2012 U.S. NATIONAL CHEMISTRY OLYMPIAD
NATIONAL EXAM - PART II

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 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 23, 2012, 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 5 for student reference. Students should be permitted to use non-programmable calculators.

DIRECTIONS TO THE EXAMINEE - PART II

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

1. [11%] The concentration of ethanol (C_2H_5OH) in aqueous solutions can be determined by reacting it with potassium dichromate ($K_2Cr_2O_7$) in acid to produce ethanoic acid (CH_3COOH) and Cr^{3+} ions.
   a. Write a balanced equation for this reaction.
   b. Describe the color change observed during this reaction.
   c. A standard solution of $K_2Cr_2O_7$ is prepared in the following manner:
      125 mL of H_2O is placed in a 250 mL volumetric flask
      70 mL of concentrated H_2SO_4 is added while swirling and cooling under running water
      0.750 g of dried $K_2Cr_2O_7$ is added and the solution is diluted to the mark on the neck of the flask with H_2O.
      i. Account briefly for the order in which the liquid solution components are mixed (H_2O, H_2SO_4, H_2O) and for the fact the initial mixture is cooled.
      ii. Calculate the $[Cr_2O_7^{2-}]$ in the 250 mL solution.
   d. 0.600 mL of a popular mouthwash is diluted to 100. mL with H_2O. When a 10.0 mL aliquot of this solution is titrated with the solution of $K_2Cr_2O_7$ prepared in c., 20.25 mL of $K_2Cr_2O_7$ are required.
      i. Calculate the number of moles of ethanol in 0.600 mL of mouthwash.
      ii. Determine the mass percentage of ethanol in this mouthwash (Assume the density of mouthwash to be 0.966 g•cm^{-3}).
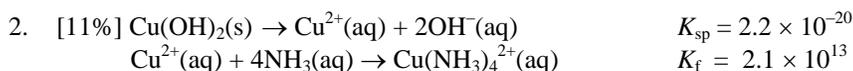
2. [11%]
$$Cu(OH)_2(s) \rightarrow Cu^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = 2.2 \times 10^{-20}$$
$$Cu^{2+}(aq) + 4NH_3(aq) \rightarrow Cu(NH_3)_4^{2+}(aq) \qquad K_f = 2.1 \times 10^{13}$$
   Use the equations and K values above to answer the questions below.
   a. Determine the solubility of $Cu(OH)_2$ in mol/L at pH = 8.00
   b. If 20.0 mL of 0.0010 M $CuSO_4$ is mixed with 50.0 mL of 0.0010 M NaOH, determine whether $Cu(OH)_2$ will precipitate. Support your answer with appropriate calculations.
   c. Write the equation for the reaction of $Cu(OH)_2$ with aqueous NH_3 and calculate the K value for this reaction.
   d. Calculate the $[NH_3]$ that would be needed to dissolve 0.100 g of $Cu(OH)_2$ in 1.00 L of H_2O.
   e. Describe what would be observed if 5.0 M NH_3 is added dropwise to a 0.10 M solution of Cu^{2+} ions.

3. [14%] A voltaic cell is constructed using solutions of $NaHSO_4$, H_2SO_3, and $MnSO_4$ with suitable electrodes. The relevant half reactions are:
$$HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow H_2SO_3(aq) + H_2O \qquad E° = 0.17 \text{ V}$$
$$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \qquad E° = -1.18 \text{ V}$$
   a. Sketch a working voltaic cell on which you
      i. identify the contents of each half-cell,
      ii. suggest a substance to be used as an electrode in the $HSO_4^-(aq)/H_2SO_3(aq)$ half-cell.
      iii. label the anode and cathode,
      iv. show the direction of electron movement in the external circuit,
      v. indicate the direction of movement of cations in the salt bridge.
   b. Write the equation for the overall cell reaction and calculate the cell potential at standard conditions.
   c. Calculate the cell potential if the $[H^+]$ is changed to pH = 1.
   d. Predict the qualitative effect on the cell potential if a solution of $Ba(NO_3)_2$ is added to both cell compartments. Justify your prediction.
      [$BaSO_3$ $K_{sp} = 8.3 \times 10^{-7}$; $BaSO_4$ $K_{sp} = 1.2 \times 10^{-10}$]
   e. Predict the qualitative effect on the cell potential if the electrode that serves as the anode is doubled in size. Justify your prediction.

4. [12%] Selected thermodynamic values for the ionization of ethanoic acid, H_3CCOOH, and trichloroethanoic acid, Cl_3CCOOH, at 25 °C are given in the table below.

	$\Delta G°$, kJ•mol^{-1}	$\Delta H°$, kJ•mol^{-1}	$\Delta S°$ J•mol^{-1}•K^{-1}	K_a (25 °C)
H_3CCOOH	27.12	−2.51		1.77×10^{-5}
Cl_3CCOOH	3.93	−13.66	−59.0	

   Use the given values to provide answers to the following questions.
   a. What is the $\Delta S°$ value for the ionization of H_3CCOOH at 25 °C?
   b. What is the K_a value for Cl_3CCOOH at 25 °C?
   c. What is the K_a value for H_3CCOOH at 35 °C?
   d. Account for the difference in the K_a values of the two acids at 25 °C in terms of their molecular structures.
   e. State whether the $\Delta S°$ values suggest an increase or a decrease in the order of the system upon ionization and offer an explanation in molecular-level terms.

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. A solution of hydrofluoric acid is added to a suspension of aluminum hydroxide.
   b. Sodium iodide solution is added to a hydrogen peroxide solution.
   c. Solutions of mercury(I) nitrate and hydrochloric acid are mixed.
   d. Solid sodium sulfide is added to water.
   e. Nitrogen dioxide is bubbled into water.
   f. 1,6-hexanedioic acid chloride is reacted with 1,6-hexanediamine.

6. [14%] A proposed reaction mechanism for the formation of nitrosyl bromide is:
   $$(1)\ NO(g) + Br_2(g) \rightarrow NOBr_2(g)$$
   $$(2)\ NOBr_2(g) + NO(g) \rightarrow 2NOBr(g)$$
   a. Write the overall equation for this reaction.
   b. Determine the rate law for this reaction if the rate determining step is the
      i. first step in the mechanism.
      ii. second step in the mechanism.
   c. State and explain how the rate determining step could be identified experimentally. Describe the experiments to be performed and the results expected for each mechanism.
   d. Sketch and label a potential energy diagram for each of the mechanisms in b., showing and labeling each step for this exothermic reaction.
   e. State and explain using chemical principles and graphs how a temperature increase would affect the reaction rate.

7. [12%] Account for the following observations in terms of atomic structure, intermolecular forces, or intramolecular forces.
   a. The stable form of nitrogen is a diatomic molecule with a low boiling point while the most stable form of phosphorus is a network solid at room temperature.
   b. The melting points of the Group I elements decrease with increasing atomic number (Li to Cs) whereas the melting points of the Group 17 elements increase with increasing atomic number (F to I).
   c. The first ionization energies of the Group II elements decrease with increasing atomic number. The first three elements (Be, Mg, Ca) show a greater change (899 to 590 kJ/mol) than the latter three (Ca, Sr, Ba) (590 to 503 kJ/mol).
   d. The Group 14 elements (C – Pb) exhibit a gradual progression from non-metallic to metallic behavior with increasing atomic number.

8. [14%] There are four structural isomers with the molecular formula C_4H_9Br. The structures of three of these are shown below. Each of these compounds can undergo a substitution reaction with hydroxide ion to form an alcohol.
   $$CH_3CH_2CH_2CH_2Br \qquad CH_3CH_2CHBrCH_3 \qquad (CH_3)_3CBr$$
   a. Which of these alkyl bromides reacts most rapidly with OH^-? Outline your reasoning.
   b. These substitution reactions may occur by either a uni-molecular (1) or a bi-molecular (2) mechanism.

(1)	(2)
$RBr \rightarrow R^+ + Br^-$	$RBr + OH^- \rightarrow ROH + Br^-$
$R^+ + OH^- \rightarrow ROH$	

   Predict which of the above alkyl bromides is most likely to react via a uni-molecular mechanism and outline your reasoning.
   c. State the properties of a solvent that would promote the uni-molecular mechanism. Outline your reasoning.
   d. Write the structure of the fourth structural isomer of C_4H_9Br. To which of the original three compounds is its reactivity most comparable? Outline your reasoning.
   e. For chiral molecules such as
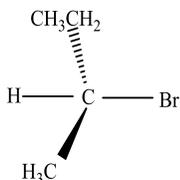
   one of the mechanisms in b. forms a product with inverted configuration while the other gives a mixture of stereoisomeric products. Assign each of these results to one of the mechanisms in b. and outline your reasoning.

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** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)	113 (Uut) (284)	114 (Uuq) (289)	115 (Uup) (288)	116 (Uuh) (293)	117 (Uus) (294)	118 (Uuo) (294)

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)

1) a. $2 \times (Cr_2O_7{}^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O)$
$3 \times (C_2H_5OH + H_2O \rightarrow CH_3COOH + 4\ e^- + 4\ H^+)$

$2\ Cr_2O_7{}^{2-} + 3\ C_2H_5OH + 16\ H^+ \rightarrow 4\ Cr^{3+} + 3\ CH_3COOH + 11\ H_2O$
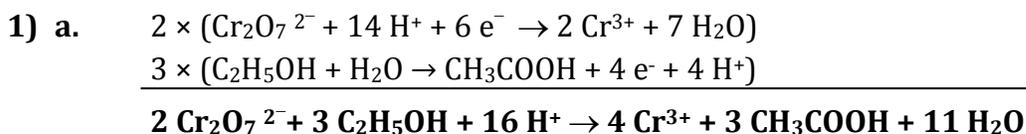
b. orange $\rightarrow$ green

c. i) Acid should be added to water to prevent spattering. Mixture is cooled to dissipate heat of dilution.

ii) $0.750\text{g} \times \dfrac{1\ \text{mol}}{294.2\text{g}}\ \times \dfrac{1}{0.250\text{L}}$ = **0.0102 M**

d. i) $0.02025\ \text{L} \times 0.0102\ \text{mol/L} = 2.066 \times 10^{-4}\ \text{mol}\ Cr_2O_7{}^{2-}$

$2.066 \times 10^{-4}\ \text{mol}\ Cr_2O_7{}^{2-} \times [3\ \text{mol}\ C_2H_5OH]/[2(Cr_2O_7){}^{2-} = 3.099 \times 10^{-4}\ \text{mol}\ C_2H_5OH$ in 10 mL

$3.099 \times 10^{-4}\ \text{mol}\ C_2H_5OH \times \dfrac{100}{10} = 3.099 \times 10^{-3}\ \text{mol}\ C_2H_5OH$ in 100 mL

ii) $0.600\ \text{mL} \times 0.966\ \dfrac{\text{g}}{\text{cm}^3} = 0.5796$ g

$3.099 \times 10^{-3}\ \text{mol} \times \dfrac{46.7\ \text{g}}{1\text{mol}} = 0.1428\ \text{g}\ C_2H_5OH$ **24.6% Ethanol**

2) a. $Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2\ OH^-$ pH = 8   pOH = 6
$k_{sp} = [Cu^{2+}] \times [OH^-]^2$
$2.2 \times 10^{-20} = [Cu^{2+}] \times [10^{-6}]^2$
$[Cu^{2+}] = 2.2 \times 10^{-8}$ M

b. $\left(\dfrac{0.0200\ \text{L} \times 1.0 \times 10^{-3}\ \text{M}}{0.0700\text{L}} \right) = 2.86 \times 10^{-4}\ \text{M}\ Cu^{2+}$

$0.0500\ \text{L} \dfrac{(1.0 \times 10^{-3}\text{M})}{0.0700\text{L}} = 7.14 \times 10^{-4}\ \text{M}\ OH^-$
$Q = (2.86 \times 10^{-4}) \times (7.14 \times 10^{-4})^2$
$Q = 1.46 \times 10^{-10} \gg K_{sp} \therefore P_{pt}$

c. $Cu(OH)_2 + 4\ NH_3 \rightarrow Cu(NH_3)_4{}^{2+} + 2\ OH^-$
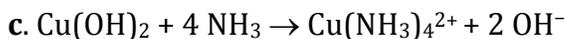
$K = K_{sp} \times K_f$

$K = (2.2 \times 10^{-20}) \times (2.1 \times 10^{13}) = 4.6 \times 10^{-7}$

d. $1\ g\ Cu(OH)_2 \times \dfrac{1\ mol}{97.54\ g} = 0.00103\ mol\ Cu(OH)_2$ in 1 L.

OH^- will be 0.00206 M

$4.6 \times 10^{-7} = [Cu(NH_3)_4] \times (OH^-)^2 = 0.00103 \times (0.00206)^2$

$[NH_3]^4 = 0.00950$

$[NH_3] = (0.00950)^{1/4}$

[NH₃] = 0.312 M

e. As the NH3 solution is added a blue precipitate will form which will dissolve as more NH3 is added to form a dark blue solution.

3) a.

b. $Mn + HSO_4{}^- + 3\ H^+ \rightarrow Mn^{2+} + H_2SO_3 + H_2O$

$\Sigma^o{}_{cell} = \Sigma^o{}_{ox} + \Sigma^o{}_{red}$ $\Sigma^o{}_{cell} = 1.18 + 0.17 = $ **1.35 V**
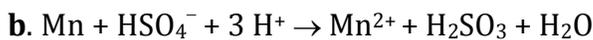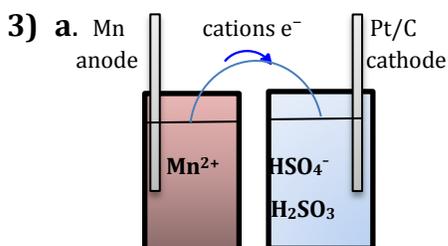
c. $\Sigma = \Sigma^o \left(\dfrac{0.0257}{n} \right) \ln \dfrac{1}{[H^+]^3}$

$\Sigma = 1.35 - \left(\dfrac{0.0257}{2} \right) \ln 10^3$

$\Sigma = 1.35 - \left(\dfrac{0.0257}{2} \right) (6.91)$

$\Sigma = 1.35 - 0.089 = $ **1.26 V**

d. $Ba(NO_3)_2$ will have no effect on the anode components. $Ba(NO_3)_2$ will react with both H_2SO_3 and $HSO_4{}^-$ in cathode compartment but $BaSO_4$ is less soluble so reaction will shift to the left, decreasing the potential.

e. There is no effect on the cell potential by changing the size of the anode. Only the solution component concentrations and gas pressures affect E.

4) a. $\Delta G^o = \Delta H^o - T\Delta S^o$

27120 J/mol $= -2510$ J/mol $- 298.15$ K $\times \Delta S^o$

$$\frac{29630 \text{ J/mol}}{-298.15 \text{ K}} = \Delta S^o$$

$\Delta S^o = -99.4$ J/mol K

b. $\Delta G^o = -RT \ln K$

$$\frac{3930 \text{ J/mol}}{(-8.314 \text{ J/mol K}) \times (298.15 \text{ K})} = \ln (K)$$

$\ln (K) = -1.58$

$K = 2.0 \times 10^{-1}$

c. $\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

$$\ln\left(\frac{K_2}{1.77 \times 10^{-5}}\right) = \frac{-2510\frac{J}{mol}}{\left(8.314\frac{J}{mol K}\right)}\left[\frac{1}{298.15} - \frac{1}{308.15}\right]$$

$$\ln\left(\frac{K_2}{1.77 \times 10^{-5}}\right) = -301.9 \times (0.003354 - 0.003245)$$

$$\ln\left(\frac{K_2}{1.77 \times 10^{-5}}\right) = -0.0329$$

$$\left(\frac{K_2}{1.77 \times 10^{-5}}\right) = 0.9677$$

$K_2 = 1.71 \times 10^{-5}$

d. Cl_3CCOOH has a greater K than H_3CCOOH because the Cl atom draw electrons from C–OH, weakening the O–H bond.

e. ΔS^o values are less than zero, suggesting an increase in order H^+ and A^- are solvated more tightly than HA with $CH_3CO_2^-$ being solvated better than larger Cl_3CO^-.

5) a. $HF + Al(OH)_3 \rightarrow Al^{3+} + F^- + H_2O$

b. $I^- + H_2O_2 \rightarrow I_2 + H_2O$ // $H_2O_2 \rightarrow H_2O + O_2$ (cat: I^-)

c. $Hg_2^{2+} + Cl^- \rightarrow Hg_2Cl_2$

d. $Na_2S + H_2O \rightarrow HS^- + 2\,Na^+ + OH^- \rightarrow H_2S + OH^- + Na^+$

e. $NO_2 + H_2O \rightarrow H^+ + NO_3^- + HNO_2$ or $NO_2^- + H^+$

f. $Cl–CO(CH_2)_4COCl + H_2N(CH_2)_6NH_2 \rightarrow -(OC(CH_2)_6CONH(CH_2)_6NH)_x - + HCl$

6) a. $2\,NO + Br_2 \rightarrow 2\,NOBr$
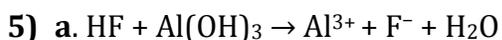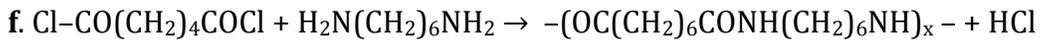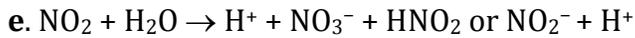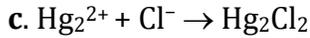
b. i) Rate $= k_1 \times [NO] \times [Br_2]$
ii) Rate $= k_2 \times [NOBr_2] \times [NO]$ Rate $= k_2 \times K[NO][Br_2][NO]$

c. The [NO] can be varied at constant [Br₂] while studying rate.
If first step is limiting: Rate $\propto [NO]$
If second step is limiting: Rate will increase $\propto [NO]^2$

d.
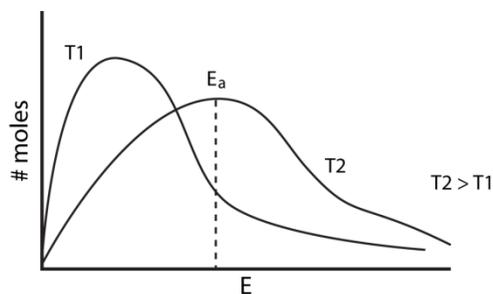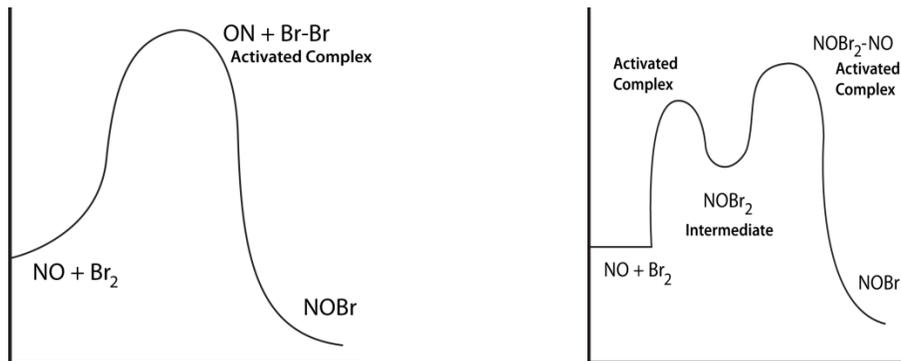
e. T↑ will increase reaction rate since at higher T more molecules will have the energy equal or greater than E_a (necessary activation energy).

7) a. The *p* orbitals in the small nitrogen atom overlap well to form strong π bonds leading to triple bonded N_2 molecules with weak intermolecular forces. The larger phosphorus atom forms weaker π bonds but, stronger σ bonds. This results in a network solid held together with single bonds.

b. The Group I elements exhibit metallic bonding with cations held together with free electrons. The attraction between the cations and electrons becomes weaker as the cations increase in size. Therefore, the melting points decrease down the family. The Group 17 elements consist of diatomic molecules, X_2. These molecules are bonded to one another with London forces which become stronger with the number of electrons in the molecule, i.e. down the family so melting points increase in that direction.

c. Ionization energies decrease with increasing size of the atoms because the electron that removed is farther from the nucleus and shielded by more inner electrons. The first three elements show a greater change because the electrons added are in *s* and *p* orbitals and screen the outermost electron more efficiently while some of the core electrons added in the latter three elements are in d orbitals which do not shield well as well as s and p.
(Give half credit for size arguments, for example, there is a greater difference in size between Be and Ca than between Ca and Ba so a greater change in ionization energy between Be and Ca).

d. The ionization energies decrease down the family making it easier for the atoms to lose electrons and form cations. The *s* and *p* orbitals combine to form bonding and antibonding orbitals. In carbon there is a large energy gap between them, making diamond an insulator. The gap is smaller in Si and Ge which behave as semiconductors with a few electrons jumping the gap. In Sn and Pb the gap is zero and electrons flow readily from the valence band to the conduction bond and they are metals.

8) a. $(CH_3)_3CBr$ will react fastest. The sterically-crowded Br atom will leave most readily. The three CH_3 groups will donate electron density to the carbon atom breaking the C–Br bond. [$CH_3CH_2CH_2Br$ will react fastest by substitution primary bromide is less hindered, faster S_N2].

b. $(CH_3)_3CBr$ will most likely react via a uni-molecular mechanism. The three CH_3 groups will donate electron density to stabilize the carbocation. The $(CH_3)_3C^+$ will be more stable relative to $(CH_3)_3CBr$ than the ions for the other two isomers.

c. An ionizing solvent with a high dielectric constant that stabilizes ions would promote the uni-molecular mechanism.

d. $(CH_3)_2CHCH_2Br$. Its reactivity would resemble that of $CH_3CH_2CH_2CH_2Br$ because they are both primary bromides.

e. The bi-molecular mechanism will give an inverted configuration because the OH^- attacks the carbon atom bonded to the Br from the back. The uni-molecular mechanism gives a mixture of products because it goes through a planar R^+ ion making either stereoisomer equally possible.