

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAM
CHEMISTRY 209
VERSION A

Date: Thursday December 12th, 2013

Time: 12:00pm – 3:00pm

FIRST NAME: Answer

LAST NAME: Key

ID.....

Q22..... Q23..... Q24..... Q25..... Q26.....

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

Please circle your lecture section number below.

Lec. 01 Dr. Sandblom

(Tu/Th 2:00 pm)

Lec. 02 Dr. E. Sullivan

(Tu/Th 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 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 3 hour exam. The answers to the long answer questions must be written in the space provided on the question sheets.

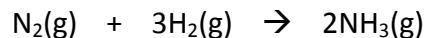
This test consists of **21 multiple choice** questions **worth 2 marks each** (total 42 marks) and **5 long answer** questions (total 40 marks). The total value for the test is **82 marks**. The exam has 17 pages; check that you have all 17 pages.

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

SECTION I - Machine graded section (Total value 42)
To be answered on provided Optical Score Sheet

1. Ammonia, an important source of fixed nitrogen that can be metabolized by plants, is produced using the Haber process in which nitrogen and hydrogen combine.



How many grams of nitrogen are needed to produce 325 grams of ammonia?

a) 1070 g
 b) 535 g
 c) 267 g
 d) 178 g
 e) 108 g

$$325 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.04 \text{ g}} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} \times \frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} = 267 \text{ g}$$

2. The decomposition of SOCl_2 is first-order in SOCl_2 . If the half-life for the reaction is 4.1 hr, how long would it take for the concentration of SOCl_2 to drop from 0.36 M to 0.045 M?

- a) 0.52 hr
 b) 1.4 hr
 c) 12 hr
 d) 33 hr
 e) > 40 hr

$$t_{1/2} = \frac{0.693}{k} \quad \therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.1 \text{ hr}} = 0.169 \text{ hr}^{-1}$$

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

$$\ln \left(\frac{0.36}{0.045} \right) = (0.169 \text{ hr}^{-1}) t$$

$$t = \frac{\ln 8}{0.169 \text{ hr}^{-1}} = 12 \text{ hr}$$

3. Dinitrogen tetraoxide, N_2O_4 , decomposes to nitrogen dioxide, NO_2 , in a first-order process. If $k = 2.5 \times 10^3 \text{ s}^{-1}$ at -5°C and $k = 3.5 \times 10^4 \text{ s}^{-1}$ at 25°C , what is the activation energy for the decomposition?

- a) 0.73 kJ/mol
 b) 58 kJ/mol
 c) 140 kJ/mol
 d) 580 kJ/mol
 e) > 1000 kJ/mol

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

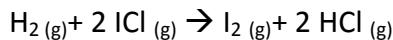
$$\ln \left(\frac{3.5 \times 10^4}{2.5 \times 10^3} \right) = \frac{E_a}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \left(\frac{1}{268 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\frac{21.9411 \text{ J/mol} \cdot \text{K}}{3.756385856 \times 10^{-4} \text{ K}} = E_a$$

$$E_a = 58410 \text{ J/mol}$$

$$= 58 \text{ kJ/mol}$$

4. The reaction between the gases iodine-monochloride and hydrogen produce two gases, iodine and hydrogen chloride as products:



The following reaction mechanism is proposed.



Predict a rate law based on this mechanism.

a) Rate = $k [\text{H}_2][\text{ICl}]$

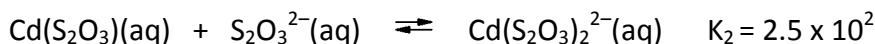
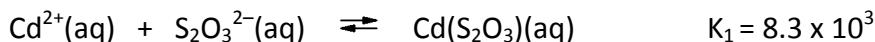
b) Rate = $k [\text{H}_2][\text{ICl}]^2$

c) Rate = $k [\text{HI}][\text{ICl}]$

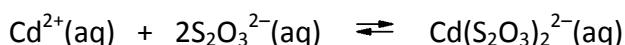
d) Rate = $k [\text{HI}][\text{HCl}]$

e) Rate = $k [\text{I}_2][\text{HCl}]^2$

5. Consider the reactions of cadmium with the thiosulfate anion.



What is the value for the equilibrium constant for the following reaction?



a) 0.030

$K = K_1 \cdot K_2$

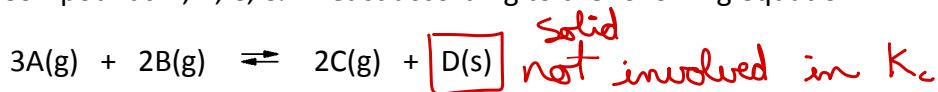
b) 33

c) 8.1×10^3

d) 8.6×10^3

e) 2.1×10^6

6. Compounds A, B, C, & D react according to the following equation:



In a 1.00 L container we have 0.855 mol of A, 1.23 mol of B, 1.75 mol of C and 2.0 mol of D. What is the value of K_c for this reaction?

a) 0.309

b) 0.601

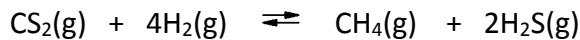
c) 1.66

d) 3.24

e) > 10

$$K_c = \frac{[C]^2}{[A]^3[B]^2} = \frac{1.75^2}{(0.855^3)(1.23^2)} = 3.24$$

7. The reaction system



is at equilibrium. Which of the following statements describes the behaviour of the system if the partial pressure of hydrogen is doubled?

a) As equilibrium is re-established, the partial pressure of carbon disulfide increases.

b) As equilibrium is re-established, the partial pressure of methane, CH_4 , decreases.

c) As equilibrium is re-established, the partial pressure of hydrogen decreases.

d) As equilibrium is re-established, the partial pressure of hydrogen sulfide decreases.

e) As equilibrium is re-established, all the partial pressures will decrease.

8. A lab technician fully dissolves 0.35 mol of cadmium nitrate, $\text{Cd}(\text{NO}_3)_2$ in 1.0 L of water. The technician then adds 0.20 mol of NaF to this solution. Which of the following statements is correct? $K_{\text{sp}} = 6.44 \times 10^{-3}$ for CdF_2 (assume overall volume stays at 1.0 L).

a) Cadmium fluoride precipitates until the solution is saturated.

b) The solution is unsaturated and no precipitate forms.

c) The solubility of cadmium fluoride is increased by the presence of additional fluoride ions. $\text{Q}_{\text{sp}} = (0.35)(0.20)^2 = 1.40 \times 10^{-2} > K_{\text{sp}}$

d) One must know K_{sp} for cadmium nitrate to make meaningful predictions on this system.

e) The presence of NaF will raise the solubility of $\text{Cd}(\text{NO}_3)_2$.

$$\text{Cd}(\text{NO}_3)_2 = 0.35 \text{ mol/L}$$

$$\text{NaF} = 0.20 \text{ mol/L}$$

$$Q_{\text{sp}} = (0.35)(0.20)^2 = 1.40 \times 10^{-2}$$

9. Calculate the molar solubility of silver phosphate, Ag_3PO_4 , in pure water. $K_{\text{sp}} = 2.6 \times 10^{-18}$

a) $4.0 \times 10^{-5} \text{ mol L}^{-1}$

$$K_{\text{sp}} = 2.6 \times 10^{-18}$$

b) $1.8 \times 10^{-5} \text{ mol L}^{-1}$

c) $4.0 \times 10^{-6} \text{ mol L}^{-1}$



d) $1.5 \times 10^{-6} \text{ mol L}^{-1}$

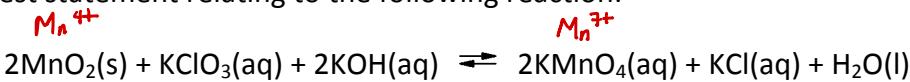
$$3s \quad s$$

e) $< 1.0 \times 10^{-6} \text{ mol L}^{-1}$

$$K_{\text{sp}} = (3s)^3 s = 27s^4 = 2.6 \times 10^{-18}$$

$$s = \sqrt[4]{\frac{2.6 \times 10^{-18}}{27}} = 1.8 \times 10^{-5}$$

10. Select the best statement relating to the following reaction:



a) Mn in MnO_2 is oxidized.

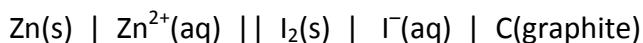
b) O in KClO_3 is the oxidizing agent.

c) K in KClO_3 is the reducing agent.

d) H in KOH is oxidized.

e) Cl in KClO_3 is the reducing agent.

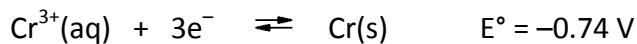
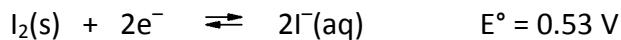
11. A voltaic cell prepared using zinc and iodine has the following cell notation.



Which of the following equations correctly represents the balanced, spontaneous, cell reaction?

- a) $2\text{I}^-(\text{aq}) + \text{Zn}^{2+}(\text{aq}) \rightleftharpoons \text{I}_2(\text{s}) + \text{Zn(s)}$
- b) $\text{I}_2(\text{s}) + \text{Zn(s)} \rightleftharpoons 2\text{I}^-(\text{aq}) + \text{Zn}^{2+}(\text{aq})$
- c) $2\text{I}^-(\text{aq}) + \text{Zn(s)} \rightleftharpoons \text{I}_2(\text{s}) + \text{Zn}^{2+}(\text{aq})$
- d) $\text{I}_2(\text{s}) + \text{Zn}^{2+}(\text{aq}) \rightleftharpoons 2\text{I}^-(\text{aq}) + \text{Zn(s)}$
- e) None of the above, since graphite must be in the equation.

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



Overall reaction:



- a) $E^\circ_{\text{cell}} = -1.27 \text{ V}$, spontaneous
- b) $E^\circ_{\text{cell}} = -1.27 \text{ V}$, nonspontaneous
- c) $E^\circ_{\text{cell}} = 1.27 \text{ V}$, spontaneous
- d) $E^\circ_{\text{cell}} = 1.27 \text{ V}$, nonspontaneous
- e) $E^\circ_{\text{cell}} = 1.54 \text{ V}$, spontaneous



15. Which of the following atoms or ions is paramagnetic?

- a) Cl^-
- b) Cd
- c) Ca
- d) Na^+
- e) B

*Without Quantum #s, all of these

16. Which of the following gives the correct orbital, set of quantum numbers and electron probability density diagram for an electron.

are possible

	Name of the Orbital		Electron Probability Density Diagram
a)	1s		
b)	2s		
c)	2p _x		
d)	2p _y		
e)	4d _{xz}		

17. Which one of the following simple, shorthand, ground state electron configurations is incorrect for the elements given?

- a) Beryllium: [He] 2s²
- b) Carbon: [He] 2s²2p²
- c) Silicon: [Ne] 3s²3p²
- d) Phosphorus: [Ne] 3s²3p³
- e) Scandium: [Ar] 4s²4d¹

*e⁻ configs for d-block elements
werent done this year -
but this one should hopefully
make sense*

↑
4s²3d¹

18. Which of the orbital diagrams gives the correct electron configuration for an atom of boron, in the ground state?

- | | 1s | 2s | 2p |
|-----------|----|----|----|
| a) | | | |
| b) | | | |
| c) | | | |
| d) | | | |
| e) | | | |

19. Which represents the shorthand electron configuration for P³⁺?

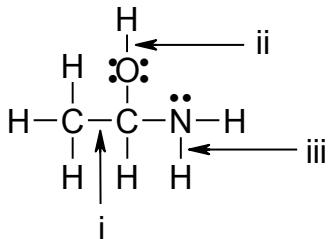
- a) [Ar]
- b)** [Ne]3s²
- c) [Ne]3s²3p³
- d) [Ne]3s²3p⁶
- e) [Ar]4p³

20. Which of the following statements is false?

- a) a H atom is larger than an H^+ ion
- b) a K^+ cation will be smaller than a Cl^- anion
- c) an O atom will be smaller than an O^{2-} anion
- d) a N atom will be smaller than an O atom
- e) an O atom will be smaller than a Te atom

21. Which of the following is the **most** polar covalent bond?

- a) i only
- b) ii only
- c) iii only
- d) i and ii only
- e) All of the above

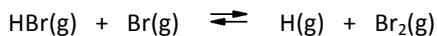


*****END OF MULTIPLE CHOICE*****

SECTION II: To be graded manually (Total value 26)
For full marks show all your work.

QUESTION 22 VALUE 6 MARKS

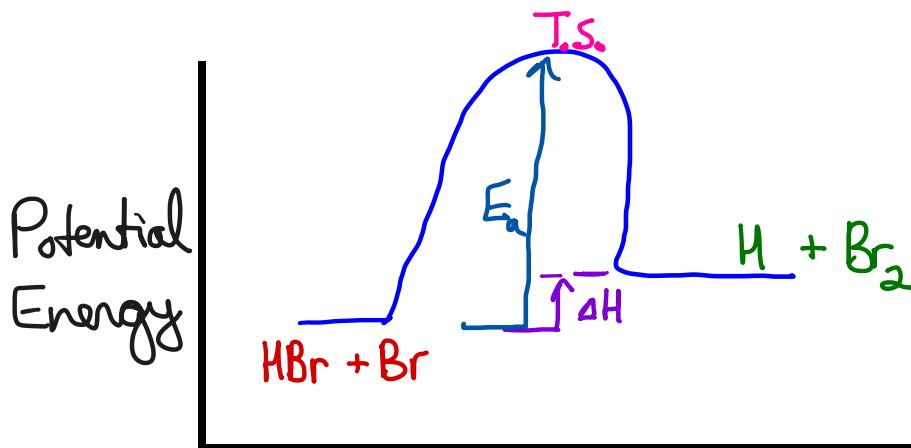
For all parts of this question, consider a reaction with this elementary step:



- This step is endothermic (ΔH is positive).
- The activation energy (E_a) for this step is bigger in magnitude than ΔH .

a) [4 points] Draw a reaction energy diagram for this elementary step. Label the following:

• Reactants (R)	• ΔH for the forward reaction
• Products (P)	• E_a for the forward reaction
• Transition state (TS)	• Both axes



b) [0.5 point] Which rate constant is bigger? Add an X to one box.

k_{reverse} (rate constant for the reverse reaction)



k_{forward} (rate constant for the forward reaction)

c) [1 point] Write one or two grammatically correct sentences explain your choice in part (b).

The reverse reaction will have a faster rate since the activation energy is lower

d) [0.5 point] Write the predicted rate law for this step.

$$\text{Rate} = k[\text{HBr}][\text{Br}]$$

QUESTION 23 VALUE 10 MARKS

In Experiment #4, Sue and Stu Dent used potentiometric titrations to prepare a 1:1 buffer of butyric acid (C_3H_7COOH) and sodium butyrate (C_3H_7COONa).

- a) [1 point] Write the balanced equation for the neutralization of OH^- by butyric acid.



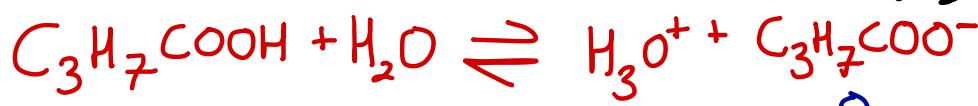
- b) [2 points] Calculate the equilibrium constant for the reaction in part (a) given that the K_a for butyric acid is 1.51×10^{-5}

$$K_b = \frac{[C_3H_7COO^-]}{[C_3H_7COOH][OH^-]} \quad K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.51 \times 10^{-5}} = 6.62 \times 10^{-10}$$

$$K_b = \frac{[C_3H_7COOH][OH^-]}{[C_3H_7COO^-]} \quad \therefore K = \frac{1}{K_b} = \frac{1}{6.62 \times 10^{-10}} = 1.51 \times 10^9$$

- c) [2 points] Before the titration starts, calculate the pH of the 0.13 M solution of butyric acid.

~2 sig figs for answer



I	0.13		
C	-x	+x	+x
E	0.13-x	x	x

assume small
 $\therefore 0.13 - x \approx 0.13$

$$K_a = \frac{[H_3O^+][C_3H_7COO^-]}{[C_3H_7COOH]} = \frac{x^2}{0.13} = 1.51 \times 10^{-5}$$

$$x^2 = 1.96 \times 10^{-6}$$

$$x = 1.40 \times 10^{-3} M = [H_3O^+]$$

$$pH = -\log [H_3O^+] = -\log (1.40 \times 10^{-3}) = 2.85$$

*↑
2 sig figs*

- d) [3 points] How many mL of 0.1032 M NaOH will Sue & Stu need to add to make the 1:1 buffer when they are provided with 25.00 mL of 0.13 M butyric acid?

$$\text{# mole of acid} = 0.13 \text{ mol/L} \times 0.0250 \text{ L} = 3.3 \times 10^{-3} \text{ mol}$$

1:1 ratio of $\text{C}_3\text{H}_7\text{COOH}$: $\text{C}_3\text{H}_7\text{COO}^-$

\therefore must add $\frac{1}{2}$ the # of moles of NaOH so we have a 1:1 buffer.

$$\text{# mole of NaOH} = \frac{3.3 \times 10^{-3} \text{ mol}}{2} = 1.65 \times 10^{-3} \text{ mol}$$

$$\therefore 1.65 \times 10^{-3} \text{ mol} \times \frac{1 \text{ L}}{0.1032 \text{ mol}} = 0.015988 \text{ L}$$

\therefore 16 mL of NaOH needs to be added.

- e) [2 point] Calculate the pH of the 1:1 buffer.

$$\text{pH} = \text{p}K_a + \log \left(\frac{\text{base}}{\text{acid}} \right)$$

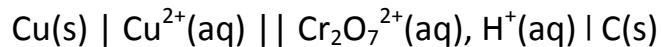
$$\text{pH} = -\log K_a + \cancel{\log (1)}^0$$

$$\text{pH} = -\log (1.51 \times 10^{-5})$$

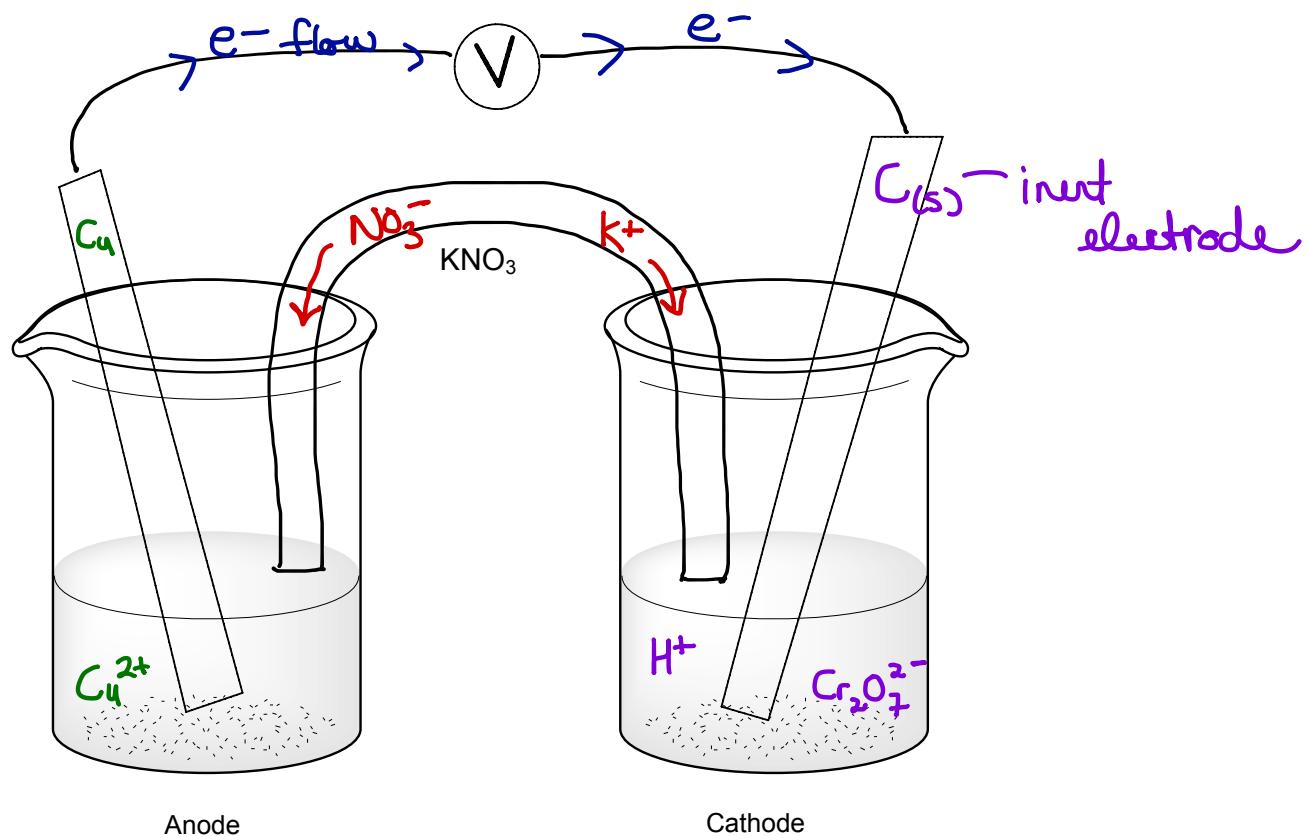
$$\text{pH} = 4.821$$

QUESTION 24 VALUE 4 MARKS

Consider the line cell notation for voltaic cell below and complete the diagram by including the following:



- Active and inactive half-cell components for both half-cells
- Direction of electron flow
- Direction of flow for ions in the salt bridge



QUESTION 25 VALUE 6 MARKS

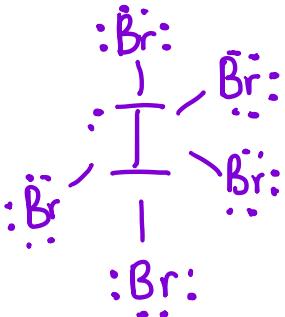
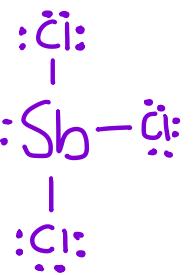
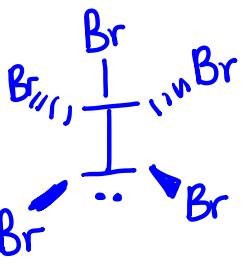
Every diagram drawn in the table below was drawn by a person just learning about chemistry. Become the professor and grade the work of the student by associating each diagram with **one of the statements A through F** below to explain why a given structure is incorrect or correct (Any error could occur more than once).

- A. The formal charges are not minimized.
- B. The central atom cannot have an expanded octet.
- C. The partial charges/dipoles are drawn incorrectly.
- D. The formal charges have not been included.
- E. Lone pairs are missing.
- F. The structure is correct.

Diagram	Letter(s) for the error(s)	Diagram	Letter(s) for the error(s)
	F		E
	D		B
	C		A

QUESTION 26 VALUE 14 MARKS

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 and net polarity. Enter your answers in the appropriate boxes. **Note: Lewis structures need to show all electron groups and all non-zero formal charges.**

Molecule	IBr_5	SO_2	SbCl_3	CO_2
Lewis structure (2D)				
VSEPR structure (3D)				
Electron-group arrangement	Octahedral	trigonal planar	tetrahedral	linear
Molecular Shape	Square pyramidal	Bent or V-shaped	trigonal pyramidal	linear
Bond Angles	$<90^\circ, <180^\circ$	$<120^\circ$	$<109.5^\circ$	180°
Hybridization	Sp^3d^2	Sp^2	Sp^3	sp

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

1													18				
1A													8A				
1 H 1.008	2 Be 9.012												2 He 4.003				
3 Li 6.941													10 Ne 20.18				
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 B 10.81	14 C 12.01	15 N 14.01	16 O 16.00	17 F 19.00	18 Ne 20.18
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 (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	58 Hf 178.5	59 Ta 180.9	60 W 183.9	61 Re 186.2	62 Os 190.2	63 Ir 192.2	64 Pt 195.1	65 Au 197.0	66 Hg 200.6	67 Tl 204.4	68 Pb 207.2	69 Bi 209.0	70 Po (209)	71 At (210)	72 Rn (222)
87 Fr (223)	88 Ra (227)	89** Ac (261)	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, HNO₃, H₂SO₄, HClO₄

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

Constants:	Conversion factors:													
Gas constant, R	$0.08205 \text{ L atm mol}^{-1} \text{ K}^{-1}$													
	$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$													
Avogadro's number: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$	$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$													
Faraday: $F = 96,485 \text{ C / mol electrons}$	$1 \text{ Pa} = 1 \text{ kg m s}^{-2}$													
Planck's constant $h = 6.626 \times 10^{-34} \text{ Js}$	$T \text{ K} = T^\circ \text{C} + 273.15$													
Speed of light, $c = 2.998 \times 10^8 \text{ m/s}$	$1 \text{ L atm} = 101.3 \text{ J}$													
Rydberg constant, $R = 1.09678 \times 10^{-7} \text{ m}^{-1}$	$1 \text{ atm} = 760.0 \text{ torr} = 101.3 \text{ kPa} = 760.0 \text{ mm Hg} = 1.013 \text{ bar}$													
	$1 \text{ L} = 10^{-3} \text{ m}^3$													
	$1 \text{ C} = 1 \text{ J/V}$													
	$1 \text{ A} = 1 \text{ C s}^{-1}$													
	STP conditions: $0^\circ \text{C}, 1 \text{ atm}$													

$$[A]_t = -kt + [A]_0 \quad \ln[A]_t = -kt + \ln[A]_0 \quad \frac{I}{[A]_t} = kt + \frac{I}{[A]_0} \quad \ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

$$t_{1/2} = \frac{[A]_0}{2k} \quad t_{1/2} = \frac{0.693}{k} \quad t_{1/2} = \frac{1}{k[A]_0} \quad k = Ae^{\frac{-E_a}{RT}} \quad \ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad PV = nRT \quad K_p = K_c (RT)^{4n} \quad ax^2 + bx + c = 0$$

$$\text{pH} = -\log[\text{H}^+] \quad K_w = K_a K_b \quad K_{sp} = I / K_d \quad K_f = I / K_d \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{cong. base}]}{[\text{cong. acid}]}\right) \quad \text{or} \quad \text{pOH} = \text{p}K_b + \log\left(\frac{[\text{cong. acid}]}{[\text{cong. base}]}\right)$$

$$E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad E = E^\circ - \frac{0.0592}{n_e} \log Q \quad E^\circ = \frac{0.0592}{n_e} \log K \quad \text{or} \quad nFE^\circ = RT \ln K$$

$$q = It \quad q = n_e F \quad c = \lambda v \quad E = hv \quad E = mc^2 \quad \frac{1}{\lambda} = R \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad \Delta E = -R_H \left(\frac{Z^2}{n_f^2} - \frac{Z^2}{n_i^2} \right)$$

$$E = -R_H \left(\frac{Z}{n} \right)^2 \quad \text{or} \quad E_n = -\frac{Rhc}{n^2} \quad \text{for single electron species}$$