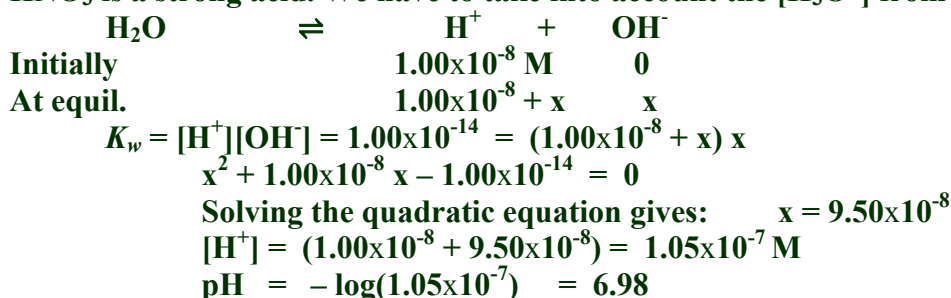
- A) The reactants will be favored because ammonia is a stronger base than the sulfate anion.
- B) The products will be favored because the hydrogen sulfate ion is a stronger acid than the ammonium ion.**
- C) Neither reactants nor products will be favored because all of the species are weak acids or 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.

The answer “B” is obvious from a comparison of the K_a values!

7. What is the pH of a 1.0 L aqueous solution containing 1.0×10^{-8} mol of HNO_3 ?

- A) 8.00
- B) 7.02
- C) 7.00
- D) 6.98**
- E) 6.00

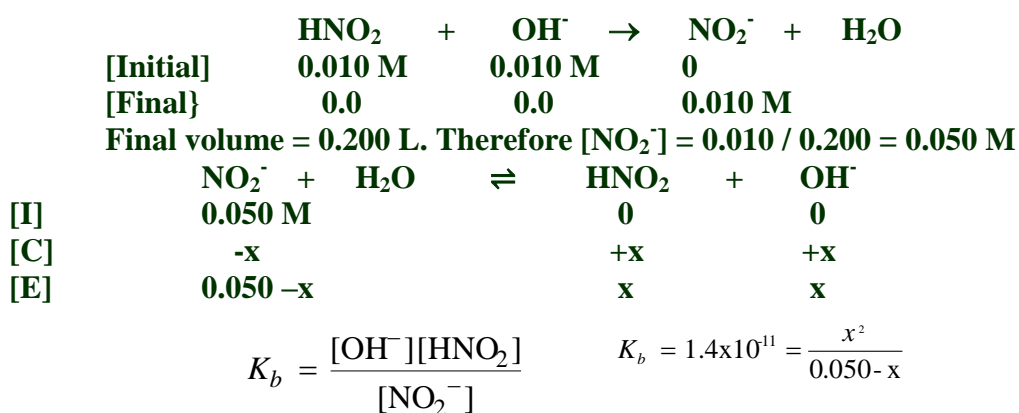
HNO_3 is a strong acid. We have to take into account the $[\text{H}_3\text{O}^+]$ from water.



8. Exactly 100 mL of 0.10 M HNO_2 are titrated with 100 mL of a 0.10 M KOH solution. What is the pH at the equivalence point? (K_a for $\text{HNO}_2 = 7.1 \times 10^{-4}$)

- A) 2.22
B) 7.00
C) 7.92
D) 8.07
E) 11.9

(defined in lab)



$x = [\text{OH}^-] = 8.39 \times 10^{-7}$ Therefore, $\text{pOH} = 6.08$ and $\text{pH} = 7.92$

9. Buffer solutions with the component concentrations shown below were prepared. Which of them should have the **lowest** pH?

- A) $[\text{CH}_3\text{COOH}] = 0.25 \text{ mol L}^{-1}$, $[\text{CH}_3\text{COO}^-] = 0.25 \text{ mol L}^{-1}$
B) $[\text{CH}_3\text{COOH}] = 0.75 \text{ mol L}^{-1}$, $[\text{CH}_3\text{COO}^-] = 0.75 \text{ mol L}^{-1}$
C) $[\text{CH}_3\text{COOH}] = 0.75 \text{ mol L}^{-1}$, $[\text{CH}_3\text{COO}^-] = 0.25 \text{ mol L}^{-1}$
D) $[\text{CH}_3\text{COOH}] = 0.25 \text{ mol L}^{-1}$, $[\text{CH}_3\text{COO}^-] = 0.75 \text{ mol L}^{-1}$
E) $[\text{CH}_3\text{COOH}] = 1.00 \text{ mol L}^{-1}$, $[\text{CH}_3\text{COO}^-] = 1.00 \text{ mol L}^{-1}$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \quad \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \text{ for } \frac{0.25}{0.25} = \frac{0.75}{0.75} = \frac{1.00}{1.00} = 0$$

$$\log \frac{0.75}{0.25} = \log 3 = 0.477 \quad \text{Therefore } \text{pH} = \text{p}K_a + 0.477$$

$$\log \frac{0.25}{0.75} = \log 0.333 = -0.477 \quad \text{Therefore } \text{pH} = \text{p}K_a - 0.477$$

10. Barium sulfate (BaSO_4) is a slightly soluble salt, with $K_{\text{sp}} = 1.1 \times 10^{-10}$. What mass of Ba^{2+} ions will be present in 1.0 L of a saturated solution of barium sulfate?

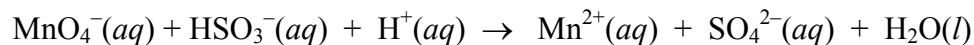
- A) $< 10^{-7} \text{ g}$
- B) $1.0 \times 10^{-5} \text{ g}$
- C) **0.0014 g**
- D) 0.0024 g
- E) $> 0.05 \text{ g}$

$$K_{\text{sp}} = 1.1 \times 10^{-10} = (\text{S})(\text{S})$$

$$\text{S} = 1.049 \times 10^{-5} \text{ M of Ba}^{2+}$$

$$137.3 \times 1.049 \times 10^{-5} = 1.44 \times 10^{-3} \text{ g of Ba}^{2+}$$

11. Balance the following redox equation using the smallest integers possible and select the correct coefficient for the hydrogen sulfite ion, HSO_3^- .



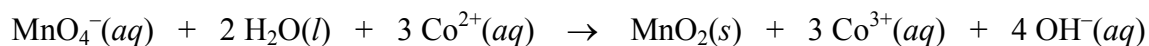
- A) 1
- B) 2
- C) 3
- D) **5**
- E) 10



12. Calculate E°_{cell} and indicate whether the overall reaction shown is spontaneous or nonspontaneous:



Overall reaction:



- 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) $E^\circ_{\text{cell}} = 1.23 \text{ V}$, nonspontaneous
E) $E^\circ_{\text{cell}} = -0.05 \text{ V}$, nonspontaneous

Cathode, reduction; the 2nd reaction – Anode, oxidation, the 1st reaction = $0.59 - 1.82 = -1.23 \text{ V}$

[REDACTED]

[REDACTED]

[REDACTED]

17. Which of the following would represent **diamagnetic** species?

- i. Ca $4s^2$ **Both electrons paired. Therefore, diamagnetic**
- ii. Ge $4s^2 4p^2$ **p electrons unpaired**
- iii. Se $4s^2 4p^4$ **two p electrons unpaired**

- 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: $F > Br > Na$
- 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 single lone pair of electrons on the central atom/s?

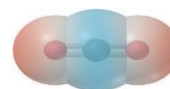
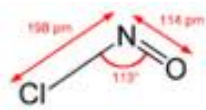
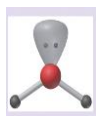
- i. SbF_3
- ii. BrCl_3
- iii. PCl_5



- A) **i only**
- B) ii only
- C) iii only
- D) i & ii only
- E) All of them will

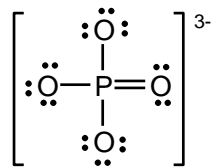
21. Which of the following compound(s) has(have) bent molecular shape(s)?

- i. SO_2
- ii. NOCl
- iii. CO_2



- 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 ___ **0** ___ and an oxidation number of ___ **5** ___.

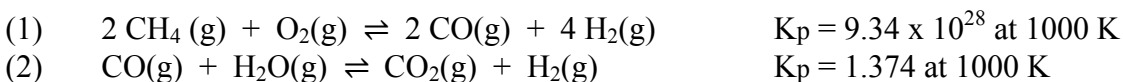


- A) 0, -3
B) 0, 5
C) 5, -3
D) 5, 5
E) 3, 5

***** END OF MULTIPLE CHOICE QUESTIONS SECTION *****

SECTION II: To be graded manually (Total value 28)Answers must be written in non-erasable ink to be considered for re-grading!**For full marks show all your work.**

23. Using methane (CH_4) and steam ($\text{H}_2\text{O}(\text{g})$) as a source of hydrogen (H_2) for ammonia (NH_3) synthesis requires high temperatures. Rather than burning CH_4 separately to heat the mixture, it is more efficient to inject some O_2 into the reaction mixture. All the H_2 is, thus, released for the synthesis, and the heat of reaction for the combustion of CH_4 helps to maintain the required temperature. Imagine the reaction, occurring in two steps, as follows:


 Marks
6

- (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? $K_p = (9.34 \times 10^{28}) (1.888) = 1.76339 \times 10^{29} = 1.76 \times 10^{29}$
- (c) What is K_c for the overall reaction? $\Delta n = \text{mol of gaseous prods} - \text{mol of gaseous reacts} = 8 - 5 = 3$

$$K_p = K_c(RT)^{\Delta n} \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.76339 \times 10^{29}}{[(0.08314 \text{ bar L/mol K})]^3} = 3.01713 \times 10^{23} = 3.02 \times 10^{23}$$

- (d) A mixture of 2.0 mol of CH_4 , 1.0 mol of O_2 , and 2.0 mol of steam ($\text{H}_2\text{O}(\text{g})$), 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?

The initial total pressure is given as 30. bar. To find the final pressure use the relationship between pressure and amount (mol) of gas:

$$n_{\text{initial}} / P_{\text{initial}} = n_{\text{final}} / P_{\text{final}}$$

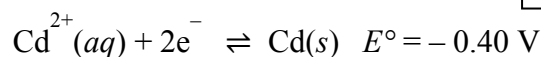
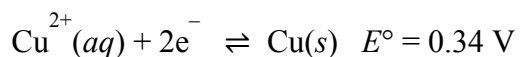
Total mol of gas initial = 2.0 mol CH_4 + 1.0 mol O_2 + 2.0 mol H_2O = 5.0 mol

Total mol of gas final = 2.0 mol CO_2 + 6.0 mol H_2 = 8.0 mol (from mole ratios)

$$P_{\text{final}} = (30. \text{ bar.reactants}) \left[\frac{8 \text{ mol products}}{5 \text{ mol reactants}} \right] = 48. \text{ bar}$$

24. A voltaic cell has one half-cell with a Cu bar in a 1.00 mol/L Cu^{2+} salt, and the other half-cell with a Cd bar in the same volume of a 1.00 mol/L Cd^{2+} salt.

Marks 8



a) Find E°_{cell} and K .

The half-reactions are: **Oxidation:** $\text{Cd}(\text{s}) \rightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{e}^{-} \quad E^{\circ} = -0.40 \text{ V}$

Reduction: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s}) \quad E^{\circ} = 0.34 \text{ V}$

Overall: $\text{Cd}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cd}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.34 \text{ V} - (-0.40 \text{ V}) = 0.74 \text{ V}$$

$$\ln K = \frac{nFE^{\circ}_{\text{cell}}}{RT}$$

$$\ln K = (2) (96485 \text{ C/mol}) (0.74 \text{ V}) / (8.314 \text{ J/molK}) (298 \text{ K}) = 57.636 \text{ Therefore, } K = 1.07 \times 10^{25}$$

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

The cell reaction is: $\text{Cu}^{2+}(\text{aq}) + \text{Cd}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Cd}^{2+}(\text{aq})$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - [(8.314 \text{ J/molK}) (298 \text{ K}) / (2) (96485 \text{ C/mol})] \ln Q$$

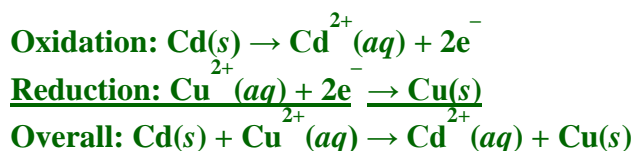
$$E = 0.74 \text{ V} - \frac{(8.314 \text{ J/mol K}) (298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{[\text{Cd}^{2+}]}{[\text{Cu}^{2+}]}$$

An increase in the cadmium conc. by 0.95 mol/L requires an equal decrease in the copper conc. since the mole ratios are 1:1. Thus, when $[\text{Cd}^{2+}] = 1.95 \text{ M}$, $[\text{Cu}^{2+}] = (1.00 - 0.95) \text{ M} = 0.05 \text{ M}$.

$$E = 0.74 \text{ V} - \frac{(8.314 \text{ J/mol K}) (298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \frac{[1.95]}{[0.05]} \quad E = 0.69296 \text{ V} = 0.69 \text{ V}$$

$$E = 0.74 \text{ V} - \frac{0.0257}{2} \ln \frac{[1.95]}{[0.05]} \quad E = 0.74 \text{ V} - \frac{0.0592}{2} \log \frac{[1.95]}{[0.05]}$$

- 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 $[\text{Cu}^{2+}]$ at equilibrium.

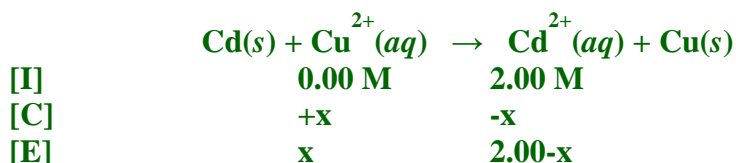


At equilibrium, $E_{\text{cell}} = 0$,

Use Nernst equation to determine the $[\text{Cu}^{2+}]$.

Let the copper ion completely react to give $[\text{Cu}^{2+}] = 0.00 \text{ mol/L}$ and $[\text{Cd}^{2+}] = 2.00 \text{ mol/L}$.

The system can now go to equilibrium giving $[\text{Cu}^{2+}] = +x \text{ mol/L}$ and $[\text{Cd}^{2+}] = (2.00 - x) \text{ mol/L}$.



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{(8.314 \text{ J/mol K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln Q \quad 0.00 = 0.74 \text{ V} - \frac{(8.314 \text{ J/mol K})(298 \text{ K})}{(2)(96485 \text{ C/mol})} \ln \left(\frac{2.00 - x}{x} \right)$$

Assume x is negligible compared to 2.00.

$$57.636 = \ln(2.00 / x) \quad \text{or} \quad 1 \times 10^{25} = 2.00 / x \quad \text{Therefore, } x = 1.9 \times 10^{-25} \text{ mol/L Cu}^{2+}$$

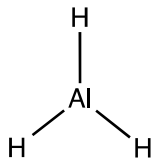
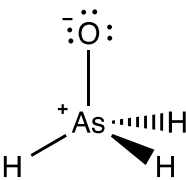
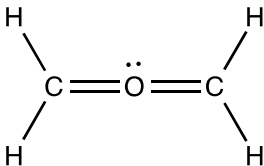
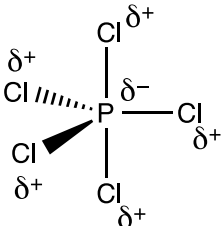
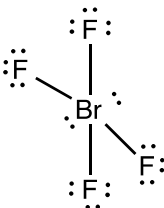
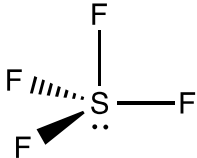
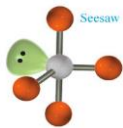
$$E = 0.74 \text{ V} - \frac{0.0257}{2} \ln \frac{[2.00]}{[x]}$$

$$E = 0.74 \text{ V} - \frac{0.0592}{2} \log \frac{[2.00]}{[x]}$$

25. 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 error	VSEPR Diagram	Letter for the error
	G		A
	B		C
	D	 	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	Trigonal planar	Tetrahedral	Trigonal bipyramid	Trigonal bipyramid
Molecular geometry	Trigonal planar	Tetrahedral	T-shaped	Linear
Bond angles	120	109.5	< 90, < 180	180
Net Polarity	Slightly polar	Non-polar	Polar	Non-polar
Hybridization	s p ²	s p ³	s p ³ d	s p ³ d

*****END OF WRITTEN ANSWER SECTION*****

Periodic Table

Lanthanides *Actinides **

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

Conversion factors:

Conversion factors:

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \qquad 1 \text{ Pa} = 1 \text{ kg m s}^{-2}$$
$$T_{\text{K}} = T_{\text{°C}} + 273.15$$
$$1 \text{ L atm} = 101.3 \text{ J}$$
$$1 \text{ atm} = 760.0 \text{ torr} = 101.3 \text{ kPa} = 760.0 \text{ mm Hg} = 1.013 \text{ bar}$$
$$1 \text{ L} = 10^{-3} \text{ m}^3$$
$$1 \text{ C} = 1 \text{ J/V} \qquad 1 \text{ A} = 1 \text{ C s}^{-1}$$

STP conditions: 0 °C, 1 atm

Electrochemical standard state: 1 atm, 1M, 25 °C

$$c = \lambda \nu \qquad E = h\nu \qquad E = mc^2 \qquad \frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad \Delta E = -R_H \left(\frac{Z^2}{n_f^2} - \frac{Z^2}{n_i^2} \right)$$