2019-20 MOCK
USNCO - Part II

42	6	19	92	50	27
Mo	C	K	U	Sn	Co
95.96	12.01	39.10	238.03	118.71	58.93

CONTEST WRITERS

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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 **USNCO 2081**, 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 have 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,**	**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 two for student reference.

Students should be permitted to use non-programmable calculators. The use of a programmable calculator, cell phone, or any other device that can access the internet or make copies or photographs during the exam is grounds for disqualification.

DIRECTIONS TO THE EXAMINEE

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 on a coversheet. Answer all of the questions in order and use both sides of the paper. 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".

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

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

$R = 0.08314\ \text{L bar mol}^{-1}\ \text{K}^{-1}$

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

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

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

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

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

$0\ °\text{C} = 273.15\ \text{K}$

1 atm = 1.013 bar = 760 mm Hg

Specific heat capacity of H_2O = $4.184\ \text{J g}^{-1}\ \text{K}^{-1}$

EQUATIONS

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

$$\ln K = \left(\frac{-\Delta H^{\circ}}{R}\right)\left(\frac{1}{T}\right) + \text{constant}$$

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

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** 78.97	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** 95.95	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 **Nh** (286)	114 **Fl** (289)	115 **Mc** (289)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (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. [12%] "Queenbee substance" **Q** contains 65.2% carbon and 8.75% hydrogen and no other element except oxygen. **Q** is known to be acidic and titration of 43.7 mg of this compound required 23.7mL of 0.0100 M aqueous sodium hydroxide to reach the equivalence point. The molecular weight of **Q** was determined to be less than 200.

a. Determine the molecular formula of **Q**

Q reacts with hydrogen in the presence of finely divided platinum metal to afford a new compound **A**. Further reduction of **A** with sodium borohydride in ethanol gives substance **B**. Compound **B** was readily dehydrated upon warming with strong sulfuric acid to afford an alkene **C**. The ^{13}C NMR of **C** revealed amongst other features the presence of a methyl group attached to a double bond.

b. What functional groups are consistent with the above reactions?

c. Ozonolysis of **C** followed by an oxidative work up gave only two fragments, ethanoic acid and a straight chain dicarboxylic acid **D**. Similar cleavage of **Q** itself yielded oxalic acid (ethanedioic acid) and a substance **E** which contained a carboxylic acid group.

d. Draw the structural formulas for compounds **A-E** and **Q**

2. [12%] The acidity constant of HCN can be determined through electrochemistry. An ion selective electrode is used to measure the cell potentials in 9 different solutions containing different concentrations of NaCN at different pH environments. The temperature was 25 °C in all experiments. The instrumental readings were as follows: (1 ppm = 1 mg/L)

	1.00 ppm NaCN	10.0 ppm NaCN	100 ppm NaCN
0.01 M NaOH	497.3 mV	438.2 mV	379.1 mV
0.001 M NaOH	497.7 mV	438.6 mV	379.5 mV
pH = 7.5 buffer	598.9 mV	539.8 mV	480.7 mV

a. Determine how many electrons are being transferred per mole of Cyanide in the primary reaction which determines the cell potential

b. Write a reaction which transfers the correct number of moles of electrons per mole of cyanide according to your result in part a.

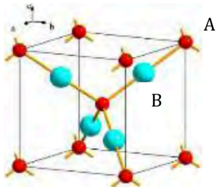
c. Calculate the acid dissociation constant of HCN based on these measurements

0.10 moles of $FeCl_2$ and 1.0 moles of NaCN are dissolved in a pH=7.5 buffer to final volume 1L, forming an iron cyanide complex with formation constant $K_f = 8 \times 10^{36}$.

d. Write the reaction for the formation of the Iron Cyanide complex

e. Calculate the cell potential in mV of the equilibrated solution

3. [16%] One of the first materials used in solid state electronics was red copper (I) oxide.



Interest in Cu_2O is renewed nowadays because it could be a non-toxic and cheap component of solar cells.

The two figures above depict the cubic unit cell of the Cu_2O crystal. The lattice constant of the structure is 427.0 pm.

a. i) Which of the atoms (A or B) is copper?
ii) What are the coordination numbers of the A and B atoms in the unit cell
iii) Which basic structure (BCC, FCC, diamond, etc.) is formed by the B atoms

b. Calculate the density of pure copper(I) oxide in g cm^{-3}

A common defect in this crystal is some copper atoms missing with the oxygen lattice unchanged. The composition of one such crystal sample was studied, and 0.2% of all copper atoms were found to be in oxidation state +2.

c. What percentage of normal copper sites are empty in the crystal sample? What is *x* in the empirical formula $Cu_{2-x}O$ of the crystal?

Copper(I) oxide can be produced in a number of ways. Heating copper in air is a common method in the synthesis of semiconductor Cu_2O. In a pure oxygen atmosphere, the three species containing copper (Cu(s), Cu_2O(s) or CuO(s)) can potentially interconvert.

	ΔH_f° kJ mol^{-1}	S° J mol^{-1} K^{-1}
Cu (s)	0	65
O_2 (g)	0	244
CuO (s)	-156	103
Cu_2O (s)	-170	180

d. Determine the temperature ranges, if any, of thermodynamic stability of copper and its oxides between 500 and 1500 K in a 105 Pa oxygen atmosphere.

4. [11%] The reaction of acetone with bromine produces bromoacetone. In a mechanistic study, the reaction was followed in several kinetic experiments at 25 °C in aqueous solution by measuring the concentration of Br_2 using a spectrophotometric method. The following kinetic curve was recorded when the initial concentrations were $[Br_2]_0 = 0.520$ mmol/dm^3, $[C_3H_6O]_0 = 0.300$ mol/dm^3, and $[HClO_4]_0 = 0.050$ mol/dm^3.

a. i) Give the chemical equation of the reaction assuming that acetone is in excess.
ii) Which is the limiting reagent in this experiment?

b. What is the order of reaction with respect to the limiting reagent?

The time where the characteristic break point occurs on the kinetic curve is called the reaction time and was determined in aqueous solution at 25 °C. The following table gives the reaction time in several different experiments (′ denotes minutes, ″ denotes seconds):

$[Br_2]_0$ mmol/L	$[C_3H_6O]_0$ mmol/L	$[HClO_4]_0$ mmol/L	reaction time
0.151	300	50	5’56”
0.138	300	100	2’44”
0.395	300	100	7’32”
0.520	100	100	30’37”
0.520	200	100	15’13”
0.520	500	100	6’09”
0.520	300	200	4’55”
0.520	300	400	2’28”

c. Determine the rate law for the reaction and the rate constant

A different, electrochemical method allowed detection of much smaller concentrations of Br_2. The half life of the limiting reagent was then determined in a few experiments

$[Br_2]_0$ μmol/L	$[C_3H_6O]_0$ mmol/L	$[HClO_4]_0$ mol/L	$t_{1/2}$ (s)
1.20	3.0	0.100	24
1.50	3.0	0.100	23
1.50	1.0	0.100	71
1.50	0.4	0.100	177
1.50	3.0	0.030	23
1.50	3.0	0.400	24

d. Determine the rate law for the reaction and the rate constant

e. Propose a detailed mechanistic explanation for the observed rate laws

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. Solutions of Silver Nitrate and Sodium Phosphate are stirred

b. Barium metal is mixed with aqueous Potassium Permanganate in basic solution

c. Copper (I) Oxide is dissolved in sulfuric acid

d. Oxalyl Chloride is stirred with water

e. Cyclopentadiene is reacted with 1,4-dichloro-2-butene

f. Butyne is treated with aqueous acid and Mercury (II) Sulfate

6. [12%] Nitrogen trifluoride is a surprisingly stable compound that was first prepared in the melt electrolysis of a mixture of ammonium fluoride and hydrogen fluoride.

a. On which electrode does nitrogen trifluoride form? Write a balanced chemical equation for the electrode half reaction for the formation of NF_3.

Fluoroamine (NH_2F) and difluoroamine(NHF_2) are very unstable materials formed as side products in the electrolysis.

b. Which of NF_3, NHF_2 or NH_2F is expected to condense at the lowest temperature? Explain.

Tetrafluoroammonium ion (NF_4^+) and its corresponding salt can form from NF_3 with elementary fluorine in the presence of an appropriate reagent.

c. Propose a suitable reagent and write a balanced chemical equation for the reaction.

NF_4^+ ions form stable salts with a number of anions. These are very sensitive to humidity, because NF_4^+ ion hydrolyzes forming NF_3 and O_2. Interestingly nitrogen trifluoride always forms quantitatively, while the quantity of oxygen is often less than expected due to side reactions.

d. Write a balanced chemical equation for the hydrolysis of NF_4^+. Write a balanced chemical equation for a possible side reaction that can decrease the theoretically expected O_2:NF_3 mole ratio.

7. [14%] The chemistry of Vanadium and the transition metals is dominated by coordination complexes, best discussed through a d-electron molecular orbital approach. An important Vanadium complex is Vanadium Carbonyl complex (formula: $V(CO)_x$, where x is some integer). Based off the number of electrons $V(CO)_x$ possesses in the $n=4$ energy level, it is expected to be unstable and dimerize into the bulky $V_2(CO)_{2x}$.

a. i. What is the formula for the monomeric Vanadium Carbonyl complex?

ii. Draw the d orbital splitting diagram for $V(CO)_x$.

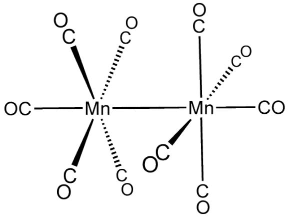
b. i. Explain why the monomer form is dominant over the dimer.

Upon gaining or losing an electron, the stability of the complex can increase.
ii. What is the most stable ion of $V(CO)_x$? Why?

Another Vanadium complex, $[V(NO)_2L_2]^+$ (L is an arbitrary ligand) demonstrates an unusual property of the NO ligand. Namely, NO donates 3 electrons to the bonded metal center (whereas typical ligands such as CO donate 2 electrons), while simultaneously stabilizing electron density in electron rich metal centers.

c. Explain how the NO ligand is able to both donate a third electron to the bonded metal center, and also withdraw electron density from the bonded metal center.

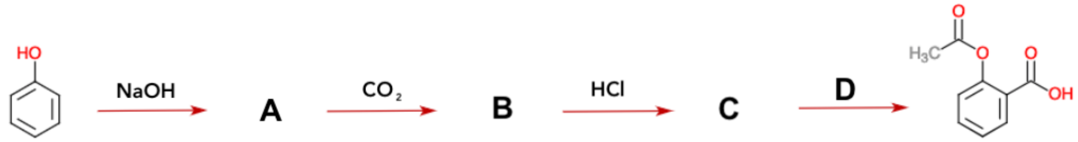
A related dimeric transition metal complex is $Mn_2(CO)_{10}$. It's 3D structure shows a staggered arrangement of CO ligands on the two Manganese centers. Upon irradiation with UV light, the Mn-Mn bond breaks first.



d. i. Explain why $Mn_2(CO)_{10}$ exhibits a staggered geometry.

ii. Which orbital transition in $Mn_2(CO)_{10}$ explains the breaking of the Mn-Mn bond? What orbitals on each respective atom are involved in the formation of this bond?

8. [12%] The chemistry of aromatic compounds is of constant interest in organic chemistry. Phenol can be converted to Aspirin via the following 4 step process.



a. Give the structures of the intermediates **A-C** and propose a reagent **D** that could be used for the conversion of **C** into Aspirin.

Adding Sodium Metal to liquid Ammonia creates a blue colored reducing solution of electrons solvated in ammonia. Reacting benzene with this solution and an alcohol (birch reduction conditions), forms 1,4-cyclohexadiene.

b. What is the basic role of Ethanol in this reaction?

c. Reaction of **A** with Bromomethane produces Methoxy Benzene. Under Birch reduction conditions on Methoxy Benzene, two structural isomers are formed. Draw the isomers and explain which one is formed in greater yield.

Scratch Page

Question Breakdown

#.	*Type*	*%*	*Description*	*Source*
1.	Quantitative Analysis		Organic Structure Determination	1998 Prep #23
2.	Kinetics		Standard Kinetics	2008 Prep #27
3.	Analytical		Complexometric Titration	2013 Prep #15
4.	Thermo/Physical		Copper Oxide Thermo + Unit Cell	2016 ICHO #2
5.	Reaction Prediction		Predict Reactions	Original
6.	Inorganic		NF_3 chemistry	2016 ICHO #1
7.	Inorganic		Vanadium Carbonyl Complexes	Original
8.	Organic		Organic Synthesis/Puzzle	Original/Clayden