



# 2013 U.S. NATIONAL CHEMISTRY OLYMPIAD NATIONAL EXAM - PART II



Prepared by the American Chemical Society Olympiad Examinations Task Force

## OLYMPIAD EXAMINATIONS TASK FORCE

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### DIRECTIONS TO THE EXAMINER - PART II

**Part II** of this test requires that student answers be written in a response booklet with blank pages. Only this "Blue Book" is graded for a score on **Part II**. Testing materials, scratch paper, and the "Blue Book" should be made available to the student only during the examination period. All testing materials including scratch paper should be turned in and kept secure until **April 15, 2013**, after which tests can be returned to students and their teachers for further study.

Allow time for the student to read the directions, ask questions, and fill in the required information on the "Blue Book". When the student has completed **Part II**, or after one hour and forty-five minutes have elapsed, the student must turn in the "Blue Book", **Part II** of the testing materials, and all scratch paper. Be sure that the student has supplied all of the information requested on the front of the "Blue Book," and that the same identification number used for **Part I** has been used again for **Part II**.

There are three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest breaks between parts.

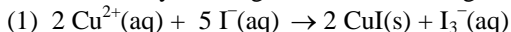
<b>Part I</b>	<b>60 questions</b>	<b>single-answer multiple-choice</b>	<b>1 hour, 30 minutes</b>
<b>Part II</b>	<b>8 questions</b>	<b>problem-solving, explanations</b>	<b>1 hour, 45 minutes</b>
<b>Part III</b>	<b>2 lab questions</b>	<b>laboratory practical</b>	<b>1 hour, 30 minutes</b>

A periodic table and other useful information are provided on page 4 for student reference. Students should be permitted to use non-programmable calculators.

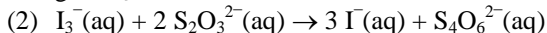
### DIRECTIONS TO THE EXAMINEE - PART II

**DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO.** **Part II** requires complete responses to questions involving problem-solving and explanations. **One hour and forty-five minutes** are allowed to complete this part. Be sure to print your name, the name of your school, and your identification number in the spaces provided on the "Blue Book" cover. (Be sure to use the same identification number that was coded onto your Scantron sheet for **Part I**.) Answer all of the questions in order, and use both sides of the paper. Do not remove the staple. Use separate sheets for scratch paper and do **not** attach your scratch paper to this examination. When you complete **Part II** (or at the end of one hour and forty-five minutes) you must turn in all testing materials, scratch paper, and your "Blue Book". **Do not forget to turn in your U.S. citizenship/ Green Card Holder statement before leaving the testing site today.**

1. [12] A compound contains only C, H, O and Cu. It is analyzed for its carbon and hydrogen content by combustion. The copper content is obtained by reacting it with  $\text{I}^-$  according to equation (1),



and reacting the  $\text{I}_3^-$  formed with standard thiosulfate,  $\text{S}_2\text{O}_3^{2-}$  according to equation (2).



- a. The combustion of a 0.250 g sample of the compound produces 0.504 g of  $\text{CO}_2$  and 0.0743 g of  $\text{H}_2\text{O}$ . Determine the mass percentages of carbon and hydrogen in the compound.
- b. In the analysis for  $\text{Cu}^{2+}$ , a 0.115 g sample of the compound is reacted with concentrated nitric acid, evaporated to dryness and the residue is dissolved in  $\text{H}_2\text{O}$ . The  $\text{Cu}^{2+}$  in the resulting solution is reacted with excess  $\text{I}^-$  and the resulting  $\text{I}_3^-$  is titrated with 0.0320 M  $\text{S}_2\text{O}_3^{2-}$ , requiring 11.75 mL.
- i. Name the indicator used for the titration of  $\text{I}_3^-$  with  $\text{S}_2\text{O}_3^{2-}$  and describe the color change observed.
- ii. Determine the moles of  $\text{Cu}^{2+}$  and calculate the mass percentage of Cu in the compound.
- c. Find the mass percentage of oxygen and write the empirical formula for the compound.
- d. A solution prepared by dissolving 0.100 g of this compound in 15.00 g of benzene,  $\text{C}_6\text{H}_6$ , freezes at 5.436 °C. Find the molar mass and molecular formula of the compound. [ $\text{C}_6\text{H}_6$  m.p. = 5.490 °C,  $k_f = 4.90 \text{ }^\circ\text{C}\cdot\text{m}^{-1}$ ]

2. [14] Some thermodynamic properties of liquid and gaseous benzene are given below.

	$\Delta H_f^\circ$ , kJ•mol <sup>-1</sup>	$S^\circ$ , J•mol <sup>-1</sup> •K <sup>-1</sup>	$\Delta H^\circ_{\text{combustion}}$ , kJ•mol <sup>-1</sup>
$\text{C}_6\text{H}_6(l)$	48.7	173.3	-3273
$\text{C}_6\text{H}_6(g)$	82.9	269.0	NA

- a. Calculate the vapor pressure of benzene at 25 °C in mm Hg.
- b. Calculate the enthalpy change associated with the hypothetical reaction:  $\text{C}_6\text{H}_6(l) \rightarrow 6\text{C}(s) + 3\text{H}_2(g)$  for 1.50 g of  $\text{C}_6\text{H}_6$ .
- c. Write a balanced equation for the complete combustion of one mole of benzene.
- d. Use the bond energies below to calculate an estimated bond energy of the carbon-carbon bonds in benzene.

Bond	C–H	C–O	C=O	C≡O	H–O	O–O	O=O
Energy, kJ/mol	414	351	799	1070	464	142	498

- e. 1.50 g of benzene is burned in a bomb calorimeter with a heat capacity of 5.99 kJ/°C submerged in 1.00 kg of water at 22.50 °C. Determine the final temperature of the system. [Specific heat of  $\text{H}_2\text{O}(l) = 4.18 \text{ J}\cdot\text{g}^{-1}\cdot^\circ\text{C}^{-1}$ ]
3. [10] The thermal decomposition of peroxyntic acid,  $\text{HO}_2\text{NO}_2$ , has been studied and found to be first-order. The rate constant was determined to be  $2.1 \times 10^{-1} \text{ s}^{-1}$  at 331 K and  $1.1 \text{ s}^{-1}$  at 342 K.
- a. Calculate the half-life of  $\text{HO}_2\text{NO}_2$  at 331 K in seconds.
- b. For a sample of  $\text{HO}_2\text{NO}_2$  with an initial concentration of  $7.1 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$ , calculate the concentration of  $\text{HO}_2\text{NO}_2$  after 0.40 minutes at 331 K.
- c. Sketch a graph for the decomposition of  $\text{HO}_2\text{NO}_2$  at 331 K for three half-lives and predict the fraction remaining after five half-lives.
- d. Calculate the activation energy of the reaction.
4. [14] A 0.0343 mol sample of  $\text{XCl}_3(g)$  is added to an evacuated 1.50 L glass bulb. The bulb is sealed, heated to 100 °C and the following equilibrium is established:  $2\text{XCl}_3(g) \rightleftharpoons 2\text{X}(g) + 3\text{Cl}_2(g)$   
At equilibrium, the final pressure in the bulb is 0.800 atm.
- a. Calculate the pressure of  $\text{XCl}_3(g)$  in the bulb at 100 °C if no reaction had occurred.
- b. Calculate the equilibrium partial pressures of
- i.  $\text{XCl}_3(g)$ ,
- ii.  $\text{X}(g)$ ,
- iii.  $\text{Cl}_2(g)$ .
- c. Determine the value at 100 °C of:
- i.  $K_p$ .
- ii.  $\Delta G^\circ$  in kJ•mol<sup>-1</sup>.
- d. Calculate the value of  $K_c$  at 100 °C.
- e. Write an expression that can be used to solve for the concentration of  $\text{XCl}_3$  at equilibrium when 0.0500 mole of  $\text{XCl}_3$  is placed in an evacuated 2.00 L glass bulb at 100 °C. You need not solve this expression.

5. [12] Write net equations for each of the reactions below. Use ionic and molecular formulas as appropriate and omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the equations or specify physical states.

- Calcium sulfite is heated to a high temperature in a vacuum.
- Solutions of sodium oxalate and acidified solution potassium permanganate are mixed.
- Solutions of magnesium sulfate and barium hydroxide are mixed.
- Gaseous dimethylamine and hydrogen chloride are mixed.
- Toluene is reacted with chlorine in the presence of aluminum chloride.
- Carbon-11 undergoes positron emission during a PET scan.

6. [13] Consider the highly reactive molecule  $\text{SF}_3\text{Cl}$ .

- Draw all of the possible structures of  $\text{SF}_3\text{Cl}$  with S as the central atom.
- Use VSEPR theory to predict the most stable structure in a. and justify your answer.
- Recent calculations predict that the two structures that are lowest in energy differ by about 0.2 kJ/mol. Identify the second lowest energy structure and justify your answer.
- Nuclear magnetic resonance (NMR) spectroscopy can be used to distinguish between atoms in different environments in a molecule. State and account for the number of unique F-19 signals if  $^{19}\text{F}$  NMR were carried out on  $\text{SF}_3\text{Cl}$  at
  - a low temperature (e.g.  $-80^\circ\text{C}$ )
  - room temperature in solution.
- While selenium and tellurium can potentially form  $\text{SeF}_3\text{Cl}$  and  $\text{TeF}_3\text{Cl}$ , an  $\text{OF}_3\text{Cl}$  species is not known even though oxygen has the same valence electron configuration. Account for this difference in the behavior of oxygen.

7. [10] Consider two solutions, each of which contains two volatile components. The vapor pressure of each of these components at  $25^\circ\text{C}$  is given in the table below.

Substance	$\text{CCl}_4$	$\text{CHCl}_3$	$\text{CH}_3\text{C(O)CH}_3$
Vapor pressure at $25^\circ\text{C}$ , torr	98.8	172.5	222

- Solution 1 consists of chloroform and carbon tetrachloride, which form an ideal solution.
  - Describe an ideal solution in terms of the interactions of the component molecules and explain why  $\text{CCl}_4$  and  $\text{CHCl}_3$  form an ideal solution.
  - Sketch a graph of vapor pressure vs. mole fraction  $\text{CHCl}_3$  for a  $\text{CHCl}_3\text{-CCl}_4$  solution at  $25^\circ\text{C}$  and predict the vapor pressure of a solution that is 0.30 mole fraction  $\text{CHCl}_3$ .
  - Describe how the composition of the vapor over this solution compares with the composition of the solution. Justify your answer.
- Propanone,  $\text{CH}_3\text{C(O)CH}_3$ , and chloroform mix with the release of heat.
  - Describe or sketch clearly the interaction between the propanone and chloroform molecules that is responsible for the heat release.
  - Use the axes from a. to sketch a graph of vapor pressure vs. mole fraction  $\text{CHCl}_3$  and account for its appearance.

8. [15] There are four isomeric alcohols with the formula  $\text{C}_4\text{H}_{10}\text{O}$ .

- Write structural formulas for these four compounds.
- One of the four alcohols is chiral (stereogenic). Write stereochemical structures for the two enantiomeric forms of this compound. Comment on any differences in their chemical and physical properties.
- Three of the alcohols in a. undergo oxidation to form aldehydes or ketones. Write structures for these products and account for the fact that the fourth alcohol does not react in this way.
- Several compounds exist with this formula but a different functional group. Name the functional group and write structures for all the compounds with this functional group.

ABBREVIATIONS AND SYMBOLS					
amount of substance	<i>n</i>	Faraday constant	<i>F</i>	molar mass	<i>M</i>
ampere	A	free energy	<i>G</i>	mole	mol
atmosphere	atm	frequency	<i>ν</i>	Planck's constant	<i>h</i>
atomic mass unit	u	gas constant	<i>R</i>	pressure	<i>P</i>
Avogadro constant	<i>N<sub>A</sub></i>	gram	g	rate constant	<i>k</i>
Celsius temperature	°C	hour	h	reaction quotient	<i>Q</i>
centi- prefix	c	joule	J	second	s
coulomb	C	kelvin	K	speed of light	<i>c</i>
density	d	kilo- prefix	k	temperature, K	<i>T</i>
electromotive force	<i>E</i>	liter	L	time	<i>t</i>
energy of activation	<i>E<sub>a</sub></i>	measure of pressure mm Hg		vapor pressure	VP
enthalpy	<i>H</i>	milli- prefix	m	volt	V
entropy	<i>S</i>	molal	<i>m</i>	volume	<i>V</i>
equilibrium constant	<i>K</i>	molar	M		

CONSTANTS
$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$1 F = 96,500 \text{ C}\cdot\text{mol}^{-1}$
$1 F = 96,500 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$
$c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
$0 \text{ }^\circ\text{C} = 273.15 \text{ K}$
$1 \text{ atm} = 760 \text{ mm Hg}$

EQUATIONS		
$E = E^\circ - \frac{RT}{nF} \ln Q$	$\ln K = \left( \frac{-\Delta H}{R} \right) \left( \frac{1}{T} \right) + \text{constant}$	$\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

## PERIODIC TABLE OF THE ELEMENTS

1	PERIODIC TABLE OF THE ELEMENTS																18						
1A																	8A						
1 <b>H</b> 1.008	2 <b>He</b> 4.003																						
3 <b>Li</b> 6.941	4 <b>Be</b> 9.012																	5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31	3 <b>B</b> 10.81	4 <b>C</b> 12.01	5 <b>N</b> 14.01	6 <b>O</b> 16.00	7 <b>F</b> 19.00	8 <b>Ne</b> 20.18	9 <b>Na</b> 22.99	10 <b>Mg</b> 24.31	11 <b>Al</b> 26.98	12 <b>Si</b> 28.09	13 <b>P</b> 30.97	14 <b>S</b> 32.07	15 <b>Cl</b> 35.45	16 <b>Ar</b> 39.95								
19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.88	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80						
37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3						
55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	57 <b>La</b> 138.9	72 <b>Hf</b> 178.5	73 <b>Ta</b> 180.9	74 <b>W</b> 183.8	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 <b>Tl</b> 204.4	82 <b>Pb</b> 207.2	83 <b>Bi</b> 209.0	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)						
87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89 <b>Ac</b> (227)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 <b>Ds</b> (281)	111 <b>Rg</b> (272)	112 <b>Cn</b> (285)	113 <b>Uut</b> (284)	114 <b>Uuq</b> (289)	115 <b>Uup</b> (288)	116 <b>Uuh</b> (293)	117 <b>Uus</b> (294)	118 <b>Uuo</b> (294)						

58 <b>Ce</b> 140.1	59 <b>Pr</b> 140.9	60 <b>Nd</b> 144.2	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.4	63 <b>Eu</b> 152.0	64 <b>Gd</b> 157.3	65 <b>Tb</b> 158.9	66 <b>Dy</b> 162.5	67 <b>Ho</b> 164.9	68 <b>Er</b> 167.3	69 <b>Tm</b> 168.9	70 <b>Yb</b> 173.0	71 <b>Lu</b> 175.0
90 <b>Th</b> 232.0	91 <b>Pa</b> 231.0	92 <b>U</b> 238.0	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)



1. a.  $0.504 \text{ g CO}_2 \times \frac{1 \text{ mol}}{44.01 \text{ g}} = 0.01145 \text{ mol C} \times 12.01 = 0.1375 \text{ g C}$

$$0.0743 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.01 \text{ g}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 8.25 \times 10^{-3} \text{ mol H}$$

$$8.25 \times 10^{-3} \text{ mol H} \times 1.008 \text{ g} = 8.317 \times 10^{-3} \text{ g H}$$

$$\text{Mass \% C} = \left( \frac{0.1375 \text{ g C}}{0.250 \text{ g compd}} \right) \times 100 = 55.0 \% \text{ C}$$

$$\text{Mass \% H} = \left( \frac{8.317 \times (10^{-3}) \text{ g H}}{0.250 \text{ g compd}} \right) \times 100 = 3.327 \% \text{ H}$$

b. i. Starch indicator. Blue solution turns colorless with excess  $\text{I}_3^-$ .

ii.  $0.0320 \frac{\text{mol}}{\text{L}} \times 0.01175 \text{ L} = 3.76 \times 10^{-4} \text{ mol S}_2\text{O}_3^{2-} \equiv 3.76 \times 10^{-4} \text{ mol Cu}^{2+}$

$$3.76 \times 10^{-4} \text{ mol Cu}^{2+} \times \left( \frac{63.54 \text{ g}}{\text{mol}} \right) = 0.02389 \text{ g Cu}$$

$$\% \text{ Cu} = \left( \frac{0.02389 \text{ g Cu}}{0.115 \text{ g compd}} \right) \times 100 = 20.77\%$$

c.  $55.0 \% \text{ C} + 3.33 \% \text{ H} + 20.77 \% \text{ Cu} = 79.1 \% \rightarrow 100 - 79.1 = 20.9 \% \text{ O}$

$55.0 \text{ C} \div 12.01 = 4.58 \div 0.327 = 14$	}	$\text{C}_{14} \text{H}_{10} \text{O}_4 \text{Cu}$
$3.33 \text{ H} \div 1.008 = 3.30 \div 0.327 = 10$		
$20.9 \text{ O} \div 16.0 = 1.31 \div 0.327 = 4.0$		
$20.77 \div 63.54 = 0.327 \div 0.327 = 1$		
		$\Sigma \text{ FM} = 305$

d.  $\Delta T = 5.436 \text{ }^\circ\text{C} - 5.490 \text{ }^\circ\text{C} = -0.054 \text{ }^\circ\text{C}$        $\Delta T -0.054 \text{ }^\circ\text{C}$

$$-0.054 \text{ }^\circ\text{C} = (-4.90 \text{ }^\circ\text{C/m})m$$

$$m = -0.054 \text{ }^\circ\text{C} / (-4.90 \text{ }^\circ\text{C/m})$$

$$m = 0.011 \text{ mol/kg} \times 0.015 \text{ kg}$$

$$m = 1.65 \times 10^{-4} \text{ mol}$$

$$\text{MM} = 0.100 \text{ g} / 1.65 \times 10^{-4} \text{ mol}$$

$$\text{MM} = 605 \text{ g/mol}$$

$$\text{MM} \sim 2 \times \text{FM}$$

$$\text{Molecular Formula} = \text{C}_{28}\text{H}_{20}\text{O}_8\text{Cu}_2$$

$$2. \text{ a. } \Delta G_1^\circ = \Delta H_1^\circ - T \Delta S_1^\circ = 48700 \text{ J/mol} - 298 \text{ K} \times 173.3 \text{ J/mol K} = -2943 \text{ J/mol}$$

$$\Delta G_g^\circ = \Delta H_g^\circ - T \Delta S_g^\circ = 82900 - 298 \times 269 = 82900 - 80162 = 2738 \text{ J/mol}$$

$$\Delta G_{1 \rightarrow v}^\circ = 2738 - (-2943) = 5681 \text{ J/mol}$$

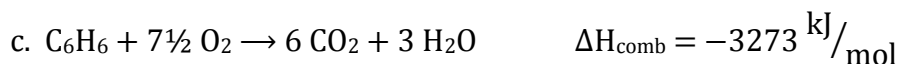
$$\Delta G_{1 \rightarrow v}^\circ = -RT \ln(K)$$

$$5681 \text{ J} = -8.314 \text{ J/mol} \times 298 \text{ K} \times \ln(K)$$

$$\ln(K) = -2.293 \quad K = 0.101 \text{ atm} = 76.7 \text{ mmHg}$$

$$\text{b. } 1.50 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol}}{78.11 \text{ g}} = 0.0192 \text{ mol}$$

$$\Delta H = (0.0192 \text{ mol} \times -48700 \text{ J/mol}) = -935 \text{ J}$$



$$\text{d. } \Delta H_{\text{comb}} = 12 \text{ BE}_{\text{C=O}} + 6 \text{ BE}_{\text{HO}} + [6 \text{ BE}_{\text{C-H}} + 6 \text{ BE}_{\text{C-C}} + 7.5 \text{ BE}_{\text{O=O}}]$$

$$-3273 = - [12(799) + 6(464)] + [6(414) + 6 \text{ BE}_{\text{C-C}} + 7.5(498)]$$

$$-3273 = - [9588 + 2784] + [2484 + 3735 + 6 \text{ BE}_{\text{C-C}}]$$

$$-3273 = - 12372 + [6219 + 6 \text{ BE}_{\text{C-C}}]$$

$$-3273 + 12372 - 6219 = 6 \text{ BE}_{\text{C-C}}$$

$$6 \text{ BE}_{\text{C-C}} = 2880$$

$$\text{BE}_{\text{C-C}} = 480$$

$$\text{e. } 1.50 \text{ g C}_6\text{H}_6 \times \frac{\text{mol}}{78.11 \text{ g}} = 0.0192 \text{ mol}$$

$$0.0192 \text{ mol} \times 3273 \text{ kJ/mol} = 62.8 \text{ kJ released}$$

$$5.99 \text{ kJ/}^\circ\text{C} + 4.18 \text{ kJ/}^\circ\text{C} = 10.17 \text{ kJ/}^\circ\text{C}$$

$$62.8 \text{ kJ} \times \frac{1^\circ\text{C}}{10.17 \text{ kJ}} = 6.18^\circ\text{C}$$

$$22.50^\circ\text{C} + 6.18^\circ\text{C} = 28.68^\circ\text{C final T}$$

$$3. \text{ a. } \ln\left(\frac{a_0}{a}\right) = kt \quad \ln(2) = 0.21 \text{ s}^{-1} \times t_{1/2} \quad \frac{0.693}{0.21 \text{ s}^{-1}} = t_{1/2} \quad t_{1/2} = 3.3 \text{ s}$$

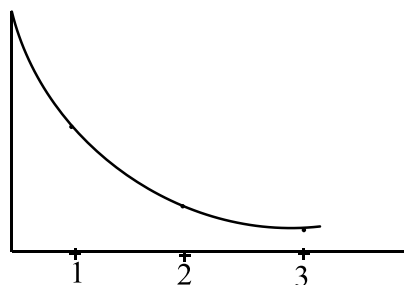
$$\text{b. } \ln(7.1 \times 10^{-8}) = 0.21 \text{ s}^{-1}$$

$$0.21 \text{ s}^{-1} \times 24 \text{ s} = 5.04$$

$$7.1 \times 10^{-8/x} = 154.4$$

$$x = 4.60 \times 10^{-10} \text{ M}$$

c.



$$\left(\frac{1}{2}\right)^5 = \frac{1}{32}$$

Half lives

$$\begin{aligned} \text{d. } \ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{1.1}{0.21} &= \frac{E_a}{8.314} \left( \frac{1}{331} - \frac{1}{342} \right) \\ (8.314) \times \ln(5.24) &= E_a (0.0030 - 0.00292) \\ (8.314) \times (1.66) &= E_a \times (9.7 \times 10^{-5}) \\ E_a &= 142030 \text{ J} = 142.0 \text{ kJ} \end{aligned}$$

$$4. \text{ a. } PV = nRT \quad P = \frac{0.0343 \text{ mol}}{1.50 \text{ L}} \times (0.0821 \text{ L atm/mol K}) \times 373 \text{ K} = 0.700 \text{ atm}$$

$$\begin{aligned} \text{b. } P_1 &= P_{\text{XCl}_3} + P_x + P_{\text{Cl}_2} \\ 0.800 &= 0.70 - x + x + 1.5x \\ 0.800 - 0.700 &= 1.5x \\ x &= 0.067 \end{aligned}$$

$$P_{\text{XCl}_3} = 0.700 - 0.067 = 0.633$$

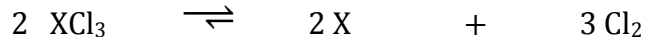
$$P_x = 0.067$$

$$P_{\text{Cl}_2} = 0.099$$

$$\text{c. i. } K_p = \frac{P_x^2 \times P_{\text{Cl}_2}^3}{P_{\text{XCl}_3}^2} = \frac{0.067^2 \times 0.099^3}{0.633^2} = \frac{4.36 \times 10^{-6}}{4.01 \times 10^{-1}} = 1.09 \times 10^{-5}$$

$$\begin{aligned} \text{ii. } \Delta G^\circ &= -RT \ln(K_p) = -8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times 373 \text{ K} \times \ln(1.09 \times 10^{-5}) = \\ &35552 \text{ J/mol} \end{aligned}$$

$$\begin{aligned} \text{d. } K_p &= K_c \times (RT)^{\Delta n} \\ 1.09 \times 10^{-5} &= K_c \times (0.0821 \times 373)^3 \\ K_c &= \frac{1.09 \times 10^{-5}}{2.872 \times 10^4} = 3.80 \times 10^{-10} \end{aligned}$$



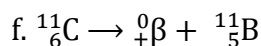
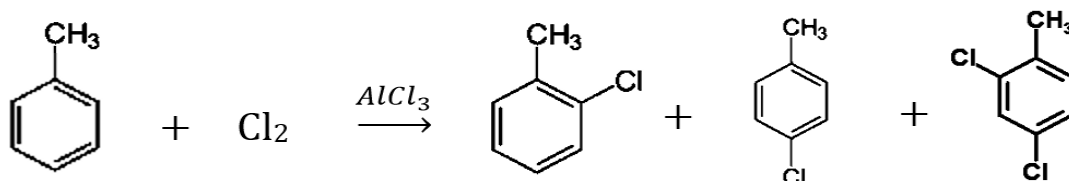
e.

I	$\frac{0.0500}{2}$	0	0
$\Delta$	-x	x	1.5x
E	(0.0500 - x)	x	1.5x

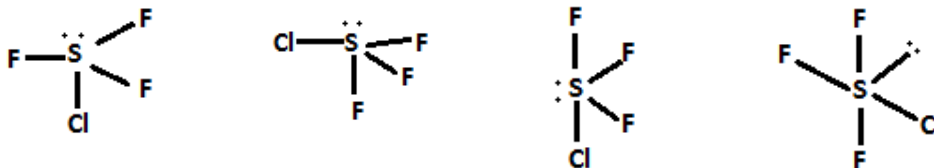
$$(3.8 \times 10^{-10}) = \frac{x^2 \times (1.5x)^3}{(0.025 - x)}$$

5. a.  $\text{CaSO}_3 \rightarrow \text{CaO} + \text{SO}_2$   
 b.  $\text{Na}_2\text{C}_2\text{O}_4^{2-} + \text{H}^+ + \text{MnO}_4^- \rightarrow \text{Na}^+ + \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$   
 c.  $\text{Mg}^{2+} + \text{SO}_4^{2-} + \text{Ba}^{2+} + \text{OH}^- \rightarrow \text{Mg}(\text{OH})_2 + \text{BaSO}_4$   
 d.  $(\text{CH}_3)_2\text{NH} + \text{HCl} \rightarrow (\text{CH}_3)_2\text{NH}_2^+ \text{Cl}^-$

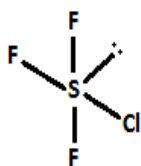
e.



6. a.



b.



Structure is correct for most stable. Lone pair of electrons and the least electronegative atom (Cl) are in the equatorial plane at 120 degrees apart with very electronegative F atoms in axial positions, drawing bonding pairs of electrons away from S.

c.

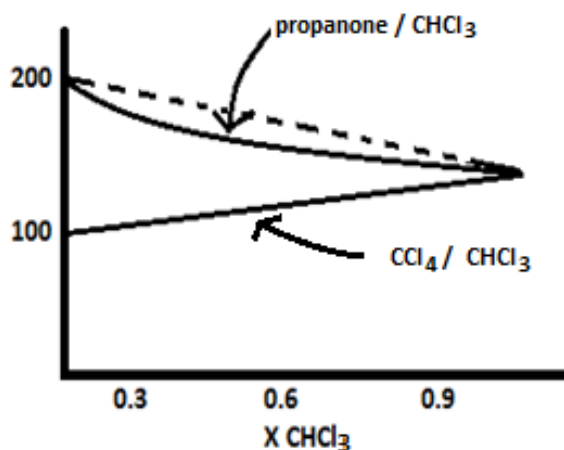


Structure is correct for second most stable. Cl is in an apical position but the lone pair is still in the equatorial plane, minimizing its repulsion of the bonding pairs of electrons.



- d. i. At  $-80\text{ }^{\circ}\text{C}$  there are 2 signals in a ratio of 2 (apical) to 1 (equatorial).  
 ii. At room temperature there will be 1 signal as the molecule reorganizes and the signals average.
- e. The central atom  $\text{X F}_3 \text{Cl}$  has ten electrons around it. While  $\text{S}_1 \text{Se}$  and  $\text{Te}$  can all accommodate ten electrons, O (with fewer orbitals available) cannot do so.

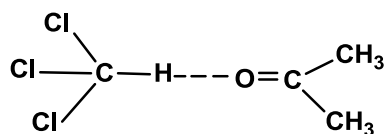
7. a. i. An ideal solution is one in which the forces between the molecules in the individual components are comparable to the forces between the molecules of the different components. The  $\text{CCl}_4\text{--CCl}_4$  attractions and  $\text{CHCl}_3\text{--CHCl}_3$  attractions are similar to the  $\text{CCl}_4\text{--CHCl}_3$  attractions.
- ii.



$$\begin{aligned} \text{VP} &= (.30 \times 172.5) + (0.70 \times 98.8) \\ \text{VP} &= 51.75 + 69.16 \\ \text{VP} &= 120.9 \text{ mmHg} \end{aligned}$$

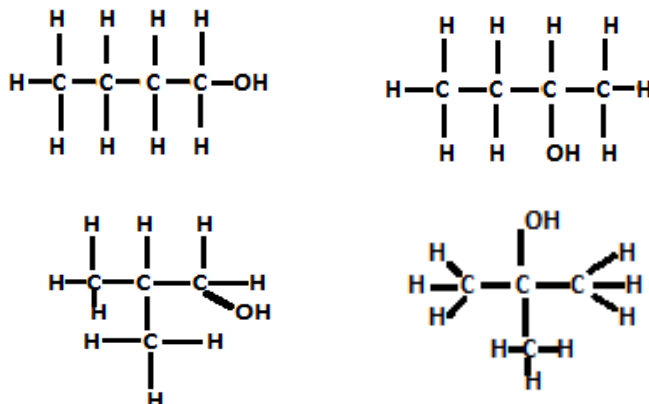
- iii. Vapor will be richer in  $\text{CHCl}_3$  than solution because  $\text{CHCl}_3$  has a higher VP.

- b. i.

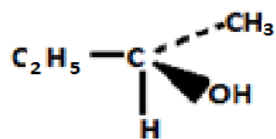
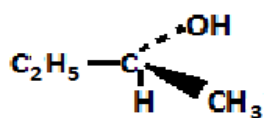


- ii. The V.P. curve will lie below the straight line due to the greater interactions between the different types of molecules than between similar ones.

8. a.

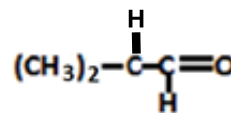
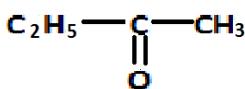
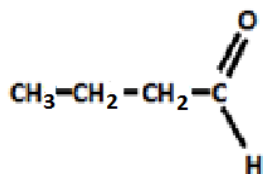


b.



Chemical properties are the same except for their interaction with chiral substrates. The two forms will rotate plane polarized light in opposite directions.

c.



$(\text{CH}_3)_3\text{C}-\text{OH}$  cannot be oxidized because C has 4 bonds.

d. ether

