



# 2003 U. S. NATIONAL CHEMISTRY OLYMPIAD

## NATIONAL EXAM—PART II



Prepared by the American Chemical Society Olympiad Examinations Task Force

### OLYMPIAD EXAMINATIONS TASK FORCE

**Arden P. Zipp, State University of New York, Cortland  
Chair**

Peter E. Demmin (retired), Amherst Central High School, NY

David W. Hostage, Taft School, CT

Alice Johnsen, Bellaire High School, TX

Jerry D. Mullins, Plano Senior High School, TX

Ronald O. Ragsdale, University of Utah, UT

Amy Rogers, College of Charleston, SC

#### 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 27, 2003, 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.

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

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

#### DIRECTIONS TO THE EXAMINEE—PART II

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

**Not valid for use as an USNCO National Exam after April 27, 2003.**

Distributed by the ACS DivCHED Examinations Institute, University of Wisconsin-Milwaukee, Milwaukee, WI.  
All rights reserved. Printed in U.S.A.

1. (12%) 0.1152 g of a compound containing carbon, hydrogen, nitrogen and oxygen are burned in excess oxygen. The gases produced are treated further to convert nitrogen-containing products into  $N_2$ . The resulting mixture of  $CO_2$ ,  $H_2O$  and  $N_2$  and excess  $O_2$  is passed through a  $CaCl_2$  drying tube, which gains 0.09912 g. The gas stream is bubbled through water where the  $CO_2$  forms  $H_2CO_3$ . Titration of this solution to the second endpoint with 0.3283 M NaOH requires 28.81 mL. The excess  $O_2$  is removed by reaction with copper metal and the  $N_2$  is collected in a 225.0 mL measuring bulb where it exerts a pressure of 65.12 mmHg at 25 °C. In a separate experiment the molar mass of this compound is found to be approximately  $150 \text{ g}\cdot\text{mol}^{-1}$ .

a. Calculate the number of moles of

- i.  $H_2O$
- ii.  $CO_2$
- iii.  $N_2$

b. Determine the mass in the original compound of

- i. C
- ii. H
- iii. N
- iv. O

c. Find the empirical formula of the compound.

d. Find the molecular formula.

2. (13%) The enthalpy of combustion of liquid octane,  $C_8H_{18}(l)$  to gaseous products, is  $-5090 \text{ kJ}\cdot\text{mol}^{-1}$ . Use this value to answer the questions below, assuming a temperature of 100 °C.

a. Write a balanced equation for the complete combustion of liquid octane  $C_8H_{18}(l)$ .

b. Determine the molar enthalpy of formation,  $\Delta H_f^\circ$ , for liquid octane,  $C_8H_{18}(l)$ .

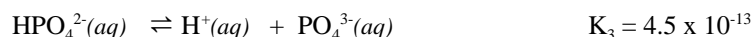
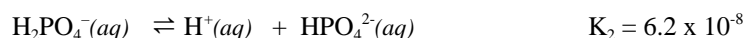
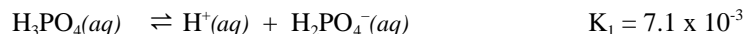
$$[\Delta H_f^\circ \text{ kJ}\cdot\text{mol}^{-1}; CO_2(g) -393.5, H_2O(g) -241.8]$$

c. Calculate the value of the internal energy change,  $\Delta E^\circ$ , for the combustion reaction.

d. If  $\Delta G^\circ$  for the combustion is  $-5230 \text{ kJ}\cdot\text{mol}^{-1}$  of octane, calculate the value of  $\Delta S^\circ$ . Comment on the sign of  $\Delta S^\circ$  relative to the equation written above.

e. State whether the heat associated with the combustion of liquid octane in a bomb calorimeter represents  $\Delta H^\circ$  or  $\Delta E^\circ$ . Explain your reasoning.

3. (13%) Phosphoric acid,  $H_3PO_4$ , ionizes according to the equations,



a. Write the equilibrium expression for the ionization of  $H_3PO_4$  and find the pH of a 1.5 M solution of  $H_3PO_4$ .

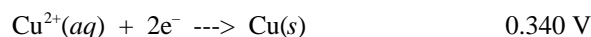
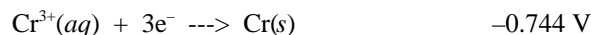
b. A student is asked to prepare a phosphate buffer with a pH of 7.00. Identify the species that should be used in this solution and calculate their ratio.

c. Assume that 50.0 mL of the buffer solution in b. are available in which the more abundant buffer species has a concentration of 0.10 M. Determine the  $[H^+]$  in this solution after  $2.0 \times 10^{-3}$  mol of NaOH are added.

d. Determine the  $[H^+]$  in a 0.20 M solution of  $Na_3PO_4$ .

4. (13%) An electrochemical cell is constructed with a piece of copper wire in a 1.00 M solution of  $Cu(NO_3)_2$  and a piece of chromium wire in a 1.00 M solution of  $Cr(NO_3)_3$ .

The standard reduction potentials for  $Cr^{3+}(aq)$  and  $Cu^{2+}(aq)$  are:



a. Write a balanced equation for the spontaneous reaction that occurs in this cell and calculate the potential it produces.

b. Sketch a diagram for this cell.

i. Label the anode.

ii. Show the direction of electron flow in the external circuit.

iii. Show the direction of movement of nitrate ions. Explain.

c. The cell is allowed to operate until the  $[Cu^{2+}] = 0.10 \text{ M}$ .

i. Find the  $[Cr^{3+}]$ .

ii. Calculate the cell potential at these concentrations.

- 
- 
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.
- Water is added to magnesium nitride.
  - Excess carbon dioxide is bubbled through a solution of calcium hydroxide.
  - Acidic solutions of potassium dichromate and iron(II) chloride are mixed.
  - Solutions of lead acetate and sulfuric acid are mixed.
  - Excess concentrated sodium hydroxide is added to a solution of zinc nitrate.
  - Fluorine-18 undergoes positron emission.
6. (14%) Account for the following observations about chemical kinetics.
- Reactions involving molecular chlorine often have nonintegral rate laws.
  - The rates of exothermic reactions increase when their temperatures are increased.
  - Two reactions, A and B, have rate constants that are equal at 25°C but the rate constant for reaction A is much greater than that for reaction B at 35°C.
  - The rates of reactions catalyzed by complex molecules, such as enzymes, increase with an increase in temperature up to a certain point above which they decrease again.
7. (12%) The atoms C, N and O can be arranged in three different orders to form negative ions, i.e.  $\text{CNO}^-$ ,  $\text{CON}^-$ , and  $\text{NCO}^-$ . Salts of one of these ions are stable. Salts of one are explosive and salts of one are unknown at this time.
- Write Lewis electron dot structures for each atomic arrangement.
  - For each arrangement,
    - find the formal charge on each atom.
    - use these formal charges to identify the most and least stable arrangements. Explain your reasoning.
  - Predict the geometry of the most stable atom arrangement and identify the type of hybridization used by the central atom in this structure.
8. (11%) Three compounds; X, Y, Z, have the formula  $\text{C}_3\text{H}_8\text{O}$ .
- Write structural formulas for three different compounds with the formula  $\text{C}_3\text{H}_8\text{O}$ .
  - The boiling points of the compounds are; X 10.8°C, Y 82.4°C, Z 97.4°C. Assign each boiling point to one of the structures in part a. and account for these boiling points on the basis of the molecular structures and the types of intermolecular forces in each.
  - A fourth compound with the formula  $\text{C}_2\text{H}_4\text{O}_2$ , has the same molar mass as the three compounds above and boils at 117.9°C. Propose a structure for this compound and account for its higher boiling point.

---

---

**END OF PART II**

---

---

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

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

### USEFUL EQUATIONS

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$\ln K = \left( \frac{-\Delta H}{R} \right) \left( \frac{1}{T} \right) + c$$

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

## PERIODIC TABLE OF THE ELEMENTS

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

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

---

---

**2003 U.S. NATIONAL  
CHEMISTRY OLYMPIAD  
KEY FOR NATIONAL EXAM – PART II**

1.

*Facts from the problem.*

- 0.1152 g sample contains C, H, N, O.
- 0.0912 g H<sub>2</sub>O are recovered.
- Conversion of carbon dioxide to carbonic acid has 1 to 1 stoichiometry,  
•  $1 \text{ CO}_2 \rightarrow 1 \text{ H}_2\text{CO}_3$ .
- Carbonic acid is titrated with 28.81 mL of 0.3283 M NaOH
- $\text{H}_2\text{CO}_3 + 2 \text{ NaOH} \rightarrow \text{Na}_2\text{CO}_3 + 2 \text{ H}_2\text{O}$
- Volume of N<sub>2</sub> collected is 225.0 mL at 65.12 torr and 25 °C.
- Molar mass of the substance is 150 g/mol

a. i. H<sub>2</sub>O (1 pt)

$$\text{moles H}_2\text{O} = 0.09912 \text{ g} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 5.501 \times 10^{-3} \text{ mol H}_2\text{O}$$

ii. CO<sub>2</sub> (2 pts)

$$\text{moles CO}_2 = \frac{0.3283 \text{ mol NaOH}}{\text{L soln}} \times 0.02881 \text{ L soln} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol NaOH}} = 4.729 \times 10^{-3} \text{ mol CO}_2$$

iii. N<sub>2</sub> (1 pt)

$$\text{moles N}_2 = \frac{pV}{RT} = \frac{(65.12 \text{ torr})(0.2250 \text{ L})}{(62.4 \text{ L} \cdot \text{torr} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} = 7.879 \times 10^{-4} \text{ mol N}_2$$

b. i. C (1 pt)

$$\text{g C} = 4.729 \times 10^{-3} \text{ mol CO}_2 \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} = 0.05680 \text{ g C}$$

ii. H (1 pt)

$$\text{g H} = 5.501 \times 10^{-3} \text{ mol H}_2\text{O} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.01109 \text{ g H}$$

iii. N (1 pt)

$$\text{g N} = 7.879 \times 10^{-4} \text{ mol N}_2 \times \frac{2 \text{ mol N}}{1 \text{ mol N}_2} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} = 0.02208 \text{ g N}$$

iv. O (1 pt)

$$\begin{aligned} \text{g O} &= \text{g sample} - (\text{g C} + \text{g H} + \text{g N}) \\ &= 0.1152 \text{ g} - (0.05680 \text{ g} + 0.01109 \text{ g} + 0.02208 \text{ g}) \\ &= 0.1152 \text{ g} - 0.08997 \text{ g} = 0.02523 \text{ g O} \end{aligned}$$

c. Find the empirical formula of the compound. (2 pts)

$$\text{C} : 0.05680 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.729 \times 10^{-3} / 1.576 \times 10^{-3} = 3.001 \approx 3$$

$$\text{H} : 0.01109 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 1.100 \times 10^{-2} / 1.576 \times 10^{-3} = 6.980 \approx 7$$

$$\text{N} : 0.02208 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 1.576 \times 10^{-3} / 1.576 \times 10^{-3} = 1.000 = 1$$

$$\text{O} : 0.02523 \text{ g N} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.577 \times 10^{-3} / 1.576 \times 10^{-3} = 1.001 \approx 1$$

Therefore the empirical formula is  $\text{C}_3\text{H}_7\text{NO}$

d. Find the molecular formula. (2 pts)

The molar mass of the empirical formula is 73.10

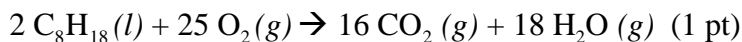
Compare this molar mass to the measured molar mass.

$$\frac{150 \text{ g} \cdot \text{mol}}{73.1 \text{ g} \cdot \text{mol}} = 2.05 \approx 2$$

Therefore the molecular formula is  $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$

2.

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



b. Determine the molar enthalpy of formation,  $\Delta H_f^\circ$ , for liquid octane,  $\text{C}_8\text{H}_{18}(l)$ . (4 pts)

$$\Delta H_{rxn} = 8\Delta H_f(\text{CO}_2) + 9\Delta H_f(\text{H}_2\text{O}) - \Delta H_f(\text{C}_8\text{H}_{18})$$

$$-5090 \text{ kJ} = 8(-393.5) \text{ kJ} + 9(-241.8) \text{ kJ} - \Delta H_f(\text{C}_8\text{H}_{18})$$

$$\Delta H_f(\text{C}_8\text{H}_{18}) = -3148 - 2176.2 + 5090 \text{ kJ}$$

$$= -234.2 \text{ kJ}$$

c. Calculate the value of the internal energy change,  $\Delta E^\circ$ , for the combustion reaction. (4 pts)

$$\Delta H = \Delta E + \Delta nRT \text{ so } \Delta E = \Delta H - \Delta nRT$$

$$= -5090000 \text{ J} - (4.5 \text{ mol})(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(373 \text{ K})$$

$$= -5090000 \text{ J} - 13955 \text{ J}$$

$$= -5104000 \text{ J} = -5104 \text{ kJ/mol C}_8\text{H}_{18}(l)$$

d. If  $\Delta G^\circ$  for the combustion is  $-5230 \text{ kJ} \cdot \text{mol}^{-1}$  of octane, calculate the value of  $\Delta S^\circ$ . Comment on the sign of  $\Delta S^\circ$  relative to the equation written above. (3 pts)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-5230 \text{ kJ} \cdot \text{mol}^{-1} = -5090 \text{ kJ} \cdot \text{mol}^{-1} - 373 \text{ K} (\Delta S^\circ)$$

so

$$\Delta S^\circ = \frac{-5090 \text{ kJ} \cdot \text{mol}^{-1} + 5230 \text{ kJ} \cdot \text{mol}^{-1}}{373 \text{ K}}$$

$$= 0.375 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

The increase in  $\Delta S^\circ$  is consistent with the formation of more moles of gas during the reaction.

e. State whether the heat associated with the combustion of liquid octane in a bomb calorimeter represents  $\Delta H^\circ$  or  $\Delta E^\circ$ . Explain your reasoning. (1 pt)

Heat in a bomb calorimeter is  $\Delta E^\circ$  (q at constant volume) - no credit unless there is a discussion of zero work under constant volume.

3.

a. Write the equilibrium expression for the ionization of  $H_3PO_4$  and find the pH of a 1.5 M solution of  $H_3PO_4$ . (1 pt for equation, 1 pt for solution)

$$K_a = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

for a 1.5 M solution, assuming no initial concentration of reactants and that the amount of phosphoric acid that reacts is small compared to the original volume,

$$7.1 \times 10^{-3} = \frac{x^2}{1.5}$$

Solving for x,  $x = \sqrt{1.5(7.1 \times 10^{-3})} = 0.103$ .

Use successive approximations to check that the amount of reacting phosphoric acid doesn't change the answer... plug in 1.397 ( $1.5 - 0.103 = 1.397$ ) rather than 1.5,

$x = \sqrt{1.397(7.1 \times 10^{-3})} = 0.100$  the change is small enough to accept this answer.

b. A student is asked to prepare a phosphate buffer with a pH of 7.00. Identify the species that should be used in this solution and calculate their ratio. (1 pt for correct identification of salts, 1 pt for solution of ratio)

To obtain a pH of 7 the  $K_a$  should be close to 7. In this case it would be  $K_{a2}$ . Thus the species that would be present in this buffer should be  $H_2PO_4^- (aq)$  and  $HPO_4^{2-} (aq)$ .

The ratio can be found by the equation,

$$6.2 \times 10^{-8} = 1.0 \times 10^{-7} \left( \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \right) \text{ and the ratio is, } \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.62 \text{ or } \frac{0.62}{1}$$

c. Assume that 50.0 mL of the buffer solution in b. are available in which the more abundant buffer species has a concentration of 0.10 M. Determine the  $[H^+]$  in this solution after  $2.0 \times 10^{-3}$  mol of NaOH are added. (1 pt for correct calculation of each concentration)

$H_2PO_4^- (aq)$  is the more abundant species in the buffer from part b.

$0.050 \text{ L} \times 0.10 \text{ mol} \cdot \text{L}^{-1} H_2PO_4^- = 0.0050 \text{ mol } H_2PO_4^-$  initially

0.0020 mol of  $OH^-$  is added, so the amount of  $H_2PO_4^- (aq)$  left is (1 to 1 stoichiometry)

$0.0050 - 0.0020 = 0.0030 \text{ mol } H_2PO_4^- (aq)$

If the concentration of  $H_2PO_4^- (aq)$  is 0.10 M the ratio calculated earlier indicates that the initial concentration of  $HPO_4^{2-} (aq)$  must be  $0.62 \times 1 = 0.062 \text{ M}$ , so

$0.050 \text{ L} \times 0.062 \text{ mol} \cdot \text{L}^{-1} HPO_4^{2-} = 0.0031 \text{ mol } HPO_4^{2-}$  initially

and 0.0020 mol are formed in the reaction so there is 0.0051 mol  $HPO_4^{2-} (aq)$  present.

Calculating the amount of hydrogen ion present,

$$6.2 \times 10^{-8} = [H^+] \frac{0.0051}{0.0030}, \text{ solving for } [H^+] \text{ gives, } 3.65 \times 10^{-8} \text{ M}$$

- d. Determine the  $[H^+]$  in a 0.20 M solution of  $Na_3PO_4$ . (1 pt for determining  $K_b$ , 1 pt for noting the need for successive approximation in the calculation of phosphate ion, 1 pt for final solution)



$$K_b = \frac{K_w}{K_{a3}} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-13}} = 0.0222$$

Obtain concentration of hydroxide, initially assume no reaction of phosphate and let  $x = [OH^-]$ ,

$$0.0222 = \frac{x^2}{0.20} \text{ so } x = [OH^-] = 6.67 \times 10^{-2} \text{ now for phosphate, } 0.20 - 0.0667 = 0.1333$$

$$0.0222 = \frac{x^2}{0.1333} \text{ so } x = [OH^-] = 5.44 \times 10^{-2} \text{ now for phosphate, } 0.20 - 0.0544 = 0.1456$$

$$0.0222 = \frac{x^2}{0.1456} \text{ so } x = [OH^-] = 5.70 \times 10^{-2} \text{ now for phosphate, } 0.20 - 0.0570 = 0.143$$

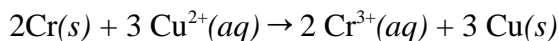
$$0.0222 = \frac{x^2}{0.143} \text{ so } x = [OH^-] = 5.63 \times 10^{-2} \text{ which is acceptably close to the previous iteration, now use}$$

$K_w$  to calculate  $[H^+]$ ,

$$[H^+] = \frac{1.0 \times 10^{-14}}{5.63 \times 10^{-2}} = 1.77 \times 10^{-13}$$

4.

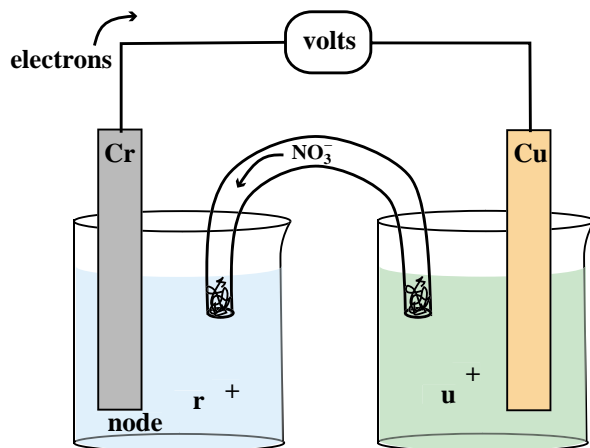
- a. Write a balanced equation for the spontaneous reaction that occurs in this cell and calculate the potential it produces. (3 pts)



$$E^{\circ} = E_{ox} + E_{red} = 0.744 + 0.340 = 1.084 \text{ V}$$

- b. Sketch a diagram for this cell. (5 pts for sketch with proper labels. Points taken off for incorrectly labeled components, etc.)

- Label the anode.
- Show the direction of electron flow in the external circuit.
- Show the direction of movement of nitrate ions. Explain.





- c. The cell is allowed to operate until the  $[\text{Cu}^{2+}] = 0.10 \text{ M}$ .
- Find the  $[\text{Cr}^{3+}]$ . (2 pts)
  - Calculate the cell potential at these concentrations. (3 pts)

$[\text{Cu}^{2+}]$  goes from 1.0 M to 0.10 M, so  $\Delta[\text{Cu}^{2+}]$  is  $-0.90$

$\Delta[\text{Cr}^{3+}] = 0.90 \times 2/3 = 0.60$  so,  $[\text{Cr}^{3+}] = 1.60$

plug these values into the equation,

$$E = E^\circ - \frac{RT}{nF} \left( \frac{[\text{Cr}^{3+}]^2}{[\text{Cu}^{2+}]^3} \right)$$

$$E = 1.084 - \frac{0.0257}{6} \left( \frac{(1.60)^2}{(0.10)^3} \right) = 1.05 \text{ V}$$

5. (Note that balanced chemical equations are not required.)

(1 pt for each reactant and 2 points for products (usually 1 for each product) then the total point value was multiplied by 2/3 to scale to 12 pts)

- $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{NH}_3$
- $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$
- $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} + \text{H}^+ \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + \text{H}_2\text{O}$
- $\text{Pb}^{2+} + \text{C}_2\text{H}_3\text{O}_2^- + \text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + \text{HC}_2\text{H}_3\text{O}_2$
- $\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn}(\text{OH})_4^{2-}$
- ${}^{18}_9\text{F} \longrightarrow {}^{18}_8\text{O} + {}^0_{+1}\beta$

6.

a. (3 pts)  $\text{Cl}_2$  often dissociates to Cl atoms, which react individually. If these atoms participate in the rate determining step the overall rate equation is proportional to  $[\text{Cl}\cdot] = [\text{Cl}_2]^{1/2}$

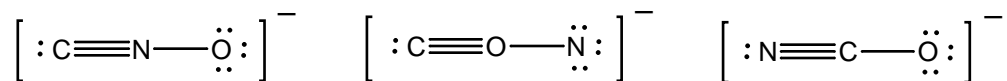
b. (3 pts) All reactions increase in rate with an increase in temperature due to an increase in the collision frequency and the increase in fraction of species with high velocities. Higher velocity particles impart more energy to collisions in which they participate so those collisions are more likely to exceed  $E_a$ . The exothermicity or endothermicity of a reaction has no bearing on its kinetics or the effect of temperature.

c. (4 pts) Reactions A and B must have different activation energies. When the  $\log$  (or  $\ln$ ) of the rate is constant for a reaction is plotted versus  $1/T$  the slope is the  $E_a$ . Reactions A and B have different slopes which cross at  $25^\circ\text{C}$ . The  $E_a$  for reaction A is greater because an increase in temperature affects its rate constant more.

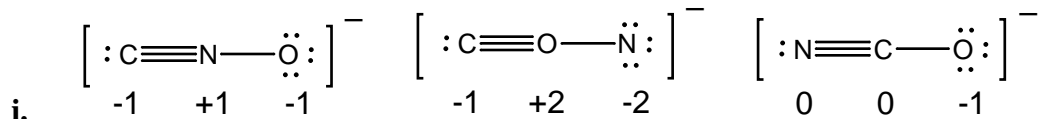
d. (4 pts) Reaction rates increase with higher temperature because of an increase in collision rate and an increase in the fraction of molecules that have the necessary energy to react. At still higher temperatures the enzyme is denatured so that it no longer is an effective catalyst.

7. (1 pt for each correct Lewis structure (3 total)  
 1 pt for correct formal charges on each Lewis structure (3 total)  
 1 pt for correct identification of most stable structure / 1 pt for correct reasoning  
 1 pt for correct identification of least stable structure / 1 pt for correct reasoning  
 1 pt for correctly identifying the structure as linear  
 1 pt for correct hybridization.)

a.



b.



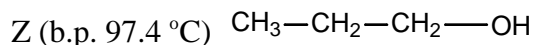
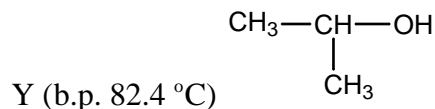
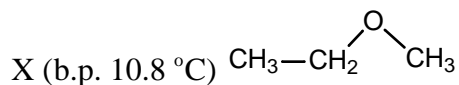
ii. N C O is the most stable arrangement because the formal charges are the lowest in this structure.

C O N is the least stable structure because the formal charges are the greatest in this structure

c. N C O as drawn would be linear because there are two charge centers around the central atom. The central atom will be sp hybridized.

8.

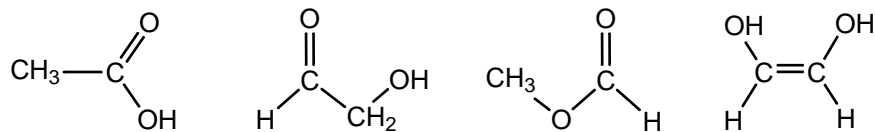
a. The structural formulas would be, (1 pt for each)



Compound Y and Z would have hydrogen bonding where compound X would not. Therefore X would have the weakest intermolecular forces and the lowest boiling point (of 10.8 °C) (2 pts)

b. The linear shape of compound Z would allow for stronger dispersion forces than compound Y. Therefore Y should have a lower boiling point than Z. (4 pts)

c. The possible Lewis structures include,



All of these would have increased hydrogen-bonding relative to the three compounds in part a.