2024 U.S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM PART II

Prepared by the American Chemical Society Chemistry Olympiad Examinations Task Force

DIRECTIONS TO THE EXAMINER

Part II of this test requires that student answers be written in this test booklet in the spaces provided underneath the questions. Part II test booklet and scratch paper should be made available to the student only during the examination period. All testing materials including scratch paper should be collected from students after the examination. Only test booklets should be shipped to the USNCO office immediately after the national exam and no later than **April 22, 2024**.

When the student has completed **Part II**, or after one hour and forty-five minutes have elapsed, the student must turn in **Part II** of the testing materials and all scratch paper. Be sure that the student has supplied 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 two for student reference.

Students should be permitted to use only 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 use the same identification number you used for **Part I and write it on top of each page in the indicated fields**. 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 and scratch paper.

STUDENT USNCO ID:

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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	year	y

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 °C = 273.15 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

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

PERIODIC TABLE OF THE ELEMENTS

1 **1A**	**2** **2A**	**3** **3B**	**4** **4B**	**5** **5B**	**6** **6B**	**7** **7B**	**8** **8B**	**9** **8B**	**10** **8B**	**11** **1B**	**12** **2B**	**13** **3A**	**14** **4A**	**15** **5A**	**16** **6A**	**17** **7A**	**18** **8A**
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** 78.97	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)**

Question 1 (page 1 of 2) USNCO ID Number:

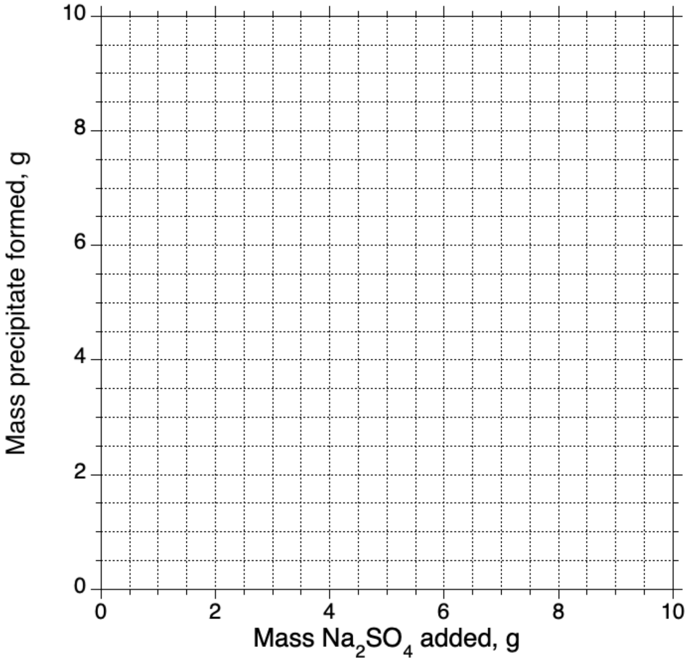
1. [10%] An unknown salt MX_2 is a group 2 metal halide.

   a. 10.00 g MX_2 dissolves in 50.0 g water to give a homogeneous solution. The freezing point of this solution is –4.50 °C. What is the molar mass of MX_2? For water, $K_f = 1.86$ °C/m.

   b. 10.00 g Na_2CO_3 and 10.00 g MX_2 are mixed in 200.0 mL of water. A precipitate of MCO_3 forms. What is the pH of the supernatant? The K_a of H_2CO_3 is 4.3×10^{-7} and the K_a of HCO_3^- is 4.7×10^{-11}

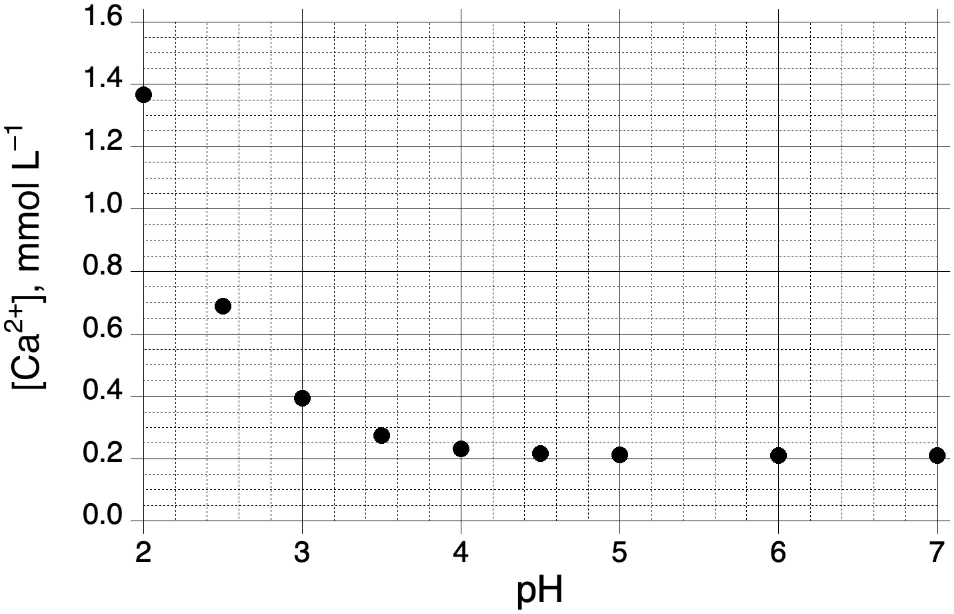
   c. A solution of 10.00 g MX_2 in water is treated with excess silver nitrate. The precipitate is dried; the mass of the dried compound is 15.2 g. What is the identity of MX_2?

d. A sample of 10.00 g MX_2 dissolved in 50 mL water is treated with increasing amounts of Na_2SO_4 up to 10 g in total. How will the mass of precipitate formed vary with the mass of added Na_2SO_4? Graph your answer on the grid provided.



e. What color flame test does MX_2 give?

2. [13%] A sample of solid calcium fluoride is suspended in water in an unreactive container and stirred until it achieves equilibrium. The pH of the solution is lowered by careful addition of nitric acid, and the pH and concentration of $Ca^{2+}(aq)$ are noted at several points as shown on the graph below. Note that the units on the *y* axis are millimoles per liter.



a. Determine the K_{sp} of CaF_2 from the data provided.

b. Qualitatively, what is the cause for the increase in solubility of CaF_2 at low pH?

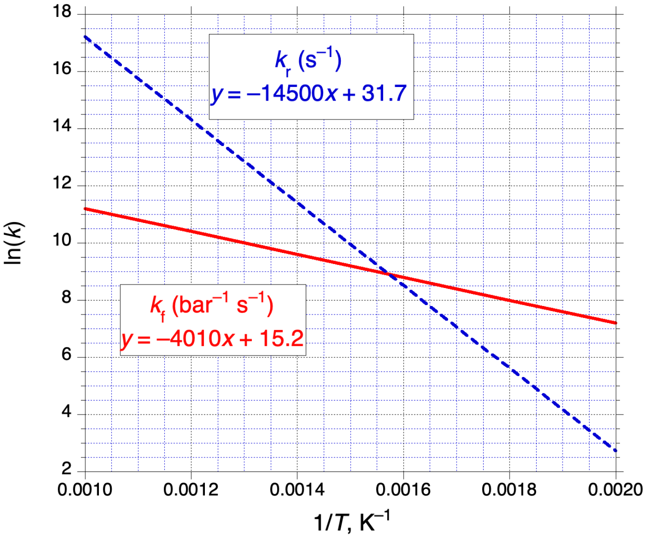
c. From the data provided, determine the K_a of HF.

d. How many moles of HNO_3 must be added to the CaF_2/water mixture to achieve a pH = 3.00 in this experiment? The volume of solution is 1.00 L.

e. Carbon dioxide dissolves in water at 25 °C and 1 atm pressure to the extent of 0.0345 mol L^{-1}. An aliquot of the solution taken from the above experiment at pH = 5 is stirred under 1 atm CO_2 and the pH slowly raised by addition of solid NaOH until $CaCO_3$ just begins to precipitate. What is the pH of the solution at this point? The K_{sp} of $CaCO_3$ is 8.7×10^{-9}, the K_a of aqueous CO_2 ("H_2CO_3") is 4.3×10^{-7}, and the K_a of HCO_3^- is 4.7×10^{-11}.

3. [13%] Ethene, C_2H_4, can react in the gas phase in the presence of radicals *R* to form polyethylene as shown in the equation below. Here *n* is the degree of polymerization. The forward reaction is second-order while the reverse reaction is first-order. The values of these rate constants are independent of the degree of polymerization *n* and the identity of *R*.

$$C_2H_4(g) + \bullet CH_2(CH_2)_{2n}CH_2R \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \bullet CH_2(CH_2)_{(2n+2)}CH_2R$$



a. A sample of polyethylene has an average degree of polymerization *n* = 1200. How many polymer chains are present in 1.0 g of this material?

b. Calculate Δ*H*° and Δ*S*° for the polymerization reaction.

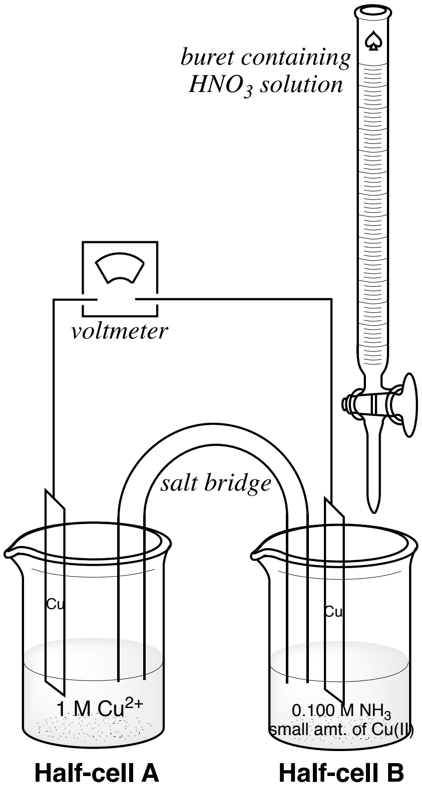
c. The bond dissociation enthalpy (BDE) for a typical carbon-carbon single bond is 345 kJ mol^{-1}. From the data given, what is the BDE of the carbon-carbon double bond in ethene?

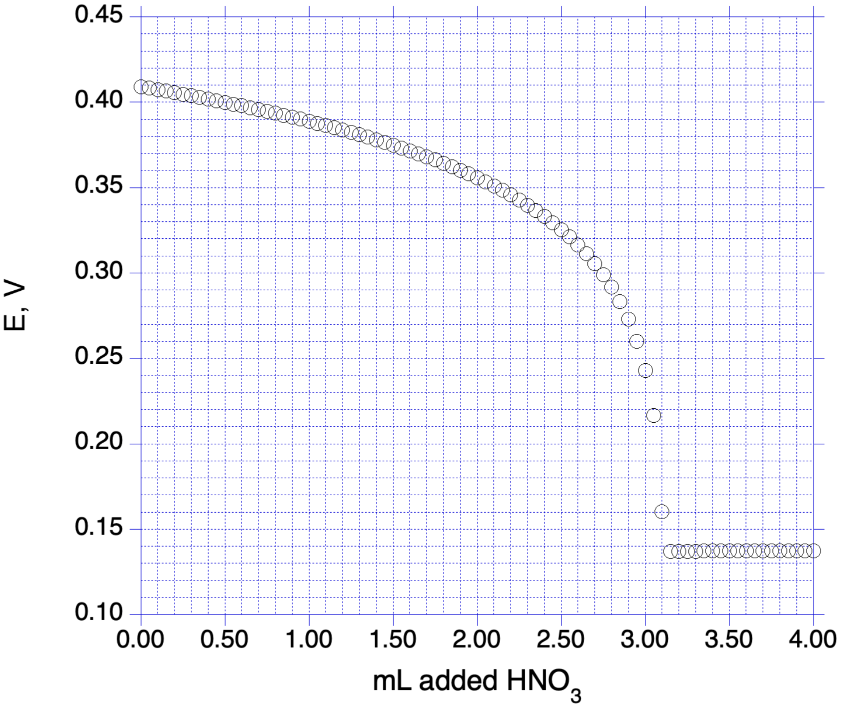
d. Ethene is charged to a fixed vessel at 25 bar and 720 K. Traces of radical are then added to initiate polymerization. What is the percent conversion of ethene into polymer at equilibrium under these conditions?

e. In the presence of a catalyst for the polymerization reaction, the forward rate constant as a function of temperature is $\ln(k_f) = -3050(1/T) + 21.0$. By what factor does the catalyst accelerate the rate of the forward reaction at 500 K?

f. By what factor does the catalyst change the rate of the reverse reaction at 500 K?

4. [13%] Copper(II) forms a complex ion with ammonia, $Cu(NH_3)_4^{2+}$, with $K_f = 1.7 \times 10^{13}$. An electrochemical cell is set up as shown below at 298 K. Half-cell **A** contains 100 mL of 1.00 M $Cu(NO_3)_2$, while half-cell **B** contains 100 mL of a solution that contains a small amount of copper(II) and is 0.100 M in NH_3. A solution of nitric acid is slowly added to half-cell **B** and the potential measured by the voltmeter is recorded as a function of the added volume of HNO_3.





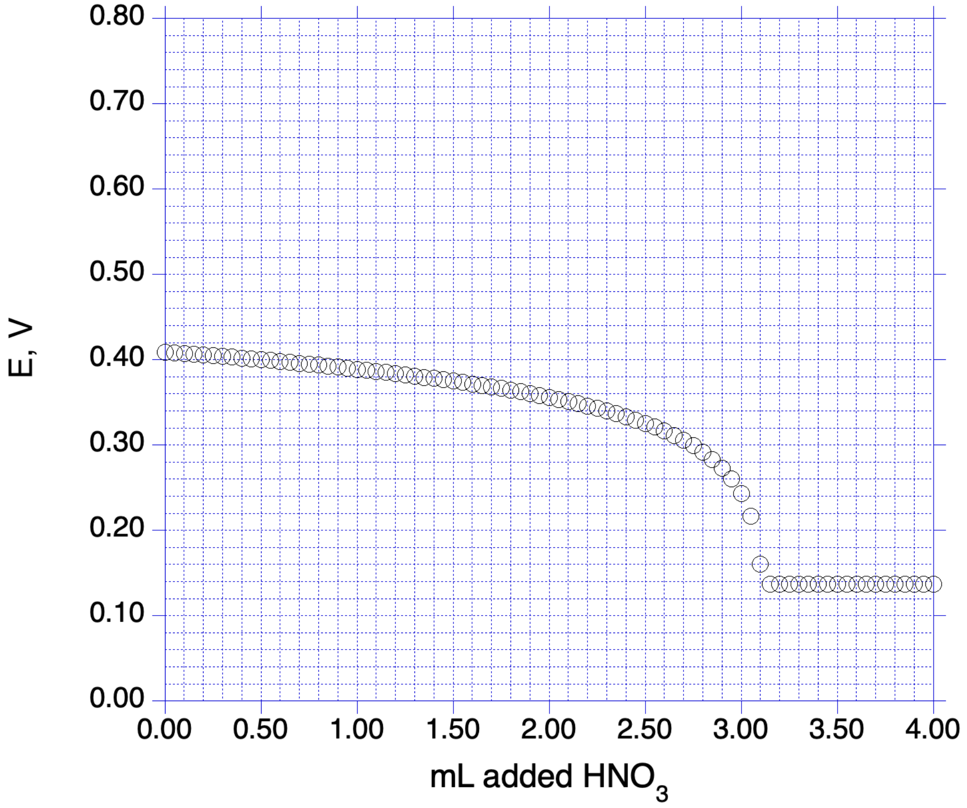
a. Which half-cell is the cathode and which is the anode? Justify your answer.

b. Qualitatively explain the shape of the graph.

c. What is the total concentration of copper(II) in the solution in half-cell **B**?

d. What is the concentration of nitric acid in the buret?

e. Suppose that the experiment is set up again with silver metal in place of copper metal and silver(I) ion in place of copper(II) ion, but with all concentrations and all other reagents identical. What would the graph of *E* vs. mL added HNO_3 look like in this experiment? Sketch your result on the grid below (the graph shown above is redrawn for your convenience), and explain your answer. Silver(I) forms a complex ion with ammonia, $Ag(NH_3)_2^+$, with $K_f = 1.7 \times 10^7$.



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, and clearly show stereochemistry where relevant. You need not balance the equations or show the phase of the species.

a. Aqueous ammonia and acetic acid are mixed.

b. Sodium iodate is added to an excess of hydriodic acid.

c. Manganese(IV) oxide is added to concentrated aqueous hydrochloric acid.

d. Propyl benzoate is heated with aqueous sodium hydroxide.

e. Calcium oxide and graphite are heated to 2200 °C.

f. Iodine-124 undergoes radioactive decay by electron capture.

6. [14%] Consider the properties of the group 1 elements, whose valence shell electron configuration is ns^1, in the table below.

Element M	n	First ionization energy, kJ mol^{-1}	Energy required to excite the valence electron to the $(n+1)s$ orbital, kJ mol^{-1}	Molar density of solid MCl, mol cm^{-3}
H	1	1312	984	0.0403
Li	2	520	325	0.0507
Na	3	496	308	0.0371
K	4	420	252	0.0266
Rb	5	403	241	0.0232
Cs	6	376	222	0.0237

a. Rationalize the observed trend in first ionization energies with increasing n.

b. Suppose a hydrogen atom were excited to its $2s^1$ state. If that excited state atom were to transfer its electron to Cs^+ to form a ground-state Cs atom, how much energy would that reaction absorb or release?

c. All but one of the atoms listed in the table have an excited state that is significantly lower in energy than the $(n+1)s^1$ state described in the table. Explain this observation, noting which atom is the exception and why.

d. All but one of the atoms listed in the table have an excited state that is modestly higher in energy (38 – 55 kJ mol^{-1}) than the $(n+1)s^1$ state described in the table. Explain this observation, noting which atom is the exception and why.

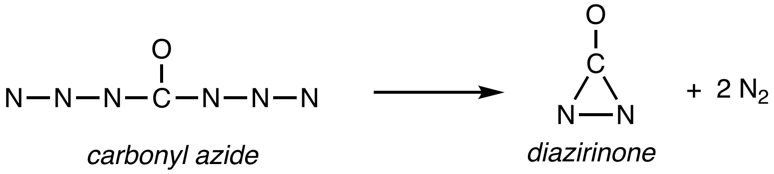
e. The compounds MCl(s) show a smooth decrease in their molar densities, except that HCl(s) is less dense than expected from the trend and CsCl(s) is more dense than expected. Explain this periodic trend, and give reasons for the two exceptions to the trend.

f. ^{137}Cs (136.9070895 amu) undergoes radioactive decay to give a stable product whose atomic mass is 136.9058274 amu. What type of radioactive decay is this, and what is the identity of the decay product?

g. Calculate the energy, in kJ mol^{-1}, released by the radioactive decay of ^{137}Cs.

Question 7 (page 1 of 2) USNCO ID Number:

7. [13%] Flash vacuum pyrolysis of carbonyl azide (CON_6) at 420 °C gives low yields of a cyclic compound, diazirinone, as shown in the equation below. Note that the illustrations of carbonyl azide and diazirinone correctly show the connectivity of the atoms but are NOT correct Lewis structures. The bond dissociation enthalpies (BDE, in kJ mol^{-1}) of various bonds among carbon, oxygen, and nitrogen are given in the table.



Bond	BDE, kJ mol^{-1}	Bond	BDE, kJ mol^{-1}	Bond	BDE, kJ mol^{-1}	Bond	BDE, kJ mol^{-1}
C–O	350	C–N	290	N–N	160	N–O	200
C=O	741	C=N	615	N=N	418	N=O	480
C≡O	1080	C≡N	891	N≡N	949		

a. Draw complete Lewis structures for carbonyl azide and for diazirinone, including all lone pairs and nonzero formal charges. You need only draw one Lewis structure for each molecule, even if there are multiple possible resonance structures.

b. Diazirinone decomposes in the gas phase over the course of several days at room temperature to give carbon monoxide and nitrogen gas. Based on the given BDEs, calculate ΔH° for this decomposition reaction.

c. The actual $\Delta H°$ for the decomposition of diazirinone is –347 kJ mol^{-1}. Comment on any discrepancy you find between this value and the value you determined in part b. Be sure your comment addresses the direction of deviation of the two values.

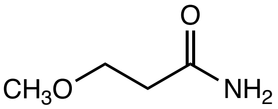
d. Will $\Delta G°$ for decomposition at 298 K be algebraically greater than, less than, or equal to $\Delta H°$ for decomposition? Briefly justify your answer.

e. There is an isomer of diazirinone that has a chain structure with the connectivity NCNO. Draw a Lewis structure for this molecule and clearly describe or sketch its geometry.

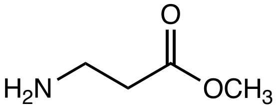
f. Would you expect acyclic NCNO to be more or less stable than diazirinone? Clearly justify your prediction.

Question 8 (page 1 of 2) USNCO ID Number:

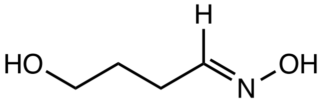
8. [12%] Consider the three isomers of $C_4H_9NO_2$ shown below:



I



II



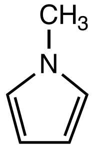
III

a. Which compound is the most basic? Justify your answer.

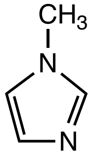
b. Draw the structures of the conjugate acids of the three compounds.

c. Draw the structure of a chiral isomer of $C_4H_9NO_2$.

Consider the two nitrogen heterocycles shown below:



IV



V

d. Which compound is more basic? Draw the structure of its conjugate acid.

e. Which compound is more reactive towards Br_2? Explain why it is more reactive and draw the structure of a major product of its reaction with Br_2.

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