2016 U.S. NATIONAL CHEMISTRY OLYMPIAD

NATIONAL EXAM - PART II

Prepared by the American Chemical Society 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 25, 2016**, 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 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.**

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ABBREVIATIONS AND SYMBOLS

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

CONSTANTS

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

$R = 0.0821\ \text{L}\bullet\text{atm}\bullet\text{mol}^{-1}\bullet\text{K}^{-1}$

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

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

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

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

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

0 °C = 273.15 K

1 atm = 760 mm Hg

Specific heat capacity of H_2O = $4.184\ \text{J}\bullet\text{g}^{-1}\bullet\text{K}^{-1}$

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** 78.96	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	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** (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)

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)

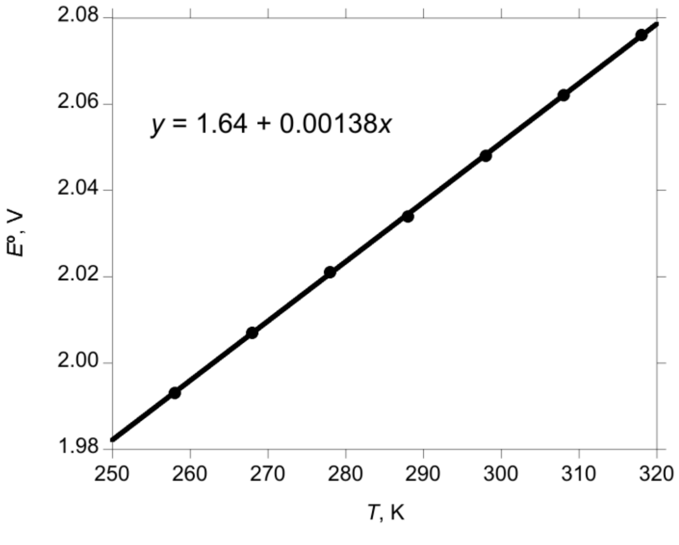
1. [12] An unknown compound **A** contains only carbon, oxygen, and chlorine.
   a. A 3.00 g sample of **A** is completely vaporized in a 1.00 L container at 70.0 ºC and exerts a pressure of 0.854 atm. What is the molar mass of **A**?
   b. A 0.300 g sample of **A** is added to 100 mL water, which results in the conversion of all the chlorine in **A** to HCl. After briefly bubbling nitrogen gas through the solution, the hydrochloric acid is titrated with 0.2000 M NaOH solution. The titration requires 30.33 mL added NaOH to reach a phenolphthalein endpoint. What is the mass percentage of chlorine in compound **A**?
   c. Propose a molecular formula for **A** and draw a reasonable Lewis structure for it
   d. Write a balanced equation for the reaction of **A** with water (as described in part (b)).

2. [12] A buffer solution is prepared from 1.00 L of 0.0500 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and 2.50 g sodium acetate, $Na(CH_3COO)$.
   a. What is the pH of this solution?
   b. 1.00 mL of a 1.00 M solution of hydrochloric acid is added to the buffer. Write an equation for the major reaction that takes place, and calculate the pH after addition.
   c. Calculate the mass of sodium hydroxide that would need to be added to 1.00 L of 0.050 M CH_3COOH to produce a solution with the same pH as the original buffer.
   d. Suppose the buffer had been made with 1.00 L of 0.0500 M chloroacetic acid, $ClCH_2COOH$, and 2.50 g sodium chloroacetate, $Na(ClCH_2COO)$. Compared to the original buffer, would this buffer have a lower pH, a higher pH, or the same pH, or can one not draw a qualitative conclusion without quantitative information about the K_a of $ClCH_2COOH$? Justify your answer.

3. [14] The lead acid storage battery is commonly used in cars. In dilute solutions, the overall reaction of a cell in this battery is:

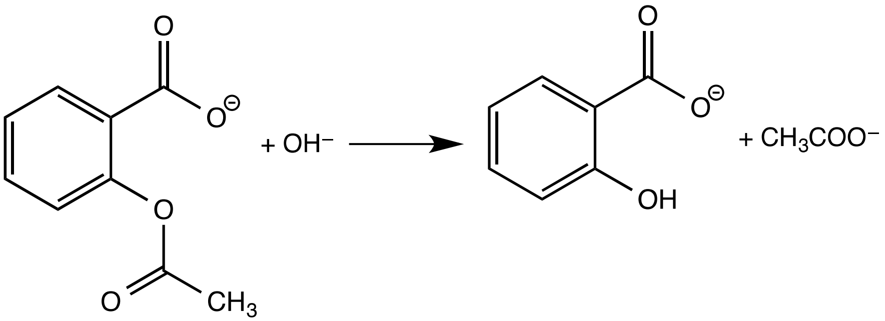
$$Pb(s) + PbO_2(s) + 4\,H^+(aq) + 2\,SO_4^{2-}(aq) \rightarrow 2\,PbSO_4(s) + 2\,H_2O(l)$$

The variation of the standard cell potential $E°$ with temperature is shown below:



   a. Sketch the setup of a cell of the lead acid storage battery, clearly showing the location of all components. Label the cathode and the anode and indicate the direction of flow of electrons through the external circuit as the cell is discharged.
   b. Calculate $\Delta G°$ for the reaction at 298 K.
   c. Calculate $\Delta H°$ for the reaction.
   d. Calculate $\Delta S°$ for the reaction.
   e. Calculate the cell potential E for the reaction at 5 ºC at pH = 5.0 and 0.10 M sulfate ion concentration.

4. [14] Acetylsalicylate ion (derived from aspirin and shown as **X** in the equation below) hydrolyzes in the presence of hydroxide ion:



X

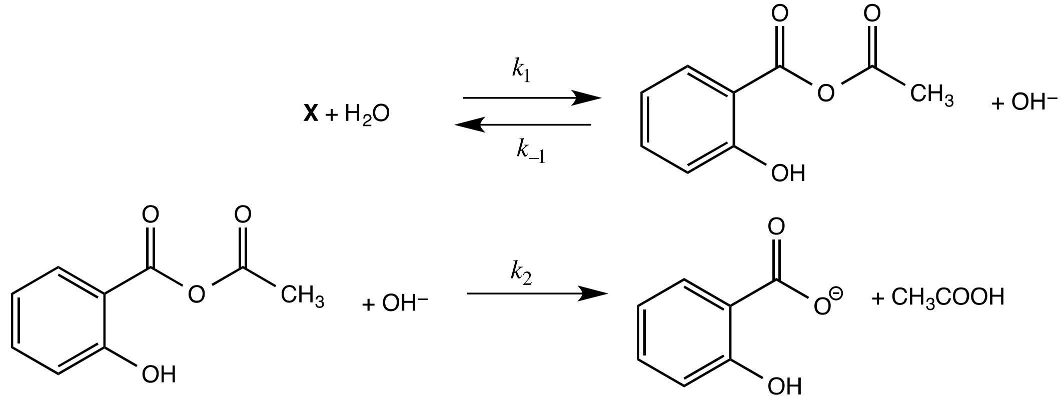
The reaction was studied at 60 ºC and was found to be first-order in **X** under all conditions. The amount of **X** was monitored over time in two different buffer solutions and the following data were obtained:

Time, s	[**X**], M pH = 10.10 buffer	[**X**], M pH = 10.60 buffer
0	3.61×10^{-4}	3.59×10^{-4}
600		1.78×10^{-4}
740	2.75×10^{-4}	

a. Since the reaction is first-order in **X**, and the concentration of hydroxide ion is held constant by the buffer solution, then for each individual run the rate can be written

$$\text{rate} = k'[\mathbf{X}]$$

Determine the value of k' for each of the two runs.
b. What is the reaction order in hydroxide ion? Give your reasoning.
c. Give the full rate law for the reaction and calculate the rate constant k.
d. The following mechanism is proposed for this reaction:

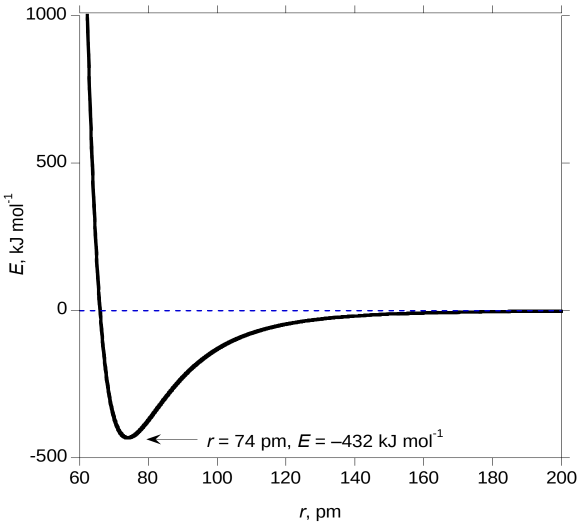


$$CH_3COOH + OH^- \xrightarrow{fast} CH_3COO^- + H_2O$$

Is this mechanism consistent with the observed rate law? If so, state which step(s) could be rate-determining. If not, explain why not.

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. A strip of copper metal is heated strongly with concentrated sulfuric acid.
   b. Solid dinitrogen pentoxide is added to water.
   c. Lead(II) carbonate is added to hydrobromic acid.
   d. Freshly precipitated manganese(IV) oxide is added to a solution of hydrogen peroxide.
   e. Chlorine is combined with toluene (methylbenzene) in the presence of ultraviolet light.
   f. Tritium (^{3}H) undergoes radioactive decay.

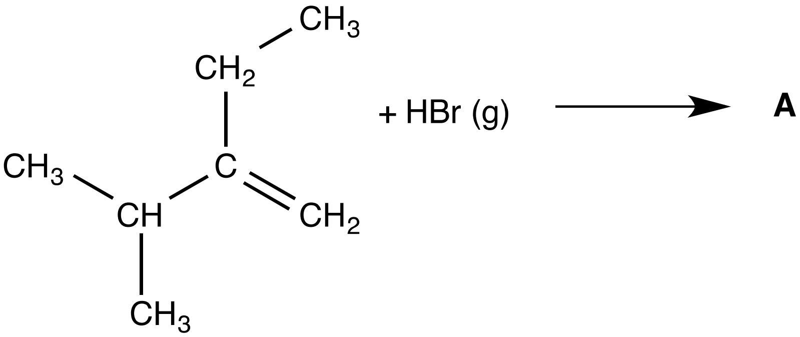
6. [12] The plot below shows the energy of two hydrogen atoms as a function of their internuclear separation *r*:



   a. Explain why the potential energy decreases as the internuclear separation decreases from 120 pm to 80 pm.
   b. Explain why the potential energy increases as the internuclear separation decreases from 70 pm to 60 pm.
   c. Calculate the longest wavelength of light that has sufficient energy to break a H–H bond.
   d. The vibrational frequency of $H_2(g)$ is 1.32×10^{14} Hz. What percentage of the H–H bond dissociation energy is required to excite a molecular vibration of H_2?
   e. Will $H_2(g)$ absorb infrared radiation due to its molecular vibration? Explain why or why not.

7. [12] Explain the following observations about the properties of the Group 15 halides.
   a. Phosphorus pentachloride in the gas phase has two different kinds of P–Cl bonds: three P–Cl bonds that are relatively short (202 pm) and two that are relatively long (214 pm).
   b. In the solid state, phosphorus pentachloride is an ionic compound.
   c. The F–N–F bond angle in nitrogen trifluoride is larger than the F–P–F bond angle in phophorus trifluoride (102.5 º vs. 96.3 º).
   d. Arsenic trifluoride is a volatile liquid (mp –8.5 ºC, bp 60.4 ºC), while antimony trifluoride is a nonvolatile solid (mp 292 ºC, bp 376 ºC).
   e. Antimony trichloride reacts with chlorine to form antimony pentachloride, while bismuth trichloride does not react with chlorine.

8. [12] Consider the reaction below:



a. When conducted in the dark, the reaction gives rise to a product **A** that consists of a single structural isomer. Draw the structure for **A** and account for the selectivity of its formation in terms of the reaction mechanism.
b. Does **A** exist in stereoisomeric forms? If so, draw structures of the stereoisomers of **A**, clearly showing their stereochemistry. If not, explain why not.
c. Carrying out the reaction in the light or in the presence of peroxides results in significant amounts of an isomeric product **B**. Draw the structure of **B** and explain why it is formed under these conditions.
d. Treatment of **A** with strong bases results in the formation of four isomeric alkenes. Draw structures of the four alkenes and indicate which is the predominant product.

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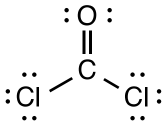
2016 USNCO Part II Exam Answers

1.a. $n = PV/RT = (0.854 \text{ atm})(1.00 \text{ L})/(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(343.2 \text{ K}) = 0.0303 \text{ mol}$
$3.00 \text{ g}/0.0303 \text{ mol} = 99.0 \text{ g/mol}$

b. $0.03033 \text{ L NaOH soln} \times 0.2000 \text{ mol L}^{-1} = 0.06066 \text{ mol NaOH}$
There were thus $0.06066 \text{ mol Cl} \times 35.45 \text{ g mol}^{-1} = 0.2150 \text{ g Cl}$ in the sample
$(0.2150 \text{ g Cl}/0.300 \text{ g sample}) \times 100\% = 71.7\%$ Cl by mass

c. In 99.0 g (1 mol) **A**, there is $(0.717 \times 99.0 \text{ g})/(35.45 \text{ g mol}^{-1} \text{ Cl}) = 2 \text{ mol Cl}$
The remaining mass in 1 mol **A** is $99.0 \text{ g mol}^{-1} - (2 \times 35.45 \text{ g mol}^{-1}) = 28.1 \text{ g mol}^{-1}$
The only combination of atomic masses of C and O that is close to 28 g mol^{-1} is C_1O_1.
So the molecular formula is $COCl_2$:



d. $COCl_2(g) + H_2O(l) \rightarrow CO_2(g) + 2\ HCl(aq)$

2.a. $1.00 \text{ L} \times 0.050 \text{ mol L}^{-1} = 0.0500 \text{ mol } CH_3COOH$
$2.50 \text{ g Na}[CH_3COO]/82.04 \text{ g mol}^{-1} = 0.0305 \text{ mol } CH_3COO^-$
$pH = pK_a + \log([CH_3COO^-]/[CH_3COOH]) = 4.74 + \log(0.0305/0.0500) = 4.53$

b. $CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$ [very favorable]
$pH = 4.74 + \log(\{0.0305 - 0.001\}/\{0.0500 + 0.001\}) = 4.50$

c. To achieve the same pH, one would need the same ratio of conjugate acid to conjugate base, so $(\text{mol } CH_3COOH)/(\text{mol } CH_3COO^-) = 1.64$.
If x is the number of mol NaOH added, then $(0.0500 \text{ mol} - x)/x = 1.64$

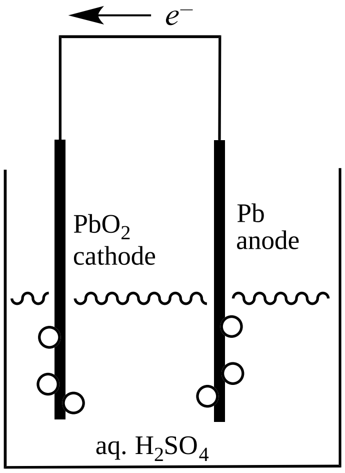
$$0.0500 \text{ mol} = 2.64x$$

$$x = 0.0189 \text{ mol NaOH}$$

$$0.0189 \text{ mol NaOH} \times 40.0 \text{ g mol}^{-1} = 0.756 \text{ g NaOH}$$

d. The electron-withdrawing character of Cl compared with H means that $ClCH_2COOH$ will be more acidic (have a lower pK_a) than CH_3COOH. The higher molar mass of $Na(ClCH_2COO)$ means that one is adding fewer moles of base to the chloroacetic acid buffer than one did to the acetic acid buffer (the number of moles of acid are the same in both cases). Both these factors will contribute to a lower pH of the $ClCH_2COOH/ClCH_2COO^-$ buffer.

3.a.



○ = $PbSO_4(s)$

b. $E^o = 1.64\ \text{V} + (0.00138\ \text{V K}^{-1})T$

At 298 K, $E^o = 2.05$ V

$\Delta G^o = -nFE^o = -(2)(96500\ \text{J V}^{-1}\ \text{mol}^{-1})(2.05\ \text{V}) = -396\ \text{kJ mol}^{-1}$

c. Since $\Delta G^o = \Delta H^o - T\Delta S^o = -nFE^o$:

$$E^o = -(\Delta H^o/nF) + T(\Delta S^o/nF) = 1.64\ \text{V} + T(0.00138\ \text{V K}^{-1})$$

Thus $\Delta H^o = -(2)(96500\ \text{J V}^{-1}\ \text{mol}^{-1})(1.64\ \text{V}) = -317\ \text{kJ mol}^{-1}$

d. From the analysis in (c), $\Delta S^o = (2)(96500\ \text{J V}^{-1}\ \text{mol}^{-1})(0.00138\ \text{V K}^{-1}) = +266\ \text{J mol}^{-1}\ \text{K}^{-1}$

e.

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

$$E = (1.64\ \text{V} + (0.00138\ \text{V K}^{-1})\bullet 278\ \text{K}) - \frac{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(278\ \text{K})}{(2)(96500\ \text{J V}^{-1}\ \text{K}^{-1})}\ln\left(\frac{1}{[H^+]^4[SO_4^{2-}]^2}\right)$$

$$E = 2.024\ \text{V} - (0.0120\ \text{V})\ln\left(\frac{1}{[1.0\times 10^{-5}]^4[0.10]^2}\right)$$

$$E = 1.42\ \text{V}$$

4. a. Under these "pseudo" first-order conditions, $\ln([\mathbf{X}]/[\mathbf{X}]_0) = -k't$.
At pH = 10.10, $\ln([2.75 \times 10^{-4}]/[3.61 \times 10^{-4}]) = -k'(740\ \text{s})$, so $k' = 3.68 \times 10^{-4}\ \text{s}^{-1}$.
At pH = 10.60, $\ln([1.78 \times 10^{-4}]/[3.59 \times 10^{-4}]) = -k'(600\ \text{s})$, so $k' = 1.17 \times 10^{-3}\ \text{s}^{-1}$.

b. At pH = 10.10, $[\text{OH}^-] = 10^{10.10-14} = 1.26 \times 10^{-4}$ M
At pH = 10.60, $[\text{OH}^-] = 10^{10.60-14} = 3.98 \times 10^{-4}$ M
Between the two runs, $[\text{OH}^-]$ increases by a factor of 3.16; the pseudo-first-order rate constant k' increases by a factor of 3.18. Thus, k' is directly proportional to $[\text{OH}^-]$. Since

$$\text{Rate} = k'[\mathbf{X}] = k[\text{OH}^-]^m[\mathbf{X}]$$

where m is the reaction order in hydroxide, we thus have $m = 1$.

c. $\text{Rate} = k[\text{OH}^-][\mathbf{X}]$
Since $k[\text{OH}^-] = k'$ for either run, we have $k = (3.68 \times 10^{-4}\ \text{s}^{-1})/(1.26 \times 10^{-4}\ \text{M}) = 2.92\ \text{M}^{-1}\ \text{s}^{-1}$. (Using the data from the second run gives $k = 2.94\ \text{M}^{-1}\ \text{s}^{-1}$, in good agreement.)

d. If the first step of the mechanism were rate-limiting, then $\text{Rate} = k_1[\mathbf{X}]$. This is inconsistent with the first-order dependence on OH^-. If the second step is rate-limiting, then $\text{Rate} = K_1k_2[\mathbf{X}]$, also inconsistent with the first-order dependence on OH^-. So, regardless of the rate-limiting step this mechanism is predicted to have a zeroth-order dependence on OH^-, so it is not consistent with the experimental data. (More generally, if one applies the steady-state approximation to the intermediate, one concludes that $\text{Rate} = k_1k_2[\mathbf{X}]/(k_{-1} + k_2)$, which is always zeroth-order in OH^-.)

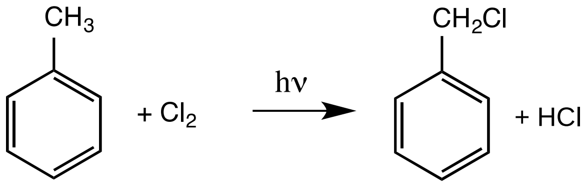
5. a. $\text{Cu}(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{CuSO}_4(s) + \text{SO}_2(g) + \text{H}_2\text{O}(l)$
($\text{Cu}^{2+} + \text{SO}_4^{2-}$ [or HSO_4^-] is OK in lieu of CuSO_4; $\text{H}_3\text{O}^+ + \text{HSO}_4^-$ is OK in lieu of H_2O)

b. $\text{N}_2\text{O}_5(s) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)$

c. $\text{PbCO}_3(s) + \text{H}_3\text{O}^+(aq) + \text{Br}^-(aq) \rightarrow \text{PbBr}_2(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$

d. $\text{H}_2\text{O}_2(aq) \rightarrow \text{H}_2\text{O}(l) + \text{O}_2(g)$ [$\text{MnO}_2(s)$ catalyzes the reaction]

e.



f. $^3\text{H} \rightarrow {}^3\text{He} + \beta$

6. a. The attraction of the electrons for the nucleus of the other atom causes the energy to decrease as the separation decreases, in this range.

b. As the nuclei get very close, the nuclear-nuclear repulsion overwhelms the electron-nucleus attraction, causing the energy to increase as the internuclear separation gets closer than the equilibrium distance.

c. BDE = 432 kJ mol^{-1} = 7.17×10^{-19} J/molecule
7.17×10^{-19} J = hc/λ, so $\lambda = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{8} \text{ m s}^{-1})/(7.17 \times 10^{-19} \text{ J})$
$\lambda = 2.77 \times 10^{-7}$ m = 277 nm

d. $E = h\nu = (6.626 \times 10^{-34} \text{ J s})(1.32 \times 10^{14} \text{ s}^{-1}) = 8.75 \times 10^{-20}$ J. This is $\{(8.75 \times 10^{-20} \text{ J})/(7.17 \times 10^{-19} \text{ J})\}\bullet 100\% = 12.2\%$ of the BDE.

e. While the frequency is in the infrared range, there will be no absorption of light because absorption of IR light requires a change in dipole moment of the molecule as it vibrates. H_2 is symmetrical and always has a zero dipole moment, regardless of its vibrational excitation.

7. a. PCl_5 adopts a pentagonal bipyramidal structure, with two axial and three equatorial bonds. The two axial bonds are best described as three-center, four-electron bonds, and so are longer than the more covalent equatorial bonds.

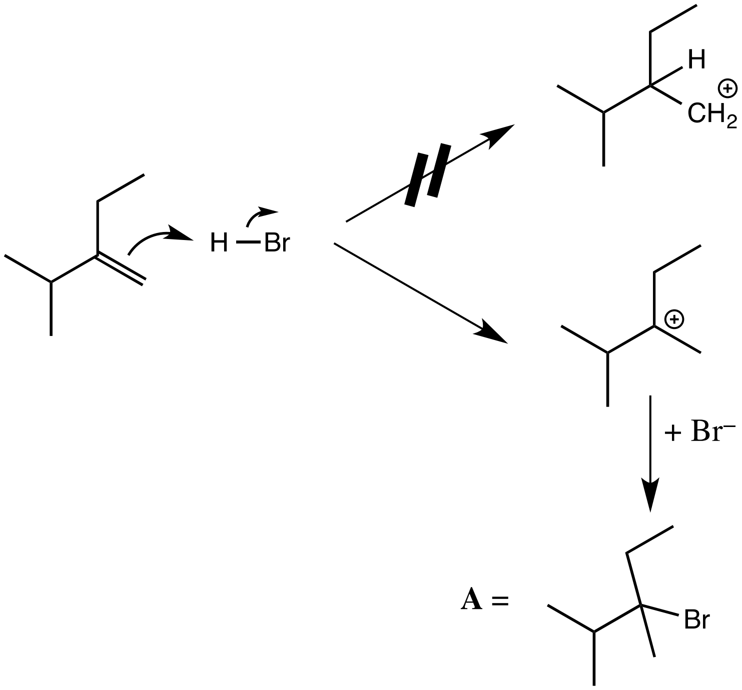
b. PCl_5 disproportionates to PCl_4^+ and PCl_6^- in the solid state.

c. The 2*p* orbitals are anomalously contracted because there are no 1*p* orbitals to shield them. This makes them similar in size to the 2*s* orbitals, so both *s* and *p* orbitals are significantly involved in bonding of the $n = 2$ elements like N. In contrast, the 3*s* orbitals are much less involved in the bonding of phosphorus compounds than the 3*p* orbitals. Pure *p* orbitals would form an ideal angle of 90º between bonds, while pure sp^3 hybrids would form angles of 109.5º. Neither NF_3 nor PF_3 is ideal in this respect, but the larger angle in NF_3 is consistent with greater *s* orbital participation in bonding.

d. Sb is larger and less electronegative than As. This means that there is greater ionic character in the Sb-F bond, and a greater possibility of forming close Sb–F--Sb contacts, increasing the intermolecular forces between SbF_3 units in the solid.

e. The 6*s* orbital in Bi is anomalously contracted and low in energy, due to the lanthanide contraction and relativistic effects. Thus Bi(V) is much more oxidizing than is Sb(V), and Cl_2 is an insufficiently strong oxidant to oxidize $BiCl_3$ to $BiCl_5$ (the latter compound is unknown).

8. a.

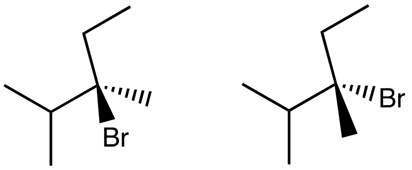


primary carbocation, disfavored

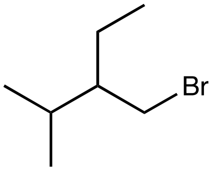
tertiary carbocation, favored

A =

b. **A** exists as a pair of enantiomers:

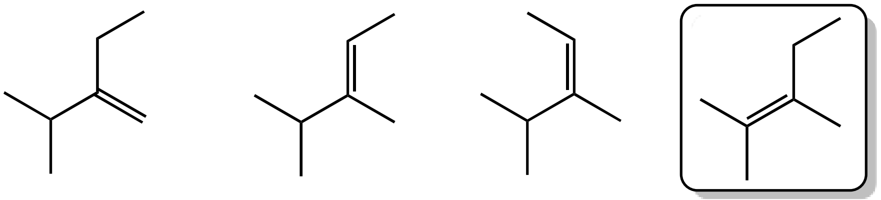


c. **B** =



In the presence of light or peroxides, a radical chain mechanism can take place. Br• is the chain carrier, and it adds preferentially to the less substituted carbon of the alkene, since that generates the more stable tertiary alkyl radical. Abstraction of H• from HBr by this radical forms **B** and reforms Br•, which continues the chain.

d.



major product
(most substituted alkene)