STUDENT USNCO ID:

ACS USNCO
U.S. National Chemistry Olympiad

2026 U.S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM PART II

Prepared by the American Chemical Society Chemistry Olympiad Examinations Task Force

OLYMPIAD EXAMINATIONS TASK FORCE

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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. The 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 21, 2026**.

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 used the same identification number used for **Part I** 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 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.

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

CONSTANTS
$R = 8.314$ J mol^{-1} K^{-1}
$R = 0.08314$ L bar mol^{-1} K^{-1}
$F = 96{,}500$ C mol^{-1}
$F = 96{,}500$ J V^{-1} mol^{-1}
$N_A = 6.022 \times 10^{23}$ mol^{-1}
$h = 6.626 \times 10^{-34}$ J s
$c = 2.998 \times 10^{8}$ m s^{-1}
0 °C = 273.15 K
1 atm = 1.013 bar = 760 mm Hg
Specific heat capacity of H_2O = 4.184 J g^{-1} 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																	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%] An unknown compound **X** contains only carbon, hydrogen, and oxygen.

   a. When burned, 1.00 g of **X** produces 2.00 g of carbon dioxide and 0.818 g of water. What is the empirical formula of **X**?

   b. A 1.68 g sample of **X** is introduced into a 2.00 L evacuated flask. The flask is slowly heated until the liquid evaporates completely, which occurs at 62.3 °C. At this temperature, the pressure in the flask is 200.0 mmHg. What is the molar mass of **X**, and what is its molecular formula?

   c. The melting point of **X** is 11.8 °C and its normal boiling point is 101.1 °C. Calculate the standard enthalpy and entropy of vaporization of **X**.

d. What types of intermolecular forces are likely present in liquid **X**? Justify your answer.

e. The unit cell of crystalline **X** at its melting point has a volume of 241.5 $Å^3$ and the density of the solid is 1.211 g cm^{-3}. How many molecules of **X** are present in the unit cell?

f. The density of liquid **X** at its melting point is 1.034 g cm^{-3}. Will the melting point increase, decrease, or stay the same as the pressure is increased?

2. [14%] The nickel(II) ion forms a variety of colored complex ions, including green $Ni(H_2O)_6^{2+}$, violet $Ni(NH_3)_6^{2+}$ ($K_f = 2.0 \times 10^8$), and yellow $Ni(CN)_4^{2-}$ ($K_f = 2.0 \times 10^{31}$).

a. Explain the trend in colors among the three complex ions.

b. How many unpaired electrons does each of the three complex ions have?

c. To 1.00 L of a 0.01 M solution of $Ni(NO_3)_2$ is slowly added ammonia. Initially, a green precipitate of $Ni(OH)_2$ ($K_{sp} = 2.0 \times 10^{-15}$) is formed. What is the pH of the solution at the point where the precipitate just begins to form?

d. By the time 0.600 mol of NH_3 have been added to the solution in c., the solution has become homogeneous and violet in color. Calculate the concentration of $Ni^{2+}(aq)$ in this solution.

e. Nickel sulfide is quite insoluble ($K_{sp} = 4.0 \times 10^{-20}$). 0.010 mol of NiS is suspended in 1.00 L of a solution buffered at pH = 10.00. Ammonia is then bubbled through this solution until the nickel sulfide just dissolves. Show that no solid $Ni(OH)_2$ will be present at this point. For H_2S, $pK_{a1} = 7.05$ and $pK_{a2} = 19.0$.

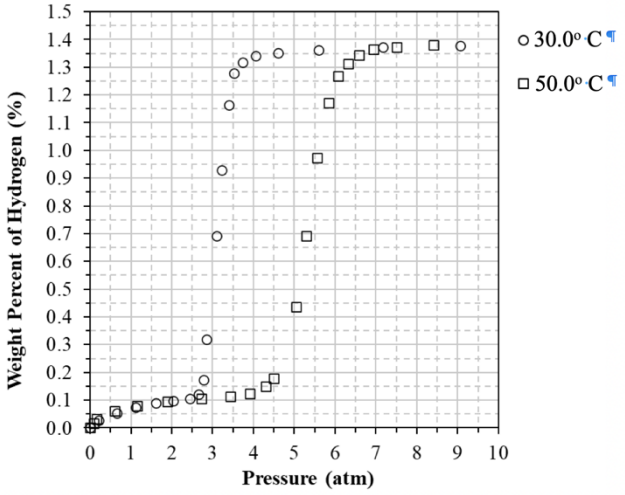
f. Calculate the number of moles of NH_3 added to the solution in part e. (The pK_a of NH_4^+ is 9.25.)

3. [12%] Lanthanum pentanickel, $LaNi_5(s)$, is under consideration for solid-state hydrogen storage. $LaNi_5(s)$ is a conductive metallic crystal, and it forms hydrides in two phases:
   - an α phase α-$LaNi_5H_x(s)$ observed at lower H_2 pressure, characterized as a solid-state solution
   - a β phase β-$LaNi_5H_{6.39}(s)$ observed at higher H_2 pressure, characterized by metal-hydrogen bonding

Species	$\Delta H°_f$, kJ mol^{-1}	$S°$, J mol^{-1} K^{-1}	Species	$\Delta H°_f$, kJ mol^{-1}	$S°$, J mol^{-1} K^{-1}
$H_2(g)$	0	130.7	$LaNi_5(s)$	–162	217
$Ni(s)$	0	29.9	α-$LaNi_5H_x(s)$	–186	223
$La(s)$	0	56.9	β-$LaNi_5H_{6.39}(s)$	?	?

a. Calculate $\Delta G°_f$ of $LaNi_5(s)$ at 298 K.

$LaNi_5(s)$ is placed in vacuum chambers, one at 30.0 °C and one at 50.0 °C. Pure $H_2(g)$ is added to each chamber, and the weight-percent hydrogenation of $LaNi_5(s)$ is recorded as a function of pressure.



b. Show that the maximum degree of hydrogenation x for α-$LaNi_5H_x(s)$ is approximately 0.43.

c. Calculate $\Delta G°_{rxn}$ at 30 °C and at 50 °C for the hydrogenation of the α phase to the β phase.

d. Calculate $\Delta H°_f$ and $S°$ for β-$LaNi_5H_{6.39}(s)$.

4. [12%] Iodomethane, CH_3I, hydrolyzes irreversibly in dilute solution via two distinct pathways:

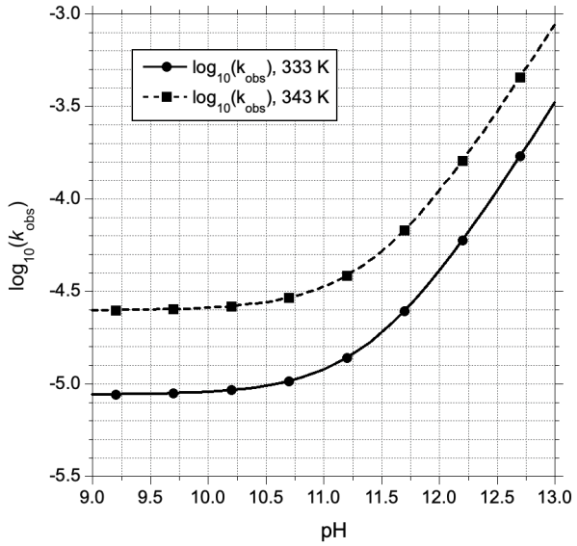
$$CH_3I(aq) + H_2O(l) \rightarrow CH_3OH(aq) + H^+(aq) + I^-(aq) \qquad \text{Rate} = k_1[CH_3I]$$

$$CH_3I(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + I^-(aq) \qquad \text{Rate} = k_2[CH_3I][OH^-]$$

a. A solution is prepared by dissolving enough methyl iodide in pure water to make a 0.0500 M solution. After 1.50 h at 89.9 °C, the concentration of iodide in this solution is measured to be 0.0311 M. What is the value of k_1 at 89.9 °C?

b. What would the concentration of iodide be in this solution after 3.00 h at 89.9 °C?

The hydrolysis of iodomethane is studied in strongly buffered solutions as a function of pH. Under these conditions, the reaction is always found to be first order in iodomethane, with an observed first-order rate constant k_{obs} that varies with pH. The logarithms of k_{obs} (with k_{obs} measured in units of s^{-1}) for the reaction studied at 333 K as a function of pH are shown with filled circles and a solid line on the graph below.



c. What are the values of k_1 and k_2 for the reaction at 333 K?

d. The analogous data for the reaction studied at 343 K are shown on the graph (filled squares, dashed line). Which has a larger activation energy, reaction 1 or reaction 2? Explain your reasoning.

e. The value of k_2 for CH_3CH_2I is significantly smaller than the value of k_2 for CH_3I at a given temperature. Rationalize this difference based on the structures of the transition states for these reactions.

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 phases of the species.

a. Sulfur dioxide is bubbled through barium hydroxide solution.

b. Phosphorus pentachloride is heated with phosphorus(V) oxide.

c. Cobalt(II) nitrate is dissolved in concentrated aqueous hydrochloric acid.

d. Iron(II) ammonium sulfate reacts with potassium dichromate in dilute sulfuric acid.

e. Bromine is added to 4-nitrotoluene in the presence of anhydrous iron(III) bromide.

f. Acetone (2-propanone) is added to an aqueous solution of hydroxylamine.

6. [13%] A metallic alloy contains all of the group 11 metals (copper, silver, and gold).

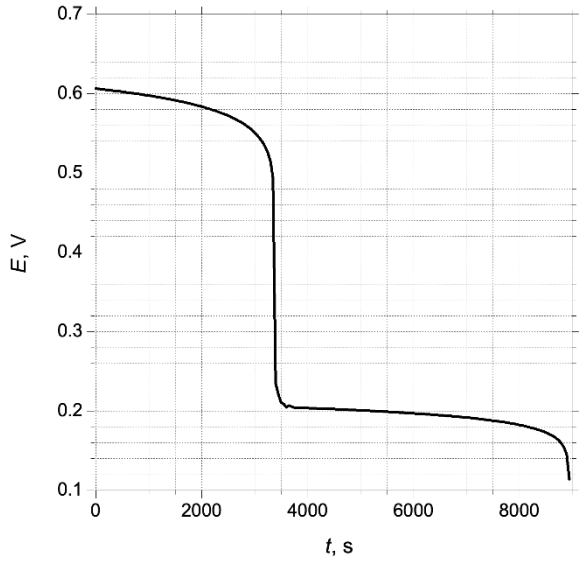
Half-reaction	$E°$, V
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+0.34
$Ag^{+}(aq) + e^- \rightarrow Ag(s)$	+0.80
$Au^{+}(aq) + e^- \rightarrow Au(s)$	+1.83
$Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$	+1.52
$AuCl_4^-(aq) + 3\ e^- \rightarrow Au(s) + 4\ Cl^-(aq)$	+0.93

a. 0.1000 g of this alloy is dissolved in 10 mL of 6 M nitric acid (a large excess), which leaves behind 0.0325 g of unreacted metallic gold. Explain why gold does not dissolve in nitric acid, but does dissolve in aqua regia, which is a mixture of nitric and hydrochloric acids.

b. What is the formation constant K_f for the $AuCl_4^-$ complex ion?

c. To the filtrate from part a. is added aqueous ammonia to give a total volume of 50.0 mL, with the final pH of the solution equal to 4.00. What fraction of the Cu(II) ion in solution is in the form of $Cu(NH_3)_4^{2+}$? The K_f of $Cu(NH_3)_4^{2+}$ is 1.7×10^{13} and the pK_a of NH_4^+ is 9.25.

d. The solution from part c. is subjected to constant-current electrolysis with a platinum cathode and its potential measured relative to a half-cell with a silver anode in a large volume of 1.000 M NaBr (with some silver bromide present). The electrolysis is carried out with a constant current of 12.0 mA and the potential measured as a function of time to give the graph shown below. What is the percent by mass of copper and silver in the alloy?



e. What is the K_{sp} of AgBr?

7. [13%] Boron and hydrogen form a number of interesting compounds.

a. Give the electron configuration and the number of unpaired electrons in both the ground state of atomic B and its lowest-energy excited state.

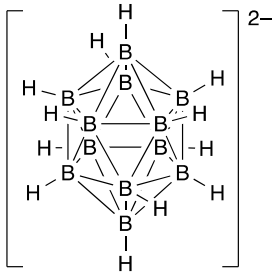
b. Which requires more energy to excite, the ground state of atomic B to its lowest excited state or the ground state of atomic H to its lowest excited state? Justify your answer.

c. In the gas phase at low pressure, the binary compound BH_3 can be observed. Clearly describe or depict its geometry and explain its bonding.

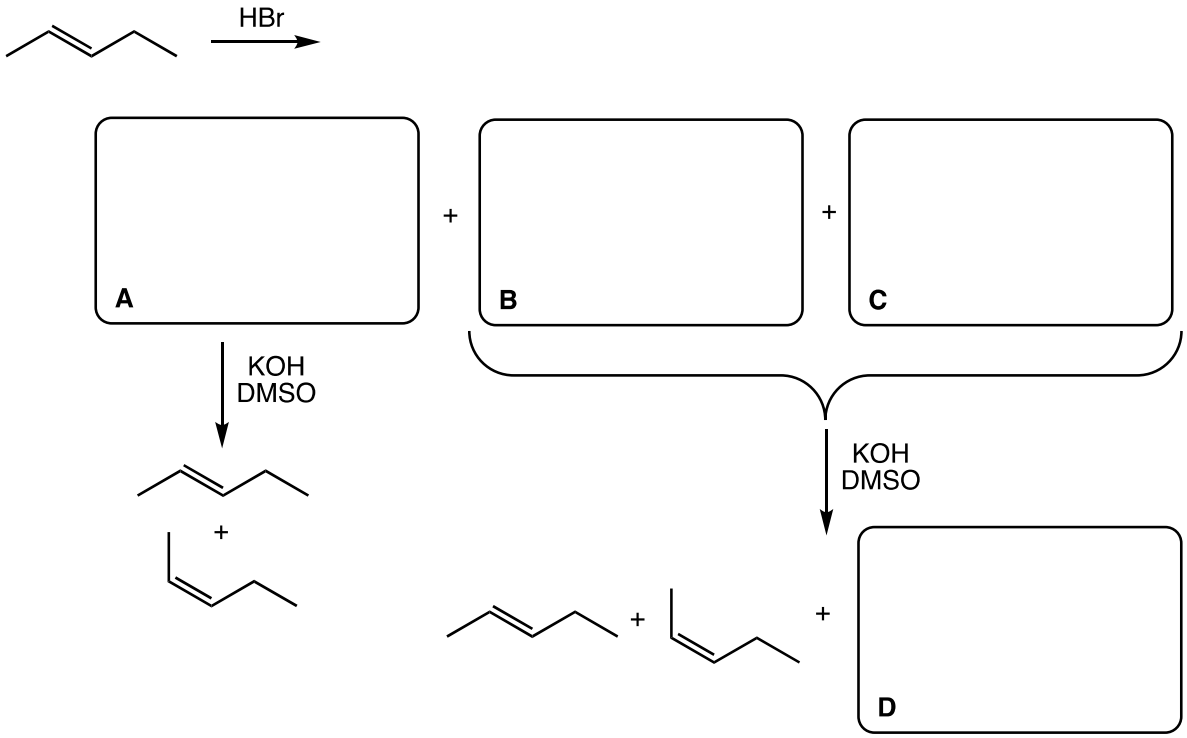
d. At higher pressures or in condensed phases, BH_3 dimerizes to form diborane, B_2H_6. Clearly describe or depict the geometry and explain the bonding in diborane.

e. Boron and hydrogen form the anionic species borohydride, BH_4^-. Draw a Lewis structure of BH_4^-, making sure to include all lone pairs and nonzero formal charges.

f. Boron and hydrogen also form a series of dianions $B_nH_n^{2-}$, including the icosahedral species $B_{12}H_{12}^{2-}$ illustrated below. Carboranes are neutral compounds with the formula $C_2B_{10}H_{12}$, where two of the boron atoms in $B_{12}H_{12}^{2-}$ are replaced with carbon while retaining the same icosahedral structure. How many isomers of carborane are possible? Draw or clearly describe them.



8. [12%] (*E*)-2-pentene reacts with hydrogen bromide to give three compounds, **A**, **B**, and **C**. Compound **A** reacts with potassium hydroxide in dimethyl sulfoxide to give (*E*)-2-pentene and its (*Z*) isomer as the only alkene products. In contrast, compounds **B** and **C** react with KOH in DMSO to give not only (*E*)- and (*Z*)-2-pentene but also another alkene **D**.



a. Draw structures for compounds **A**–**D**, clearly indicating stereochemistry if applicable.

b. What is the relationship (constitutional isomers, enantiomers, diastereomers, or not isomers) between compounds **A** and **B**?

c. What is the relationship (constitutional isomers, enantiomers, diastereomers, or not isomers) between compounds **B** and **C**?

d. (*E*)-2-pentene has a melting point of –140 °C and a normal boiling point of 37 °C, while (*Z*)-2-pentene has a melting point of –180 °C and a boiling point of 37 °C. Explain why the (*E*) isomer has a significantly higher melting point, but essentially the same boiling point, as the (*Z*) isomer.

e. No alkenes with the formula C_5H_{10} are chiral. Draw the structure of a chiral alkene with the formula C_6H_{12}.

2026 USNCO Part 2 SOLUTIONS

1. a. 2.00 g CO_2/(44.01 g mol^{-1}) = 0.0454 mol C = 0.545 g C

0.818 g H_2O/(18.02 g mol^{-1}) = 0.0454 mol H_2O = 0.0908 mol H = 0.0915 g H

1.00 g **X** – 0.545 g C – 0.0915 g H = 0.364 g O = 0.0227 mol O

Mol ratio of C : H : O = 2 : 4 : 1, so empirical formula is C_2H_4O

b. $PV = nRT$

[(200.0 mmHg)/(760 mmHg/atm)]*(1.013 bar atm^{-1}) = 0.2666 bar

(0.2666 bar)(2.00 L) = n(0.08314 L bar mol^{-1} K^{-1})(335.5 K)

n = 0.0191 mol

M = (1.68 g)/(0.0191 mol) = 87.9 g mol^{-1}

Since the molar mass of C_2H_4O = 44.1 g mol^{-1}, the molecular formula must be double the empirical formula, $C_4H_8O_2$

c. We have two temperatures at which we know the vapor pressure: 0.2666 bar at 335.5 K (from part b) and 1 atm (1.013 bar) at 374.3 K.

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{1.013\text{ bar}}{0.2666\text{ bar}}\right) = -\frac{\Delta H^\circ}{8.314\text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{374.3\text{ K}} - \frac{1}{335.5\text{ K}}\right)$$

$$\Delta H^\circ_{vap} = 35.92\text{ kJ mol}^{-1}$$

At 374.3 K, K_{eq} = 1.013, so

$$\Delta G^\circ_{vap} = -RT\ln(1.013) = -0.0402\text{ kJ mol}^{-1} = \Delta H^\circ_{vap} - T\Delta S^\circ_{vap}$$

$$-0.0402\text{ kJ mol}^{-1} = 35.92\text{ kJ mol}^{-1} - (374.3\text{ K})\Delta S^\circ_{vap}$$

$$\Delta S^\circ_{vap} = 96.1\text{ J mol}^{-1}\text{ K}^{-1}$$

d. There are of course London dispersion forces present, and these are probably the only forces that are significant, given that the enthalpy of vaporization is modest and the entropy is about what one would expect from Trouton's rule. Hydrogen bonding in particular is unlikely because the boiling point is lower than one would expect for a molecule of this size with hydrogen bonding present. Thus, for example, *n*-propanol, C_3H_7OH, has a very similar normal boiling point of 97 °C despite having one fewer carbon and one fewer oxygen atom than this compound.

e. $\frac{1.211\ g}{1\ cm^3} \times \frac{10^{-24}\ cm^3}{1\ Å^3} \times \frac{241.5\ Å^3}{1\ unit\ cell} \times \frac{1\ mol}{88.1\ g} \times \frac{6.022 \times 10^{23}\ molecules}{1\ mol}$ = 2 molecules/unit cell

f. Higher pressures favor the denser phase, which for **X** is the solid. Therefore the melting point will increase with increasing pressure.

2. a. The complexes absorb the complementary colors of those shown, so green $Ni(H_2O)_6^{2+}$ absorbs red light, violet $Ni(NH_3)_6^{2+}$ absorbs yellow light, and yellow $Ni(CN)_4^{2-}$ absorbs violet light. Thus the complexes are listed in increasing energy of the absorbed light. These d^8 complexes absorb light when an electron is promoted from a nonbonding *d* orbital to an antibonding *d* orbital. The strength of the bonding increases in the order of $H_2O < NH_3 < CN^-$ (increasing Lewis basicity, increasing ligand field strength), corresponding to a greater difference in energy between nonbonding and antibonding orbitals.

b. Octahedral d^8 complexes such as $Ni(H_2O)_6^{2+}$ or $Ni(NH_3)_6^{2+}$ have two unpaired electrons. Square planar d^8 complexes such as $Ni(CN)_4^{2-}$ have no unpaired electrons.

c. At the point of precipitation, $[Ni^{2+}] = 0.010$ M and

$$[Ni^{2+}][OH^-]^2 = [0.010][OH^-]^2 = 2.0 \times 10^{-15}$$

$$[OH^-] = 4.47 \times 10^{-7}$$

$$pH = 14 + \log_{10}[OH^-] = 7.65$$

d. Almost all the nickel will be complexed in this solution, so $[NH_3] = 0.600 - 6(0.010) = 0.54$ M. (The solution is highly basic, so the amount of ammonia in the form of NH_4^+ is negligible.) From the formation equilibrium,

$$\frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} = \frac{[0.010]}{[Ni^{2+}][0.54]^6} = 2.0 \times 10^8$$

$$[Ni^{2+}] = 2.0 \times 10^{-9} \text{ M}$$

e. Since the nickel sulfide has just dissolved, all the sulfur is in solution either as H_2S, HS^-, or S^{2-}. At pH = 10, almost all the sulfur will be in the form of HS^-, so $[HS^-] = 0.0100$ M. One can calculate $[S^{2-}]$ using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log_{10}([S^{2-}]/[HS^-])$$

$$10.00 = 19.0 + \log_{10}([S^{2-}]/[0.0100])$$

$$[S^{2-}] = 1.0 \times 10^{-11} \text{ M}$$

From the K_{sp} of NiS, which is valid because the NiS has just barely dissolved:

$$[Ni^{2+}][S^{2-}] = 4.0 \times 10^{-20}$$

$$[Ni^{2+}][1.0 \times 10^{-11}] = 4.0 \times 10^{-20}$$

$$[Ni^{2+}] = 4 \times 10^{-9} \text{ M}$$

At pH = 10.00, $[OH^-] = 1.0 \times 10^{-4}$ M. One can calculate Q_{sp} for $Ni(OH)_2$:

$$Q_{sp} \text{ for } Ni(OH)_2 = [Ni^{2+}][OH^-]^2 = [4 \times 10^{-9}][1.0 \times 10^{-4}]^2 = 4.0 \times 10^{-17}$$

Since $Q_{sp} < K_{sp}$ ($= 2.0 \times 10^{-15}$), no $Ni(OH)_2$ will precipitate under these conditions.

f. From part e., $[Ni^{2+}] = 4 \times 10^{-9}$ M. Since there is no solid, this means that almost all the nickel must be present in the form of $Ni(NH_3)_6^{2+}$, so $[Ni(NH_3)_6^{2+}] = 0.010$ M. From the complexation equilibrium:

$$\frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} = \frac{[0.010]}{[4 \times 10^{-9}][NH_3]^6} = 2.0 \times 10^8$$

$$[NH_3] = 0.48 \text{ M}$$

This is the amount of *free* ammonia present, but to determine the number of moles of ammonia *added*, one needs to account for the other forms of ammonia present. This includes NH_3 bound to Ni^{2+}, which amounts to 6 × (0.010 mol) = 0.060 mol. It also includes NH_4^+, which is related to $[NH_3]$ via the acid-base equilibrium:

$$pH = pK_a + \log_{10}([NH_3]/[NH_4^+])$$

$$10.00 = 9.25 + \log_{10}([0.48]/[NH_4^+])$$

$$[NH_4^+] = 0.085 \text{ M}$$

Since the volume of solution is 1.00 L, the number of moles of ammonia that need to be added is 0.48 mol + 0.060 mol + 0.085 mol = 0.63 mol ammonia.

3. a. For the reaction

$$La(s) + 5\ Ni(s) \rightarrow LaNi_5(s)$$

$$\Delta H°_{rxn} = (-162) - (0 + 5[0])\ kJ\ mol^{-1} = -162\ kJ\ mol^{-1}$$

$$\Delta S°_{rxn} = (217) - (56.9 + 5[29.9])\ J\ mol^{-1}\ K^{-1} = 10.6\ J\ mol^{-1}\ K^{-1}$$

$$\Delta G°_{rxn,\ 298K} = \Delta G°_{f,\ 298K}\ of\ LaNi_5(s) = \Delta H°_{rxn} - (298\ K)\Delta S°_{rxn}$$

$$\Delta G°_{f,\ 298K}\ of\ LaNi_5(s) = -165\ kJ\ mol^{-1}$$

b. The maximum mass% of H in α-$LaNi_5H_x(s)$ is 0.10%. So in 100. g of α-$LaNi_5H_x(s)$, there are 0.10 g/(1.008 g mol^{-1}) = 0.099 mol H and 99.9 g/(432.35 g mol^{-1}) = 0.231 mol $LaNi_5$. So x = 0.099/0.231 = 0.43.

c. The balanced reaction is:

$$\alpha\text{-}LaNi_5H_{0.43} + 2.98\ H_2(g) \rightarrow \beta\text{-}LaNi_5H_{6.39}$$

If ΔG_{rxn} (nonstandard; not the standard $\Delta G°$) is positive, then the α phase is stable, while if it is negative the β phase is stable. The two phases can coexist if $\Delta G_{rxn} = 0$. The hydrogen pressure at which the two phases coexist can be read from the steep part of the graphs, i.e., 3.1 bar at 30 °C and 5.4 bar at 50 °C. At these pressures,

$$\Delta G = 0 = \Delta G° + RT\ln(Q)$$

$$\Delta G° = -RT\ln(Q) = -RT\ln(P_{H2}{}^{-2.98})$$

$$\Delta G°(30\ °C) = -R(303.2\ K)\ln[(3.1)^{-2.98}] = 8.50\ kJ\ mol^{-1}$$

$$\Delta G°(50\ °C) = -R(323.2\ K)\ln[(5.4)^{-2.98}] = 13.5\ kJ\ mol^{-1}$$

d. One can get $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ for the hydrogenation reaction in (c) by solving the two simultaneous equations:

$$8.50\ kJ\ mol^{-1} = \Delta H°_{rxn} - (303.2\ K)\Delta S°_{rxn}$$

$$\underline{13.5\ kJ\ mol^{-1} = \Delta H°_{rxn} - (323.2\ K)\Delta S°_{rxn}}$$

$$\Delta H°_{rxn} = -67.3\ kJ\ mol^{-1},\ \Delta S°_{rxn} = -250.\ J\ mol^{-1}\ K^{-1}$$

From the tabulated values:

$$\Delta H°_{rxn} = \Delta H°_f(\beta) - (-186\ kJ\ mol^{-1}) - 2.98(0) = -67.3\ kJ\ mol^{-1}$$

$$\Delta H°_f(\beta\text{-}LaNi_5H_{6.39}(s)) = -253\ kJ\ mol^{-1}$$

$$\Delta S°_{rxn} = S°(\beta) - (223\ J\ mol^{-1}\ K^{-1}) - 2.98(130.7\ J\ mol^{-1}\ K^{-1}) = -250.\ J\ mol^{-1}\ K^{-1}$$

$$S°(\beta\text{-}LaNi_5H_{6.39}(s)) = 362\ J\ mol^{-1}\ K^{-1}$$

4. a. If $[I^-] = 0.0311$ M, then $[CH_3I] = 0.0500 - 0.0311 = 0.0189$ M. Since this is a first-order reaction,

$$\ln([CH_3I]) = \ln([CH_3I]_0) - k_1 t$$

$$\ln(0.0189) = \ln(0.0500) - k_1(5400\text{ s})$$

$$k_1 = 1.80 \times 10^{-4}\text{ s}^{-1}$$

b.
$$\ln([CH_3I]) = \ln([CH_3I]_0) - k_1 t$$

$$\ln([CH_3I]) = \ln(0.0500) - (1.80 \times 10^{-4}\text{ s}^{-1})(10800\text{ s})$$

$$[CH_3I] = 7.16 \times 10^{-3}\text{ M}$$

$$[I^-] = 0.0500\text{ M} - 0.0072\text{ M} = 0.0428\text{ M}$$

c. Because the reactions take place in a buffer solution, the concentration of hydroxide ion is constant throughout each run, so rate = $(k_1 + k_2[OH^-])[CH_3I]$. Thus, $k_{obs} = k_1 + k_2[OH^-]$. At low pH, the concentration of hydroxide becomes very small and k_{obs} approaches k_1 asymptotically. From the graph, $\log_{10}(k_1) = -5.06$, $k_1 = 8.7 \times 10^{-6}\text{ s}^{-1}$.

The value of k_2 can be inferred from any point on the graph at higher pH. An easy value to pick is at pH = 13.0, where $\log_{10}(k_{obs}) = -3.48$, $k_{obs} = 3.31 \times 10^{-4}\text{ s}^{-1}$.

$$k_{obs} = k_1 + k_2[OH^-]$$

$$3.31 \times 10^{-4}\text{ s}^{-1} = 8.7 \times 10^{-6}\text{ s}^{-1} + k_2[0.10\text{ M}]$$

$$k_2 = 3.2 \times 10^{-3}\text{ M}^{-1}\text{ s}^{-1}$$

d. At pH = 9, hydrolysis is essentially only taking place by reaction 1. The difference in the graphs at this pH, 0.46 log units, indicates that the reaction 1 is faster at 343 K by a factor of $10^{0.46} = 2.9$. At pH = 13, hydrolysis is taking place almost completely (> 95%) by reaction 2. The difference in the graphs is slightly smaller here, only 0.42 log units corresponding to a factor of 2.6. Reaction 1 therefore has a greater temperature-dependence than reaction 2, and since $k = Ae^{-Ea/RT}$, reaction 1 must therefore have the greater activation energy.

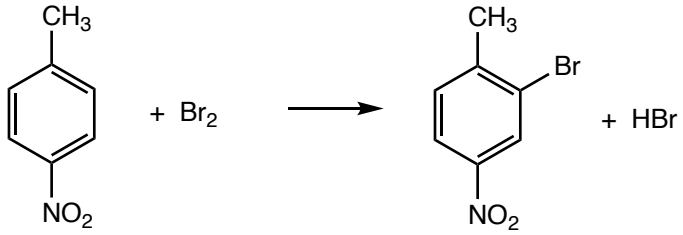
e. Reaction 2 is bimolecular, with hydroxide ion approaching the carbon 180° away from the iodide in the transition state of the (so-called S_N2) reaction. Since the coordination number of carbon increases from 4 to 5 in the transition state, substitution of methyl for hydrogen at the carbon makes it more difficult to attain the transition state due to increased steric crowding. Thus the activation energy is higher for CH_3CH_2I and the value of k_2 correspondingly smaller.

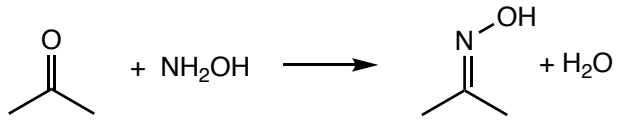
5. a. $Ba^{2+}(aq) + SO_2(g) + OH^-(aq) \rightarrow BaSO_3(s) + H_2O(l)$

   b. $PCl_5(s) + P_4O_{10}(s) \rightarrow POCl_3(l)$

   c. $Co(NO_3)_2(s) + Cl^-(aq) \rightarrow CoCl_4^{2-}(aq) + NO_3^-(aq)$

   d. $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq) + H_2O(l)$

   e. 

   f. 

6. a. The redox potential of Au to form either $Au^+(aq)$ or $Au^{3+}(aq)$ is so high that nitric acid is not a strong enough oxidant to allow this reaction. However, chloride ion binds strongly to Au^{3+}, so that in aqua regia the relevant couple is the $AuCl_4^-$/Au couple, which has a lower potential.

b.

$$Au^{3+}(aq) + 3e^- \rightarrow Au(s) \qquad \Delta G° = -3F(1.52\text{ V})$$

$$\underline{Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3e^-} \qquad \underline{\Delta G° = -3F(-0.93\text{ V})}$$

$$Au^{3+}(aq) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) \qquad \Delta G° = -3F(0.59\text{ V})$$

$$\Delta G° = -170.8\text{ kJ mol}^{-1} = -RT\ln(K_f) = -(8.314\text{ J mol}^{-1}\text{ K}^{-1})(298\text{ K})\ln(K_f)$$

$$K_f = 8.6 \times 10^{29}$$

c. Since the nitric acid was employed in large excess over the dissolving metals, the moles of acid present will be close to those initially present, i.e. $(6\text{ mol L}^{-1})(0.010\text{ L}) = 0.060$ mol. Since the final pH = 4, essentially all the acid is neutralized (with little excess ammonia), so $[NH_4^+] = 0.060\text{ mol}/0.050\text{ L} = 0.12$ M. From the pH,

$$pH = pK_a + \log_{10}([NH_3]/[NH_4^+])$$

$$4.00 = 9.25 + \log_{10}([NH_3]/[0.12])$$

$$[NH_3] = 6.7 \times 10^{-6}\text{ M}$$

From the complex ion equilibrium,

$$[Cu(NH_3)_4^{2+}]/[Cu^{2+}(aq)] = K_f[NH_3]^4$$

$$[Cu(NH_3)_4^{2+}]/[Cu^{2+}(aq)] = 3.4 \times 10^{-8}$$

Since this ratio is so tiny, it is essentially equal to the fraction of complexed copper.

d. The first equivalence point, where all the Ag^+ has been reduced to Ag(*s*), occurs at 3400 s. This corresponds to $(3400\text{ s})(0.0120\text{ C s}^{-1})/(96500\text{ C mol}^{-1}) = 4.23 \times 10^{-4}$ mol Ag = 0.0456 g Ag = 45.6% of the 0.1000 g alloy sample. The percent Cu can be obtained by difference, given the 32.5% Au, as 21.9%. (Using the second equivalence point in the potentiometric titration at 8950 s gives 21.9% Cu as well.)

e. The initial potential, 0.61 V, is essentially a concentration cell between the Ag^+ in the analyte $(= 4.23 \times 10^{-4}\text{ mol}/0.0500\text{ L} = 8.46 \times 10^{-3}$ M) and the Ag^+ in the AgBr/Br^- solution. So $0.61\text{ V} = (RT/F)\ln([8.46 \times 10^{-3}]/[Ag^+])$, which gives $[Ag^+] = 4.1 \times 10^{-13}$ in the AgBr reference cell. Since $[Br^-] = 1.00$ M in this cell, then $K_{sp} = 4.1 \times 10^{-13}$.

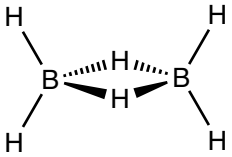
7. a. Ground state B is $1s^2 2s^2 2p^1$ with one unpaired electron.

   Lowest-energy excited state B is $1s^2 2s^1 2p^2$ with three unpaired electrons.

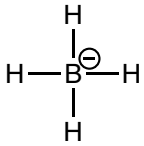
   b. B takes much less energy to excite than H. (Quantitatively, B requires 3.55 eV to excite while H requires 10.20 eV.) The energy difference between *s* and *p* orbitals with the same principal quantum number is less than the difference in energy between orbitals of different principal quantum number. The difference between $n = 1$ and $n = 2$ is especially large, since E is proportional to $-1/n^2$, making the H 2*s* excited state especially high in energy. Boron's higher Z_{eff} is not enough to outweigh these effects. (The more favorable exchange energy of the quartet excited state of B also contributes to its relatively low energy.)

   c. BH_3 has six valence electrons and can thus form three two-center two-electron bonds. It has a trigonal planar geometry.

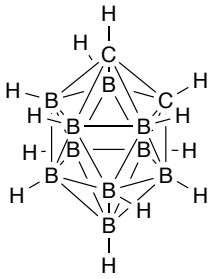
   d. B_2H_6 has only twelve valence electrons and can thus not form seven two-center two-electron bonds (as in, for example, C_2H_6 with 14 valence electrons). Instead, it has a structure where the two boron atoms are bridged by two hydrogens, forming two three-center two-electron bonds. Each B also has two terminal hydrogens bonded with two-center two-electron bonds. The overall geometry is that of two tetrahedra joined along an edge:



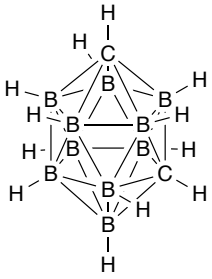
   e.



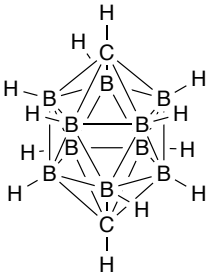
   f. Three possible isomers: so-called "ortho" with two carbons bonded to one another; "meta" with two carbons separated by one boron; and "para" with two carbons separated by two boron atoms.



ortho

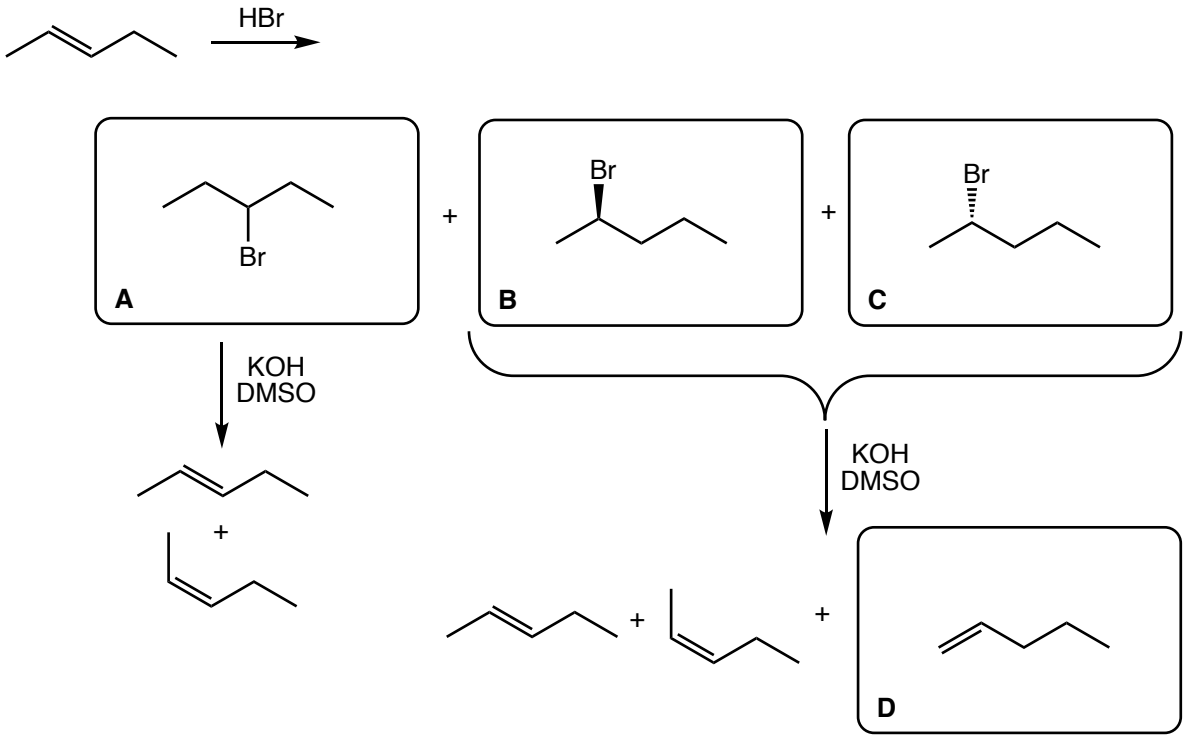


meta



para

8. a.



b. Constitutional isomers

c. Enantiomers

d. Melting points of molecular solids depend strongly on how well the molecules can pack together in the crystal. Molecules with more regular shapes (such as the zigzag-shaped *E* isomer) can pack more tightly and thus have higher melting points than irregularly shaped molecules (such as the curlicue-shaped *Z* isomer). Boiling points are not very sensitive to the details of shape (since the liquid is not arranged regularly), but rather to surface area. The two isomers are both tube shaped and have the same surface area and thus very similar boiling points. (A branched isomer, such as 2-methyl-1-butene, has a smaller surface area and thus weaker intermolecular forces and a correspondingly lower boiling point, 31 °C.)

e.  or its enantiomer. These are the only chiral alkenes with the formula C_6H_{12}.