2001 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 22, 2001, 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.

**Not valid for use as an USNCO National Exam after April 22, 2001.**

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. (10%) The mass percent of MnO_2 in a sample of a mineral is determined by reacting it with a measured excess of As_2O_3 in acid solution, and then titrating the remaining As_2O_3 with standard $KMnO_4$. A 0.225 g sample of the mineral is ground and boiled with 75.0 mL of 0.0125 M As_2O_3 solution containing 10 mL of concentrated sulfuric acid. After the reaction is complete, the solution is cooled, diluted with water, and titrated with 2.28×10^{-3} M $KMnO_4$, requiring 16.34 mL to reach the endpoint. *Note:* 5 mol of As_2O_3 react with 4 mol of MnO_4^-.

   a. Write a balanced equation for the reaction of As_2O_3 with MnO_2 in acid solution. The products are Mn^{2+} and AsO_4^{3-}.

   b. Calculate the number of moles of

      i. As_2O_3 added initially.

      ii. MnO_4^- used to titrate the excess As_2O_3.

      iii. MnO_2 in the sample.

   c. Determine the mass percent of MnO_2 in the sample.

   d. Describe how the endpoint is detected in the $KMnO_4$ titration.

2. (15%) The presence of CO_3^{2-}, HCO_3^- and CO_2 in body fluids helps to stabilize the pH of these fluids despite the addition or removal of H^+ ions by body processes. Answer the following questions about solutions containing these species in varying combinations at 25 °C. K_1 and K_2 for H_2CO_3 are 4.2×10^{-7} and 4.7×10^{-11}, respectively.

   a. Write balanced equations to represent the processes responsible for K_1 and K_2.

   b. Calculate the $[H^+]$ and pH expected for

      i. 0.033 M solution of H_2CO_3, which is the saturation point of CO_2 at 25 °C.

      ii. 1:1 mixture of H_2CO_3 and HCO_3^-.

      iii. 1:1 mixture of HCO_3^- and CO_3^{2-}.

      iv. 0.125 M solution of CO_3^{2-}.

   c. The "normal" pH in blood plasma is 7.40. Identify the components that would provide the best buffer at this pH and calculate their ratio.

   d. The value of K_1 is based on the assumption that all of the CO_2 dissolved in water exists in the form of H_2CO_3. However, recent evidence suggests that an additional equilibrium exists as represented by this equation.

   $$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$
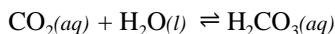
   When the "true" concentration of $H_2CO_{3(aq)}$ is taken into account, $K_1 = 2 \times 10^{-4}$. Use this information to determine the percent of dissolved CO_2 that is actually present as $H_2CO_{3(aq)}$.

3. (12%) Glucose, $C_6H_{12}O_6$, is readily metabolized in the body.

   a. Write a balanced equation for the metabolism of $C_6H_{12}O_6$ to CO_2 and H_2O.

   b. Calculate $G°_{metabolism}$ for glucose. Given: The free energy of formation, G_f^o, is -917 kJ·mol^{-1} for $C_6H_{12}O_{6(s)}$; -394.4 kJ·mol^{-1} for $CO_{2(g)}$; -237.2 kJ·mol^{-1} for $H_2O_{(l)}$.

   c. If $H°$ for this process is -2801.3 kJ, calculate $S°$ at 25 °C.

   d. One step in the utilization of energy in cells is the synthesis of ATP^{4-} from ADP^{3-} and $H_2PO_4^-$, according to this equation.

   $$ADP^{3-} + H_2PO_4^- \quad ATP^{4-} \quad G° = 30.5 \text{ kJ·mol}^{-1}$$

      i. Calculate the number of moles of ATP^{4-} formed by the metabolism of 1.0 g of glucose.

      ii. Calculate the equilibrium constant, K, for the formation of ATP^{4-} at 25 ˚C.

4. (11%) The corrosion of iron is an electrochemical process that involves the standard reduction potentials given here at 25 °C.

      $Fe^{2+}_{(aq)} + 2e^- \quad Fe_{(s)}$ $E° = -0.44$ V

      $O_{2(g)} + 4H^+_{(aq)} + 4e^- \quad 2H_2O_{(l)}$ $E° = +1.23$ V

   a. Calculate the voltage for the standard cell based on the corrosion reaction. $2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \quad 2Fe^{2+}_{(aq)} + 2H_2O_{(l)}$

   b. Calculate the voltage if the reaction in Part **a** occurs at pH = 4.00 but all other concentrations are maintained as they were in the standard cell.

   c. For the reaction $Fe(OH)_{2(s)} + 2e^- \quad Fe_{(s)} + 2OH^-_{(aq)}$, $E° = -0.88$ V. Use this information with one of the given standard potentials to calculate the K_{sp} of $Fe(OH)_2$.

d. An iron object may be protected from corrosion by coating it with tin. This method works well as long as the tin coating is intact. However, when the coating is penetrated, the corrosion of the iron is actually accelerated. Use electrochemical principles to account for both of these observations. The standard reduction potential for tin is:

$$Sn^{2+}(aq) + 2e^- \quad Sn(s) \qquad E^\circ = -0.14 \text{ V}$$
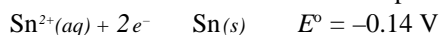
5. (14%) Write net equations for each of these reactions. Use appropriate ionic and molecular formulas for the reactants and products. Omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the reactions. All reactions occur in aqueous solution unless otherwise indicated.

   a. Solid calcium hydrogen carbonate is heated to a very high temperature.

   b. Solid potassium sulfite is added to a solution of hydrochloric acid.

   c. Solutions of barium hydroxide and sulfuric acid are mixed.

   d. A tin(II) chloride solution is added to an acidic solution of potassium dichromate.

   e. Concentrated hydrochloric acid is added to a solution of sodium hypochlorite.

   f. Nitrogen-16 undergoes $^-$ decay.

6. (13%) Answer these questions pertaining to chemical kinetics.

   a. Determine the reaction rate at 10 seconds from the graph. Show your work.

   b. Using the same units for the reaction rate as in Part **a**, and assuming concentrations in mol·L^{-1}, give the units for the rate constant of a reaction with an order of:

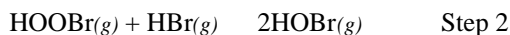   **i.** zero   **ii.** one   **iii.** two

   c. Consider this reaction: $4HBr(g) + O_2(g) \quad 2H_2O(l) + 2Br_2(g)$

   i. Express the reaction rates for HBr and Br_2 in this reaction relative to that of O_2.

   ii. Explain why this reaction is unlikely to occur by direct collision of four HBr molecules with one O_2 molecule.

   d. This mechanism has been suggested for the reaction in Part **c**:

$$HBr(g) + O_2(g) \quad HOOBr(g) \qquad \text{Step 1}$$
$$HOOBr(g) + HBr(g) \quad 2HOBr(g) \qquad \text{Step 2}$$
$$HOBr(g) + HBr(g) \quad H_2O(g) + Br_2(g) \qquad \text{Step 3}$$

   Give the rate equation in terms of reactants expected for this reaction if the rate-determining step is:

   i. Step 1   **ii.** Step 2   **iii.** Step 3

   Assume in each case that the steps before the rate-determining step are in rapid equilibrium. Outline your reasoning in each case.

7. (13%) A certain element, **X**, forms the fluorides XF_3 and XF_5. Element **X** also reacts with sodium to form Na_3X.

   a. Give the symbol of an element that behaves in this way.

   b. For both XF_3 and XF_5;

   i. write Lewis electron dot structures.

   ii. describe the electron pair and molecular geometries.

   iii. give the hybridization of the **X** atom.

   c. The bonds in XF_5 are not all the same length. Identify the longer bonds and account for this behavior.

   d. Another element, **Y**, in the same family as **X**, forms YF_3 but not YF_5. Identify element **Y** and account for its inability to form YF_5.

8. (12%) Account for each observation with appropriate atomic or molecular properties.

   a. Carbon dioxide has a higher vapor pressure than sulfur dioxide at the same temperature.

   b. Hydrogen chloride has a lower normal boiling point than either hydrogen fluoride or hydrogen bromide.

   c. Calcium oxide has a much higher melting point (2580 °C) than potassium fluoride (858 °C).

   d. Tin(II) chloride is an ionic compound (mp = 240 °C) while tin(IV) chloride is a covalent compound (bp = 114 °C).
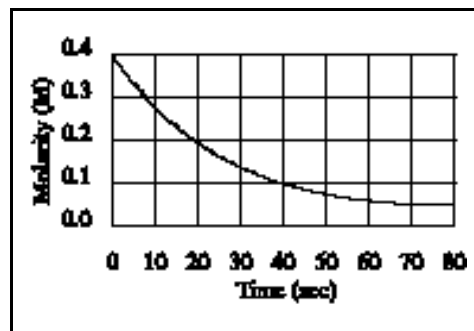
END OF PART II

ABBREVIATIONS AND SYMBOLS

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

CONSTANTS

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

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

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

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

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

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

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

USEFUL EQUATIONS

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

PERIODIC TABLE OF THE ELEMENTS

1 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)

2001 U. S. NATIONAL CHEMISTRY OLYMPIAD
KEY for NATIONAL EXAM—PART II

1. **a.** $2MnO_2 + As_2O_3 + H_2O \rightarrow 2Mn^{2+} + 2AsO_4^{3-} + 2H^+$

b. i. $0.0750 \text{ L} \times \dfrac{0.0125 \text{ mol}}{\text{L}} = 9.38 \times 10^{-4} \text{ mol As}_2O_3$

   ii. $0.01634 \text{ L} \times \dfrac{2.28 \times 10^{-3} \text{ mol}}{\text{L}} = 3.73 \times 10^{-5} \text{ mol MnO}_4^-$

   $3.73 \times 10^{-5} \text{ mol MnO}_4^- \times \dfrac{5 \text{ mol As}_2O_3}{4 \text{ mol MnO}_4^-} = 4.66 \times 10^{-5} \text{ mol As}_2O_3 \text{ left}$

   iii. $9.38 \times 10^{-4} - 4.66 \times 10^{-5} = 8.91 \times 10^{-4} \text{ mol As}_2O_3 \text{ react with MnO}_2$

   $8.91 \times 10^{-4} \text{ mol As}_2O_3 \times \dfrac{2 \text{ mol MnO}_2}{1 \text{ mol As}_2O_3} = 1.78 \times 10^{-3} \text{ mol MnO}_2$

c. $1.78 \times 10^{-3} \text{ mol MnO}_2 \times \dfrac{86.94 \text{ g MnO}_2}{\text{mol MnO}_2} = 0.155 \text{ g MnO}_2$

   $\text{mass \% MnO}_2 = \dfrac{0.155 \text{ g MnO}_2}{0.225 \text{ g sample}} \times 100 = 68.9\% \text{ MnO}_2 \text{ in sample}$

d. The endpoint corresponds to a slight purple (pink) color due to excess $MnO_4^-{}_{(aq)}$.

2. **a.** Process responsible for K_1 $H_2CO_{3(aq)} \rightleftharpoons H^+{}_{(aq)} + HCO_3^-{}_{(aq)}$

   Process responsible for K_2 $HCO_3^-{}_{(aq)} \rightleftharpoons H^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$

b. i. $K_1 = \dfrac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]}$ $4.2 \times 10^{-7} = \dfrac{\left[H^+\right]^2}{(0.033)}$ $\left[H^+\right] = 1.2 \times 10^{-4}$ $pH = 3.93$

   ii. $\left[H_2CO_3\right] = \left[HCO_3^-\right]$ $K_1 = \left[H^+\right]$ $\left[H^+\right] = 4.2 \times 10^{-7}$ $pH = 6.38$

   iii. $\left[HCO_3^-\right] = \left[CO_3^{2-}\right]$ $K_2 = \left[H^+\right]$ $\left[H^+\right] = 4.7 \times 10^{-11}$ $pH = 10.33$

   iv. $CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + OH^-{}_{(aq)}$

   $\left[OH^-\right] = \sqrt{\dfrac{K_w}{K_a} \times \left[CO_3^{2-}\right]}$

   $\left[OH^-\right] = \sqrt{\dfrac{1.0 \times 10^{-14}}{4.7 \times 10^{-11}} \times 0.125}$

   $\left[OH^-\right] = \sqrt{2.7 \times 10^{-5}}$ $\left[OH^-\right] = 0.0052$ $pOH = 2.28$

   $\left[H^+\right] = 1.9 \times 10^{-12}$ $pH = 11.72$

c. $pH = 7.40$ $\left[H^+\right] = 4.0 \times 10^{-8}$ Components of the best buffer: H_2CO_3 and HCO_3^-

   $4.2 \times 10^{-7} = 4.0 \times 10^{-8} \times \dfrac{HCO_3^-}{H_2CO_3}$ $\dfrac{HCO_3^-}{H_2CO_3} = 10.5$

d. $\dfrac{4.2 \times 10^{-7}}{2 \times 10^{-4}} = 2 \times 10^{-3}$ or 0.002

Because the ratio of the two K values is 0.002, 0.2% of dissolved CO_2 is actually H_2CO_3.

3. **a.** $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$
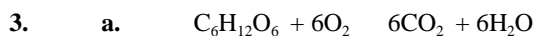
b. $\Delta G^o_{metabolism} = 6\, \Delta G^o_{CO_2} + 6\, \Delta G^o_{H_2O} - \Delta G^o_{C_6H_{12}O_6}$

$= 6 \text{ mol}(-394.4 \text{ kJ mol}^{-1}) + 6 \text{ mol}(-237.2 \text{ kJ mol}^{-1}) - (-917 \text{ kJ mol}^{-1})$

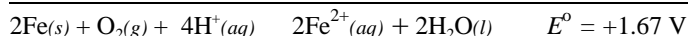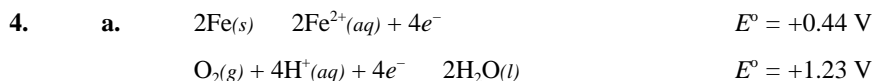$= -2366.4 \text{ kJ} - 1423.2 \text{ kJ} + 917 \text{ kJ}$

$= -2873 \text{ kJ}$

c. $\Delta G^o = \Delta H^o - T\,\Delta S^o$

$-2873 \text{ kJ} = -2801.3 \text{ kJ} - 298 \text{ K}\,\Delta S^o \quad (298 \text{ K}\,\Delta S^o = 72 \text{ kJ} \quad \Delta S^o = 0.24 \text{ kJ/K} \quad \text{or } 240 \text{ J/K}$

d. i. $1.0 \text{ g } C_6H_{12}O_6 \times \dfrac{1 \text{ mol}}{180 \text{ g}} = 5.6 \times 10^{-3} \text{ mol } C_6H_{12}O_6$
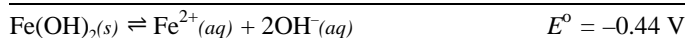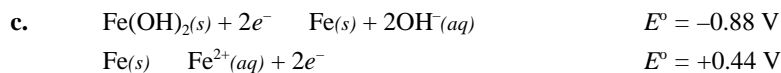
$5.6 \times 10^{-3} \text{ mol } C_6H_{12}O_6 \times \dfrac{2872.6 \text{ kJ}}{\text{mol}} = 16 \text{ kJ}$

$16 \text{ kJ} \times \dfrac{1 \text{ mol ATP}}{30.5 \text{ kJ}} = 0.52 \text{ mol ATP formed}$

ii. $\Delta G^o = -RT \ln K \quad \dfrac{30.5 \times 10^3 \text{J}}{\text{mol}} = \dfrac{-8.314 \text{ J}}{\text{mol K}} (298 \text{ K})\ln K \quad \ln K = -12.31 \quad K = 4.5 \times 10^{-6}$

4. **a.** $2Fe_{(s)} \longrightarrow 2Fe^{2+}_{(aq)} + 4e^-$ $\qquad\qquad\qquad E^o = +0.44$ V

$O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$ $\qquad\qquad E^o = +1.23$ V

$\overline{2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad E^o = +1.67 \text{ V}}$

b. $E = E^o - \dfrac{RT}{nF} \ln \dfrac{\left[Fe^{2+}\right]^2}{\left[H^+\right]^4 \left(P_{O_2}\right)}$

$= 1.67\text{V} - \dfrac{(8.314 \text{ J/ mol K})(298 \text{ K})}{(96{,}500 \text{ J/V})(4 \text{ mol})} \ln \dfrac{1}{\left(1.0 \times 10^{-4}\right)^4 (1)}$

$= 1.67 - (0.00642)(+36.84)$

$= 1.43$ V

c. $Fe(OH)_{2(s)} + 2e^- \longrightarrow Fe_{(s)} + 2OH^-_{(aq)}$ $\qquad\qquad E^o = -0.88$ V

$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$ $\qquad\qquad\qquad E^o = +0.44$ V

$\overline{Fe(OH)_{2(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad\qquad E^o = -0.44 \text{ V}}$

$\Delta G^o = -nFE^o = -RT \ln K_{sp}$

$\ln K_{sp} = \dfrac{nFE^o}{RT} \qquad \ln K_{sp} = \dfrac{(2 \text{ mol}) (96{,}500 \text{ J V}^{-1}) (-0.44 \text{ V})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = -34.28 \qquad K_{sp} = 1.30 \times 10^{-15}$

d. When iron is coated with Sn, the reaction $Sn \longrightarrow Sn^{2+} + 2e^-$ takes place. If the tin coating is broken, the reaction $Sn^{2+} + Fe \longrightarrow Sn + Fe^{2+}$ becomes spontaneous. Iron becomes the anode and is oxidized more readily.

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

    a. $Ca(HCO_3)_2 \longrightarrow CaO + H_2O + 2CO_2$ (partial credit for $CaCO_3$)

    b. $K_2SO_3 + H^+ \longrightarrow K^+ + H_2O + SO_2$ (partial credit for H_2SO_3)

    c. $Ba^{2+} + OH^- + H^+ + SO_4^{2-} \longrightarrow H_2O + BaSO_4$

    d. $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow Cr^{3+} + Sn^{4+} + H_2O$ (partial credit for $SnCl_4$)

    e. $H^+ + Cl^- + OCl^- \longrightarrow Cl_2 + H_2O$ (partial credit for $HClO$)

    f. $^{16}_{7}N \longrightarrow ^{\ \ 0}_{-1}\beta + ^{16}_{8}O$

6.   **a.**   Tangent to curve at 10 seconds: $\dfrac{M}{T} = \dfrac{-0.39M}{32\ s} = -0.012\ M\ s^{-1}$

    b. *i.*   rate $= k$ units are $M \cdot s^{-1}$

       ii.   rate $= k\ [\ ]$ units are s^{-1}

      iii.   rate $= k\ [\ ]^2$ units are $M^{-1} \cdot s^{-1}$

    c. *i.*   Expressed in symbols: $\dfrac{-d[O_2]}{dt} = \dfrac{-d[HBr]}{4dt} = \dfrac{d[Br_2]}{2dt}$

               This shows that the rate of disappearance of HBr is 4 times that of O_2 and the rate of production of Br_2 is twice the rate of disappearance of O_2.
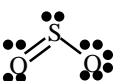
      ii.   More than mono- or bi-molecular steps improbable.

    d. *i.*   rate $= k\ [HBr]\ [O_2]$ Rate is proportional to reactants in the rate-limiting step.

      ii.   rate $= k\ [HBr]^2\ [O_2]$ [HOOBr] in the rate equation must be stated in terms of the previous equilibrium.

     iii.   rate $= k\ [HBr]^2\ [O_2]^{1/2}$ [HOBr] in the rate equation must be stated in terms of the previous equilibria.

7.   **a.**   Phosphorus (P) and arsenic (As) might behave in this manner.

    b. *i.*
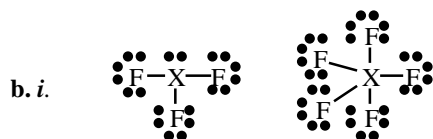
      ii. XF_3 Electron pair geometry is tetrahedral; atom geometry is trigonal pyramidal.

                XF_5 Electron pair geometry and atom geometry are both trigonal bipyramidal.

     iii. XF_3 X is sp^3 hybridized.

                XF_5 X is dsp^3 hybridized.

    c.   Axial bonds in XF_5 are longer than the equatorial bonds. The axial bonds are p/d hybrids and the equatorial bonds are s/p^2 hybrids. Another acceptable explanation is that the axial bonds at 90° are repelled more than the equatorial bonds at 120°.

    d. Y could be N; N has no d orbitals. Another acceptable explanation is that N is too small to accommodate five F atoms.

                Y could be Bi; Bi can't easily be oxidized to +5.

8.   **a.** CO_2 is linear and therefore nonpolar.

SO₂ is bent and therefore polar.

The polar substance will bond more strongly and have the lower vapor pressure.

b.   The boiling point of HCl is less than the boiling point of HF because HF forms hydrogen bonds which are harder to break than van der Waals forces.

Both HCl and HBr are attracted by van der Waals forces. However, HBr has more electrons and therefore has stronger van der Waals forces. As a result, the boiling point of HCl is less than the boiling point of HBr.

c. Ca^{2+} and O^{2-} ions are attracted about four times as strongly as K^+ and F^- ions. Ions with a +2 charge are attracted more strongly than ions with a +1 charge. In addition, the calcium-to-oxygen distance is less than the potassium-to-fluoride distance, leading to an increased force of attraction for the shorter bond.

d.   Tin(II) chloride is ionic. Tin(IV) chloride is covalent. The +4 charge on tin causes it to attract electrons more strongly from chloride ion, making the bonds covalent.