



2010 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 26, 2010, 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 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.

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

CONSTANTS
$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$1 F = 96,500 \text{ C}\cdot\text{mol}^{-1}$
$1 F = 96,500 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$
$c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
$0^\circ\text{C} = 273.15 \text{ K}$

PERIODIC TABLE OF THE ELEMENTS

1											18						
1A											8A						
1 H 1.008											13 B 10.81	14 C 12.01	15 N 14.01	16 O 16.00	17 F 19.00	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 B	4 C	5 N	6 O	7 F	8 Ne	9 Na	10 Mg	11 Al 26.98	12 Si 28.09	13 P 30.97	14 S 32.07	15 Cl 35.45	16 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 Uub (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)

1. (12%) 5.60 g of solid carbon is placed in a rigid evacuated 2.5 L container. Carbon dioxide is added to the container to a final pressure of 1.50 atm at 298 K.
- Calculate the number of moles of each reactant in the container originally.
 - The container is heated to 1100 K and the following reaction occurs: $\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO(g)}$ $\Delta H^\circ = 173 \text{ kJ}$
 - Calculate the pressure in the container at this temperature before the reaction takes place.
 - When equilibrium is reached the pressure inside the container is 1.75 times that calculated in **b.i**. Determine the equilibrium partial pressures of $\text{CO}_2(\text{g})$ and CO(g) .
 - Write the equilibrium expression for this reaction, K_p .
 - Calculate the value of K_p for this reaction at 1100 K.
 - Predict the effect on the number of moles of carbon monoxide of each of the following changes made to this system at equilibrium. Give reasons for your predictions.
 - The volume of the container is increased to 5.0 L.
 - The pressure inside the container is increased by adding helium.
 - The temperature of the system is increased to 1200 K.
 - The amount of solid carbon is increased to 6.00 g.
2. (14%) Green plants utilize sunlight to convert CO_2 and H_2O to glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and O_2 .
- Write a balanced equation for this process.
 - Use the information in the accompanying table to calculate
 - ΔH°
 - ΔS°
 - ΔG° at 298 K for this reaction.

Substance	ΔH_f° kJ/mol	S° J/mol·K
$\text{CO}_2(\text{g})$	-393.5	213.2
$\text{H}_2\text{O(l)}$	-285.8	69.9
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1273.3	212.1
$\text{O}_2(\text{g})$		205.0

- Comment on the spontaneity of this reaction at 25°C and other temperatures.
 - Green plants use light with wavelengths near 600 nm for this process. Calculate
 - the energy of a 600 nm photon,
 - ΔG° for the formation of one molecule of glucose by the reaction in 2a,
 - the minimum number of 600 nm photons required to make one molecule of glucose by the reaction in 2a.
 - All of the photosynthesis on earth in a year stores 3.4×10^{18} kJ of solar energy.
 - Use the ΔG° for the photosynthetic reaction to calculate the number of moles of CO_2 removed from the atmosphere by photosynthesis each year.
 - Determine the mass of carbon that is fixed annually by photosynthesis.
3. (14%) A 0.125 g piece of vanadium reacts with nitric acid to produce 50.0 mL of a yellow solution of vanadium ions in their highest oxidation state.
- Calculate the number of moles of vanadium dissolved and the molarity of vanadium ions in this solution.
 - Write the electron configuration of a neutral gaseous vanadium atom.
 - Give the oxidation state of vanadium in the yellow solution and outline your reasoning.
 - A 25.0 mL portion of this yellow solution is reduced with excess zinc amalgam under an inert atmosphere to give a violet solution. A 10.0 mL aliquot of this violet solution is titrated with a solution of $2.23 \times 10^{-2} \text{ M KMnO}_4$ in acid forming Mn^{2+} . A volume of 13.20 mL of the MnO_4^- solution is required to convert the vanadium back to yellow. Determine the:
 - number of moles of MnO_4^- used in this titration,
 - mole ratio of vanadium ions to MnO_4^- ions in this titration,
 - oxidation number change for vanadium in this titration and the oxidation state of vanadium ions in the violet solution.
 - When 2.00 mL of the violet solution are mixed with 1.00 mL of the original yellow solution, a green solution results. When this ratio is reversed a bright blue solution is formed. Determine the oxidation states of the green and blue vanadium ions. Support your answers with calculations.

4. (12%) The reaction $\text{NO(g)} + \text{O}_3\text{(g)} \rightarrow \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$ is first order in each reactant with an activation energy, E_a , of 11.7 kJ/mol and a rate constant of $k = 1.2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C.
- Calculate the value of the pre-exponential factor, A, in the equation $k = A e^{-E_a/RT}$.
 - Would the A factor for the chemical reaction $\text{NO(g)} + \text{N}_2\text{O(g)} \rightarrow \text{NO}_2\text{(g)} + \text{N}_2\text{(g)}$ be expected to be larger or smaller than the A factor in the above reaction if each reaction occurs in a single step? Outline your reasoning.
 - Calculate the rate constant for this reaction at 75 °C.
 - The following two-step mechanism has been proposed for this reaction:

$$\begin{array}{ll} \text{O}_3\text{(g)} \rightarrow \text{O}_2\text{(g)} + \text{O(g)} & \text{Step 1} \\ \text{NO(g)} + \text{O(g)} \rightarrow \text{NO}_2\text{(g)} & \text{Step 2} \end{array}$$
 State and explain whether this mechanism is consistent with the observed rate law.

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.
- Solutions of hydrochloric acid and silver acetate are mixed.
 - A small piece of potassium is added to water.
 - Concentrated hydrochloric acid is added to a solution of cobalt(II) sulfate.
 - An acidified potassium dichromate solution is added to a tin(II) chloride solution.
 - Methyl ethanoate (methyl acetate) is reacted with a sodium hydroxide solution.
 - Carbon-14 undergoes beta decay.

6. (12%) Account for the following observations on the basis of electrochemical principles. The Standard Reduction Potentials are provided.

$2 \text{HOCl(aq)} + 2 \text{H}^+\text{(aq)} + 2 \text{e}^- \rightarrow \text{Cl}_2\text{(g)} + 2 \text{H}_2\text{O(l)}$	$E^\circ = 1.61 \text{ V}$
$\text{Cl}_2\text{(g)} + 2 \text{e}^- \rightarrow 2 \text{Cl}^-\text{(aq)}$	$E^\circ = 1.36 \text{ V}$
$\text{O}_2\text{(g)} + 4 \text{H}^+\text{(aq)} + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O(l)}$	$E^\circ = 1.23 \text{ V}$
$\text{Cu}^{2+}\text{(aq)} + 2 \text{e}^- \rightarrow \text{Cu(s)}$	$E^\circ = 0.34 \text{ V}$
$\text{Sn}^{2+}\text{(aq)} + 2 \text{e}^- \rightarrow \text{Sn(s)}$	$E^\circ = -0.14 \text{ V}$
$\text{Fe}^{2+}\text{(aq)} + 2 \text{e}^- \rightarrow \text{Fe(s)}$	$E^\circ = -0.44 \text{ V}$
$\text{Zn}^{2+}\text{(aq)} + 2 \text{e}^- \rightarrow \text{Zn(s)}$	$E^\circ = -0.76 \text{ V}$

- In a voltaic cell made with Cu metal in a 1.0 M CuSO_4 and Zn metal in 1.0 M ZnSO_4 the Zn is the anode and the cell potential is more than 1.0 V. When aqueous sodium sulfide is added to the CuSO_4 solution the cell potential decreases substantially.
 - Iron metal corrodes readily in moist air but this corrosion can be prevented when iron is coated with tin or zinc. Corrosion is prevented when the zinc coating is intact or broken. In contrast, corrosion is prevented by coating iron with tin only as long as the tin coating remains intact but actually occurs faster when there is a break in the tin coating.
 - In acid solution chloride and hypochlorite ions react to form chlorine gas whereas in basic solution chlorine gas reacts to form chloride and hypochlorite ions.
7. (12%) Two stable allotropes of oxygen are dioxygen (O_2) and ozone (O_3).
- Describe the geometry of ozone and state the hybridization of each of the oxygen atoms.
 - Ozone has a nonzero dipole moment. Account for this fact and predict the direction of the dipole moment.
 - Dioxygen is weakly attracted to strong magnetic fields (i.e. is paramagnetic), while ozone is weakly repelled by magnetic fields (i.e. is diamagnetic). Account for these observations in terms of the bonding in the two molecules.
 - The most stable allotrope of sulfur is the cyclic S_8 molecule while S_2 is a highly unstable gas. In contrast, O_2 is the most stable allotrope of oxygen and O_8 is unknown. Account for these differences in the relative stability of the allotropes of these two elements.
8. (12%) There are four structural isomers with the formula $\text{C}_4\text{H}_9\text{Cl}$, one of which exists in optically active forms.
- Write structural formulas for these four isomers.
 - Identify the isomer that exists in optically active forms and describe the difference in behavior of these two forms.
 - Each of these isomers reacts with OH^- ions to eliminate a molecule of HCl.
 - Give the name and molecular formula for the family of compounds formed by this elimination reaction.
 - Write a structural formula for each of the elimination products.
 - Identify the elimination product that can exist in different isomeric forms and draw structures for these forms.