



2015 U.S. NATIONAL CHEMISTRY OLYMPIAD NATIONAL EXAM - PART II



Prepared by the American Chemical Society 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 20, 2015**, after which tests can be returned to students and their teachers for further study.

Allow time for the student to read the directions, ask questions, and fill in the required information on the "Blue Book". When the student has completed **Part II**, or after one hour and forty-five minutes have elapsed, the student must turn in the "Blue Book", **Part II** of the testing materials, and all scratch paper. Be sure that the student has supplied all of the information requested on the front of the "Blue Book," and that the same identification number used for **Part I** has been used again for **Part II**.

There are three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest breaks between parts.

Part I	60 questions	single-answer multiple-choice	1 hour, 30 minutes
Part II	8 questions	problem-solving, 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 4 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.**

1. [12] A salt containing chromium, chlorine, and water has the formula $\text{CrCl}_n(\text{H}_2\text{O})_m$.
- A sample of the salt is electrolyzed for 1310 s using a current of 1.24 A and deposits 0.292 g metallic Cr. What is the value of n in the salt?
 - A 3.000 g sample of the chromium salt is heated carefully at 600 °C to drive off any water in the salt, until the sample achieves a constant mass of 1.783 g. What is the value of m in the salt?
 - A 0.300 g sample of the chromium salt is dissolved in 10 mL water to which a few drops of Na_2CrO_4 solution have been added. A 0.400 M solution of silver nitrate is titrated quickly into the solution until the appearance of a dark red color; this requires 2.81 mL of the AgNO_3 solution.
 - Write balanced chemical equations for the reaction taking place during the titration and the reaction that takes place at the endpoint.
 - How many moles of chloride are detected in this titration per mole of chromium present?
 - Propose an explanation for the result in part (c)(ii).
2. [14] *L*-leucine hydrochloride, $[(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_3^+)\text{COOH}]^+\text{Cl}^-$, is used as the dietary supplement for the essential amino acid leucine. It is a diprotic acid with $\text{p}K_{\text{a}1} = 2.36$ and $\text{p}K_{\text{a}2} = 9.60$. To 50.0 mL of a 0.100 M solution of leucine hydrochloride is gradually added 0.500 M NaOH solution.
- What is the initial pH of the 0.100 M leucine hydrochloride solution?
 - What volume of 0.500 M NaOH must be added to achieve a pH of 3.50?
 - After being deprotonated once, leucine hydrochloride forms a species with an overall charge of zero. Draw the Lewis structure of this neutral species.
 - What is the maximum concentration of this species in the titration?
 - For each of the indicators listed below, state whether its color will change abruptly (over the course of addition of < 0.2 mL NaOH) during the titration of leucine hydrochloride. If it will, specify the volume of NaOH at which the color change will take place. If it will not, explain why not.

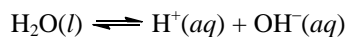
Methyl red (color change from pH = 4.4 to 6.2)

Phenolphthalein (color change from pH = 8.3 to 10.0)

3. [12] Consider the thermodynamic data given below:

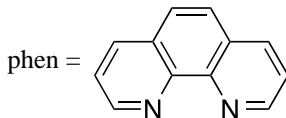
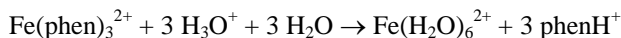
Species	$\Delta H_f^\circ, \text{kJ}\cdot\text{mol}^{-1}$	$S^\circ, \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$\text{H}^+(\text{aq})$	0	0
$\text{OH}^-(\text{aq})$	-229.9	
$\text{H}_2\text{O}(\text{l})$	-285.83	69.95

The autoionization of water can be described according to the equation below. Its equilibrium constant, K_w , is 1.0×10^{-14} at 25 °C.

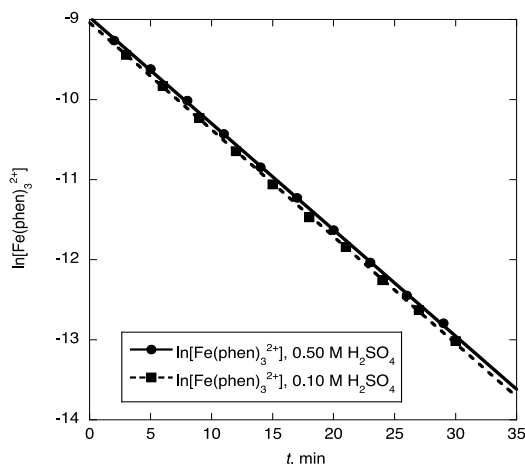


- Calculate ΔH° for the autoionization of water.
 - Calculate ΔG° (at 298 K) for the autoionization of water.
 - Calculate ΔS° for the autoionization of water and rationalize its sign.
 - Calculate S° for $\text{OH}^-(\text{aq})$.
 - Calculate K_w at 50 °C.
4. [12] Write net equations for each of the 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.
- Dilute solutions of cesium bromide and silver nitrate are combined.
 - Phosphorus(V) oxide is added to water.
 - Potassium chromate is added to dilute hydrochloric acid.
 - Solutions of hydriodic acid and hydrogen peroxide are mixed.
 - tert*-Butanol (2-methyl-2-propanol) is heated with sulfuric acid.
 - Technetium-99 undergoes beta decay.

5. [14] In strongly acidic solution, the dark red complex $\text{Fe}(\text{phen})_3^{2+}$ dissociates to the nearly colorless $\text{Fe}(\text{H}_2\text{O})_6^{2+}$.



The reaction was carried out at 42.3 °C and the concentration of $\text{Fe}(\text{phen})_3^{2+}$ was determined using visible absorption spectroscopy. Plots of the natural logarithm of $[\text{Fe}(\text{phen})_3^{2+}]$ as a function of time are shown at sulfuric acid concentrations of 0.50 M (circles) and 0.10 M (squares).



- a. What is the order of the reaction with respect to $\text{Fe}(\text{phen})_3^{2+}$? Explain your answer.
- b. What is the order of the reaction with respect to H_3O^+ ? Explain your answer.
- c. What is the value of the rate constant at 42.3 °C?
- d. The experiment is run again, but at 52.3 °C. The rate constant is determined to be 3.5 times larger than the rate constant at 42.3 °C. What is the activation energy for the reaction?
- e. Coordination complexes can be viewed as arising via a Lewis acid-base interaction. Sketch the structure of the complex $\text{Fe}(\text{phen})_3^{2+}$ and identify the Lewis acid and Lewis base. What is the coordination geometry around the iron?
6. [12] For each of the properties below, state whether H_2O or H_2S has the greater value, and justify your answer.
- Heat of fusion
 - Bond angle
 - Acid dissociation constant (K_a)
 - Stretching frequency in the infrared spectrum
7. [12] Chlorine is an industrially and biologically important element.
- Give the ground state electron configuration for gas-phase atomic Cl.
 - Draw a Lewis structure for molecular chlorine, including all lone pairs and any formal charges.
 - Which would have a greater first ionization energy, atomic Cl or molecular chlorine? Justify your answer.
 - Which would have a larger radius, atomic Cl or the chloride ion (Cl^-)? Justify your answer.
 - Explain why the oxoanions ClO^- , ClO_2^- , ClO_3^- , and ClO_4^- all form stable salts, but the oxoanion ClO_5^- is unknown.
8. [12] There are three structurally isomeric ethers with the formula $\text{C}_3\text{H}_6\text{O}$.
- Draw structural formulas for these three compounds.
 - Can any of the compounds you drew in (a) exist in stereoisomeric forms? If so, draw clear 3-D representations of the isomeric forms. If not, explain why not.
 - There are four other isolable compounds with the formula $\text{C}_3\text{H}_6\text{O}$ that are *not* ethers. Draw the structure of one such compound, and identify all functional groups present in the molecule.
 - Would you expect the molecule you drew in (c) to have a lower boiling point than any of the $\text{C}_3\text{H}_6\text{O}$ ethers, a higher boiling point than any of the $\text{C}_3\text{H}_6\text{O}$ ethers, or a boiling point within the range of those exhibited by the $\text{C}_3\text{H}_6\text{O}$ ethers? Justify your answer.

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

CONSTANTS
$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$F = 96,500 \text{ C}\cdot\text{mol}^{-1}$
$F = 96,500 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$
$c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
$0^\circ\text{C} = 273.15 \text{ K}$
$1 \text{ atm} = 760 \text{ mm Hg}$
Specific heat capacity of $\text{H}_2\text{O} = 4.184 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$

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

PERIODIC TABLE OF THE ELEMENTS																																		
1																	18																	
1A																	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 78.96	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 95.94	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	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
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)																	

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)
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1. [12 pts.]

a. $(1310 \text{ s})(1.24 \text{ A})/(96485 \text{ C/mol}) = 0.0168 \text{ mol electrons}$

$$0.292 \text{ g Cr}/(52.00 \text{ g/mol}) = 5.62 \times 10^{-3} \text{ mol Cr}$$

$$0.0168 \text{ mol electrons}/(5.62 \times 10^{-3} \text{ mol Cr}) = 2.99 \text{ mol electrons/mol Cr}$$

Thus Cr must be in the +3 oxidation state, $n = 3$.

b. $3.000 \text{ g} - 1.783 \text{ g} = 1.217 \text{ g H}_2\text{O}/(18.02 \text{ g/mol}) = 0.06754 \text{ mol H}_2\text{O}$

$$1.783 \text{ g CrCl}_3/(158.35 \text{ g/mol}) = 0.01126 \text{ mol CrCl}_3$$

$$m = 0.06754 \text{ mol H}_2\text{O}/0.01126 \text{ mol CrCl}_3 = 6$$

c. i. During the titration, $\text{Ag}^+ (aq) + \text{Cl}^- (aq) \rightarrow \text{AgCl} (s)$

At the endpoint, $2 \text{Ag}^+ (aq) + \text{CrO}_4^{2-} (aq) \rightarrow \text{Ag}_2\text{CrO}_4 (s)$

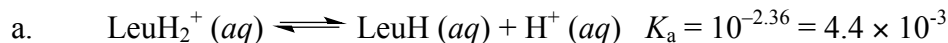
ii. $\text{Mol Cr salt} = 0.3000 \text{ g}/(266.47 \text{ g/mol}) = 1.126 \times 10^{-3} \text{ mol}$

$$\text{Mol Ag}^+ \text{ added} = \text{mol Cl}^- \text{ present} = (0.400 \text{ mol/L}) \times (2.81 \times 10^{-3} \text{ L}) = 1.12 \times 10^{-3} \text{ mol}$$

There is thus 1.00 mol Cl^- titrated per mol Cr.

d. Presumably two of the chlorides are bonded directly to the Cr(III) ion and therefore do not react rapidly with $\text{Ag}^+ (aq)$; the salt is likely best formulated $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2 \text{H}_2\text{O}$.

2. [14 pts.]



If $x = [\text{H}^+] = [\text{LeuH}]$, then $[\text{LeuH}_2^+] = 0.100 - x$.

$$\frac{[\text{LeuH}][\text{H}^+]}{[\text{LeuH}_2^+]} = \frac{[x]^2}{[0.100 - x]} = 4.4 \times 10^{-3}$$

$$x^2 = 4.4 \times 10^{-4} - (4.4 \times 10^{-3})x$$

$$x^2 + (4.4 \times 10^{-3})x - 4.4 \times 10^{-4} = 0$$

$$x = \frac{-4.4 \times 10^{-3} \pm \sqrt{(4.4 \times 10^{-3})^2 + 4(4.4 \times 10^{-4})}}{2} = 0.019 \text{ M} = [\text{H}^+]$$

$$\text{pH} = -\log_{10}[\text{H}^+] = 1.72$$

Since ~20% of the leucine hydrochloride is ionized, neglecting its ionization (i.e., assuming $[\text{LeuH}_2^+]_{\text{final}} = [\text{LeuH}_2^+]_{\text{initial}}$) is not a great approximation. If this approximation is made, then one calculates $[\text{H}^+] = 0.021 \text{ M}$, $\text{pH} = 1.68$.

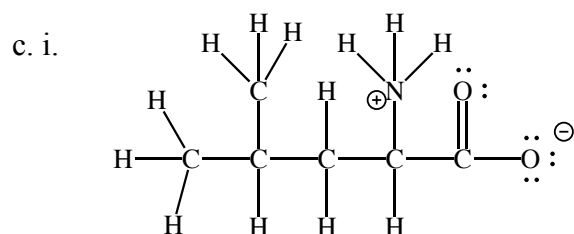
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b. $3.50 = 2.36 + \log_{10} \frac{[\text{LeuH}]}{[\text{LeuH}_2^+]}$

(mol LeuH)/(mol LeuH₂⁺) = 13.8

Since (mol LeuH) + (mol LeuH₂⁺) = 5.00 × 10⁻³ mol, then we must have 4.66 × 10⁻³ mol LeuH, which would have required 4.66 × 10⁻³ mol NaOH to form.

Volume added NaOH = (4.66 × 10⁻³ mol)/(0.500 mol/L) = 9.32 mL.



ii. The concentration of this species is maximized at the first equivalence point, where 10.0 mL NaOH have been added. [LeuH] = 0.00500 mol/0.0600 L = 0.0833 M.

d. Methyl red: Will change pH abruptly at the first equivalence point (where the pH will jump abruptly from about 4.4 to about 7.6), at 10.00 mL added NaOH.

Phenolphthalein: The buffer range of LeuH/Leu⁻ is from about pH = 8.6 to 10.6. This is where the pH will change very slowly as NaOH is added, so the color of phenolphthalein will change very slowly as well.

3. [12 pts.]

a. $\Delta H^\circ = (-229.9 \text{ kJ/mol}) - (-285.8 \text{ kJ/mol}) = +55.9 \text{ kJ/mol}$

b. $\Delta G^\circ = -RT \ln K_{\text{eq}} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln(1.0 \times 10^{-14}) = +79.9 \text{ kJ/mol}$

c. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 $79.9 \text{ kJ/mol} = 55.9 \text{ kJ/mol} - (298 \text{ K})(\Delta S^\circ)$

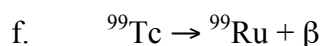
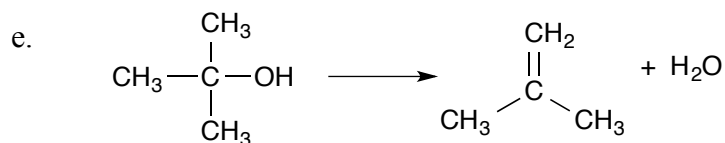
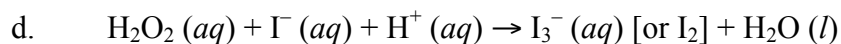
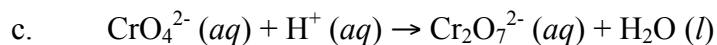
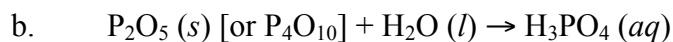
$\Delta S^\circ = -80.5 \text{ J/mol}\cdot\text{K}$

The entropy change is negative because the ions strongly order the solvent molecules around them (much more so than the neutral water).

d. $-80.5 \text{ J/mol}\cdot\text{K} = (S^\circ \text{ of OH}^- (aq)) - (69.95 \text{ J/mol}\cdot\text{K})$
 $S^\circ \text{ of OH}^- (aq) = -10.6 \text{ J/mol}\cdot\text{K}$

e. At 50 °C, $\Delta G^\circ = 55.9 \text{ kJ/mol} - (323 \text{ K})(-80.5 \text{ J/mol}\cdot\text{K}) = 81.9 \text{ kJ/mol}$
 $\ln(K_w) = -\Delta G^\circ/RT = (-81900 \text{ J/mol})/(8.314 \text{ J/mol}\cdot\text{K})(323 \text{ K}) = -30.5$
 $K_w = 5.7 \times 10^{-14}$

4. [12 pts.]



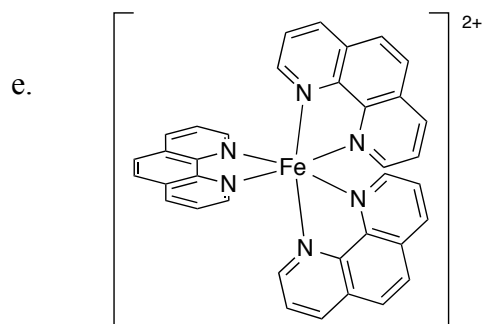
5. [14 pts.]

a. $\ln([\text{Fe}(\text{phen})_3^{2+}])$ decreases linearly with time, which is characteristic of a 1st-order process, so the order in $\text{Fe}(\text{phen})_3^{2+}$ is 1.

b. The slope of the line does not depend on the concentration of H^+ , which says that the rate is independent of $[\text{H}^+]$. Therefore the order in H^+ is zero.

c. The slope of the line is $-k$. From the graph, the slope is about $(-4)/(30 \text{ min})$, so $k = 0.13 \text{ min}^{-1} = 2.2 \times 10^{-3} \text{ s}^{-1}$.

d. $\ln(3.5) = (E_a/8.314 \text{ J/mol}\cdot\text{K})([1/315.4 \text{ K}] - [1/325.4 \text{ K}])$
 $E_a = 107 \text{ kJ/mol}$



Phen is the Lewis base, Fe^{2+} the Lewis acid.

The coordination geometry at Fe is octahedral.

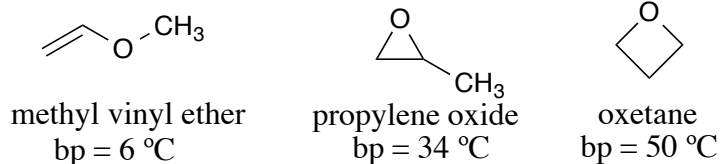
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6. [12 pts.]
- a. H₂O has the greater heat of fusion. O-H---O hydrogen bonds are possible in water, while the S-H bonds in H₂S are not polar enough to support hydrogen bonding. This leads to stronger intermolecular forces in water and hence a larger heat of fusion.
- b. H₂O has the larger bond angle. The 2s orbital is significantly involved in bonding in H₂O, which makes the angle close to the tetrahedral angle of 109.5° (actually 105°). In H₂S, the 3s orbital is much smaller than the 3p orbital, so the latter dominates the bonding, and the angle is close to the angle between p orbitals, 90° (actually 92°).
- c. H₂S has the larger K_a. The larger S has less electron-electron repulsion, stabilizing the anionic conjugate base. (Explanations involving bond strength are possible as well.)
- d. H₂O has the larger stretching frequency. ν is proportional to $\sqrt{k/\mu}$, where k is the force constant of the bond and μ is the reduced mass of the bond. H₂O has both (slightly) smaller reduced masses and (significantly) stronger bonds, so its stretching frequencies are higher than those in H₂S.
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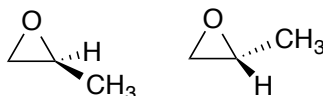
7. [12 pts.]
- a. $1s^2 2s^2 2p^6 3s^2 3p^5$ or [Ne] $3s^2 3p^5$
- b. $\text{:}\ddot{\text{Cl}}\text{---}\ddot{\text{Cl}}\text{:}$
- c. Cl has a higher ionization energy than Cl₂. The highest-lying electrons in Cl₂ are π^* , so they are higher in energy, and hence require less energy to ionize, than the 3p electrons in atomic chlorine. (The experimental values are 13.0 eV for Cl, 11.5 eV for Cl₂ [Frost, D. C.; McDowell, C. A.; Vroom, D. A. *J. Chem. Phys.* **1967**, *46*, 4255-4259].)
- d. Cl⁻ would have a larger radius, since it has an additional electron.
- e. Cl has 7 valence electrons. An oxoanion with the formula ClO₅⁻ would require an oxidation state of +9 for Cl, which would require removing core electrons. This is not energetically feasible.

8. [12 pts.]

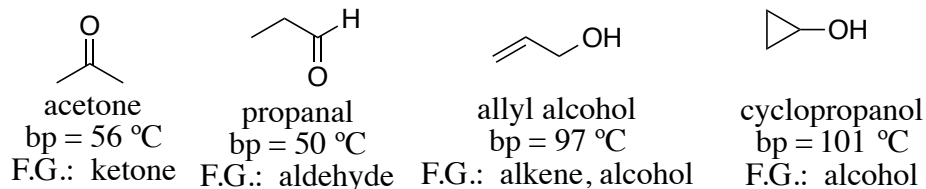
a.



b. Only propylene oxide can exist in stereoisomeric forms (a pair of enantiomers, shown below).



c.



Note that the three enols with the formula C_3H_6O are not isolable, since they rapidly isomerize (tautomerize) to either acetone or propanal.

d. The two alcohols boil at much higher temperatures than any of the ethers, since the O-H group can participate in hydrogen bonding, leading to strong intermolecular forces. The two carbonyl compounds boil higher than most of the ethers, since the carbonyl group is more polar than the ether linkage. The exception is oxetane, which has a similar boiling point to acetone and propanal, since the cyclic (and small-ring) structure makes the ether unusually polar. Thus, for either of the carbonyl compounds, either "higher-boiling than any of the ethers" or "within the range of boiling points of the ethers" would be accepted as an answer.