2011 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 18, 2011, 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 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 questions	laboratory practical	1 hour, 30 minutes

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 statement before leaving the testing site today.

1. (11%) An organic acid containing only C, H, and O has the elemental composition by mass:

Element	% by mass
C	40.7
H	5.1

   a. Determine the empirical formula of this acid.
   b. When 1.26 g of the acid is dissolved in 20.00 g of H_2O, the solution freezes at –1.0 °C. Determine the apparent molar mass of the compound to the proper number of significant figures. Suggest an appropriate molecular formula for the compound [$K_f = -1.86$ °C•m^{-1}].
   c. When a 4.00 g portion of the solution in b. is titrated with 0.226 M NaOH, 17.8 mL is required to reach a phenolphthalein end point. Calculate the number of moles of NaOH used and the apparent molar mass of the compound.
   d. Use the results from b. and c. to draw a possible structural formula for this compound.
   e. This compound is refluxed with excess ethanol in the presence of an acid catalyst. Write a structural formula for the organic compound formed.
   f. Suppose the reaction in e. does not go to completion. Outline a method to separate the organic product from the unreacted acid.

2. (11%) Pyridine, C_5H_5N, is a weak base [$K_b = 1.78 \times 10^{-9}$].
   a. Calculate the [OH^-] and pH of a 0.240 M solution of pyridine.
   b. A 20.0 mL portion of 0.240 M pyridine solution is titrated with 0.120 M HCl.
      i. Calculate the pH after 20.0 mL of the HCl solution has been added.
      ii. Calculate the pH at the equivalence point.
   c. If $MgCl_2$ is added to a 0.240 M solution of pyridine, what is the minimum [Mg^{2+}] at which $Mg(OH)_2$ will precipitate? [$K_{sp} = 5.6 \times 10^{-12}$]
   d. For a solution with [Mg^{2+}] = 0.10 M and [C_5H_5N] = 0.240M what must the [$C_5H_5NH^+$] be to just prevent the precipitation of $Mg(OH)_2$?

3. (16%) Aluminum is a highly reducing metal.
   a. The standard reduction potentials for Al^{3+}(aq) and Fe^{3+}(aq) are

   $$Al^{3+}\ (aq)\ +\ 3\ e^-\ \to\ Al\ (s) \qquad E°_{red} = -1.66\ V$$
   $$Fe^{3+}\ (aq)\ +\ 3\ e^-\ \to\ Fe\ (s) \qquad E°_{red} = -0.04\ V$$

   and the standard S° values for these species are

species	S°(J/mol K)
Al (s)	28
Fe (s)	27
Al^{3+} (aq)	–293.3
Fe^{3+} (aq)	–313.8

   i. Calculate $\Delta G°$ for the reduction of Fe^{3+}(aq) by Al at 25 °C.
   ii. Calculate $\Delta S°$ for the reduction of Fe^{3+}(aq) by Al.
   iii. Calculate $\Delta H°$ for the reduction of Fe3+(aq) by Al at 25 °C.

   b. i. Construct a Born-Haber cycle for the formation of Al_2O_3 from its elements, showing each step in the process
      $$4\ Al(s) + 3\ O_2\ (g) \to 2\ Al_2O_3(s)$$
      ii. Use the data below to calculate the lattice enthalpy of Al_2O_3(s) in kJ/mol.

Aluminum	IE_1 577.6 kJ/mol	IE_2 1816.7 kJ/mol	IE_3 2744.8 kJ/mol
$\Delta H_{sub}°$(Al)	330.0 kJ/mol		
$\Delta H°_f(Al_2O_3)$	–1675.7 kJ/mol		

Oxygen	EA_1 141.0 kJ/mol NOTE: A positive EA is exothermic.	EA_2 –1779.6 kJ/mol
BDE (O_2)	493.6 kJ/mol	

4. (12%) Consider the concentration cell consisting of two $Cu^{2+}(aq)|Cu(s)$ half-cells with different molarities. The $[Cu^{2+}]$ in the two half-cells are 2.0 M and 2.5×10^{-2} M, respectively. $[Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \ E° = 0.34 \ V]$
   a. State the E° value for the concentration cell and explain why it has this value.
   b. Calculate the cell potential, E, for the cell with the two concentrations given.
   c. Identify the anode of this cell and explain your reasoning.
   d. For each half-cell, predict whether the $[Cu^{2+}]$ will increase or decrease as the cell operates.
   e. For the half reaction $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$, E° = –0.26 V.
       i. Write a balanced equation for the reaction in a standard voltaic cell made with the $V^{3+}(aq)/V^{2+}(aq)$ and $Cu^{2+}(aq)/Cu(s)$ half-cells and calculate the E° value for this cell.
       ii. Identify the $Cu^{2+}(aq)|Cu(s)$ half-cell (2.0 M or 2.5×10^{-2} M) that would yield the greater E value in combination with the $V^{3+}(aq)/V^{2+}(aq)$ half-cell. Explain.
       iii. Write an expression that could be used to calculate the E value for specific $[Cu^{2+}]$, $[V^{2+}]$, and $[V^{3+}]$.

5. (12%) Write net equations for each of the reactions 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.
   a. Sodium peroxide is added to water.
   b. Barium carbonate is treated with sulfuric acid.
   c. Lithium metal is heated in nitrogen gas.
   d. Concentrated hydrochloric acid is added to aqueous sodium hypochlorite.
   e. 2-methyl-2-propanol is mixed with cold hydrobromic acid.
   f. Uranium-238 emits an alpha particle followed by a beta particle.

6. (12%) Account for the following observations about the elements in Group 14 (C - Pb) and their compounds in terms of bonding principles.
   a. Carbon (in the form of diamond) and silicon have the same tetrahedral structure but very pure silicon is a semiconductor while diamond is an electrical insulator.
   b. Carbon and silicon both form tetrachlorides, but while CCl_4 does not react with H_2O at 25 °C, $SiCl_4$ reacts violently with H_2O at 25 °C.
   c. Carbon forms compounds containing chains of carbon atoms but the tendency of the elements in the family to bond to one another in this fashion decreases with increasing atomic number.
   d. Germanium, tin, and lead form stable chlorides in which they exhibit oxidation states of +2 and +4 but the +4 state decreases in stability relative to the +2 state with increasing atomic number.

7. (12%) Account for each of the following results of chemical kinetics experiments.
   a. When solid $Pb(NO_3)_2$ and solid KI are shaken together the mixture slowly turns yellow as PbI_2 is formed, but when aqueous solutions of the two reactants are combined a yellow precipitate of PbI_2 forms immediately.
   b. For most chemical reactions the initial reaction rate is faster than the rates at later times.
   c. 1 M solutions of compounds A and B decompose at identical initial rates at 25 °C. At 15 °C a 1 M solution of compound B shows a higher initial decomposition rate than a 1 M solution of compound A at that temperature.
   d. The rate equation for the reaction: $2 \ NO_2 + F_2 \rightarrow 2 \ NO_2F$ does not include a second order dependence on NO_2.

8. (14%) Explain the following observations about aromatic compounds.
   a. Benzene, C_6H_6, does not undergo addition reactions as alkenes do despite being highly unsaturated.
   b. Benzene is converted to bromobenzene on reaction with bromine. This reaction requires a Lewis acid catalyst.
   c. In the presence of a Lewis acid catalyst methylbenzene reacts faster with bromine than benzene does whereas nitrobenzene reacts more slowly.
   d. There are three possible isomers of dibromobenzene, $C_6H_4Br_2$, of which two are the major products formed when bromobenzene is reacted with Br_2 in the presence of a Lewis acid catalyst. Draw and name each of the three possible isomers, identify the two major products and account for this behavior.

ABBREVIATIONS AND SYMBOLS

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

CONSTANTS

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

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

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

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

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

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

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

$0\ °C = 273.15 \text{ K}$

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 1A																	18 8A
1 **H** 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	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	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	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** 180.9	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)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (**277**)	113 (Uut)	114 (Uuq)	115 (Uup)	116 (Uuh)	117 (Uus)	118 (Uuo)

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)	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** (262)

CELEBRATE THE INTERNATIONAL YEAR OF CHEMISTRY!

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2011

1. a. C $40.7 \div 12.011 = 3.39 \div 3.39 = 1$ $\quad \times 2 = 2 \rightarrow C_2$
    H $5.1 \div 1.008 = 5.06 \div 3.39 = 1.5$ $\quad \times 2 = 3 \rightarrow H_3$
    O $54.2 \div 16.00 = 3.39 \div 3.39 = 1$ $\quad \times 2 = 2 \rightarrow O_2$

    Empirical Formula: $C_2H_3O_2$

    b. $\Delta T = km$ $\quad -1.93 = -1.86m$ $\qquad m = 1.04$

    $m = \dfrac{1.20 g/mm}{kg}$ $\quad 1.04 = \dfrac{1.20/mm}{0.0100}$ $\quad M = \dfrac{1.20}{0.0104} = 116$ $\quad \dfrac{116}{59} = 2\ C_4H_6O_4$

    Molecular Formula: $C_4H_6O_4$

    c. $(4.00g \div 21.26) \times (1.26) = 0.237g$ compound
    $(0.226 mol/L) \times (0.0178L) = 0.00402$ mol NaOH
    $(0.237g \div 0.00402 mol) = 58.9/mol (\times 2 = 117.8/mol \qquad \therefore 2$ COOH/mol$)$

    d. **Structural Formula:** $HOOC\ CH_2\ CH_2\ COOH$

    e. **Structural Formula**
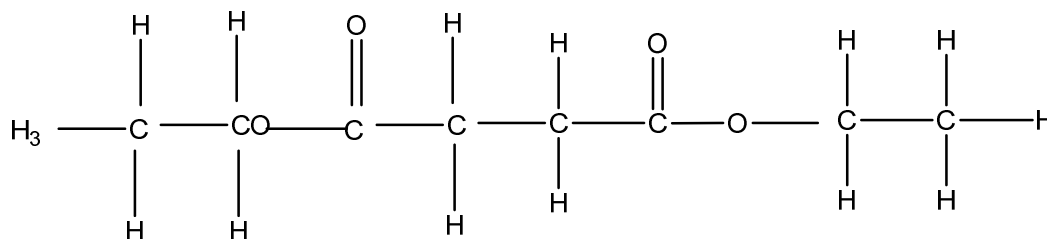
    f. Aqueous solution of NaOH is added to mixture. Acid is converted to salt. Organic solvent (eg. C_6H_{14} or $C_2H_2Cl_2$) is added to extract product while salt remains in H_2O phase.

2 a.

$$K_b = \frac{[pyH^+][OH^-]}{[py]} \qquad 1.78 \times 10^{-9} = \frac{[OH^-]^2}{0.240} \qquad [OH^-] = 2.07 \times 10^{-5} \quad pOH = 4.68$$

$$pH = 9.32$$

b. (i).

(0.240M pyridine)×(0.0200L)=0.0048mol pyridine

(0.120M HCl)×(0.0200L)=0.0024mol HCl

$$K_b = \frac{\left[pyH^+\right]\left[OH^-\right]}{\left[py\right]} \quad K_b = \left[OH^-\right] \quad \left[OH^-\right] = 1.78\times10^{-9} \quad pOH=8.75 \quad pH=5.25$$

(ii) Equivalence point

(20.00mL pyridine)(0.240M) + (40.00mL) (0.120M HCl)

0.0800M pyH⁺

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.78\times10^{-9}} = \frac{\left[H^+\right]\left[py\right]}{\left[pyH^+\right]} \quad 5.62\times10^{-6} = \frac{\left[H^+\right]^2}{0.080} \quad \left[H^+\right] = 6.70\times10^{-4}, pH=3.17$$

c.

$$K_{sp} = \left[Mg^{2+}\right]\left[OH^-\right]^2 \quad \left[OH^-\right] = 2.07\times10^{-5}$$

$$\left[Mg^{2+}\right] = \frac{5.6\times10^{-12}}{(2.07\times10^{-5})^2} = 1.3\times10^{-2}$$

d.

$$\left[Mg^{2+}\right] = 0.10 \quad \left[OH^-\right] = \sqrt{\frac{5.6\times10^{-12}}{0.10}} = 7.48\times10^{-6}$$

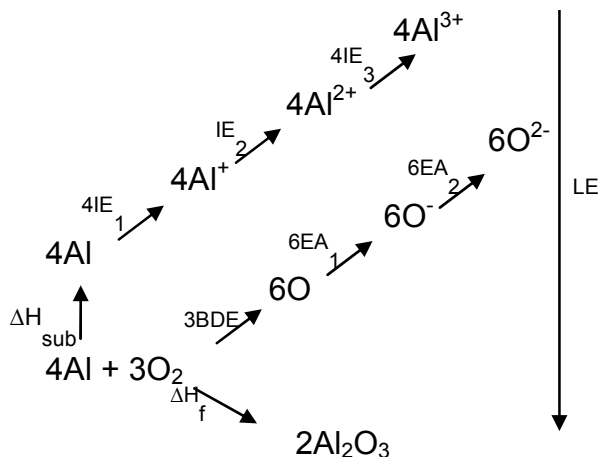$$1.78\times10^{-9} = \frac{\left[pyH^+\right]\left[7.48\times10^{-6}\right]}{0.240}$$

$$\left[pyH^+\right] = 5.71\times10^{-5}$$

3. a. (i). $E^0 = E^0_{red} - E^0_{ox}$ $E^0 = 0.04V - (-1.66V)$ $E^0 = 1.62V$
            $\Delta G^0 = -nFE^0$ $\Delta G^0 = -3\times(96500J/mol\ V)\times1.62V$ $\Delta G^0 = -468990J$

   (ii). $\Delta S^0 = S^0_{Al^{3+}} + S^0_{Fe} - \left[S^0_{Al} + S^0_{Fe^{3+}}\right]$
           $\Delta S^0 = -293.3 + 27 - [28-313.8]$
           $\Delta S^0 = -266.3 - [-285.8]$
           $\Delta S^0 = 19.5J/K$

   (iii). $\Delta G^0 = \Delta H^0 - T\Delta S^0$
           $\Delta H^0 = -468990J + 298\times(19.5J/K)$
           $\Delta H^0 = -463.2kJ$

   b. (i).

The diagram shows a Born-Haber cycle:

- $4Al + 3O_2$ → (via ΔH_f) → $2Al_2O_3$
- $4Al$ → (via ΔH_{sub}) → $4Al$
- $4Al$ → (via $4IE_1$) → $4Al^+$
- $4Al^+$ → (via IE_2) → $4Al^{2+}$
- $4Al^{2+}$ → (via $4IE_3$) → $4Al^{3+}$
- $6O$ ← (via $3BDE$)
- $6O$ → (via $6EA_1$) → $6O^-$
- $6O^-$ → (via $6EA_2$) → $6O^{2-}$
- $6O^{2-}$ → (via LE) → $2Al_2O_3$

(ii). $2\ \Delta H_f = 4\ \Delta H_{sub} + 4(IE_1 + IE_2 + IE_3) + 3BDE - 6(EA_1 + EA_2) - LE$

$2(-1675.7kJ) = 4(330.0) + 4(5139.1) + 3(493.6) - 6(141) + 6(1779.6) - LE$

$-3351.4 = 1320 + 20556.4 + 1480.8 - 846 + 10677.6 - 2LE$

$LE = 3351.4 + 1320 + 20556.4 + 1480.8 + 9831.6$

$= 36540.2kJ \times 2mol$

$= \mathbf{18270kJ/mol}$

4. a. E^0 is 0 because the 2 half-cells have the same material.

   b.

   $$E = E^0 - \frac{RT}{nF}\ln\frac{\left[Cu^{2+}\right]_d}{\left[Cu^{2+}\right]_c} \quad E = 0 - \frac{0.0257}{2}\ln\frac{2.5\times10^{-2}}{2.0} \quad E = \frac{-0.0257}{2}\times(-4.38) = 0.056V$$

   c. The anode is the half-cell with $[Cu^{2+}] = 2.5\times10^{-2}$. Oxidation occurs more readily in this half-cell because the $[Cu^{2+}]$ is lower.

   d. $[Cu^{2+}]$ will increase in the half-cell with $[Cu^{2+}]_{init} = 2.5\times10^{-2}M$ and decrease in half-cell with $[Cu^{2+}] = 2.0M$

   e. (i). $2V^{2+} + Cu^{2+} \rightarrow 2V^{3+} + Cu \qquad E^0 = 0.034V - (-0.26V) \qquad E^0 = 0.60V$

      (ii). Because Cu^{2+} is undergoing reduction in this cell (and Cu^{2+} is a reactant) the higher $[Cu^{2+}]_{(2.0M)}$ will give the greater E value.

      (iii). $E = E^0 - \frac{0.0257}{2}\ln\frac{\left[V^{3+}\right]^2}{\left[V^{2+}\right]^2\left[Cu^{2+}\right]}$

5. a. $Na_2O_2 + H_2O \rightarrow 2Na^+ + O_2H^- + OH^-$

   b. $BaCO_3 + 2H^+ + SO_4^{2-} \rightarrow BaSO_4 + H_2O + CO_2$

   c. $6Li + N_2 \rightarrow 2Li_3N$

   d. $OCl^- + 2H^+ + Cl^- \rightarrow Cl_2 + H_2O$

   e. $H_3CCOH(CH_3)_2 + H^+ + Br^- \rightarrow H_3CCBr(CH_3)_2 + H_2O$

   f. $^{238}_{92}U \rightarrow {}^4_2He + {}^{234}_{90}Th \rightarrow {}^{234}_{91}Pa + {}^0_{-1}\beta$

6. a. Electrons are held in covalent bonds between C atoms in diamond. Electrons in Si (with a lower IE) can be excited to move through lattice. Valence band (fully occupied) and conduction band (empty) are widely separated in energy. In Si the

energy gap between the occupied valence band and the empty conduction band is small enough that some electrons are excited at room temperature.

b. The carbon atom in CCl_4 is protected from H_2O attack by the Cl atoms. C has no orbitals available to bond with H_2O. Si is larger, allowing H_2O access and has d orbitals available to bond with H_2O molecule in addition to having a more polar bond (Si-Cl vs. C-Cl)

c. C-C bonds are very strong because of the substantial overlap of the orbitals. Bond strength decreases down the family because the larger orbitals do not overlap as efficiently leading to weaker bonds.

d. +2 and +4 oxidation states result from the involvement of electrons from p or $s+p$ orbitals, respectively. Electrons in s orbitals become less available for bonding as atoms become larger due to penetration of s orbitals and their greater attraction to higher charged nuclei.

7. a. Lead and iodide ions in the two solids react when they come into contact with one another, which occurs only infrequently so the reaction is slow. When dissolved in H_2O the ions are free to move and react quickly when the solutions are mixed.

    b. Reaction rates are typically proportional to the concentration of reactant. Because [Reactant] decreases as the reaction proceeds the rate will decrease also.

    c. Decomposition of A and B has different activation energies which leads to different variations with temperature. The two rate vs. temperature lines cross at 25°C giving the same rates. Since B has a higher rate at 15°C its E_a must be lower than that for compound A.

    d. The ratio of atoms in the stoichiometric equation often has little to do with the order in the rate equation. The mechanism apparently has at least one NO_2 that participates in the reaction after the rate determining step.
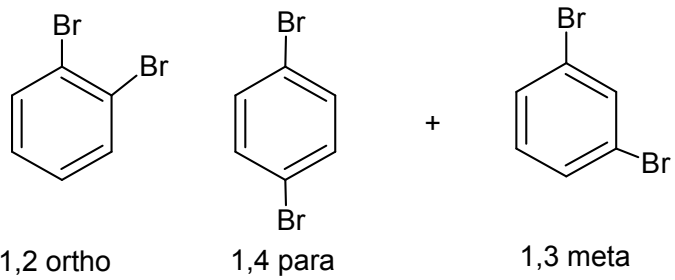
8. a. The π electrons in C_6H_6 are delocalized so that sites do not exist where addition could occur.

    b. C_6H_6 can undergo substitution reactions by an electrophilic mechanism. Interaction of Br_2 with a Lewis acid catalyst (such as $FeBr_3$) produces $FeBr_4^-$ and Br^+. The Br^+ can attack the electron-rich C_6H_6 ring, leading to substitution.

    c. A CH_3 group contributes electron density to a C_6H_6 ring relative to a H atom. Higher electron density in ring leads to faster substitution. A NO_2 group withdraws electron density from a C_6H_6 ring (relative to H) producing a slower reaction.

    d. Br is an ortho-para director increasing electron density more at those positions so substitution occurs there preferentially.

1,2 ortho   1,4 para   1,3 meta

major products