2004 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 19, 2004, after which tests can be returned to students and their teachers for further study.

Allow time for the student to read the directions, ask questions, and fill in the requested information on the "Blue Book". When the student has completed **Part II**, or after **one hour and forty-five minutes** has elapsed, the student must turn in the "Blue Book", **Part II** of the testing materials, and all scratch paper. Be sure that the student has supplied all of the information requested on the front of the "Blue Book," and that the same identification number used for **Part I** has been used again for **Part II**.

There are three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest-breaks between parts.

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

A periodic table and other useful information are provided on the back page for student reference. Students should be permitted to use non-programmable calculators.

DIRECTIONS TO THE EXAMINEE–PART II

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

1. (12 %) A solution of copper(II) sulfate that contains 15.00% $CuSO_4$ by mass has a density of 1.169 g/mL. A 25.0 mL portion of this solution was reacted with excess concentrated ammonia to form a dark blue solution. When cooled, filtered and dried, 6.127 g of a dark blue solid were obtained. A 0.195 g sample of the solid was analyzed for ammonia by titrating with 0.1036 M hydrochloric acid solution, requiring 30.63 mL to reach the equivalence point. A 0.150 g sample was analyzed for copper (II) by titrating with 0.0250 M EDTA, (which reacts with Cu^{2+} in a 1:1 ratio). The endpoint was reached after 24.43 mL of the EDTA were added. A 0.200 g sample was heated at 110 °C to drive off water, producing 0.185 g of the anhydrous material.

   a. Determine the molarity of Cu^{2+} ions in the original solution.
   b. Find the number of moles of Cu^{2+} in the 25.0 mL portion.
   c. Calculate the percentages by mass in the prepared compound of;
         i. NH_3
         ii. Cu^{2+}
         iii. H_2O
         iv. SO_4^{2-}
   d. Use the results in part c. to determine the formula of the compound.
   e. Assuming that Cu^{2+} is the limiting reactant in the synthesis, determine the percent yield.

2. (16%) $2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$ $\Delta H° = -198$ kJ $\Delta S° = -168$ J·K^{-1}

   Ozone reacts with nitrogen dioxide according to the equation above.
   a. Calculate $\Delta H_f°$ for $NO_2(g)$ in kJ·mol^{-1}. [$\Delta H_f°$ kJ·mol^{-1}; $O_3(g)$ 143, $N_2O_5(g)$ 11]
   b. Account for the sign of $\Delta S°$.
   c. Calculate the value of $\Delta G°$ at 25 °C.
   d. State and explain how the spontaneity of this reaction will vary with increasing temperature.
   e. Use the rate data below to determine the rate law for the reaction of $NO_2(g)$ and $O_3(g)$

$NO_2(g)$, M	$O_3(g)$, M	Rate M·s^{-1}
0.0015	0.0025	4.8×10^{-8}
0.0022	0.0025	7.2×10^{-8}
0.0022	0.0050	1.4×10^{-7}

   f. Calculate the specific rate constant and give its units.
   g. The following mechanisms have been proposed for this reaction. Discuss the suitability of each to account for the rate law obtained.

 | Mechanism I | | Mechanism II | |
   |---|---|---|---|
   | $NO_2 + NO_2 \rightarrow NO_3 + NO$ | slow | $NO_2 + O_3 \rightleftharpoons NO_3 + O_2$ | fast |
   | $NO_3 + NO_2 \rightarrow N_2O_5$ | fast | $NO_3 + NO_2 \rightarrow N_2O_5$ | slow |
   | $NO + O_3 \rightarrow NO_2 + O_2$ | fast | | |

   h. Describe and account for any change expected in the rate of this reaction as the temperature is increased.

3. (10%) A popular lecture demonstration involves the sequential precipitation and dissolution of several slightly soluble silver compounds beginning with a $[Ag^+] = 0.0050$ M. Use the information below to answer the following questions about this demonstration.
       [K_{sp} values; AgCl 1.8×10^{-10}, AgBr 5×10^{-13}, AgI 8.3×10^{-17}, Ag_2SO_4 1.4×10^{-5}]
   a. What must the $[SO_4^{2-}]$ be in order to start precipitation in a solution in which $[Ag^+] = 0.005$ M?
   b. State the order in which the halide ions should be added to a concentration of 0.10 M so that each precipitate will form from the $[Ag^+]$ in equilibrium with the previous precipitate. Support your answer with appropriate calculations.
   c. As a way of making this demonstration more striking, one of the silver halides in this series is dissolved by adding aqueous ammonia before precipitating the next silver halide. Which silver halide(s) dissolve in 0.60 M NH_3? Support your answer with calculations. [K_f Ag(NH_3)$_2^+$ 1.7×10^7]

4. (12%) Aluminum metal is obtained commercially by electrolyzing Al_2O_3 mixed with cryolite (Na_3AlF_6).

    a. Explain why electrolysis is used rather than heating the Al_2O_3 either directly or in the presence of C (as is done to extract Fe or Zn from their ores).

    b. State the purpose of the Na_3AlF_6.

    c. Write the two half-reactions that occur during electrolysis and indicate which of the two occurs at the cathode

    d. How many moles of electrons must pass through the cell to produce 5.00 kg of Al? (Assume 100% efficiency.)

    e. Determine the current required (in amperes) if the aluminum in d. is produced in 10.0 hours.

    f. Calculate the volume of gas formed in the process in d. at 25 ˚C and 720 mmHg.

5. (12%) Write net equations for each of the combinations of reactants below. Use appropriate ionic and molecular formulas and omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the equations. All reactions occur in aqueous solution unless otherwise indicated.

    a. Concentrated nitric acid is added to iron(II) sulfide.

    b. Acetic acid is added to solid calcium phosphate.

    c. Small pieces of aluminum metal are added to concentrated sodium hydroxide solution.

    d. Solutions of chromium(III) sulfate and barium hydroxide are mixed.

    e. Concentrated hydrochloric acid is added to an aqueous solution of cobalt(II) nitrate.

    f. Bromine gas is added to propene.

6. (16%) Account for the following statements or observations in terms of atomic-, ionic- or molecular-level explanations.

    a. Magnesium exists as +2 ions rather than +1 ions in all of its compounds despite the fact that the second ionization energy of a magnesium atom is more than twice as great as the first ionization energy.

    b. Titanium forms ions with different charges (+2, +3 and +4). The first two of these ions are colored while the last is colorless.

    c. Carbon dioxide (CO_2) is a gas at room temperature but silicon dioxide (SiO_2) is a high melting solid.

    d. Nitrogen forms NF_3 but not NF_5 whereas phosphorus forms PF_3 and PF_5. The trifluorides are both trigonal pyramidal and the pentafluoride is trigonal bipyramidal.

7. (12%) Explain these observations about nuclei.

    a. Elements with even atomic numbers tend to have more stable isotopes than elements with odd atomic numbers.

    b. Carbon-14 decays with the loss of a β^- particle while carbon-10 decays with the loss of a β^+.

    c. Carbon-14 ($t_{1/2}$ = 5730 years) can be used to determine the age of organic materials that died between approximately 500 and 50,000 years ago.

8. (10%) A student is asked to determine the molar mass of an unknown monoprotic carboxylic acid by freezing point depression. The student dissolves 0.029 g of the unknown acid in 10. mL of water and obtains the cooling curve shown.
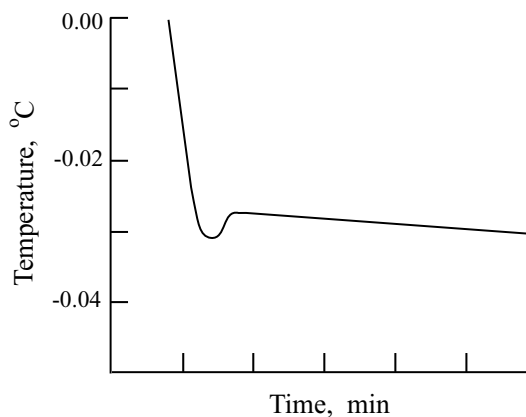
    a. Account for the shape of the curve including the
        i. downward slope of the final portion of the curve.
        ii. depression before the final portion of the curve.

    b. Give the value of the freezing point of the solution and calculate the molality of the solute. [K_f = -1.86 ˚C·m^{-1}]

    c. Determine the molar mass of the acid.

    d. When the student titrates a solution of the acid in water, a molar mass of 120. g·mol^{-1} is determined. Compare these results with those in part c. and offer an explanation for this behavior.

END OF PART II

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

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

PERIODIC TABLE OF THE ELEMENTS

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (277)				

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

CHEMISTRY OLYMPIAD

KEY FOR NATIONAL EXAM – PART II

1.

a. $1.1169 \dfrac{g}{L} \times \dfrac{0.1500 \text{ g Cu}}{1.000 \text{ g solution}} \times \dfrac{1 \text{ mol}}{159.62 \text{ g}} = 1.099$ M

b. $1.099 \dfrac{\text{mol}}{L} \times 0.025 \text{ L} = 0.0275$ mol $CuSO_4$

c. i. $0.1036 \dfrac{\text{mol}}{L} \times 0.03063 \text{ L} = 0.003173$ mol HCl $= 0.003173$ mol NH_3

0.003173 mol $NH_3 \times 17.034 \dfrac{g}{\text{mol}} = 0.05405$ g NH_3

% $NH_3 = \dfrac{0.05405 \text{ g } NH_3}{195 \text{ g sample}} \times 100 = 27.7\%$ NH_3

ii. 0.02443 L EDTA $\times 0.0250 \dfrac{\text{mol}}{L} = 6.11 \times 10^{-4}$ mol EDTA $\equiv 6.11 \times 10^{-4}$ mol Cu^{2+}

6.11×10^{-4} mol $Cu^{2+} \times 63.55 \dfrac{g}{\text{mol}} = 0.03881$ g EDTA

% EDTA $= \dfrac{0.03881 \text{ g EDTA}}{150 \text{ g sample}} \times 100 = 25.9\%$ EDTA

iii. 0.200 g compound - 0.185 g anhydrous compound $= 0.015$ g H_2O

% $H_2O = \dfrac{0.0150 \text{ g } H_2O}{0.200 \text{ g sample}} \times 100 = 7.5\%$ H_2O

iv. % $SO_4 = 100 - [27.7 + 25.88 + 7.5] = 38.92$ %

d. Assume 100 g; calculate moles using molar mass; divide all results by the smallest number

27.7 g $NH_3 \times \dfrac{1 \text{ mol}}{17.03 \text{ g}} = 1.627 / 0.405 = 4.02$

25.88 g $Cu \times \dfrac{1 \text{ mol}}{63.55 \text{ g}} = 0.407 / 0.405 = 1.00$

7.5 g $H_2O \times \dfrac{1 \text{ mol}}{18.02 \text{ g}} = 0.416 / 0.405 = 1.03$

38.9 g $SO_4 \times \dfrac{1 \text{ mol}}{96.1 \text{ g}} = 0.405 / 0.405 = 1$

Based on these results, we can see the molecular formula is, $Cu(NH_3)_4SO_4 \cdot H_2O$
whose molar mass is 245.28 g/mol

e. $245.28 \dfrac{g}{\text{mol}} \times 0.275 \text{ mol} = 6.76$ g is the theoretical yield

% yield $= \dfrac{6.127 \text{ g}}{6.76 \text{ g}} \times 100 = 90.7\%$

2.

a. $\Delta H^{0}_{rxn} = \Delta H^{0}_{f}(N_2O_5) + \Delta H^{0}_{f}(O_2) - [2\Delta H^{0}_{f}(NO_2) + \Delta H^{0}_{f}(O_3)]$

-198 kJ $= 11$ kJ $+ 0 - [2\Delta H^{0}_{f}(NO_2) + 143$ kJ$]$ so, $\Delta H^{0}_{f}(NO_2) = 33$ kJ

b. $\Delta S° < 0$ because 3 moles of gas are converted into 2 moles of gas.

c. $\Delta G° = \Delta H° - T\Delta S° = -198000$ J $- 298$ K$(-168$ J/K$) = -148$ kJ

d. Spontaneity will decrease as temperature increases because the entropy change of the process is negative. This makes the contribution of the $T\Delta S^\circ$ term to the free energy positive. As temperature rises, this term contributes more to the free energy and because it is positive, the spontaneity must decrease.

e. Looking at the table we see from comparing experiments 1&2 that when $[NO_2]$ increases by a factor of 1.5 the rate of reaction also increases by 1.5, so it is first order in $[NO_2]$. From experiments 2&3 we see that an increase in the $[O_3]$ by a factor of 2.0 increases the rate of reaction by 2.0 so the reaction is also first order in $[O_3]$.

f. The rate law is, $rate = k[NO_2][O_3]$

$4.8\times10^{-8}\ M^{-1}s^{-1} = k(0.0015\ M)(0.0025\ M)$ so k = 0.0128 L mol^{-1} s^{-1}

g. Mechanism #1 would suggest a rate law of $rate = k[NO_2]^2$ and mechanism #2 would suggest a rate law of, $rate = k[NO_2]^2[O_3]$. Neither of these mechanisms is consistent with the observed rate law.

h. The rate of the reaction would be expected to increase with an increase in temperature. Collision rate increases as temperature increases and a larger fraction of collisions have the energy necessary for reaction (Ea).

3.

a. $K_{sp} = [Ag^+]^2[SO_4^{2-}]$ so $[SO_4^{2-}] = \dfrac{[Ag^+]^2}{K_{sp}} = \dfrac{1.4\times10^{-5}}{(0.005)^2} = 0.56$ M

b. Cl^- then Br^- then I^-.
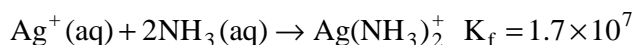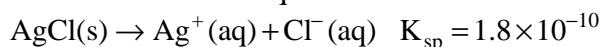
For Cl, $1.8\times10^{-10} = [Ag^+](0.10)$, so $[Ag^+] = 1.8\times10^{-9}$,

for $5\times10^{-13} = [Ag^+](0.10)$, so $[Ag^+] = 5\times10^{-13}$

and for $8.3\times10^{-17} = [Ag^+](0.10)$, so $[Ag^+] = 8.3\times10^{-17}$
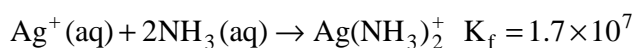
The $[Ag^+]$ in equilibrium with AgCl in 0.1 M Cl^- is sufficient to cause precipitation of AgBr in 0.1 M Br^-. In turn, the $[Ag^+]$ in equilibrium with AgBr in 0.1 M Br^- will cause precipitation of AgI in 0.1 M I^-. However, the reverse order of addition of the anions would not lead to this behavior.

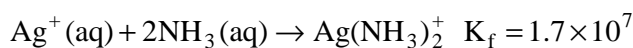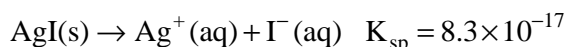**c.** We need the net equilibrium constant for the combined reaction in each case.

$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)\quad K_{sp} = 1.8\times10^{-10}$

$Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+\quad K_f = 1.7\times10^7$

So $K = K_{sp} \times K_f = 3.06\times10^{-2}$

and

$AgBr(s) \rightarrow Ag^+(aq) + Br^-(aq)\quad K_{sp} = 5\times10^{-12}$

$Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+\quad K_f = 1.7\times10^7$

So $K = K_{sp} \times K_f = 8.5\times10^{-7}$

and

$AgI(s) \rightarrow Ag^+(aq) + I^-(aq)\quad K_{sp} = 8.3\times10^{-17}$

$Ag^+(aq) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+\quad K_f = 1.7\times10^7$

So $K = K_{sp} \times K_f = 1.41\times10^{-9}$

Now calculate the reaction quotient, Q, for the given case (using chloride as the example),

$AgCl(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+ + Cl^-(aq)$
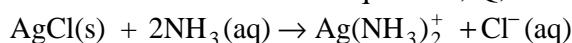
So, $Q = \dfrac{[Cl^-]\left[Ag(NH_3)_2^+\right]}{[NH_3]^2} = \dfrac{(0.10)(0.005)}{(0.60)^2} = 1.39\times10^{-3}$

This value is smaller than only one of the calculated values for the net equilibrium constant (the case of chloride) so the silver chloride is the only one that will dissolve in 0.60 M NH_3.

4.

    a. Al-O bonds are too strong to be broken by simple heating of the oxide, even in the presence of carbon. The heat of formation of Al_2O_3 is much more negative than that of CO_2, so the reaction: $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$ is endothermic.

    b. Na_3AlF_6 is added to lower the melting point of Al_2O_3. Lowering the melting point also lowers the amount of energy needed to carry out the process.

    c. $Al^{3+} + 3e^- \rightarrow Al$ (cathode) and $2O^{2-} \rightarrow O_2 + 4e^-$

    d. 5.00×10^3 g Al $\times \dfrac{1 \text{ mol}}{26.98 \text{ g}} = 185.3$ mol Al and 185.3 mol Al $\times \dfrac{3 \text{ mol } e^-}{1 \text{ mol Al}} = 556$ mol e^-

    e. We need to determine the charge (in coulomb) and time (in seconds) to calculate current.

    556 mol $e^- \times \dfrac{96500 \text{ C}}{1 \text{ mol } e^-} = 5.365 \times 10^7$ C and 10.0 hours $\times \dfrac{60 \text{ min}}{1 \text{ hour}} \times \dfrac{60 \text{ sec}}{1 \text{ min}} = 3.6 \times 10^4$ sec

    so, $\dfrac{(5.365 \times 10^7 \text{C})}{(3.6 \times 10^4 \text{ sec})} = 1490$A

    f. 556 mol $e^- \times \dfrac{1 \text{ mol } O_2}{4 \text{ mol } e^-} = 139$ mol O_2

    Now use Ideal Gas Law, $V = \dfrac{nRT}{P} = \dfrac{(139 \text{ mol } O_2)(0.0821 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})}{720 \text{ mmHg} \times \left(\dfrac{1 \text{ atm}}{760 \text{ mmHg}}\right)} = 3590$ L

5.

    a. $H^+ + NO_3^- + FeS \rightarrow NO_2 + Fe^{3+} + S + H_2O$

    b. $HC_2H_3O_2 + Ca_3(PO_4)_2 \rightarrow Ca^{2+} + C_2H_3O_2^- + HPO_4^{2-}$

    c. $Al + H_2O + OH^- \rightarrow Al(OH)_4^- + H_2$

    d. $Cr^{3+} + SO_4^{2-} + Ba^{2+} + OH^- \rightarrow Cr(OH)_3 + BaSO_4$

    e. $Co^{2+} + Cl^- \rightarrow CoCl_4^{2-}$

    f. $Br_2 + CH_3CHCH_2 \rightarrow CH_3CHBrCH_2Br$

6.

    a. The Mg^{2+} ion is smaller and has a higher charge than the Mg^+ ion, so the lattice energy that arises when Mg^{2+} ions form compounds is much greater than what would be observed if Mg^+ ions formed compounds. The increase in lattice energy more than offsets the larger ionization energy of the Mg^{2+} ion.

    b. Ti (atomic number 24) has a valence electron configuration of $4s^2 3d^2$ and can form +2 ions by losing it's two 4s electrons, +3 ions by losing the two 4s electrons and one 3d electron and +4 by losing all four of the valence electrons. The +2 and +3 ions are colored because of electronic transitions between d orbitals. The +4 ion does not exhibit color because it has no valence d-electrons to undergo electronic transitions.

    c. Carbon dioxide (O=C=O) molecules are nonpolar and interact with each other only through weak dispersion forces. These weak forces are easily overcome so CO_2 is a gas at room temperature. SiO_2 doesn't have the same molecular formula, because Si does not form double bonds as readily as carbon does. Si-O form single bonds that lead to a network solid held together with strong, covalent bonds, so it is a solid that has a high melting point.

    d. Nitrogen can form three bonds (NF_3) but not five (NF_5) because it lacks d orbitals that are energetically available for the formation of hybrid orbitals (or alternatively, because it is too small to accommodate five atoms.) Both NF_3 and PF_3 are trigonal pyramidal because the central atom has three bonding pairs and one lone pair of electrons (leading to sp^3 hybridization). PF_5 is trigonal bipyramidal because it has five bonding pairs (leading to dsp^3 hybridization.)

7.

    a. Even numbers of protons can pair up, which makes nuclei more stable. These more stable nuclei can accommodate a wider range of n/p ratios.

    b. Light nuclei are more stable when the n/p is close to 1/1. C-14 loses a β^- because it's n/p ratio of 8/6 is too high, so a neutron is converted to a proton, giving a n/p ratio of 7/7. C-10 loses a β^+, thereby converting a proton to a neutron and changing its n/p ration from 4/6 to 5/5.

    c. The difference in radioactivity between a fresh sample of C-14 containing material and a sample between 500 years and 50,000 years old can be used to determine the age of the historical sample. Samples less than 500 years old produce too little difference from new samples to provide reliable dates. Samples older than 50,000 years contain too little C-14 to provide sufficient radioactivity ("counts" measured) to give reliable dates.

8.

    a. **i.** As the solution cools, the water freezes, leaving a more concentrated solution. The more concentrated the solution, the lower the freezing temperature, so the line slopes downward once the solution starts to freeze.
    ii. The depression of the freezing point is due to supercooling of the solution before crystallization begins.

    b. The freezing point is approximately –0.026 °C. $\Delta T = k_f m$ so $m = \dfrac{\Delta T}{k_f} = \dfrac{-0.026}{1.86} = 0.014 m$

    c. The molality is 0.014 mol / kg water, so the molar mass can be calculated,

$$\left(0.014 \frac{\text{mol}}{\text{kg}}\right) \times (0.01 \text{ kg}) = 1.4 \times 10^{-4} \text{ mol} \text{ and the molar mass is } \frac{0.029 \text{ g}}{1.4 \times 10^{-4} \text{ mol}} = 207 \text{ g/mol}$$

    d. The molar mass determination by freezing point depression is roughly twice as great as that determined by titration. Carboxylic acids tend to dimerize in solution so the freezing point depression experiment, which observes the number of particles rather than their chemical properties, overestimates the molar mass by almost a factor of two (dimers take two particles and combine them into one.)