

# 2018 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

**Part II** of this test requires that student answers be written in a response booklet with blank pages. Only this "Blue Book" is graded for a score on **Part II**. Testing materials, scratch paper, and the "Blue Book" should be made available to the student only during the examination period. All testing materials including scratch paper should be turned in and kept secure until **April 23, 2018**, 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.

<b>Part I</b>	<b>60 questions</b>	<b>single-answer multiple-choice</b>	<b>1 hour, 30 minutes</b>
<b>Part II</b>	<b>8 questions</b>	<b>problem-solving, explanations</b>	<b>1 hour, 45 minutes</b>
<b>Part III</b>	<b>2 lab questions</b>	<b>laboratory practical</b>	<b>1 hour, 30 minutes</b>

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 in the spaces provided on the "Blue Book" cover. (Be sure to use the same identification number that was coded onto your Scantron sheet for **Part I**.) Answer all of the questions in order, and use both sides of the paper. Use separate sheets for scratch paper and do **not** attach your scratch paper to this examination. When you complete **Part II** (or at the end of one hour and forty-five minutes) you must turn in all testing materials, scratch paper, and your "Blue Book". **Do not forget to turn in your U.S. citizenship/Green Card Holder statement before leaving the testing site today.**

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

CONSTANTS
$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$
$F = 96,500 \text{ C mol}^{-1}$
$F = 96,500 \text{ J V}^{-1} \text{ mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J s}$
$c = 2.998 \times 10^8 \text{ m s}^{-1}$
$0 \text{ }^\circ\text{C} = 273.15 \text{ K}$
1 atm = 1.013 bar = 760 mm Hg
Specific heat capacity of H <sub>2</sub> O = $4.184 \text{ J g}^{-1} \text{ K}^{-1}$

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

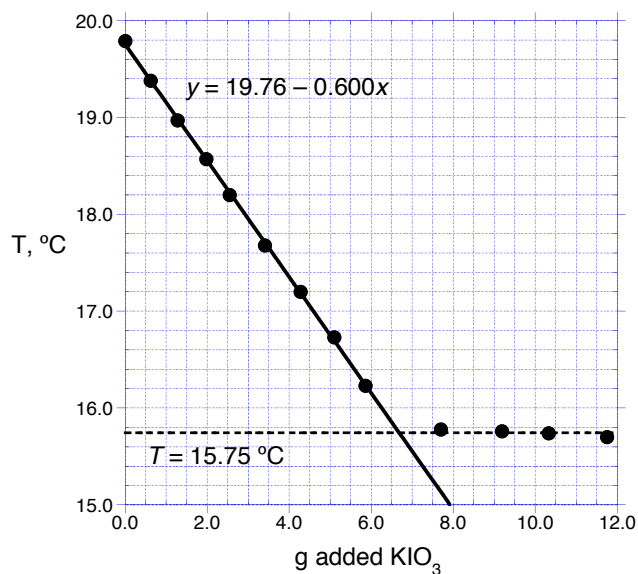
1	PERIODIC TABLE OF THE ELEMENTS																18
1A																	8A
1 <b>H</b> 1.008	2 <b>He</b> 4.003																
3 <b>Li</b> 6.941	4 <b>Be</b> 9.012															10 <b>Ne</b> 20.18	
11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31	13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95										
19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.88	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.97	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80
37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.95	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3
55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	57 <b>La</b> 138.9	72 <b>Hf</b> 178.5	73 <b>Ta</b> 180.9	74 <b>W</b> 183.8	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 <b>Tl</b> 204.4	82 <b>Pb</b> 207.2	83 <b>Bi</b> 209.0	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)
87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89 <b>Ac</b> (227)	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 <b>Ds</b> (281)	111 <b>Rg</b> (272)	112 <b>Cn</b> (285)	113 <b>Nh</b> (286)	114 <b>Fl</b> (289)	115 <b>Mc</b> (289)	116 <b>Lv</b> (293)	117 <b>Ts</b> (294)	118 <b>Og</b> (294)

58 <b>Ce</b> 140.1	59 <b>Pr</b> 140.9	60 <b>Nd</b> 144.2	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.4	63 <b>Eu</b> 152.0	64 <b>Gd</b> 157.3	65 <b>Tb</b> 158.9	66 <b>Dy</b> 162.5	67 <b>Ho</b> 164.9	68 <b>Er</b> 167.3	69 <b>Tm</b> 168.9	70 <b>Yb</b> 173.0	71 <b>Lu</b> 175.0
90 <b>Th</b> 232.0	91 <b>Pa</b> 231.0	92 <b>U</b> 238.0	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)

1. [13%] An unknown monoprotic acid contains only the elements C, H, and O.
- Combustion analysis indicates that the unknown acid contains 40.0% C and 6.7% H by mass. What is its empirical formula?
  - A 1.000 g sample of the compound is dissolved in 50 mL water and titrated with 0.3000 M NaOH to a phenolphthalein endpoint, which is observed after the addition of 37.00 mL of base. What is the molar mass of the acid and what is its molecular formula?
  - The pH of the titration mixture is measured to be 3.43 after the addition of 10.00 mL of the NaOH solution. What is the  $pK_a$  of the unknown acid?
  - A different monoprotic acid with the same molar mass is titrated under the same conditions and the pH of the solution is measured after the addition of 40.00 mL NaOH solution. Explain why this measurement will not be informative about the  $pK_a$  of this acid, and estimate the pH at this point in the titration.
  - An aqueous solution of the unknown acid was found to rotate the plane of polarization of plane-polarized light (at the sodium D line). Suggest a reasonable structure for the unknown acid.
2. [12%] Potassium iodate ( $KIO_3$ ,  $M = 214.0$ ) dissolves to a limited extent in water:

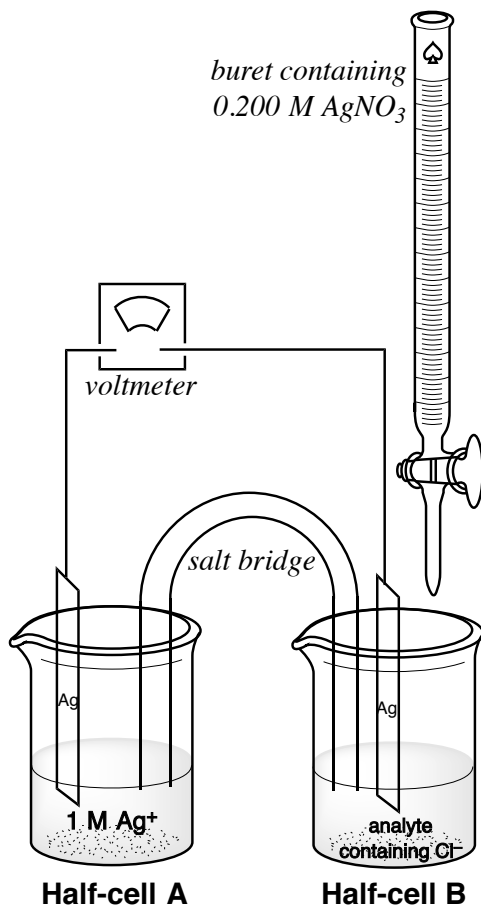


To 100.67 g water in a well-insulated container were added small portions of solid  $KIO_3$ . After each addition, the mixture was stirred extensively until the temperature stabilized. The temperatures, measured as a function of the added mass of  $KIO_3$ , are shown as solid dots below. A best-fit line through the data points below 6 g  $KIO_3$  added is given for your convenience. (You may assume that the specific heat capacity and density of the solution are the same as that of pure water at all times during the experiment and may neglect the heat capacity of the insulated container.)



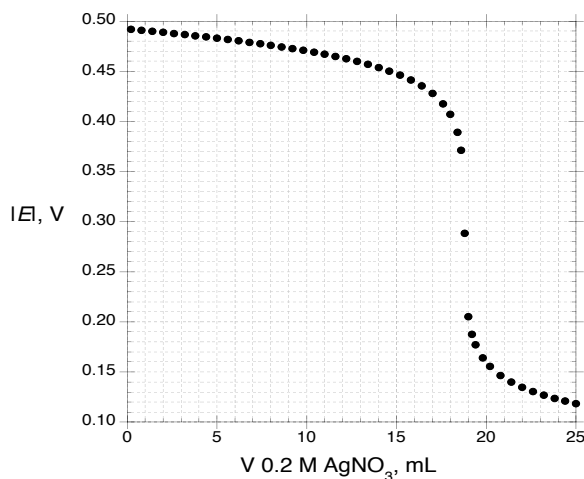
- Calculate  $K_{sp}$  for  $KIO_3$  (that is,  $K_{eq}$  for the dissolution reaction given above).
- Calculate  $\Delta H^\circ$  for the dissolution reaction of  $KIO_3$ .
- Calculate  $\Delta S^\circ$  for the dissolution reaction of  $KIO_3$ .
- One might expect dissolution reactions of ionic solids to invariably take place with large positive  $\Delta S^\circ$  values, since an ordered solid is forming mobile ions in solution. In fact,  $\Delta S^\circ$  values for such reactions are often small in magnitude and are frequently negative. Explain why.

3. [12%] The amount of chloride in an unknown sample can be determined by potentiometric titration, which uses an electrochemical cell shown schematically below:



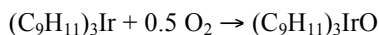
- a. During the titration, when some of the 0.200 M AgNO<sub>3</sub> solution has been added to the analyte, which half-cell (A or B) contains the anode of the electrochemical cell? Explain your reasoning.

A saline solution, consisting of NaCl dissolved in 5% dextrose solution, is analyzed using this technique. 100.0 g of the saline solution is placed in half-cell B and the voltage from the voltmeter is recorded as a function of the volume of added 0.200 M AgNO<sub>3</sub>:

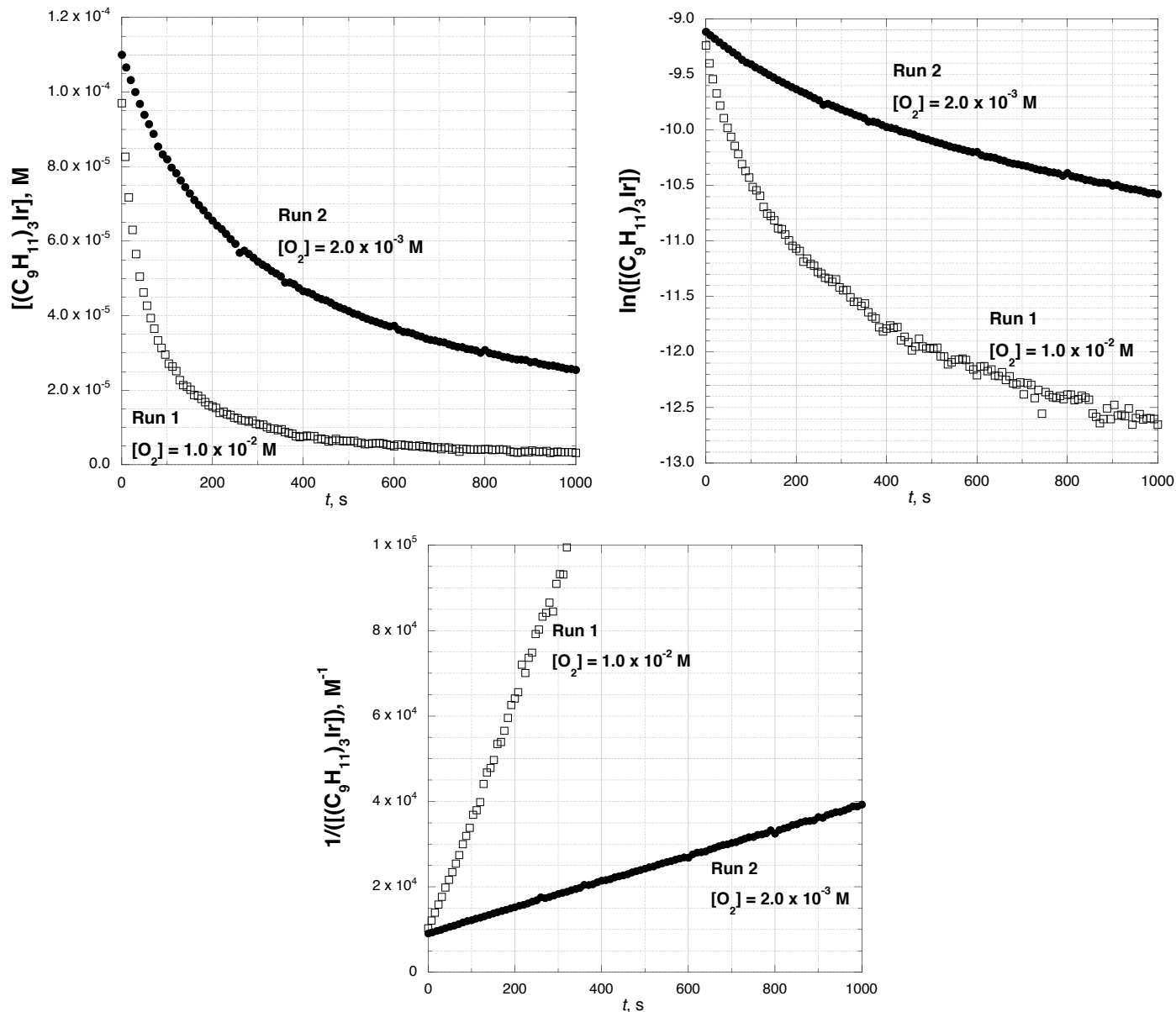


- b. Calculate the mass percentage of NaCl in the saline solution.  
 c. Calculate the concentration of free silver ion in half-cell B when 10.00 mL of titrant has been added.  
 d. Calculate the  $K_{sp}$  of AgCl(s).

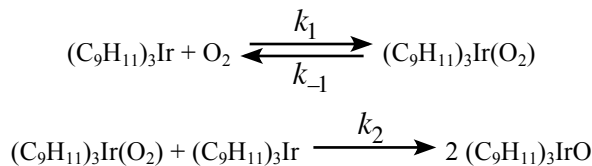
4. [12%] The air oxidation of an organoiridium compound  $(C_9H_{11})_3Ir$  takes place according to the following equation:



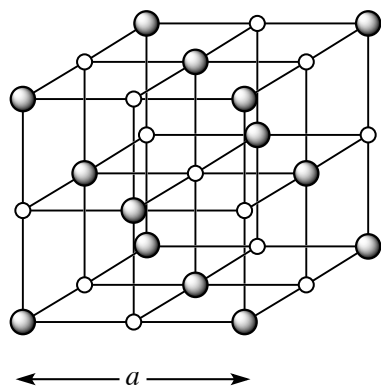
The reaction was studied with the initial  $[(C_9H_{11})_3Ir] = 1.3 \times 10^{-4} M$  under two different  $O_2$  concentrations (run 1,  $[O_2] = 1.0 \times 10^{-2} M$ ; run 2,  $[O_2] = 2.0 \times 10^{-3} M$ ). The concentration of  $(C_9H_{11})_3Ir$  was measured as a function of time; below are plotted  $[(C_9H_{11})_3Ir]$ ,  $\ln[(C_9H_{11})_3Ir]$ , and  $1/[(C_9H_{11})_3Ir]$  vs. time.



- Is the order of the reaction in  $(C_9H_{11})_3Ir$  0, 1, or 2? Justify your answer. (Even if the data are not exactly consistent with an integer order, pick the closest integer order.)
- Is the order of the reaction in  $O_2$  0, 1, or 2? Justify your answer. (Even if the data are not exactly consistent with an integer order, pick the closest integer order.)
- Calculate the rate constant for the reaction.
- The following mechanism has been proposed. Is the mechanism consistent with the observed rate law? Explain your reasoning.

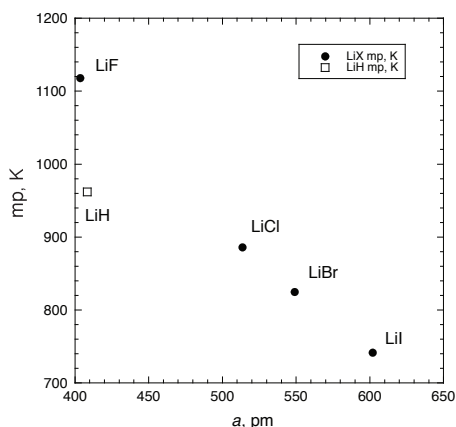


5. [12%] Write net equations for each of the reactions below. Use appropriate ionic and molecular formulas and omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the equations.
- A solution of acetic acid (ethanoic acid) is added to solid cadmium hydroxide.
  - Phosphorus tribromide and water are mixed.
  - Hydrogen sulfide gas is passed into a solution of nickel(II) perchlorate.
  - A mixture of manganese(IV) oxide and concentrated hydrochloric acid is heated.
  - Calcium carbonate is added to aqueous hydrofluoric acid.
  - A mixture of benzene with concentrated nitric and sulfuric acids is carefully heated.
6. [14%] The binary compounds of lithium  $\text{LiX}$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{and I}$ ) all crystallize in the cubic lattice known as the rock salt or  $\text{NaCl}$  lattice. One unit cell of this structure (small circles =  $\text{Li}$ , large circles =  $\text{X}$ ) is shown below. The length of the edge of the unit cell is abbreviated  $a$ .



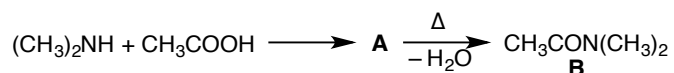
Compound	$a$ , pm
$\text{LiH}$	408.3
$\text{LiF}$	403.5
$\text{LiCl}$	513.6
$\text{LiBr}$	548.9
$\text{LiI}$	601.9

- Calculate the density of  $\text{LiCl}$ ,  $a = 513.6$  pm.
- Carbon-hydrogen bonds are invariably shorter than carbon-fluorine bonds (e.g., 108.7 pm in  $\text{CH}_4$  vs. 132.3 pm in  $\text{CF}_4$ ). However, the  $\text{Li-H}$  distances in  $\text{LiH}$  are actually slightly longer than the  $\text{Li-F}$  distances in  $\text{LiF}$ . Explain why.
- The  $a$  values of the lithium halides increase monotonically but not steadily with increasing period: The increase from fluoride to chloride is the largest, with the increase from chloride to bromide the smallest and the increase from bromide to iodide intermediate in size. Explain this pattern. What would you predict about the magnitude of the increase in  $a$  from  $\text{LiI}$  to  $\text{LiAt}$ ?
- The melting points of the lithium halides (filled circles) and of lithium hydride (open square) are graphed as a function of the unit cell edge length  $a$  below. Explain the correlation observed among the lithium halides between  $a$  value and melting point.



- The melting point of lithium hydride deviates from the value expected based on the correlation shown by the lithium halides. Explain this deviation.

7. [12%] Nitrogen forms a wide variety of binary oxides.
- What is the bond order in nitric oxide, NO? Explain your answer.
  - NO has one unpaired electron; is it principally located on nitrogen or on oxygen? Justify your answer.
  - The ionization energy of atomic N(g) is 1400 kJ mol<sup>-1</sup>. Is the ionization energy of NO(g) greater than or less than 1400 kJ mol<sup>-1</sup>? Justify your answer.
  - The molecule N<sub>2</sub>O<sub>3</sub> has been observed in two structurally isomeric forms. Draw Lewis structures of these two isomers.
8. [13%] Amides are an important class of compounds that can be formed from carboxylic acids and amines.
- Account for the following two experimental observations on the basis of structure and bonding.
    - Acetic acid, CH<sub>3</sub>COOH, is a stronger acid than ethanol, CH<sub>3</sub>CH<sub>2</sub>OH.
    - Dimethylamine, (CH<sub>3</sub>)<sub>2</sub>NH, is a stronger base than diphenylamine, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH.
  - When dimethylamine and acetic acid are mixed, they form a solid compound **A**, which upon strong heating loses water and forms the amide *N,N*-dimethylacetamide (**B**). What is the structure of the intermediate **A**?



- Experimental measurements such as those using nuclear magnetic resonance (NMR) spectroscopy indicate that all three CH<sub>3</sub> groups in *N,N*-dimethylacetamide are in distinct chemical environments, with exchange between any of these environments being very slow at room temperature. Explain this observation.
- Strong bases deprotonate *N,N*-dimethylacetamide to give an anion, C<sub>4</sub>H<sub>8</sub>NO<sup>-</sup>, while strong acids protonate *N,N*-dimethylacetamide to give a cation, C<sub>4</sub>H<sub>10</sub>NO<sup>+</sup>. Draw Lewis structures of the conjugate base and conjugate acid of *N,N*-dimethylacetamide, including formal charges and all major resonance structures if relevant.

## 2018 USNCO Part II Exam Answers

1. a. 1.000 g of the acid would contain 0.400 g C, 0.067 g H, and (by difference) 0.533 g O.

$$0.400 \text{ g C} / (12.01 \text{ g mol}^{-1}) = 0.0333 \text{ mol C}$$

$$0.067 \text{ g H} / (1.008 \text{ g mol}^{-1}) = 0.0665 \text{ mol H}$$

$$0.533 \text{ g O} / (16.00 \text{ g mol}^{-1}) = 0.0333 \text{ mol O}$$

So the empirical formula is  $\text{CH}_2\text{O}$ .

- b.  $0.03700 \text{ L titrant} \times 0.3000 \text{ mol L}^{-1} = 0.01110 \text{ mol NaOH} = 0.01110 \text{ mol unknown}$   
 $1.000 \text{ g unknown} / 0.01110 \text{ mol unknown} = 90.09 \text{ g mol}^{-1}$

Since the formula mass of  $\text{CH}_2\text{O}$  is  $30.03 \text{ g mol}^{-1}$ , there must be three formula units per molecule; the molecular formula is thus  $\text{C}_3\text{H}_6\text{O}_3$ .

- c. After 10.00 mL base have been added 10.0/37.0 of the acid has been deprotonated, while 27.0/37.0 remains protonated. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log_{10}([\text{X}^-]/[\text{HX}])$$

$$3.43 = \text{p}K_a + \log_{10}(10/27)$$

$$\text{p}K_a = 3.86$$

- d. Since this acid is also monoprotic and has the same molar mass, the endpoint will also be at 37.00 mL added base. Thus, at 40.00 mL added NaOH, essentially all the original acid will have been deprotonated, and the pH will be determined by the amount of excess NaOH added.

Specifically, 3.00 mL excess base will have been added

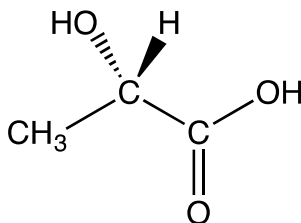
$$0.00300 \text{ L} \times 0.3000 \text{ mol L}^{-1} = 9.00 \times 10^{-4} \text{ mol excess OH}^-$$

$$\text{Total volume} = 50 \text{ mL original} + 40 \text{ mL added} = 90 \text{ mL}$$

$$[\text{OH}^-] = 9.00 \times 10^{-4} \text{ mol} / 0.090 \text{ L} = 1.0 \times 10^{-2} \text{ M}$$

$$\text{pH} = 14.0 + \log_{10}[\text{OH}^-] = 12.0$$

- e. Since a solution of the unknown acid rotates plane-polarized light, the acid must be chiral. An organic acid with a  $\text{p}K_a = 3.86$  and a formula of  $\text{C}_3\text{H}_6\text{O}_3$  must contain a carboxylic acid,  $-\text{COOH}$ . The only chiral carboxylic acid with this formula is lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , though of course one cannot determine which enantiomer is present from the given data.





2. a. The  $\text{KIO}_3$  stops dissolving when the temperature stops changing, i.e. at the intersection of the solid and dashed lines. The position of this intersection can be found by reading the graph, or by setting the equations of the two lines equal to one another:

$$19.76 - 0.600x = 15.75$$

$$x = 6.68 \text{ g KIO}_3 \text{ to make a saturated solution}$$

$$6.68 \text{ g KIO}_3 / (214.0 \text{ g mol}^{-1}) = 0.0312 \text{ mol KIO}_3$$

$$[\text{K}^+] = [\text{IO}_3^-] = 0.0312 \text{ mol} / (0.10067 \text{ L} + 0.00668 \text{ L}) = 0.291 \text{ M}$$

In the saturated solution, the dissolution reaction is at equilibrium:

$$K_{\text{eq}} = K_{\text{sp}} \text{ of KIO}_3 = [\text{K}^+][\text{IO}_3^-] = [0.291]^2 = 0.0846$$

b.  $q_{\text{solution}} = mC_p\Delta T = (107.39 \text{ g solution})(4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1})(15.75 \text{ }^\circ\text{C} - 19.76 \text{ }^\circ\text{C})$

$$q_{\text{solution}} = -1.80 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = q_{\text{rxn}} / (\text{mol reacted}) = -q_{\text{solution}} / (0.0312 \text{ mol}) = +57.8 \text{ kJ mol}^{-1}$$

- c. The temperature is not strictly constant in the experiment, but it is reasonable to use the average temperature of the experiment,  $18 \text{ }^\circ\text{C} = 291 \text{ K}$ .

$$\Delta G^\circ = -RT \ln(K_{\text{eq}}) = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(291 \text{ K}) \ln(0.0846)$$

$$\Delta G^\circ_{291 \text{ K}} = 5.98 \text{ kJ mol}^{-1}$$

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

$$5980 \text{ J mol}^{-1} = 57800 \text{ J mol}^{-1} - (291 \text{ K})(\Delta S^\circ)$$

$$\Delta S^\circ = +178 \text{ J mol}^{-1} \text{ K}^{-1}$$

- d. The increase in entropy on dissolving the highly constrained solid is counterbalanced by the decrease in degrees of freedom of the solvent. Ions in aqueous solution are surrounded by a solvent shell of water molecules that are strongly oriented by the charges on the ions and so have much smaller entropies than bulk water. This contributes a negative term to the overall change in entropy of the dissolution reaction. (In the case of  $\text{KIO}_3$ , the relatively large size and small charges on the ions means that this negative term is modest in magnitude; the overall entropy change of this dissolution is indeed rather positive.)

3. a. The concentration of  $\text{Ag}^+$  ion will always be smaller in half-cell B than it is in half-cell A (it cannot exceed  $0.2 \text{ M}$ !). Oxidation of the Ag electrode will take place in the half-cell with lower  $\text{Ag}^+$  concentration, so the anode is in half-cell B.

- b. The endpoint of the titration takes place at  $18.8 \text{ mL}$  added  $\text{AgNO}_3$ , so

$$\text{mol Cl}^- = (0.0188 \text{ L})(0.200 \text{ mol L}^{-1}) = 3.76 \times 10^{-3} \text{ mol}$$

$$(3.76 \times 10^{-3} \text{ mol NaCl})(58.44 \text{ g mol}^{-1}) = 0.220 \text{ g NaCl}$$

$$(0.220 \text{ g NaCl}) / (100.0 \text{ g saline}) \times 100\% = 0.22\% \text{ saline solution}$$

- c. At  $10.00 \text{ mL}$  added titrant, the absolute value of the cell potential is  $0.470 \text{ V}$ . From the Nernst equation:

$$E = E^\circ - (0.0591/n) \log([\text{Ag}^+]_{\text{sample}} / [\text{Ag}^+]_{\text{ref}})$$

$$0.470 \text{ V} = 0 \text{ V} - 0.0591 \cdot \log([\text{Ag}^+]_{\text{sample}} / [1])$$

$$[\text{Ag}^+] = 1.12 \times 10^{-8} \text{ M}$$

- d. At the point where 10.00 mL AgNO<sub>3</sub> has been added, essentially all the added silver ion (0.01000 L × 0.200 mol L<sup>-1</sup> = 2.00 × 10<sup>-3</sup> mol) has reacted to form AgCl(s) (since, according to part c, only about 10<sup>-9</sup> mol Ag<sup>+</sup> is still present in solution). Thus the remaining chloride ion concentration is

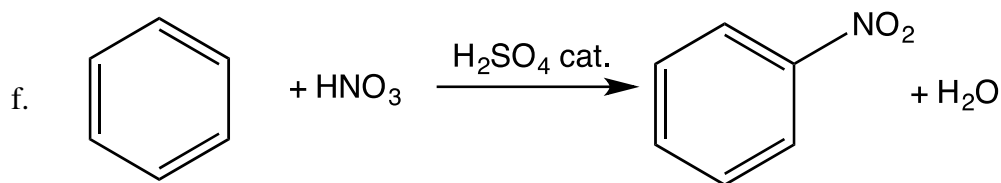
$$[\text{Cl}^-] = (3.76 \times 10^{-3} \text{ mol} - 2.00 \times 10^{-3} \text{ mol}) / (0.100 \text{ L} + 0.010 \text{ L}) = 0.016 \text{ M}$$

Since at this point there is some solid AgCl present, then

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = [1.12 \times 10^{-8}][0.016] = 1.8 \times 10^{-10}$$

Of course, there is nothing special about the 10.0-mL point in the titration; any point where the [Ag<sup>+</sup>] can be determined (from the cell potential) and the [Cl<sup>-</sup>] can be determined (from the un-precipitated amount) will work. But 10.0 mL is convenient since we already figured out [Ag<sup>+</sup>] in part c.

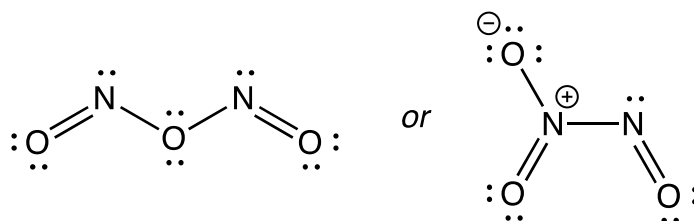
4. a. In each run, [O<sub>2</sub>] >> [(C<sub>9</sub>H<sub>11</sub>)<sub>3</sub>Ir], so [O<sub>2</sub>] is effectively constant during each run. So the order in Ir can be determined by seeing whether the [Ir] changes linearly with time (zeroth-order), whether ln([Ir]) changes linearly with time (first-order), or whether 1/[Ir] changes linearly with time (second-order). Clearly it is only the last of these that is true; the reaction must be second-order in (C<sub>9</sub>H<sub>11</sub>)<sub>3</sub>Ir.
- b. Since rate = k[O<sub>2</sub>]<sup>n</sup>[(C<sub>9</sub>H<sub>11</sub>)<sub>3</sub>Ir]<sup>2</sup>, we can see how the slope of the second-order plots (which are equal to k[O<sub>2</sub>]<sup>n</sup>) change with [O<sub>2</sub>]. The slope of run 1 ([O<sub>2</sub>] = 1.0 × 10<sup>-2</sup> M) is 280 M<sup>-1</sup>s<sup>-1</sup>, while the slope for run 2 ([O<sub>2</sub>] = 2.0 × 10<sup>-3</sup> M) is 31 M<sup>-1</sup>s<sup>-1</sup>. A decrease of [O<sub>2</sub>] by a factor of 5 results in a 9-fold decrease in rate. This is not particularly close to either n = 1 (should be a 5-fold decrease) or n = 2 (should be a 25-fold decrease), but it is closer to n = 1. (Numerically, n = log(9)/log(5) = 1.37; as directed by the instructions, this should be considered as the closest integer, n = 1.)
- c. If we use the data from run 1, k[O<sub>2</sub>] = k[1.0 × 10<sup>-2</sup> M] = 280 M<sup>-1</sup>s<sup>-1</sup>. So k for this overall third-order reaction is 2.8 × 10<sup>4</sup> M<sup>-2</sup>s<sup>-1</sup>. (Using run 2 gives k = 1.6 × 10<sup>4</sup> M<sup>-2</sup>s<sup>-1</sup>.)
- d. If step 1 is rate-determining, then Rate = k[O<sub>2</sub>][(C<sub>9</sub>H<sub>11</sub>)<sub>3</sub>Ir], which gives the wrong order in iridium. If step 2 is rate-determining, then Rate = k[(C<sub>9</sub>H<sub>11</sub>)<sub>3</sub>Ir]<sup>2</sup>[O<sub>2</sub>], which is consistent with the experimental data. So this mechanism is consistent with the data if the second step is rate-limiting (i.e., k<sub>2</sub>[(C<sub>9</sub>H<sub>11</sub>)<sub>3</sub>Ir] << k<sub>-1</sub>).
5. a. CH<sub>3</sub>COOH(aq) + Cd(OH)<sub>2</sub>(s) → Cd<sup>2+</sup>(aq) + CH<sub>3</sub>COO<sup>-</sup>(aq) + H<sub>2</sub>O(l)
- b. PBr<sub>3</sub>(l) + H<sub>2</sub>O(l) → H<sub>3</sub>PO<sub>3</sub>(aq) + H<sub>3</sub>O<sup>+</sup>(aq) + Br<sup>-</sup>(aq)
- c. Ni<sup>2+</sup>(aq) + H<sub>2</sub>S(aq) → NiS(s) + H<sup>+</sup>(aq)
- d. MnO<sub>2</sub>(s) + HCl(aq) → Mn<sup>2+</sup>(aq) + Cl<sub>2</sub>(g) + H<sub>2</sub>O(l)
- e. CaCO<sub>3</sub>(s) + HF(aq) → CaF<sub>2</sub>(s) + CO<sub>2</sub>(g) + H<sub>2</sub>O(l)



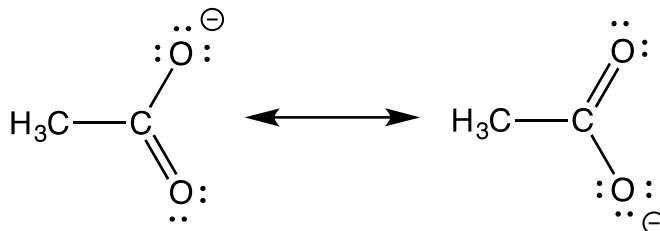
6. a. Volume of one unit cell =  $a^3 = (513.6 \text{ pm})^3 = (513.6 \times 10^{-10} \text{ cm})^3 = 1.355 \times 10^{-22} \text{ cm}^3$   
 Mass of one unit cell =  $4 \text{ LiCl} = 4(42.39 \text{ g mol}^{-1}) / (6.022 \times 10^{23} \text{ mol}^{-1}) = 2.816 \times 10^{-22} \text{ g}$   
 Density =  $(2.816 \times 10^{-22} \text{ g}) / (1.355 \times 10^{-22} \text{ cm}^3) = 2.078 \text{ g cm}^{-3}$
- b. A neutral hydrogen atom is somewhat smaller than a neutral fluorine atom (hence the smaller C–H bond compared to a C–F bond). However,  $Z_{\text{eff}}$  for F is much greater than for H, so addition of an electron to form  $\text{H}^-$  causes a much greater increase in size than addition of an electron to F to form  $\text{F}^-$ . LiH and LiF are both largely ionic, with  $\text{H}^-$  and  $\text{F}^-$  anions, respectively. The  $\text{H}^-$  ion is thus slightly larger in size than the  $\text{F}^-$  ion.
- c. As the principal quantum number  $n$  increases, the size of an atom or ion increases, though the effect generally diminishes in magnitude as  $n$  increases. The outlier in this general trend in the lithium halides is thus the LiCl vs. LiBr ( $n = 3$  to  $n = 4$ ), where the increase is smaller than expected. This is due to the inclusion for the first time of the  $d$  block elements ( $Z = 21$  to  $Z = 30$ ). The addition of these ten extra protons, which are not completely shielded by the ten extra electrons, causes the  $4p$  elements to be anomalously contracted.  
 This effect is also expected with the astatide ion  $\text{At}^-$ , due to the intervention of the  $4f$  elements (the “lanthanide contraction”). So the increase in size from LiI to LiAt is expected to be rather small, similar to or even smaller than the increase in size from LiCl to LiBr. While data are not available for astatides, this trend is seen in structures of polonides.
- d. In these ionic crystals, the interionic attractions are proportional to  $1/r$ , where  $r$  is the separation between ions. So as  $a$  is smaller, the cohesive forces are stronger, which leads to higher melting points.
- e. H is much less electronegative than F, so LiH is much less ionic than LiF. Since the cohesive energies are proportional to  $q_1q_2/r$ , and the charges on Li and H in LiH are smaller than those on Li and F in LiF, LiH has a lower melting point.

7. a. The valence molecular orbital configuration for NO is  $\sigma_{2s}^2\sigma_{2s}^*\pi_{2p}^4\sigma_{2p}^2\pi_{2p}^*1$ ; the bond order is thus  $\frac{1}{2}(8 - 3) = 2.5$ . (One could also interpolate between  $\text{NO}^+$ , with a triple bond, and  $\text{NO}^-$ , with a double bond, to get a bond order of NO of 2.5.)
- b. The  $\pi^*$  orbital in NO is made up of an antibonding combination of N  $2p$  and O  $2p$  orbitals. It is composed predominantly of the atomic orbital to which it is closer in energy. Since it is higher in energy than either atomic orbital, then the higher-lying N  $2p$  orbital makes a greater contribution to it.
- c. Since the  $\pi^*$  orbital is higher in energy than the N  $2p$  atomic orbital, an electron in it will be more easily ionized than an electron in a N  $2p$  orbital. (Since both orbitals are singly occupied, the electron-electron repulsion terms should be similar.) The experimental ionization energy of NO, 9.26 eV, is indeed smaller than that of N.

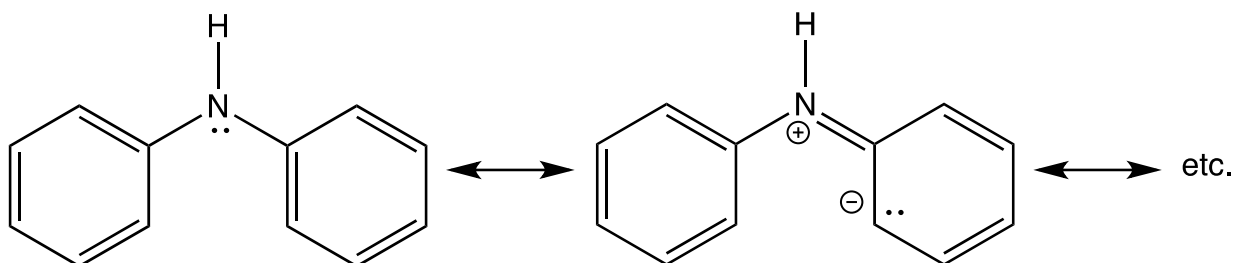
d.



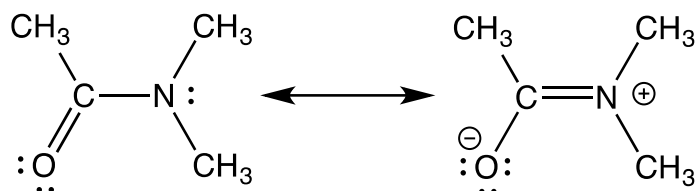
8. a. i. The conjugate base of acetic acid is strongly stabilized by resonance, while the conjugate base of ethanol is not. Since the conjugate base is stabilized, this makes it easier to remove  $\text{H}^+$  from acetic acid. (The inductive effect of the  $\text{C}=\text{O}$  group is also significant.)



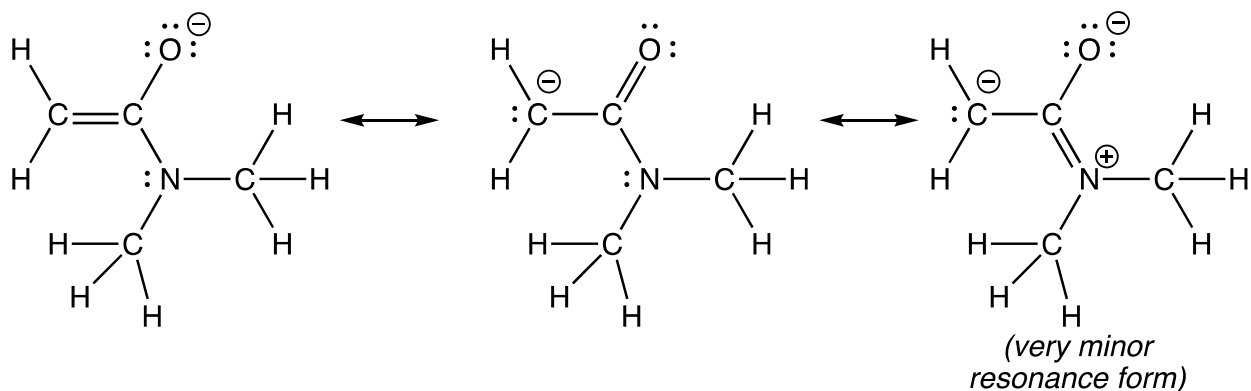
- ii. Diphenylamine is stabilized by resonance delocalization of the nitrogen lone pair into the benzene rings. Since this delocalization is lost when the nitrogen is protonated, it is more difficult to protonate diphenylamine, so it is a weaker base.



- b. **A** is the ionic compound dimethylammonium acetate,  $[(\text{CH}_3)_2\text{NH}_2][\text{CH}_3\text{COO}]$ .
- c. *N,N*-dimethylacetamide is a flat molecule (all the nonhydrogen atoms are in the same plane). This is because both the carbonyl carbon and the nitrogen atom are  $sp^2$  hybridized, with their unhybridized  $p$  orbitals parallel to each other in order to allow for  $\pi$  overlap that is required in the minor resonance structure of the amide. If the molecule twists out of planarity, this overlap, and hence the resonance stabilization, is lost, which costs a significant amount of energy. In the flat structure, the two  $\text{CH}_3$  groups on N are in different environments—one is *cis* to the oxygen and one is *trans* to it.



- d. Conjugate base:



Conjugate acid:

