ACS USNCO
U.S. National Chemistry Olympiad

2025 U.S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM PART II

Prepared by the American Chemical Society Chemistry 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 14, 2025**.

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.

Only non-programmable calculators that do not have any on-board memory space (accessed through a mini-USB or other linkage) are to be used on the ACS Local Section Exam and on the National Exam, if used. The use of an unacceptable calculator, cell phone, or any other device that can access the internet, make copies or photographs, or has access to stored information 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.

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STUDENT USNCO ID:

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

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

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

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

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

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

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

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

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

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

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

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

PERIODIC TABLE OF THE ELEMENTS

1 1A	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)

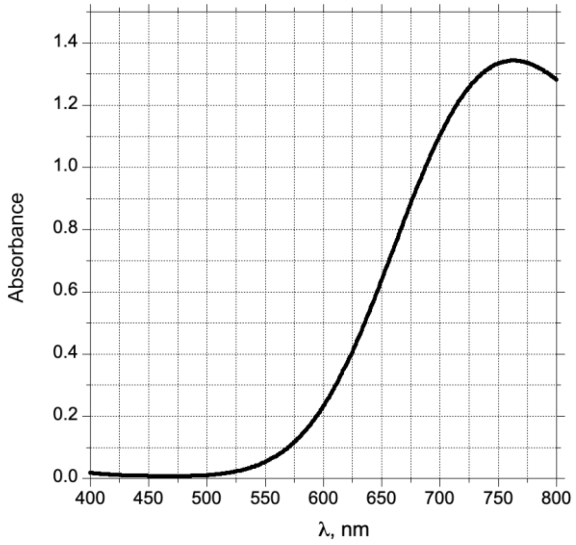
58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	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)**

1. [12%] Copper(II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, is a blue crystalline solid. Upon gentle heating, it loses water to form anhydrous $CuSO_4$, which is a white solid.

   a. When 5.000 g $CuSO_4 \cdot 5H_2O$ is heated to remove all of its water, what mass of anhydrous $CuSO_4$ will be produced?

   b. Explain the change in color on dehydration of $CuSO_4 \cdot 5H_2O$.

   c. A solution of 0.0506 g $Cu(CH_3COO)_2 \cdot H_2O$ is made up with water to a volume of 5.00 mL water. This solution in a 1-cm cuvette produces the visible spectrum shown. What wavelength would be the best choice to determine the concentration of Cu(II)?



d. A student determines the value of *n* in an unknown crystalline hydrate of copper(II) nitrate, $Cu(NO_3)_2 \bullet n\ H_2O$, by preparing 5.00 mL of an aqueous solution of a known mass of the compound and measuring its absorbance at the wavelength determined in part c. However, the student inserts the cuvette into the spectrophotometer without first wiping fingerprints from it. How will this affect the value of *n* determined in the experiment?

e. An alternative method for determining the degree of hydration of the copper nitrate is to allow a known mass of compound to react with excess KI solution, which produces a yellow-brown suspension. Write a balanced net ionic equation for this reaction.

f. The experiment in part e is carried out with 0.1000 g of the hydrated copper(II) nitrate. To the resulting mixture is added a 0.0250 M solution of sodium thiosulfate, $Na_2S_2O_3$, until the color of the mixture has just dissipated, leaving a milky white suspension. This requires 17.20 mL of added sodium thiosulfate solution. What is the value of *n* for the $Cu(NO_3)_2 \bullet n\ H_2O$?

2. [13%] Calcium oxalate, CaC_2O_4, has a K_{sp} of 2.7×10^{-9}. Oxalic acid, $H_2C_2O_4$, has two ionizable hydrogens with $pK_{a1} = 1.27$ and $pK_{a2} = 4.28$.

   a. Draw a Lewis structure for oxalate ion, $C_2O_4^{2-}$, including all bonds, lone pairs, and formal charges.

   b. Calculate the molar solubility of calcium oxalate in pure water.

   c. Calculate the molar solubility of calcium oxalate in a 0.100 M $CaCl_2$ solution.

d. A 0.100 mol sample of solid CaC_2O_4 is suspended in 1.00 L of water and HCl(*g*) is bubbled through the solution until all of the solid just dissolves. What is the pH of the final homogeneous solution? You may assume the final volume of solution is 1.00 L.

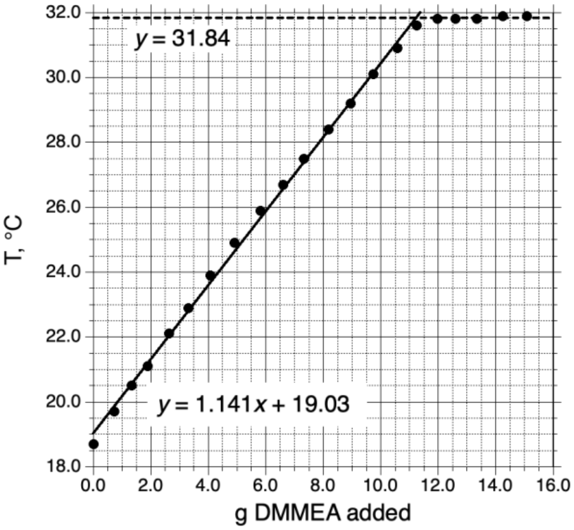
e. How many moles of HCl(*g*) are added in part d?

f. Will the molar solubility of CaC_2O_4 in 0.1 M $NaHC_2O_4$ be significantly greater than, significantly less than, or within 10% of the molar solubility of calcium oxalate in pure water? Justify your answer.

3. [12%] *N*,*N*-Dimethylethanolamine ($(CH_3)_2NCH_2CH_2OH$, DMEA, $M = 89.14$) is a Brønsted base whose conjugate acid, $DMEAH^+$, has a p$K_a = 9.22$ ($K_a = 6.0 \times 10^{-10}$). Acetic acid ($CH_3COOH$, $M = 60.05$) has a p$K_a = 4.75$ ($K_a = 1.8 \times 10^{-5}$).

a. Calculate $\Delta G°_{rxn}$ at 298 K for the acid-base reaction of DMEA with CH_3COOH.

A solution consisting of 7.84 g CH_3COOH and 107.17 g water is placed in a well-insulated (Dewar) flask. To this solution is added DMEA in small portions. After each portion of DMEA is added, the solution is stirred and the temperature measured with a digital thermometer. The data obtained are plotted at right. The solid line represents the best linear fit to the data with < 12 g added DMEA, the dashed line the average of the data with ≥ 12 g added DMMEA; both equations are given on the plot.

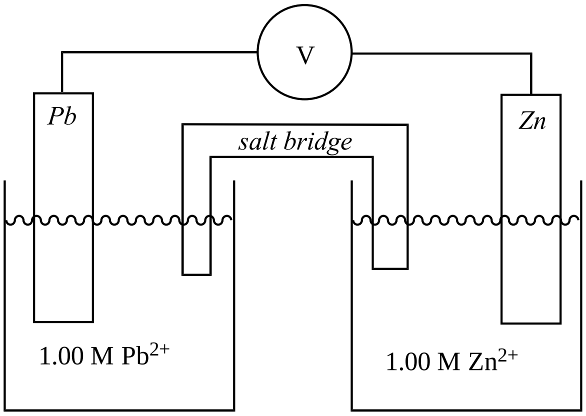


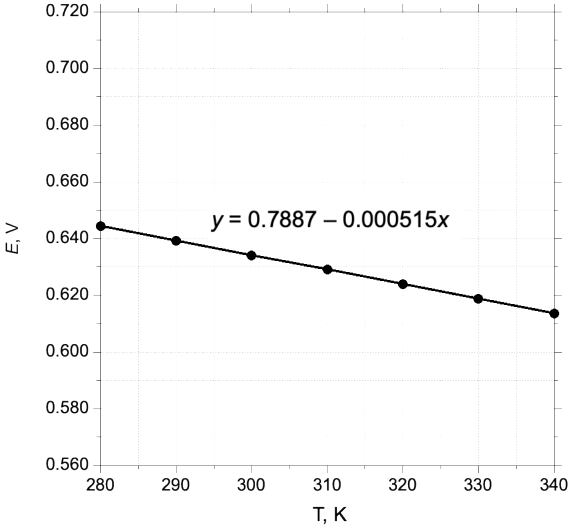
b. Calculate $\Delta H°_{rxn}$ for the reaction of DMEA with CH_3COOH. You may assume that all solutions have the same specific heat capacity as pure water.

c. Calculate $\Delta S°_{rxn}$ for the reaction of DMEA with CH_3COOH.

d. The $\Delta S°$ calculated in part c. is negative. What features of the reaction of DMEA with CH_3COOH cause it to have a negative entropy of reaction?

4. [12%] A galvanic cell is set up as follows and the cell potential measured as a function of temperature to give the graph shown.





a. Which electrode is the anode and which is the cathode?

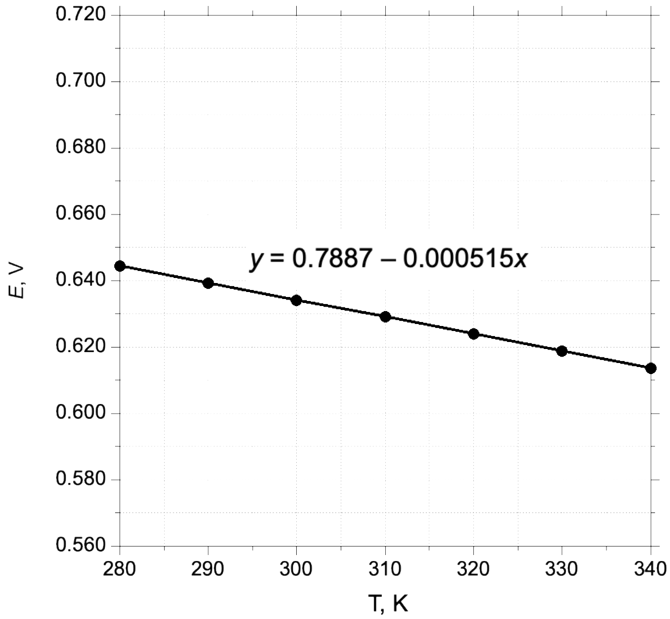
b. The standard reduction potential for $Zn^{2+}(aq)$ at 298 K is –0.762 V. What is the standard reduction potential for $Pb^{2+}(aq)$ at 298 K?

c. What are $\Delta G°$ (at 298 K), $\Delta H°$, and $\Delta S°$ for the reaction shown below?

$$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$$

d. Explain the sign of $\Delta S°$ for the reaction given in part c.

e. The temperature-dependence of the cell is remeasured with the same cell, except that the concentration of $Pb^{2+}(aq)$ in the left-hand compartment is changed to 0.100 M. Plot the results on the graph shown below (with the results shown from the standard cell given again for reference), and briefly justify your plot.



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. Carbon dioxide is bubbled through a saturated solution of barium hydroxide.

b. Potassium permanganate is mixed with iron(II) sulfate in dilute sulfuric acid.

c. Solid silver chloride is added to concentrated aqueous ammonia.

d. Phosphorus trichloride reacts with potassium chlorate.

e. *Para*-xylene (1,4-dimethylbenzene) is heated with a mixture of concentrated nitric and sulfuric acids.

f. Fluorine-18 emits a positron.

6. [13%] Oxygen has two stable allotropes, O_2 (dioxygen) and O_3 (ozone).

a. Explain why O_2 has a higher normal boiling point than either N_2 or F_2.

b. Explain why both atomic oxygen (O) and O_2 have two unpaired electrons in their ground states.

c. Molecular oxygen has an excited state with no unpaired electrons, which emits light with a wavelength of 1270 nm to return to the ground state. What is the energy (in kJ mol^{-1}) by which the excited state is higher than the ground state?

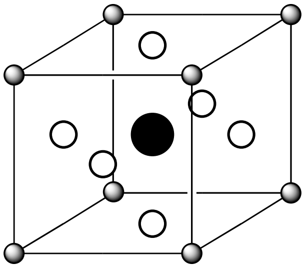
d. Explain why O_2 does not absorb light in the infrared region of the electromagnetic spectrum but O_3 does.

e. Dioxygen can be oxidized to form dioxygenyl cation (O_2^+) or reduced to form superoxide ion (O_2^-) or peroxide ion (O_2^{2-}), while ozone can be reduced to form ozonide ion (O_3^-). Among these six species, the O–O bond distances are 112 pm, 121 pm, 127 pm, 128 pm, 135 pm, and 154 pm. Fill in the table below by assigning the correct distances to the six species, and briefly justify your assignments. (You may consider 127 and 128 pm as essentially the same in this problem.)

Species	O–O distance, pm	Species	O–O distance, pm
O_2			
O_2^+		O_3	
O_2^-		O_3^-	
O_2^{2-}			

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

7. [14%] Cesium lead iodide, $CsPbI_3$, is of interest in solar photovoltaic cells. It adopts a structure called a *perovskite* whose cubic unit cell is shown below.



a. Which element corresponds to the small gray spheres, which to the medium sized white spheres, and which to the large black spheres?

• =

○ =

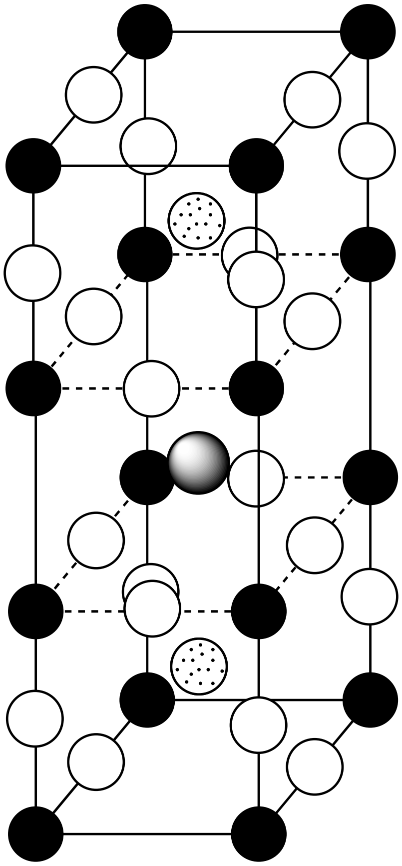
● =

b. Describe the coordination number and the identity of the nearest neighbor atoms for each of the types of atoms in $CsPbI_3$.

c. The length of the unit cell edge in $CsPbI_3$ is 628 pm. What is the density of $CsPbI_3$, in g cm^{-3}?

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

A mixed-metal oxide that is of interest in high-temperature superconductivity research, $YBa_2Cu_3O_7$, adopts a structure related to the perovskite structure. One unit cell of this structure is shown below.



d. Identify which elements correspond to the four types of spheres in the diagram.

◌ = ○ =

● = ◍ =

e. Give the oxidation numbers of each element in $YBa_2Cu_3O_7$.

f. The atoms represented by the black spheres have two different coordination geometries in the structure shown. What are the geometries? How is this observation related to the oxidation numbers you determined in part e?

8. [12%] Many organic compounds react with elemental halogens such as Br_2 or I_2.

a. Under appropriate conditions, 3-methylpentane will react with Br_2 to form a single monobromide with the formula $C_6H_{13}Br$. Give appropriate reaction conditions and the structural formula of the product.

b. Cyclohexene forms different products when reacted with Br_2 in water than when reacted in carbon tetrachloride. Give structural formulas for the products formed in the two solvents, including stereochemistry if relevant.

c. Benzene reacts with bromine in the presence of a Lewis acid catalyst. Give an example of a suitable catalyst and the structural formula of the major organic product of the reaction.

d. Cyclopentanone reacts with excess bromine in the presence of base to give a tetrabromide. Give a structural formula for the product and explain why the reaction does not give good yields of a monobromide product even when only one equivalent of Br_2 is used.

e. Acetophenone, $C_6H_5COCH_3$, reacts with excess iodine in the presence of aqueous sodium hydroxide to give a yellow precipitate and a water-soluble organic species. Give structural formulas for these two products.

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2025 USNCO Part 2 SOLUTIONS

1. a. M of $CuSO_4 \cdot 5\ H_2O = 249.70$, M of $CuSO_4 = 159.62$

   $(5.00\text{ g } CuSO_4 \cdot 5\ H_2O)/249.70\text{ g mol}^{-1} = 2.002 \times 10^{-2}\text{ mol } CuSO_4 \cdot 5\ H_2O$

   $2.002 \times 10^{-2}\text{ mol} \times 159.62\text{ g mol}^{-1} = 3.196\text{ g anhydrous } CuSO_4$

   b. Copper(II) is d^9 and is expected to show (weak) absorption of light regardless of its environment. Dehydration of copper(II) sulfate results in a change of ligands from water ligands to sulfate ligands. The blue color is due to absorption of red light at the extreme low-energy end of the visible spectrum. The change to the (weaker-field) sulfate ligands reduces the energy of the absorption into the near-infrared, so that visible light is not absorbed at all. This makes the solid appear white.

   c. The maximum absorption of light occurs at 763 nm, so that is the most sensitive wavelength to measure.

   d. The fingerprint will scatter light, increasing the apparent absorbance and thus the apparent amount of copper. This will mean that less mass will be ascribed to water, giving a smaller value of *n*.

   e. $2\ Cu^{2+}(aq) + 5\ I^-(aq) \rightarrow 2\ CuI(s) + I_3^-(aq)$

   f. The thiosulfate reacts with triiodide to form tetrathionate and iodide in the following balanced equation:

   $$2\ S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow S_4O_6^{2-}(aq) + 3\ I^-(aq)$$

   Since each 2 mol of Cu^{2+} produced one mol I_3^-, each mol of $S_2O_3^{2-}$ corresponds to one mol of Cu^{2+}:

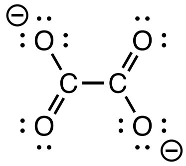
   $$(0.01720\text{ L } S_2O_3^{2-}) \times (0.0250\text{ mol L}^{-1}) = 4.30 \times 10^{-4}\text{ mol } S_2O_3^{2-} = 4.30 \times 10^{-4}\text{ mol } Cu^{2+}$$

   $$\{4.30 \times 10^{-4}\text{ mol } Cu(NO_3)_2\} \times (187.57\text{ g mol}^{-1}) = 0.0807\text{ g } Cu(NO_3)_2$$

   $$0.1000\text{ g hydrated } Cu(NO_3)_2 - 0.0807\text{ g anhyd. } Cu(NO_3)_2 = 0.0193\text{ g } H_2O$$

   $$(0.0193\text{ g } H_2O)/(18.02\text{ g mol}^{-1}) = 1.07 \times 10^{-3}\text{ mol } H_2O$$

   $$n = (1.07 \times 10^{-3}\text{ mol } H_2O)/(4.30 \times 10^{-4}\text{ mol Cu}) = 2.50$$

2. a. 

b. If the molar solubility is S, then $[Ca^{2+}] = [C_2O_4^{2-}] = S$

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = S^2 = 2.7 \times 10^{-9}$$

$$S = 5.2 \times 10^{-5} \text{ mol L}^{-1}$$

c.
$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = [0.100][C_2O_4^{2-}] = 2.7 \times 10^{-9}$$

$$[C_2O_4^{2-}] = 2.7 \times 10^{-8} \text{ mol L}^{-1}$$

Since all the oxalate comes from the dissolving calcium oxalate, this is the solubility.

d. Since all the calcium oxalate has dissolved, $[Ca^{2+}] = 0.100$ M. Since it has just dissolved, the K_{sp} expression is valid, and $[C_2O_4^{2-}] = 2.7 \times 10^{-8}$ mol L^{-1} as in part b.

The total amount of oxalate, $[C_2O_4^{2-}] + [HC_2O_4^{-}] + [H_2C_2O_4]$, must add up to 0.100 M. Since so little of it is $C_2O_4^{2-}$, we will assume that almost all of it is doubly protonated, so $[H_2C_2O_4] \approx 0.100$ M. We can relate the concentration of $C_2O_4^{2-}$ to that of $H_2C_2O_4$ by combining the two K_a equilibria:

$$\begin{array}{ll} H_2C_2O_4 \rightleftharpoons HC_2O_4^{-} + H^{+} & K_{eq} = K_{a1} = 0.054 \\ \underline{HC_2O_4^{-} \rightleftharpoons C_2O_4^{2-} + H^{+}} & \underline{K_{eq} = K_{a2} = 5.2 \times 10^{-5}} \\ H_2C_2O_4 \rightleftharpoons C_2O_4^{2-} + 2\,H^{+} & K_{eq} = K_{a1}K_{a2} = 2.8 \times 10^{-6} \end{array}$$

$$\frac{[C_2O_4^{2-}][H^+]^2}{[H_2C_2O_4]} = \frac{[2.7 \times 10^{-8}][H^+]^2}{[0.100]} = 2.8 \times 10^{-6}$$

$$[H^+] = 3.2 \text{ M}$$

$$pH = -\log_{10}[H^+] = -0.51$$

At this pH, about 1 part in 60 of the oxalate is in the form of $HC_2O_4^{-}$, so our assumption about the concentration of $H_2C_2O_4$ is indeed valid.

e. To achieve this concentration of H^+, one would need to add 3.2 mol HCl, plus 0.2 mol more to protonate the 0.1 mol of $C_2O_4^{2-}$, for a total of 3.4 mol.

f. Addition of $HC_2O_4^{-}$ cannot increase the solubility of calcium oxalate, since it cannot decrease the oxalate concentration by protonating it (since that would just replace the oxalate with another mole of oxalate!). It might be able to decrease the solubility by the common ion effect. To see if this is significant, we can calculate the concentration of $C_2O_4^{2-}$ in the 0.100 M $HC_2O_4^{-}$ solution. The major way this is formed is by deprotonation of $HC_2O_4^{-}$ by itself:

$$\begin{array}{ll} HC_2O_4^{-} + H^{+} \rightleftharpoons H_2C_2O_4 & K_{eq} = 1/K_{a1} = 18.6 \\ \underline{HC_2O_4^{-} \rightleftharpoons C_2O_4^{2-} + H^{+}} & \underline{K_{eq} = K_{a2} = 5.2 \times 10^{-5}} \\ 2\ HC_2O_4^{-} \rightleftharpoons C_2O_4^{2-} + H_2C_2O_4 & K_{eq} = K_{a2}/K_{a1} = 9.8 \times 10^{-4} \end{array}$$

$$\frac{[C_2O_4^{2-}][H_2C_2O_4]}{[HC_2O_4^{-}]^2} = \frac{[x]^2}{[0.100 - 2x]^2} = 9.8 \times 10^{-4}$$

$$\frac{[x]}{[0.100 - 2x]} = 0.031$$

$$x = 2.9 \times 10^{-3} = [C_2O_4^{2-}]$$

Since this is 56 times larger than the oxalate concentration when CaC_2O_4 is dissolved in pure water (see part b), the common ion effect will significantly decrease the solubility of calcium oxalate in the $NaHC_2O_4$ solution compared to pure water.

3. a. Reaction is $\mathrm{DMEA}(aq) + \mathrm{CH_3COOH}(aq) \rightarrow \mathrm{DMEAH^+}(aq) + \mathrm{CH_3COO^-}(aq)$

$$K_{\mathrm{eq}} = (K_\mathrm{a} \text{ of } \mathrm{CH_3COOH})/(K_\mathrm{a} \text{ of } \mathrm{DMEAH^+}) = (1.8 \times 10^{-5})/(6.0 \times 10^{-10})$$

$$K_{\mathrm{eq}} = 3.0 \times 10^4$$

$$\Delta G^\circ = -RT\ln(K_{\mathrm{eq}}) = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})\ln(3.0 \times 10^4)$$

$$\Delta G^\circ = -25500 \text{ J mol}^{-1} = -25.5 \text{ kJ mol}^{-1}$$

b. At the intersection point, $1.141x + 19.03 = 31.84$, so $x = 11.23$ g DMEA

$$\text{At this point, } q_{\mathrm{rxn}} = -q_{\mathrm{H2O}} = -mC_\mathrm{p}\Delta T$$

$$= -(7.84 \text{ g} + 107.17 \text{ g} + 11.23 \text{ g})(4.184 \text{ J mol}^{-1} \text{ K}^{-1})(31.84 \text{ °C} - 19.03 \text{ °C})$$

$$q_{\mathrm{rxn}} = -6766 \text{ J}$$

$$\Delta H^\circ_{\mathrm{rxn}} = q_{\mathrm{rxn}}/(\text{mol reacted})$$

At this point the number of moles of both reagents are equal; mol $\mathrm{CH_3COOH}$ reacted = (7.84 g)/(60.05 g mol^{-1}) = 0.131 mol.

$$\Delta H^\circ_{\mathrm{rxn}} = -6766 \text{ J}/(0.131 \text{ mol}) = -51600 \text{ J mol}^{-1} = -51.6 \text{ kJ mol}^{-1}$$

c.

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

$$-25500 \text{ J mol}^{-1} = -51600 \text{ J mol}^{-1} - (298 \text{ K})\Delta S^\circ$$

$$\Delta S^\circ = -87.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

d. The reaction produces two charged particles from two neutral ones. Charged species in aqueous solution are strongly solvated by the water, which significantly constrains the orientations of the solvent molecules around the ions. This decreases the number of ways the solvent molecules can be arranged and so decreases the entropy.

4. a. The Zn electrode is the anode and the Pb electrode is the cathode.

   b. At 298 K the (standard) cell potential is (0.7887 V) – (0.000515 V K^{-1})(298 K) = 0.635 V.

$$E°(\mathrm{Pb}^{2+}/\mathrm{Pb}) - E°(\mathrm{Zn}^{2+}/\mathrm{Zn}) = E°_{\mathrm{cell}}$$

$$E°(\mathrm{Pb}^{2+}/\mathrm{Pb}) - (-0.762\ \mathrm{V}) = 0.635\ \mathrm{V}$$

$$E°(\mathrm{Pb}^{2+}/\mathrm{Pb}) = -0.127\ \mathrm{V}$$

   c. $\Delta G° = -nFE° = -2(96500\ \mathrm{J\ V^{-1}\ mol^{-1}})(0.635\ \mathrm{V}) = -123\ \mathrm{kJ\ mol^{-1}}$

$$\Delta G° = \Delta H° - T\Delta S° = -nFE°$$

$$E° = -\Delta H°/nF + (\Delta S°/nF)(T)$$

   From the equation of the line,

$$\Delta H° = -nF(\text{intercept}) = -2(96500\ \mathrm{J\ V^{-1}\ mol^{-1}})(0.7887\ \mathrm{V}) = -152\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S° = nF(\text{slope}) = 2(96500\ \mathrm{J\ V^{-1}\ mol^{-1}})(-0.000515\ \mathrm{V\ K^{-1}}) = -99.4\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

   d. The Pb^{2+} ion is much larger and hence less tightly solvated than the Zn^{2+} ion, so it has a much more positive $S°$ value (10.5 J mol^{-1} K^{-1} compared to –112.1 J mol^{-1} K^{-1} for $Zn^{2+}(aq)$). Thus replacing Pb^{2+} in solution with Zn^{2+} results in a net ordering of the solvent molecules and a net decrease in entropy.

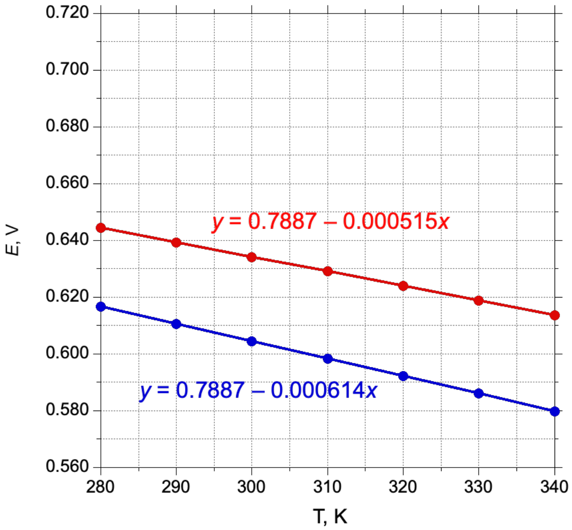
   e. Under nonstandard conditions, the Nernst equation indicates that

$$E = E° - (RT/nF)\ln([\mathrm{Zn}^{2+}]/[\mathrm{Pb}^{2+}])$$

$$E = E° - \{(8.314\ \mathrm{J\ mol^{-1}\ K^{-1}})/(2 \bullet 96500\ \mathrm{J\ mol^{-1}\ V^{-1}})\}\bullet\ln(10)\bullet T$$

$$E = E° - (9.92 \times 10^{-5}\ \mathrm{V\ K^{-1}})T$$

   So the graph will be a line with the original y-intercept but with a slope that is smaller (more negative) by 9.92×10^{-5} V K^{-1}. See blue line on the graph below.



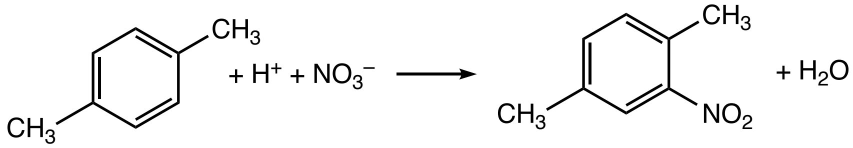
5. (Note that while phases are shown here for the sake of completeness, they are not required on the exam.)

   a. $Ba^{2+}(aq) + OH^{-}(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$

   b. $MnO_4^{-}(aq) + Fe^{2+}(aq) + H^{+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq) + H_2O(l)$

   c. $AgCl(s) + NH_3(aq) \rightarrow Ag(NH_3)_2^{+}(aq) + Cl^{-}(aq)$

   d. $PCl_3(l) + KClO_3(s) \rightarrow POCl_3(l) + KCl(s)$

   e. 

   f. $^{18}F \rightarrow {}^{18}O + \beta^{+}$

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6. a. In these nonpolar diatomic molecules, the only intermolecular forces are London dispersion forces. These interactions increase in strength with increasing numbers of electrons and with increasing polarizability of the electrons. O_2 has two more electrons than N_2, so it is expected that its boiling point will increase. The fact that F_2 has a lower boiling point must indicate that its electrons are less polarizable than those in O_2. This is characteristic of fluorine-containing molecules and is due to F's extremely high electronegativity resulting in a very low polarizability of its electrons.

   b. The ground-state electron configuration of atomic O is $1s^2 2s^2 2p^4$. Four electrons occupy the three $2p$ orbitals, so by Hund's rule, the lowest-energy configuration has two half-filled orbitals with electron spins aligned.

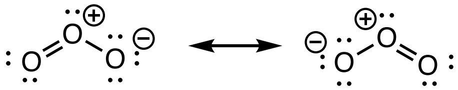
   In O_2, the occupied molecular orbitals are $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2px})^2(\pi_{2py})^2(\pi^*_{2px})^1(\pi^*_{2py})^1$. Again, with two electrons occupying the two degenerate π^* orbitals, the lowest-energy configuration has the two electrons with the same spin in different orbitals.

   c. $E = hc/\lambda$

   $E = (6.626 \times 10^{-34}\text{ J s})(2.998 \times 10^{8}\text{ m s}^{-1})/(1.270 \times 10^{-6}\text{ m}) = 1.564 \times 10^{-19}\text{ J}$

   This is the energy of one photon, the energy of a mole of photons is $(1.564 \times 10^{-22}\text{ kJ}) \times (6.022 \times 10^{23}\text{ mol}^{-1}) = 94.19\text{ kJ mol}^{-1}$

   d. To absorb light in the IR, a molecule must have a molecular vibration that causes a change in the molecule's dipole moment. O_2 has only one possible vibration (stretching the O–O bond), but that does not cause the dipole moment to change from zero. O_3 has three possible vibrations (symmetric stretch, asymmetric stretch, and bend). Because of the unsymmetrical distribution of charge in the molecule (see Lewis structures below), all of these motions cause a change in the dipole moment, so O_3 absorbs at three fundamental frequencies in the IR region (701, 1042, and 1103 cm^{-1}).



   e. According to the MO configuration in part b, the bond order in O_2 is 2.0. Electrons are added to or removed from π^* orbitals, so O_2^+ has a bond order of 2.5 while O_2^- has a bond order of 1.5 and O_2^{2-} a bond order of 1.0. The Lewis structure of O_3 (see part d) indicates that there are two O–O σ bonds and one O–O π bond, so the overall bond order is 1.5 (same as that of superoxide). The extra electron in ozonide is added to a π^* orbital, reducing the overall π bond order from 1.0 to 0.5. With the two σ bonds, this means that there are a total of 2.5 bonds distributed over the two O-O bonds, giving an O–O bond order of 1.25. Aligning the stated bond lengths with these bond orders gives the assignments in the table.

Species	O–O distance, pm	Species	O–O distance, pm
O_2	121		
O_2^+	112	O_3	127
O_2^-	128	O_3^-	135
O_2^{2-}	154		

7. a. There are 3 white spheres per unit cell, so that must be I. The coordination number of the gray spheres is 12 while that of the black spheres is 6, which is most appropriate for Cs and Pb, respectively.

◉ =	Cs
○ =	I
● =	Pb

b. Pb: coordination = 6 I atoms

Cs: coordination = 12 I atoms

I: coordination = 2 Pb atoms [the Cs–I distances are longer]

c. Unit cell volume = $(628 \times 10^{-10}\ \text{cm})^3 = 2.48 \times 10^{-22}\ \text{cm}^3$

One $CsPbI_3$ formula unit per unit cell, mass = $(720.8\ \text{g mol}^{-1})/(6.022 \times 10^{23}\ \text{mol}^{-1}) = 1.197 \times 10^{-21}\ \text{g}$

Density = $(1.197 \times 10^{-21}\ \text{g})/(2.48 \times 10^{-22}\ \text{cm}^3) = 4.83\ \text{g cm}^{-3}$

d. The elements can be assigned by the stoichiometry of the types of spheres in the unit cell.

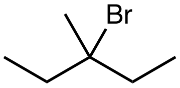
◌ = Ba ○ = O

● = Cu ◍ = Y

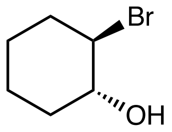
e. Y = +3, Ba = +2, O = –2. This means that Cu = +2.33 on average.

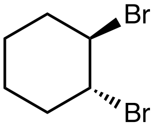
f. The Cu atoms in the middle of the unit cell are square pyramidal, while the Cu atoms on the top and bottom faces are square planar. The ratio of square pyramidal : square planar sites is 2:1. This corresponds to the two different oxidation states (two Cu(II), one Cu(III)) in the formula. Chemically, Cu(II) is often square pyramidal, while Cu(III) forms shorter bonds and is almost always square planar. So the different oxidation states are localized in the different copper sites in the crystal.

8. a. 3-bromo-3-methylpentane will be formed selectively under free radical conditions. These could be provided either by photolysis or by using a free radical initiator such as benzoyl peroxide.

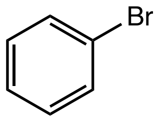


b. In water, the bromohydrin is formed, while the dibromide is formed in CCl_4. In both cases, the compounds have a *trans* stereochemistry (both as racemic mixtures, only one enantiomer of each compound is shown below).

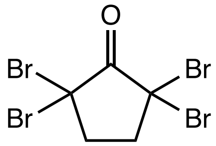




c. The product is bromobenzene. Typical Lewis acids used are $AlBr_3$ or $FeBr_3$.



d.



The reaction proceeds by rate-limiting deprotonation of the ketone at the alpha position to form an enolate, which subsequently reacts with Br_2 to form the bromoketone. Because the monobromoketone is more acidic than cyclopentanone itself, the initial product is more reactive than the starting material, leading to extensive polybromination. The tetrabromide can be formed selectively because it no longer has any acidic alpha hydrogens adjacent to the ketone.

e. This is the iodoform reaction. After iodination of the methyl group (similar to the bromination in part d), hydroxide can add to the electrophilic carbonyl and eject CI_3^-, a (relatively) stable carbanion. Protonation of this carbanion gives CHI_3, which precipitates as a yellow solid. The other product is benzoic acid, which is immediately deprotonated by the excess hydroxide, giving the soluble carboxylate salt sodium benzoate: