



2005 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 of 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 27, 2005, 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 requested information on the "Blue Book". When the student has completed **Part II**, or after **one hour and forty-five minutes** has 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.

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

A periodic table and other useful information are provided on the back page 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 statement before leaving the testing site today.

1. (15%) This question involves several reactions of copper and its compounds.
- A sample of copper metal is dissolved in 6 M nitric acid contained in a round bottom flask. This reaction yields a blue solution and emits a colorless gas which is found to be nitric oxide. Write a balanced equation for this reaction.
 - The water is evaporated from the blue solution to leave a blue solid. When the blue solid is heated further, a second reaction occurs. This reaction produces a mixture of nitrogen dioxide gas, oxygen gas and a black oxide of copper.
 - A sample of the dried gas, collected in a 125 mL flask at 35 °C and 725 mm Hg, weighed 0.205 g. Find the average molar mass of the gas and the molar NO_2/O_2 ratio in it.
 - These data were obtained for the black solid;

Mass of empty flask:	39.49 g
Mass of flask + copper metal:	40.86 g
Mass of flask + oxide of copper:	41.21 g

 Determine the formula of the oxide of copper.
 - If some of the blue solution were lost due to splattering during the evaporation, what would be the effect on the calculated percentage of copper in the black oxide? Explain.
 - If all of the blue solid were not decomposed into the black oxide during the final heating, what would be the effect on the calculated percentage of copper in the oxide? Explain.

2. (16%) Liquid hydrazine, N_2H_4 , is sometimes used as a rocket propellant.
- Write an equation for the formation of hydrazine from its elements and use the combustion equations below to derive an equation in which ΔH_f° for liquid hydrazine is expressed in terms of ΔH_1 , ΔH_2 and ΔH_3 .

$$\frac{1}{2}\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H_1$$

$$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H_2$$

$$\text{N}_2\text{H}_4(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \quad \Delta H_3$$
 - In a rocket, liquid hydrazine is reacted with liquid hydrogen peroxide to produce nitrogen and water vapor. Write a balanced equation for this reaction.
 - Calculate $\Delta H_{\text{rxn}}^\circ$ for the reaction represented in 2b.

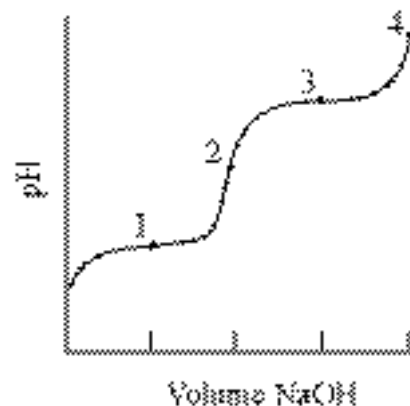
ΔH_f° kJ/mol	
$\text{N}_2\text{H}_4(\text{l})$	50.6
$\text{H}_2\text{O}_2(\text{l})$	-187.8
$\text{H}_2\text{O}(\text{g})$	-285.8

- Calculate $\Delta H_{\text{rxn}}^\circ$ for the reaction in 2b using bond dissociation energies.

Bond Dissociation Energy kJ/mol			
N-N	167	O-O	142
N=N	418	O=O	494
N≡N	942	O-H	459
N-H	386		

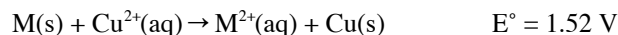
- Which value of $\Delta H_{\text{rxn}}^\circ$ (that calculated in part c or part d) is likely to be more accurate? Justify your answer.
- Calculate the maximum temperature of the combustion gases if all the energy generated in the reaction goes into raising the temperature of those gases. [The heat capacities of $\text{N}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are 29.1 J/(mol·°C) and 33.6 J/(mol·°C), respectively.]

3. (13%) A solution of alanine hydrochloride, $[\text{H}_3\text{NCH}(\text{CH}_3)\text{COOH}]^+\text{Cl}^-$, is titrated with a solution of sodium hydroxide to produce a curve similar to the one shown.



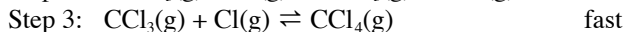
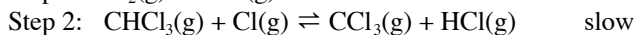
- Give the formula(s) for the major species present at the points on the titration curve.
 - 1
 - 2
 - 3
 - 4
- If K_1 and K_2 of alanine hydrochloride are 4.6×10^{-3} and 2.0×10^{-10} respectively,
 - write equations to represent the reactions responsible for K_1 and K_2 .
 - determine the pH at points 1, 2 and 3.
- Describe quantitatively how you could prepare a buffer solution with a pH = 10.0. Solutions of 0.10 M alanine hydrochloride and 0.10 M NaOH are available.

4. (10%) An electrochemical cell based on the reaction;

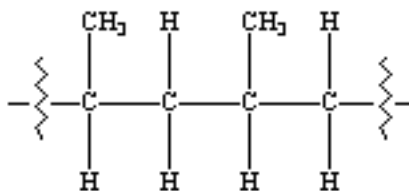


is constructed using equal volumes of solutions with all substances in their standard states.

- Use the value of the reduction potential of $Cu^{2+}(aq)$ ($E^\circ = 0.34 \text{ V}$) to determine the standard reduction potential for the reaction; $M^{2+}(aq) + 2e^- \rightarrow M(s)$
 - The cell is allowed to discharge until the $[Cu^{2+}] = 0.10 \text{ M}$. Find
 - the M^{2+} concentration in moles per liter,
 - the cell potential, E .
 - 50 mL of distilled water is added to each cell compartment of the original cell. Compare the potential of the cell after the addition of water with the potential of the original cell. Explain your answer.
5. (12%) Write net equations for each of the combinations of reactants below. Use appropriate ionic and molecular formulas 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. All reactions occur in aqueous solution unless otherwise indicated.
- Solid sodium sulfide is added to water.
 - An aqueous solution of potassium triiodide is added to a solution of sodium thiosulfate.
 - Excess aqueous sodium fluoride is added to aqueous iron(III) nitrate.
 - Strontium-90 undergoes beta decay.
 - Excess carbon dioxide is bubbled through a solution of calcium hydroxide.
 - Ethanol is warmed gently with acidified potassium dichromate.
6. (10%) This mechanism has been proposed for the reaction between chloroform and chlorine.



- Write the stoichiometric equation for the overall reaction.
 - Identify any reaction intermediates in this mechanism.
 - Write the rate equation for the rate determining step.
 - Show how the rate equation in c. can be used to obtain the rate law for the overall reaction.
 - If the concentrations of the reactants are doubled, by what ratio does the reaction rate change? Explain.
7. (14%) Xenon forms several compounds including XeF_2 , XeF_4 and XeO_3 .
- Draw a Lewis structure for each of these molecules.
 - Describe the geometry of each compound including bond angles.
 - State and explain whether each molecule is polar or nonpolar.
 - Account for the observation that these compounds are highly reactive.
8. (10%) A section of the polymer polypropylene is represented here.



- Sketch a structural formula for the monomer used to make this polymer.
- State and explain whether this polymer is an addition or a condensation polymer.
- Compare the melting points for the following polymers. Give reasons for your answers.
 - polypropylene containing 1000 monomer units **vs** polypropylene containing 10,000 monomer units
 - polypropylene **vs** a polymer in which the CH_3 group is replaced with a $CH_2CH_2CH_2CH_3$ group
 - isotactic polypropylene (all the CH_3 groups on the same side of the carbon backbone) **vs** atactic polypropylene (CH_3 groups arranged at random)

END OF PART II

ABBREVIATIONS AND SYMBOLS

amount of substance	<i>n</i>	equilibrium constant	<i>K</i>	measure of pressure	mmHg
ampere	<i>A</i>	Faraday constant	<i>F</i>	milli- prefix	<i>m</i>
atmosphere	atm	formula molar mass	<i>M</i>	molal	<i>m</i>
atomic mass unit	<i>u</i>	free energy	<i>G</i>	molar	<i>M</i>
atomic molar mass	<i>A</i>	frequency	ν	mole	mol
Avogadro constant	N_A	gas constant	<i>R</i>	Planck's constant	<i>h</i>
Celsius temperature	°C	gram	<i>g</i>	pressure	<i>P</i>
centi- prefix	<i>c</i>	heat capacity	C_p	rate constant	<i>k</i>
coulomb	<i>C</i>	hour	<i>h</i>	retention factor	R_f
electromotive force	<i>E</i>	joule	<i>J</i>	second	<i>s</i>
energy of activation	E_a	kelvin	<i>K</i>	speed of light	<i>c</i>
enthalpy	<i>H</i>	kilo- prefix	<i>k</i>	temperature, K	<i>T</i>
entropy	<i>S</i>	liter	<i>L</i>	time	<i>t</i>
				volt	<i>V</i>

CONSTANTS

$$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$1 F = 96,500 \text{ C}\cdot\text{mol}^{-1}$$

$$1 F = 96,500 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$$

USEFUL EQUATIONS

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$\ln K = \left(\frac{-\Delta H}{R} \right) \left(\frac{1}{T} \right) + c$$

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

PERIODIC TABLE OF THE ELEMENTS

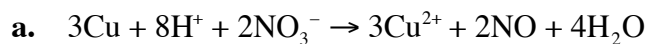
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	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 181.0	74 W 183.8	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 227.0	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		112 (277)		116 (289)		118 (293)

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
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)

CHEMISTRY OLYMPIAD

KEY FOR NATIONAL EXAM – PART II

1.



b. i.

$$MM_{ave} = \frac{mRT}{PV} = \frac{(0.205 \text{ g})(0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(308 \text{ K})}{(0.125 \text{ L})(725 \text{ mmHg} \times 1 \text{ atm} / 760 \text{ mm Hg})} = 43.5 \text{ g} \cdot \text{mol}^{-1}$$

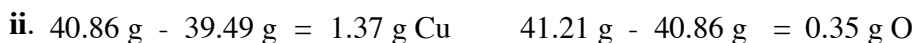
For the ratio, let x be the fraction of NO_2 ,

$$xMM_{\text{NO}_2} + (1-x)MM_{\text{O}_2} = 43.5$$

$$46x + 32(1-x) = 43.5$$

$$\text{solving for } x: x = 0.821$$

$$\frac{\text{NO}_2}{\text{O}_2} = \frac{0.821}{0.189} = \frac{4.59}{1}$$



$$1.36 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} = 0.0216 \text{ mole Cu}$$

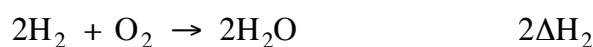
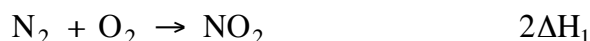
$$0.35 \text{ g O} \times \frac{1 \text{ mol O}}{16.0 \text{ g O}} = 0.0219 \text{ mole O}$$

Therefore the ratio is 1 : 1 and the formula must be CuO .

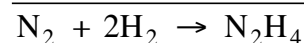
c. The lost solution will cause the mass of CuO to be too low relative to the mass of Cu . Therefore the percentage determination for copper will be too high

d. The mass of CuO will be too high. Therefore the percentage determination for copper will be too low.

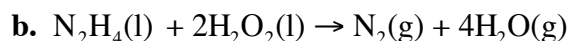
2. a. looking at $\text{N}_2 + 2\text{H}_2 \rightarrow \text{N}_2\text{H}_4$



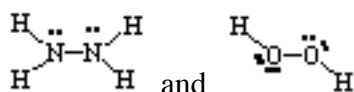
we must use the equations,



$$\Delta H_f = 2\Delta H_1 + 2\Delta H_2 - \Delta H_3$$



c. The structures of hydrazine and peroxide are,



Thus,

$$\begin{aligned}\Delta H_{\text{rxn}} &= 4 \text{ mol} \times (-285.8 \text{ kJ} \cdot \text{mol}^{-1}) - [2 \text{ mol} \times (-187.8 \text{ kJ} \cdot \text{mol}^{-1}) + 1 \text{ mol} \times (50.6 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -1143.2 + 325.0 \\ &= -818.2 \text{ kJ}\end{aligned}$$

d.

$$\begin{aligned}\Delta H_{\text{rxn}} &= \text{N}-\text{N} + 4 \text{ N}-\text{H} + 2 \text{ O}-\text{O} + 4 \text{ O}-\text{H} - [\text{N} \equiv \text{N} + 8 \text{ O}-\text{H}] \\ (\text{note: } 4 \text{ O}-\text{H} \text{ cancel from each side}) \\ &= 167 + 4(386) + 2(142) - [942 + 4(459)] \\ &= -783 \text{ kJ}\end{aligned}$$

e. ΔH from part c should be more accurate. ΔH_f values are determined for each compound individually, whereas bond energies are average values. We should expect the actual values for the compounds in this problem to vary from these averages.

f. $C = 1 \text{ mol} \times (29.1 \text{ J} \cdot \text{mol}^{-1} \cdot ^\circ\text{C}^{-1}) + 4 \text{ mol} \times (33.6 \text{ J} \cdot \text{mol}^{-1} \cdot ^\circ\text{C}^{-1})$ so $C = 163.5 \text{ J} \cdot ^\circ\text{C}^{-1}$
 $q = C\Delta T$ $818200 \text{ J} = 163.5 \text{ J} \cdot ^\circ\text{C}^{-1} \times \Delta T$ so $\Delta T = 5004 ^\circ\text{C}$.

3. a. i. $[\text{H}_3\text{NCH}(\text{CH}_3)\text{COOH}]^+$ and $^+\text{H}_3\text{NCH}(\text{CH}_3)\text{COO}^-$
ii. $^+\text{H}_3\text{NCH}(\text{CH}_3)\text{COO}^-$
iii. $^+\text{H}_3\text{NCH}(\text{CH}_3)\text{COO}^-$ and $\text{H}_2\text{NCH}(\text{CH}_3)\text{COO}^-$
iv. $\text{H}_2\text{NCH}(\text{CH}_3)\text{COO}^-$

- b. i. K_1 $[\text{H}_3\text{NCH}(\text{CH}_3)\text{COOH}]^+ \rightarrow \text{H}^+ + ^+\text{H}_3\text{NCH}(\text{CH}_3)\text{COO}^-$
 K_2 $^+\text{H}_3\text{NCH}(\text{CH}_3)\text{COO}^- \rightarrow \text{H}^+ + \text{H}_2\text{NCH}(\text{CH}_3)\text{COO}^-$
ii. $[\text{H}^+]$ at point 1 = $K_1 = 4.6 \times 10^{-3}$ so pH = 2.34
 $[\text{H}^+]$ at point 2 = $\sqrt{K_1 \times K_2} = \sqrt{9.2 \times 10^{-13}} = 9.6 \times 10^{-7}$ so pH = 6.02
 $[\text{H}^+]$ at point 3 = $K_2 = 2 \times 10^{-10}$ so pH = 9.07

c. $2.0 \times 10^{-10} = \frac{[1.0 \times 10^{-10}][\text{B}^-]}{[\text{HB}]}$ so $\frac{[\text{B}^-]}{[\text{HB}]} = \frac{2}{1}$

Take a specified volume of 0.10 M alanine hydrochloride (such as 300 mL) in which the predominant species is $[\text{H}_3\text{NCH}(\text{CH}_3)\text{COOH}]^+$. Add 0.10 M NaOH so there is 5/3 as much as there is 0.10 M alanine

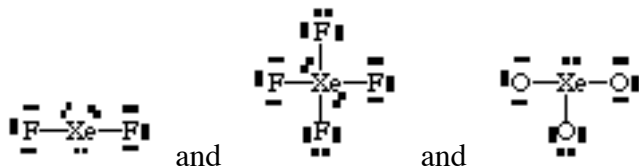
(such as 500 mL). This will give 800 mL of solution with a ratio of $\frac{[\text{H}_2\text{NCH}(\text{CH}_3)\text{COO}^-]}{[^+\text{H}_3\text{NCH}(\text{CH}_3)\text{COO}^-]} = \frac{2}{1}$.

4. a. $E_{\text{cell}}^\circ = E_{\text{ox}}^\circ + E_{\text{red}}^\circ$ and $E_{\text{ox}}^\circ = 1.52 \text{ V} - 0.34 \text{ V} = 1.18 \text{ V}$
so $E_{\text{red}}^\circ (\text{M}^{2+} + 2\text{e}^- \rightarrow \text{M}) = -1.18 \text{ V}$
b. i. If Cu^{2+} decreases to 0.10 M then M^{2+} must increase to 1.90 M
ii. $E = 1.52 - \frac{0.0257}{2} \ln \frac{1.90}{0.10} = 1.52 - 0.01285 \ln(19) = 1.52 - 0.0378 = 1.48 \text{ V}$
c. The E of the cell with dilute solutions will be the same as the original E° . Because the solutions are diluted by the same amount and the ions have the same coefficients (from the balanced chemical equation), Q in the Nernst equation is 1, and $\ln Q = 0$.

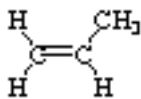
5. a. $\text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{HS}^- + \text{OH}^-$
 b. $\text{I}_3^- + \text{S}_2\text{O}_3^{2-} \rightarrow 3\text{I}^- + \text{S}_4\text{O}_6^{2-}$
 c. $\text{F}^- + \text{Fe}^{3+} \rightarrow \text{FeF}_6^{3-}$
 d. ${}^{90}_{38}\text{Sr} \rightarrow {}^{90}_{39}\text{Y} + {}^0_{-1}\beta$
 e. $\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$
 f. $\text{CH}_3\text{CH}_2\text{OH} + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}=\text{O}$ (or CH_3COOH) $+ \text{Cr}^{3+} + \text{H}_2\text{O}$

6. a. $\text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{CCl}_4 + \text{HCl}$
 b. Cl and CCl_3
 c. $\text{Rate} = k[\text{CHCl}_3][\text{Cl}]$
 d. Because this step is at equilibrium, we can express the $[\text{Cl}]$ in terms of $[\text{Cl}_2]$ by looking at the equilibrium constant expression. $K = \frac{[\text{Cl}]^2}{[\text{Cl}_2]}$ so $[\text{Cl}]^2 = K[\text{Cl}_2]$ and $[\text{Cl}] = K^{1/2}[\text{Cl}_2]^{1/2}$. Thus by substituting we get the overall expression to be: $\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$
 e. If $[\text{CHCl}_3]$ and $[\text{Cl}_2]$ are doubled, rate will increase by $(2) \cdot (2)^{1/2} = 2.83$ times.

7. a.



- b. XeF_2 is linear, 180° .
 XeF_4 is square planar, 90°
 XeO_3 trigonal pyramid, $\sim 107^\circ$
- c. XeF_2 is nonpolar. Both $\text{Xe}-\text{F}$ bond dipoles are the same size, but due to the linear geometry they offset each other.
 XeF_4 is nonpolar. All $\text{Xe}-\text{F}$ bond dipoles are the same size, but due to the square planar geometry they offset each other.
 XeO_3 is polar. The $\text{Xe}-\text{O}$ bond dipoles are the same size, and the non planar geometry leads to a net dipole.
- d. Xe has a formal positive charge in all of these compounds. This makes them good oxidizing agents.
8. a.



- b. It is an addition polymer. To form, the double bond in a monomer breaks to give a lone electron that forms bonds to other monomers. No other product(s) are formed, so it cannot be condensation.
- c. i. Polypropylene with 10,000 units melts at a higher temperature than one with 1000 units. The larger molecule, with higher molar mass has stronger dispersion forces.
 ii. Replacing CH_3 with $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ will lower the melting temperature. The bulk of this larger group will impede the packing of the polymer chains and decrease the strength of the intermolecular forces.
 iii. Isotactic polypropylene will melt at a higher temperature than atactic polypropylene. The more regular structure of the isotactic form allows better packing and stronger intermolecular forces.