



# 2002 U. S. NATIONAL CHEMISTRY OLYMPIAD

## NATIONAL EXAM—PART II

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Prepared by the American Chemical Society 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 21, 2002, 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 **1 hour, 45 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.

<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 problems</b>	<b>laboratory practical</b>	<b>1 hour, 30 minutes</b>

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.

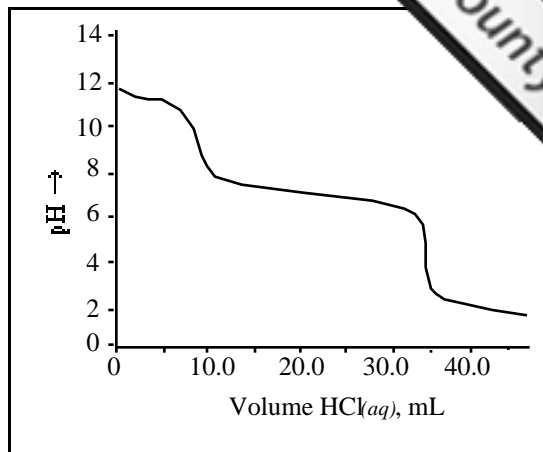
#### DIRECTIONS TO THE EXAMINEE—PART II

**DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO.** **Part II** requires complete responses to questions involving problem-solving and explanations. **1 hour, 45 minutes** is 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 1 hour, 45 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.

**Not valid for use as an USNCO National Exam after April 21, 2002.**

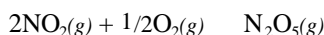
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1. (12%) The percentages of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  are to be determined in a mixture of them with  $\text{KCl}$ . A 0.500 g sample of the mixture is dissolved in 50.0 mL of deionized water and titrated with 0.115 M  $\text{HCl}$ , resulting in this pH titration curve.



- a. Write a balanced equation for the reaction that is responsible for the equivalence point that occurs at about
  - i.  $\text{pH} = 9$
  - ii.  $\text{pH} = 5$
- b. Calculate the total number of moles of acid used to reach each equivalence point if the volumes are 9.63 mL and 34.27 mL, respectively.
- c. Determine the number of grams of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  and their percentages in the original mixture.
- d. Sketch a titration curve for a solution of  $\text{Na}_2\text{CO}_3$  by itself and describe how it differs from the given curve.

2. (15%) Consider the formation of  $\text{N}_2\text{O}_5(\text{g})$  by this reaction.



For this reaction,  $H^\circ = -55.1 \text{ kJ}$  and  $S^\circ = -227 \text{ J}\cdot\text{K}^{-1}$

Additional data are given in the Table.

Type of Data	Substance	Value
$H_f^\circ$	$\text{NO}_2(\text{g})$	$+33.2 \text{ kJ}\cdot\text{mol}^{-1}$
$S^\circ$	$\text{NO}_2(\text{g})$	$239.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$S^\circ$	$\text{O}_2(\text{g})$	$205.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

a. Calculate these values.

- i.  $H_f^\circ$  of  $\text{N}_2\text{O}_5(\text{g})$
- ii.  $S^\circ$  of  $\text{N}_2\text{O}_5(\text{g})$
- iii.  $G^\circ$  of the given reaction at  $25^\circ\text{C}$
- iv.  $K_p$  of the given reaction at  $25^\circ\text{C}$

b. State and explain

- i. whether this reaction is spontaneous at  $25^\circ\text{C}$ .
- ii. how the numerical value of  $K_p$  would be affected by an increase in temperature.
- iii. how the relative amounts of reactant and product molecules would be affected by an increase in temperature.
- iv. why the  $S^\circ$  values differ for  $\text{NO}_2(\text{g})$  and  $\text{O}_2(\text{g})$  at  $25^\circ\text{C}$ .

3. (11%) Calcium ions form slightly soluble compounds with phosphate ions such as  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ , and  $\text{H}_2\text{PO}_4^-$ .

a. Write the formula and give the  $K_{sp}$  expression for the compound formed by  $\text{Ca}^{2+}$  and each of these two ions.

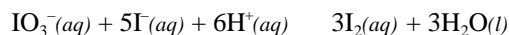
- i.  $\text{PO}_4^{3-}$
- ii.  $\text{H}_2\text{PO}_4^-$

b. Calculate the equilibrium concentration of  $\text{Ca}^{2+}$  in a saturated solution with each of the phosphate ions given in part a.

- i.  $K_{sp}$  for calcium phosphate equals  $1.0 \times 10^{-25}$ .
- ii.  $K_{sp}$  for calcium dihydrogen phosphate equals  $1.0 \times 10^{-3}$ .

c. Determine the  $[\text{H}^+]$  needed to just prevent precipitation by  $\text{H}_2\text{PO}_4^-$  in a 0.25 M  $\text{H}_3\text{PO}_4$  solution that has  $[\text{Ca}^{2+}] = 0.15 \text{ M}$ . The  $K_{a1}$  of  $\text{H}_3\text{PO}_4$  is  $7.1 \times 10^{-3}$ .

4. (14%) This reaction can be used to analyze for iodide ion.



When the rate of this reaction was studied at  $25^\circ\text{C}$ , the results in the table were obtained.

$[\text{I}^-], \text{M}$	$[\text{IO}_3^-], \text{M}$	$[\text{H}^+], \text{M}$	Reaction rate, $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
0.010	0.10	0.010	0.60
0.040	0.10	0.010	2.40
0.010	0.30	0.010	5.40
0.010	0.10	0.020	2.40

a. Use these data to determine the order of the reaction with respect to each of these species. Outline your reasoning in each case.

- i.  $\text{I}^-$
- ii.  $\text{IO}_3^-$
- iii.  $\text{H}^+$

b. Calculate the specific rate constant for this reaction and give its units.

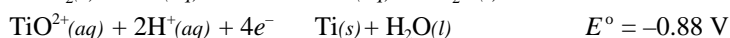
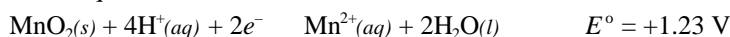
c. Based on the kinetics, discuss the probability of this reaction occurring in a single step.

d. The kinetics of reactions are often studied under pseudo first-order conditions. Describe what is meant by the term pseudo first order and illustrate how the reaction conditions above would be changed so that the  $[\text{I}^-]$  would be pseudo first order.

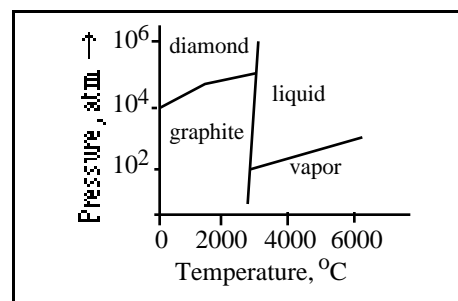
e. The activation energy for this reaction was found to be  $84 \text{ kJ}\cdot\text{mol}^{-1}$  at  $25^\circ\text{C}$ . How much faster would this reaction proceed if the activation energy were lowered by  $10 \text{ kJ}\cdot\text{mol}^{-1}$  (for example, by using a suitable catalyst)?

5. (12%) Write net equations for each of these reactions. Use appropriate ionic and molecular formulas for the reactants and products. Omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for organic substances. You need not balance the reactions. All reactions occur in aqueous solution unless otherwise indicated.
- Concentrated hydrochloric acid is added to solid manganese(IV) oxide.
  - Solutions of magnesium sulfate and barium hydroxide are mixed.
  - Solid barium peroxide is added to water.
  - A piece of copper metal is added to a solution of dilute nitric acid.
  - A solution of sodium thiosulfate is added to a suspension of solid silver bromide.
  - 2-butanol is heated with a solution of acidified potassium dichromate.
6. (12%) Chlorine trifluoride,  $\text{ClF}_3$ , is a vigorous fluorinating agent that has been used to separate uranium from the fission products in spent nuclear fuel rods.
- Write a Lewis dot structure for  $\text{ClF}_3$ .
  - Sketch and describe clearly the geometry for the  $\text{ClF}_3$  molecule.
  - Sketch one other possible geometry and explain why it is not observed.
  - Identify the hybrid orbitals that are considered to be used by the chlorine atom in  $\text{ClF}_3$ .
  - The electrical conductance of liquid  $\text{ClF}_3$  is only slightly lower than that of pure water. This behavior is attributed to the self-ionization of  $\text{ClF}_3$  to form  $\text{ClF}_2^+$  and  $\text{ClF}_4^-$ . Sketch and describe the expected structures of  $\text{ClF}_2^+$  and  $\text{ClF}_4^-$ .

7. (12%) Answer these questions about the voltaic cell based on these half-reactions.



- Write the equation for the reaction that produces a positive standard potential and then calculate that potential.
  - Identify the half-reaction that occurs at the cathode. Explain.
  - Specify the conditions that produce the standard potential.
  - State whether each of the changes listed in parts **i** - **iii** will affect the standard potential calculated in part **a** for the assembled cell. For each change, state whether the potential will increase, decrease, or remain the same. Outline your reasoning or show your calculations in each case.
    - The  $[\text{Mn}^{2+}]$  is doubled.
    - The size of the  $\text{Ti}(s)$  electrode is doubled.
    - The pH of both compartments is increased by the same amount.
8. (12%) Three common allotropic forms of carbon are diamond, graphite, and buckminsterfullerene ( $\text{C}_{60}$ ).
- Describe or sketch clearly the structure of each allotrope.
  - Compare diamond and graphite with regard to their hardness and electrical conductivity and account for any differences in behavior on the basis of the structures in part **a**.
  - Graphite is more stable than diamond (by  $2.9 \text{ kJ}\cdot\text{mol}^{-1}$ ) at room temperature and pressure. Explain why the diamonds in jewelry do not change readily into graphite.
  - Use this phase diagram for carbon to determine which has the greater density, diamond or graphite. Explain your reasoning and suggest a means of converting graphite into diamond.



END OF PART II

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

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

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

## PERIODIC TABLE OF THE ELEMENTS

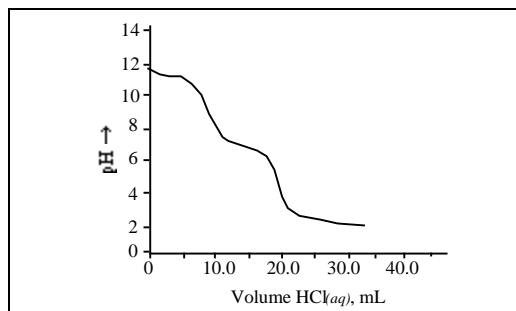
1 <b>H</b> 1.008																	2 <b>He</b> 4.003
3 <b>Li</b> 6.941	4 <b>Be</b> 9.012											5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31											13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <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> 181.0	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> 226.0	89 <b>Ac</b> 227.0	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 (269)	111 (272)	112 (277)	114 (289)					

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> 237.0	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> (260)

# 2002 U. S. NATIONAL CHEMISTRY OLYMPIAD KEY for NATIONAL EXAM—PART II

1. a. i.  $\text{pH} = 9 \quad \text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-$   
 ii.  $\text{pH} = 5 \quad \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3 \text{ or } \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2$   
 b.  $9.63 \times 10^{-3} \text{ L} \times \frac{0.115 \text{ mol}}{\text{L}} = 1.107 \times 10^{-3} \text{ mol HCl to titrate CO}_3^{2-}$   
 $3.427 \times 10^{-3} \text{ L} \times \frac{0.115 \text{ mol}}{\text{L}} = 3.941 \times 10^{-3} \text{ mol HCl to titrate HCO}_3^-$   
 c.  $1.107 \times 10^{-3} \text{ mol CO}_3^{2-} \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{\text{mol}} = 1.17 \times 10^{-1} \text{ g Na}_2\text{CO}_3$   
 $2.834 \times 10^{-3} \text{ mol HCO}_3^- \times \frac{84.01 \text{ g NaHCO}_3}{\text{mol}} = 2.38 \times 10^{-1} \text{ g NaHCO}_3$   
 $\frac{1.17 \times 10^{-1} \text{ g Na}_2\text{CO}_3}{5.00 \times 10^{-1} \text{ g mixture}} \times 100 = 23.4\% \text{ Na}_2\text{CO}_3$   
 $\frac{2.38 \times 10^{-1} \text{ g NaHCO}_3}{5.00 \times 10^{-1} \text{ g mixture}} \times 100 = 47.6\% \text{ NaHCO}_3$

d. The total volume required to reach the second equivalence point is twice that required to reach the first equivalence point because the number of moles of  $\text{HCO}_3^-$  is equal to the number of moles of  $\text{CO}_3^{2-}$ .



2. a.i.  $H_f^\circ$  of  $\text{N}_2\text{O}_5(\text{g})$   $H_{rxn}^\circ = H_f^\circ(\text{N}_2\text{O}_5) - 2 H_f^\circ(\text{NO}_2)$   
 $-55.1 \text{ kJ} = H_f^\circ(\text{N}_2\text{O}_5) - 2 \text{ mol } (33.2 \text{ kJ}\cdot\text{mol}^{-1})$   
 $H_f^\circ(\text{N}_2\text{O}_5) = +11.3 \text{ kJ}\cdot\text{mol}^{-1}$   
 ii.  $S^\circ$  of  $\text{N}_2\text{O}_5(\text{g})$   $S_{rxn}^\circ = S^\circ(\text{N}_2\text{O}_5) - (2S^\circ(\text{NO}_2) + S^\circ(\text{O}_2))$   
 $-227.0 \text{ J}\cdot\text{K}^{-1} = S^\circ(\text{N}_2\text{O}_5) - [2(-239.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) + 1/2(205.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})]$   
 $S^\circ(\text{N}_2\text{O}_5) = 355.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$   
 iii.  $G^\circ$  at  $25^\circ\text{C}$   $G^\circ = H^\circ - T S^\circ$   
 $G^\circ = -55.1 \text{ kJ} - (298 \text{ K})(-0.227 \text{ kJ}\cdot\text{K}^{-1})$   
 $G^\circ = 12.5 \text{ kJ}$   
 iv.  $K_p$  at  $25^\circ\text{C}$   $G^\circ = -RT \ln K_p$   
 $12500 \text{ J} = \frac{-8.314 \text{ J}}{\text{mol K}} (298 \text{ K}) \ln K_p \quad \ln K_p = -5.045 \quad \text{and } K_p = 6.44 \times 10^{-3}$

- b. i.** This reaction is not spontaneous at 25 °C. The value of  $G^\circ$  is positive.
- ii.** An increase in temperature will cause  $G^\circ$  to become more positive because the value of  $S^\circ$  is negative. Therefore, the numerical value of  $K_p$  will decrease.
- iii.** An increase in temperature will cause the relative amount of reactants to increase and products to decrease. This can be explained by noting that the value of  $H_{rxn}$  is negative, which means that adding heat will shift the reaction to the left. Another argument is that as the temperature increases, the value of the equilibrium constant  $K_p$  will decrease, also shifting the reaction to the left.
- iv.** The  $S^\circ$  values for  $\text{NO}_2(g)$  and  $\text{O}_2(g)$  at the same temperature are not the same because  $\text{NO}_2$ , with 3 atoms per molecule, has more possible arrangements than  $\text{O}_2$ , with only 2 atoms per molecule. This leads to a higher value for entropy, although not very much higher. The molar mass of  $\text{NO}_2$  is also higher than for  $\text{O}_2$ .

**3. a.i.**  $\text{Ca}_3(\text{PO}_4)_2 \quad K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$

**ii.**  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \quad K_{sp} = [\text{Ca}^{2+}] [\text{H}_2\text{PO}_4^-]^2$

**b.i.**  $1.0 \times 10^{-25} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$  Then, let  $3x = [\text{Ca}^{2+}]$  and  $2x = [\text{PO}_4^{3-}]$

$$1.0 \times 10^{-25} = [3x]^3 [2x]^2$$

$$1.0 \times 10^{-25} = 108x^5 \quad \text{and} \quad x^5 = 9.26 \times 10^{-28} \quad \text{and} \quad x = 3.9 \times 10^{-6}$$

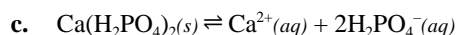
$$[\text{Ca}^{2+}] = 3(3.92 \times 10^{-6}) = 1.2 \times 10^{-5} \text{ M}$$

$1.0 \times 10^{-3} = [\text{Ca}^{2+}] [\text{H}_2\text{PO}_4^-]^2$  Then, let  $x = [\text{Ca}^{2+}]$  and  $2x = [\text{H}_2\text{PO}_4^-]$

$$1.0 \times 10^{-3} = [x] [2x]^2$$

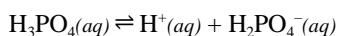
$$1.0 \times 10^{-3} = 4x^3 \quad \text{and} \quad x = 6.3 \times 10^{-2}$$

$$[\text{Ca}^{2+}] = 6.3 \times 10^{-2} \text{ M}$$



$$1.0 \times 10^{-3} = [\text{Ca}^{2+}] [\text{H}_2\text{PO}_4^-]^2$$

$$[\text{H}_2\text{PO}_4^-] = \sqrt{\frac{1.0 \times 10^{-3}}{0.15}} = \sqrt{6.67 \times 10^{-3}} = 8.2 \times 10^{-2} \text{ M}$$



$$7.3 \times 10^{-3} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$7.3 \times 10^{-3} = \frac{[x][0.082 + x]}{[0.25 - x]} \quad \text{and} \quad x = 1.7 \times 10^{-2} \text{ M}$$

Therefore, to prevent precipitation,  $[\text{H}^+]$  must be greater than  $1.7 \times 10^{-2} \text{ M}$

- 4. a. i.** First order in  $\text{I}^-$ . Compare the results of experiments 1 and 2 to see that the rate went up by a factor of 4 when the concentration of  $\text{I}^-$  went up by 4.
- ii.** Second order in  $\text{IO}_3^-$ . Compare the results of experiments 1 and 3 to see that the rate went up by 9 when the concentration of  $\text{IO}_3^-$  went up by 3.

iii. Second order in  $H^+$ . Compare the results of experiments 1 and 4 to see that the rate went up by 4 when the concentration of  $H^+$  went up by 2.

b.  $rate = k [I^-]^1 [IO_3^-]^2 [H^+]^2$

$rate = k [0.01]^1 [0.10]^2 [0.01]^2$

$k = \frac{0.60}{1.0 \times 10^{-8}} = 6.0 \times 10^7 \text{ mol}^{-4} \text{ L}^4 \text{ s}^{-1}$

c. Reaction is very unlikely to occur in one step. That would require the simultaneous collision of five particles.

d. Pseudo-first order refers to carrying out a reaction under conditions such that only one reactant changes concentration. For this reaction, pseudo-first order kinetics can be established by having a large excess of  $[IO_3^-]$  and  $[H^+]$ .

e.  $\frac{k_2}{k_1} = \frac{Ae^{-E_{a2}/RT}}{Ae^{-E_{a1}/RT}}$  and after cancelling  $A$  and combining exponents,  $\frac{k_2}{k_1} = e^{-E_{a2}/RT - E_{a1}/RT}$

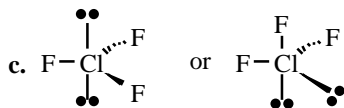
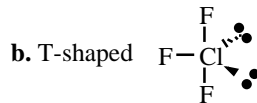
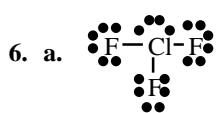
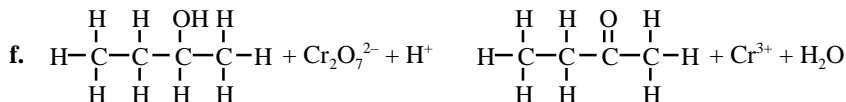
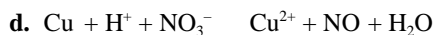
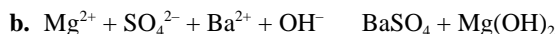
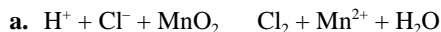
Taking the natural log and rearranging yields this expression.  $\ln \frac{k_2}{k_1} = \frac{E_{a1}}{RT} - \frac{E_{a2}}{RT}$

$\ln \frac{k_2}{k_1} = \frac{8.4 \times 10^4 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} - \frac{7.4 \times 10^4 \text{ J mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}$

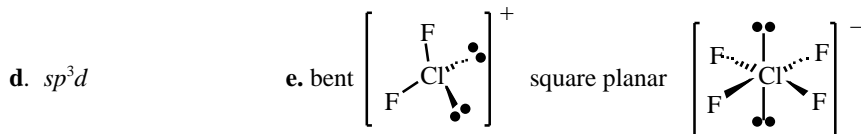
$\ln \frac{k_2}{k_1} = 33.90 - 29.87 = 4.03$  and  $\frac{k_2}{k_1} = e^{4.03}$

$\frac{k_2}{k_1} = 56.3$

5. **Note:** Balanced equations were *not* required.

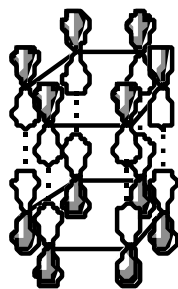
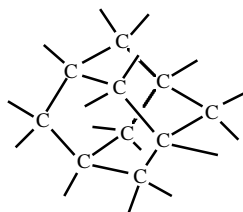


These structures are not favored because they provide less volume for the lone pairs and therefore do not minimize all repulsions.



7. a.  $\text{Ti} + 2\text{MnO}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + \text{TiO}^{2+}$   $E^\circ = 1.23 \text{ V} + 0.88 \text{ V} = 2.11 \text{ V}$
- b.  $\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$  Reduction occurs at the cathode.
- c. The conditions for standard potential are 25°C, 1 atm pressure, and 1 M concentrations.
- d. i. Doubling  $[\text{Mn}^{2+}]$  will decrease the potential because  $\text{Mn}^{2+}$  is a product. An increase in  $\text{Mn}^{2+}$  will shift the equilibrium to the left.
- ii. Doubling the size of the electrode has no effect. The electrode does not appear in the equilibrium expression nor in the Nernst equation.
- iii. Increasing pH lowers  $[\text{H}^+]$ . Because  $\text{H}^+$  appears on the left of the balanced equation, decreasing  $[\text{H}^+]$  will lower the potential. The reaction shifts to the left.

8. a. **diamond** **graphite** **C<sub>60</sub>**
- |                           |                          |                                   |
|---------------------------|--------------------------|-----------------------------------|
| $sp^3$ hybridization      | $sp^2$ hybridization     | spherical shape made up           |
| 3-dimensional tetrahedral | 2-dimensional sheets     | of hexagonal and pentagonal rings |
| network solid             | trigonal planar covalent | “soccer ball” design              |
|                           | half-filled p orbital    |                                   |
|                           | hexagonal rings          |                                   |



b. Diamond is the hardest. Diamond has 4 covalent bonds per C atom, making a very strongly bonded 3-D network solid. Graphite’s sheets have only weak forces between the sheets, allowing one to slide by the other. This makes graphite much “softer” than diamond.

All valence electrons in diamond are involved in sigma bonds, resulting in a nonconducting material. Graphite has delocalized electrons in the half-filled  $p$  orbitals (pi-bonding), allowing for electron movement from one atom to the next when an electromotive force is applied. Graphite is a good conductor.

c. Although equilibrium favors graphite at room temperature, the rate of the reaction from diamond to graphite is extremely slow because of a very high activation energy barrier.

d. The graph shows that as pressure is increased at a fixed temperature of 1000 °C, graphite is converted into diamond. Since increasing pressure should favor increasing density, one could conclude that diamond is denser than graphite. Since graphite is composed of sheets with considerable empty space between the carbon layers, converting graphite to the tetrahedral form decreases the empty space and increases density.

To prepare diamond from graphite, the graph indicates that by carrying out the process at 0 °C, a pressure of only  $10^3$  atm would be needed. However, since the rate of change would be very slow, this might not be the most ideal set of conditions. An alternate method might be to heat graphite to 2500 °C and apply a pressure of  $10^5$  atm, which should increase the rate of the conversion. Another alternate method would be to apply a pressure of  $10^3$  atm, then heat to 5000 °C to allow for liquefaction, increase pressure to  $10^6$  atm and then cool to the lower temperature.