<The Answers>

Problem	points	Problem	points	TOTAL pts
1	2+3+3+4/12	**6**	2+2+3/7	/100
2	3+4+3+4/14	**7**	6+6/12	
3	3+3/6	**8**	2x7/14	
4	3+3+3/9	**9**	4+4/8	
5	4+4/8	**10**	3+3+4/10	

전체 기준: 전개과정은 맞으나 답이나 unit 이 틀리면 -1

답은 맞으나 전개과정이 약간 틀렸을 때 -1

식을 전혀 쓰지 않고 (혹은 흔적이 전혀 없고) 답만 맞았을 때 -1 (3 pts), -2 (4 pts 이상)

1. (Total 12 pts)

(a) (2 pts) 부호 틀리면 모두 감점

		E° (volts)
$HClO_2(aq) + 2H_3O^+ + 2e^- \longrightarrow$	$HClO(aq) + 3H_2O$	1.64
$Cr_2O_7^{2-}(aq) + 14H_3O^+ + 6e^- \longrightarrow$	$2Cr_3^+ + 21H_2O$	1.33

The first half reaction (the reduction) is occurring at the cathode and the second half reaction (the oxidation) is occurring at the anode.

$\varepsilon^\circ_{cell} = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode}$ = 1.64 V - 1.33 V = 0.31 V (+2 pts, No partial points)

(b) (3 pts) $\Delta G^\circ = -nFE^\circ_{cell}$ (+1 point)

= -6 mol X 96485 C/mol X 0.31 V = -179.5 kJ (+3 pts)

(c) (3 pts) ΔG° = -RTlnK = -nFE° or E° = (0.0592/n) logK (+1 point)

Hence lnK = -ΔG°/RT,

K = exp(-ΔG°/RT) = exp(179.5 X 1000 J/mol / (8.314 J/molK X 298K)

= 2.9×10^{31} (~10^{31}, order have to correct, 2 pts)

(d) (4 pts)

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log_{10} Q \quad (\text{at } 25^\circ\text{C})}$$ by Nernst equation (+2 pts)

$Q = (0.2^3 \times 0.8 \times 1.00^8)/(0.15^3 \times [Cr^{3+}]^2)$

Hence, 0.15 V = 0.31 V – 0.0592 V / 6 X $\log((0.2^3 \times 0.8 \times 1.00^8)/(0.15^3 \times [Cr^{3+}]^2))$

6(0.15 – 0.31) V / 0.0592 V = $-\log(1.896/[Cr^{3+}]^2)$

$10^{16.216} = 1.896/[Cr^{3+}]^2$, Hence $[Cr^{3+}]$ = 1.07×10^{-8} M (~10^{-8} M, order have to correct, 2 pts)

2. (Total 14 pts)

(a) (3 pts) potential 안 써도 상관 없음

Cathode: $2\ H_3O^+(aq) + 2\ e^- \rightarrow H_2(g) + 2\ H_2O(l)$ $\qquad E^o = 0.00$ V

Anode: $3\ H_2O(l) \rightarrow (1/2)\ O_2(g) + 2\ H_3O^+(aq) + 2\ e^-$ $\qquad -E^o = -(+1.229$ V)

($6\ H_2O(l) \rightarrow O_2(g) + 4\ H_3O^+(aq) + 4\ e^-$)도 정답인정

(b) (4 pts) 각 2 pts

E(cathode) = E^o (cathode) – (0.0592 V / n_{hc}) log Q_{hc}

= 0.00 – (0.0592 V / 2) log $\{P(H_2)/[H_3O^+]^2\}$

= 0.00 – (0.0592 V / 2) log $\{1/(10^{-7})^2\}$

= – 0.414 V = E ($H_3O^+(10^{-7}$ M)|H_2(1 atm))

E(anode) = E^o (anode) – (0.0592 V / n_{hc}) log Q_{hc}

= 1.229 – (0.0592 V / 2) log $\{P(O_2)/[H_3O^+]^2\}$

= 1.229 – (0.0592 V / 2) log $\{1/(10^{-7})^2\}$

= 0.815 V = $E(O_2$(1 atm),$H_3O^+(10^{-7}$ M)|H_2O)

(c) (3 pts) each of three: 1 pt

ΔE = E(cathode) – E(anode) = – 0.414 – 0.815 V = –1.229 V (= ΔE^o)

Since $\Delta E < 0$, $\Delta G > 0$ → nonspontaneous

→ needs an external voltage, Decomposition potential of 1.229 V.

(d) (4 pts) reduction potential 계산 안하고 답만 맞는 경우 각각 0.5 pt; reduction potential 비교시,

Concentraion of NaCl using Nernst eq. 고려하지 않으면 -1 pt.

Possible half-cell reactions at electrode:

Cathode: $Na^+(0.1\ M) + e^- \rightarrow Na(s)$ $\qquad E^o\ (Na^+|Na) = -2.71$ V

$2\ H_3O^+(10^{-7}\ M) + 2\ e^- \rightarrow H_2(g) + 2\ H_2O(l)$ $\qquad E^o(H_3O^+|H_2) = 0.00$ V

Anode: $2Cl^-(0.1\ M) \rightarrow Cl_2(g) + 2\ e^-$ $\qquad -E^o(Cl_2|Cl^-) = -1.36$ V

$6H_2O(l) \rightarrow O_2(g) + 4\ H_3O^+(10^{-7}\ M) + 4\ e^-$ $\qquad -E^o(O_2,H_3O^+|\ H_2O) = -1.229$ V

$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M, $P(H_2) = P(Cl_2) = P(O_2) = 1$ atm at 25°C

>> Reduction potential for the first reaction:

$E(Na^+|Na) = E^o\ (Na^+|Na)$ – (0.0592 V / n_{hc}) log Q_{hc}

= –2.71 – (0.0592 V / 1) log $\{1/[Na^+]\}$

= –2.71 – (0.0592 V / 1) log {1/(0.1)}

= – 2.71 – 0.06 = – 2.77 V

Smaller than – 0.414 V = $E[H_3O^+(10^{-7}$ M)|H_2(1 atm)]

→ Reduction of $Na^+(aq)$ impossible! Hence hydrogen will be generated at the cathode

>> Reduction potential for the third reaction:

$E(Cl_2|Cl^-) = E^o\ (Cl_2|Cl^-) - (0.0592\ V / n_{hc}) \log Q_{hc}$

$= 1.36 - (0.0592\ V / 1) \log \{[Cl^-]/P(Cl_2)\}$

$= 1.36 - (0.0592\ V / 1) \log \{(0.1) / 1\} = 1.42\ V$

Larger than 0.815 V = $E(O_2(1\ atm), H_3O^+(10^{-7}\ M)|H_2O)$

→ reduction of $Cl_2(g)$ possible, oxidation of Cl^- is not plausible! Hence, oxygen will be generated at the anode.

3. (Total 6 pts)

(a) (3 pts)

$\frac{1}{[A]_t}$ = 2kt + $\frac{1}{[A]_0}$, so

$$\frac{1}{[I]_t} = 2kt + \frac{1}{[I]_0}$$

$$\frac{1}{[I]_{2\ min}} = (2 \times 7.0 \times 10^9\ M^{-1}\ s^{-1})(2\ min \times \frac{60\ s}{min}) + \frac{1}{0.086\ M}$$

$[I]_{2\ min}$ = 6.0 X 10^{-13} M

Hence $[I_2]$ = 0.043 M

(b) (3 pts) formular, 0.6 M, 0.42 M, 각각 1 pt

$t_{1/2}$ = $1/(2k[A]_0)$, so

For $[I]_0$ = 0.6 M,

$t_{1/2} = 1/(2k[I]_0) = 1/2 \times \frac{1}{(7.0 \times 10^9\ M^{-1}s^{-1})(0.6\ M)} = 1.2 \times 10^{-10}$ s

For [I] = 0.42 M,

$t_{1/2} = \frac{1}{k[I]_0} = \frac{1}{(7.0 \times 10^9\ M^{-1}s^{-1})(0.42\ M)} = 1.7 \times 10^{-10}$ s

4. (Total 9 pts)

(a) (3 pts) $k = A \times \exp(-E_a/RT)$

$\ln k_1 - \ln k_2 = \ln(k_1/k_2) = E_a/R \times (1/T_2 - 1/T_1)$

Hence,

$E_a = \ln(k_1/k_2) \times R \times 1/(1/T_2 - 1/T_1) = \ln(0.76/0.87) \times 8.314$ J/molK $\times 1/(1/1030\text{K} - 1/1000\text{K})$

= 38.6 kJmol^{-1}

(b) (3 pts) from $k = A \times \exp(-E_a/RT)$

$A = k / \exp(-E_a/RT) = 0.76\ \text{s}^{-1} / \exp((-38.6 \times 1000\ \text{J/mol}) / (8.314\ \text{J/molK} \times 1000\text{K})) =$

= 78.9 s^{-1}

(c) (3 pts) from $k = A \times \exp(-E_a/RT)$

k at 1100 K = $78.9\ \text{s}^{-1} \times \exp((-38.6 \times 1000\ \text{J/mol}) / (8.314\ \text{J/molK} \times 1100\text{K}))$= 1.16 s^{-1}

5. (Total 8 pts)

(a) (4 pts)

a) The enzyme is carbonic anhydrase and the substrate is carbon dioxide. Write the Michaelis-Menten rate equation (text equation 18.8), letting E stand for carbonic anhydrase

$$\frac{d[CO_2]}{dt} = \frac{\kappa_2[E]_0[CO_2]}{[CO_2]+K_m}$$

The rate of the reaction is maximized by a large concentration of CO_2. If $[CO_2] >> K_m$, then the preceding equation becomes

$$\frac{d[CO_2]}{dt} = \kappa_2[E]_0$$

Inserting the given values for κ_2 and the concentration of the enzyme gives

$$\frac{d[CO_2]}{dt} = (6\times10^5 s^{-1})(5\times10^{-6} \text{ mol L}^{-1}) = 3 \text{ mol L}^{-1} \text{ s}^{-1}$$

(b) (4 pts)

b) Rewrite text equation 18.8 for this reaction and substitute in it

$$\frac{d[CO_2]}{dt} = \frac{\kappa_2[E]_0[CO_2]}{[CO_2]+K_m}$$

$$.30(3 \text{ mol L}^{-1}\text{s}^{-1}) = \frac{(6\times10^5 \text{ s}^{-1})(5\times10^{-6} \text{ mol L}^{-1})[CO_2]}{[CO_2]+(8\times10^{-5} \text{ mol L}^{-1})}$$

Solve for $[CO_2]$

$$0.30 = \frac{[CO_2]}{[CO_2]+(8\times10^{-5} \text{ mol L}^{-1})}$$

$$\frac{1}{0.30} = \frac{[CO_2]+(8\times10^{-5} \text{ mol L}^{-1})}{[CO_2]}$$

$$3.33 = 1+\frac{8\times10^{-5} \text{ mol L}^{-1}}{[CO_2]}$$

$$[CO_2] = 3.4\times10^{-5} \text{ mol L}^{-1}$$

6. (7 pts) B 2 pts, reduced mass 2 pt, length 3 pts

We use the $\tilde{\nu}$ to find B, and then B to find r_e..

The differences $\tilde{\nu}_5$ - $\tilde{\nu}_4$ and $\tilde{\nu}_6$ - $\tilde{\nu}_5$ are 20.8 and 20.5 cm^{-1}, respectively, so

average B = $\frac{1}{2}$ (20.65) = 10.32 ± 0.2 cm^{-1}.

The reduced mass, μ, in kilograms, is

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{(1.00)(35.00)}{(1.00+35.00)} \text{amu}\left(\frac{1 g}{6.02 \ X \ 10^{23} \ amu}\right)\left(\frac{1 \ kg}{1000 \ g}\right)$$

$$= 1.615 \text{ X } 10^{-27} \text{ kg}$$

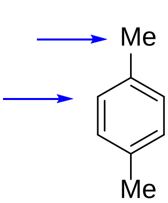
Then

$$r_e = \left[\frac{6.626 \ X \ 10^{-34} \ J \ s}{(8\pi^2)(3.0 \ X \ 10^8 m \ s^{-1})(10.32 \ X \ 10^2 \ m^{-1})(1.615 \ X \ 10^{-27} \ kg)}\right]^{1/2}$$

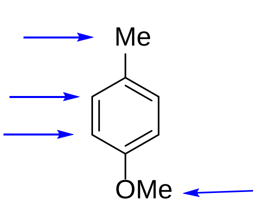
= 1.296 X 10^{-10} m (= 1.296 Å)

7. (Total 12 pts)

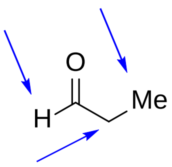
(a) (6 pts) 각 1 pt, 다 맞았을 경우 +1 pt



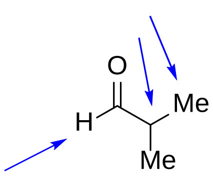
2



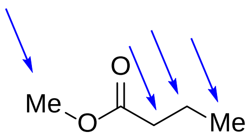
4



3

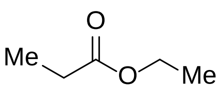


3

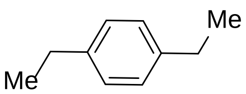


4

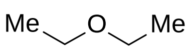
(b) (6 pts) 각 1 pt, 다 맞았을 경우 +1 pt



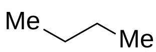
D



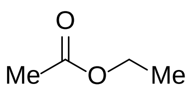
E



B



A



C

8. (Total 14 pts) **2 pts for a correct answer and -1 pt for a wrong answer**

(a) F

The LUMO of ethylene is an antibonding orbital (π^*). An additional antibonding electron means that the bond order decreases in $C_2H_4^-$ compared to C_2H

(b) F

The transfer reduces the overall bond order of the molecule by 1. The C to C bond in the molecule in the excited state should be *longer* than it was in the ground state. Because the bond is weaker, its force constant is diminished, and the vibrational frequency of the C to C stretching mode is reduced.

(c) F

Delocalization of the double bonds in benzene should lower the energy for an electronic transition. Therefore, the absorption occurs at longer wavelength in benzene.

(d) T

El-Sayed's rule

(e) F

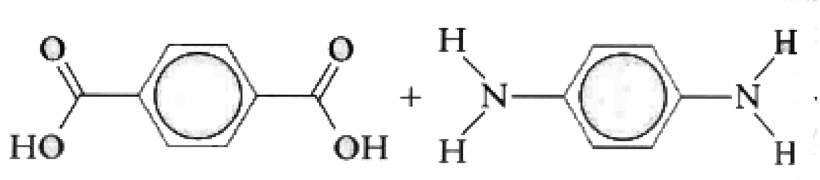
(f) T

(g) F

A strong absorption observed in the ultraviolet region of the spectrum of formaldehyde is attributed to a $\pi \rightarrow \pi^*$ transition.

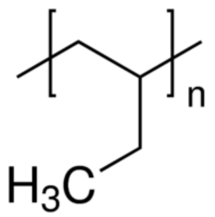
9. (Total 8 pts)

(a) (4 pts) 각 monomer 당 2 pts



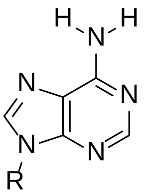
(b) (4 pts) 비슷하나 repeating unit 이 약간 틀렸을 경우 2 pts

The resulting polymer is poly(1-butene), and its repeating unit is following :

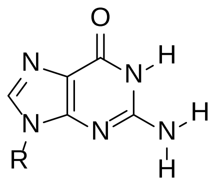


10. (Total 10 pts)

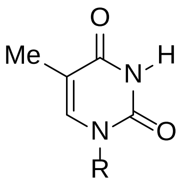
(a) (3 pts)



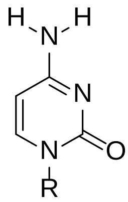
adenine



guanine

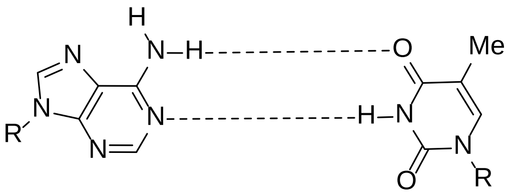


thymine



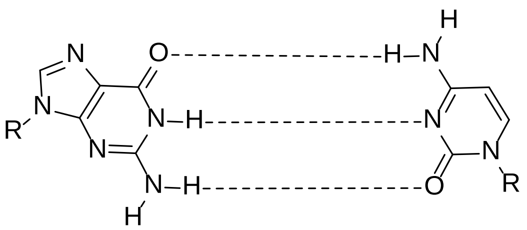
cytosine

(b) (3 pts) 각 hydrogen bonding 당 1 pt, 다 맞는 경우 +1 pt



adenine thymine

(c) (4 pts) 각 hydrogen bonding 당 1 pt, 다 맞는 경우 +1 pt



guanine cytosine

2014 FALL Semester Final Examination
For General Chemistry II (CH103)

Date: December 17 (Wed),   Time Limit: 19:00 ~ 21:00

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/12	**6**	/7	
2	/14	**7**	/12	
3	/6	**8**	/14	**/100**
4	/9	**9**	/8	
5	/8	**10**	/10	

** This paper consists of 14 sheets with 10 problems (page 11: standard reduction potentials and ^{9}H NMR chemical shifts, page 12: fundamental constants, page 13: periodic table, page 14: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the sheet.
Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.

1. Period, Location and Procedure
   1) Return and Claim Period: ***December 19 (Friday, 11:00-13:00, 2 hrs)***
   2) ***Location: Creative Learning Bldg.(E11)***

Class	***Room***
A	**407**
B	**408**
C	**409**

   3) Claim Procedure:

Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)

Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

(During the period, you can check the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it. The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 12/19 on the web.)

2. Final Confirmation
   1) Period: ***December 20(Sat) – 21(Sun)***
   2) Procedure: During this period, you can check the final score of the examination *on the website* again.

To get more information, visit the website at www.gencheminkaist.pe.kr.

1. (Total 12 pts) The following reaction occurs in an electrochemical cell (25 °C).

$$3HClO_2(aq) + 2Cr^{3+}(aq) + 12H_2O(l) \longrightarrow 3HClO(aq) + Cr_2O_7^{2-}(aq) + 8H_3O^+(aq)$$

(a) Calculate E° for this cell.

(Answer)

(b) Calculate ΔG° for this cell.

(Answer)

(c) Calculate the equilibrium constant for this reaction.

(Answer)

(d) At pH 0, with $[Cr_2O_7^{2-}]$ = 0.8 M and $[HClO_2]$ = 0.15 M, and [HClO] = 0.2 M, the cell potential is found to equal 0.15 V. Calculate the concentration of Cr^{3+} (aq) in the cell.

(Answer)

2. (Total 14 pts) Consider the electrolysis of pure water.

$$H_2O \rightarrow H_2 + 1/2\ O_2$$

(a) Write the half-cell reactions for the cathode and anode.

(Answer)

(b) Assuming that the hydrogen and oxygen are produced at atmospheric pressure, calculate the reduction potential for each half-reaction at pH = 7.

(Answer)

(c) What is the overall cell potential? Is the reaction spontaneous? How much potential should be applied for the electrolysis of pure water to occur?

(Answer)

(d) Suppose you apply 1.5 V on 0.1 M aqueous solution of NaCl. Which substances will be generated in the cathode and in the anode, respectively? (Rationalize your explanation based on the analysis of the reduction potential of each substance present in the solution.)

(Answer)

3. (Total 6 pts) Iodine atoms combine to form molecular iodine in the gas phase :

$$I(g) + I(g) \rightarrow I_2(g)$$

This reaction follows second-order kinetics with $k = 7.0 \times 10^9\ M^{-1}\ s^{-1}$ at 23 ^oC.

(a) If the initial concentration of I was 0.086 M, calculate the concentration after 2 min.

(Answer)

(b) Calculate the half-life of the reaction if the initial concentration of I is 0.6 M and if it is 0.42 M.

(Answer)

4. (Total 9 pts) The rate constant of the first-order reaction $2N_2O\ (g) \rightarrow 2N_2\ (g) + O_2\ (g)$ is 0.76 s^{-1} at 1000 K and 0.87 s^{-1} at 1030 K.

(a) Calculate the activation energy (E_a) of the reaction.

(Answer)

(b) Calculate the pre-exponential factor (A, from the Arrhrenius equation) of the reaction.

(Answer)

(c) What would be the predicted rate constant at 1100 K?

(Answer)

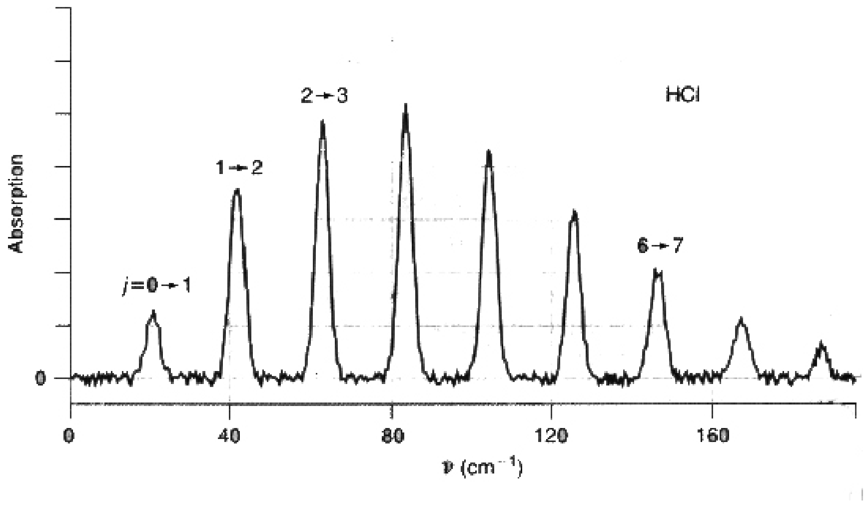
5. (Total 8 pts) The conversion of dissolved carbon dioxide in blood to HCO_3^- and H_3O^+ is catalyzed by the enzyme carbonic anhydrase. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 8\times10^{-5}$ molL^{-1} and $k_2 = 6\times10^{5}$ s^{-1}.

(a) What is the maximum rate of reaction of carbon dioxide if the enzyme concentration is 5×10^{-6} M?
(Answer)

(b) At what CO_2 concentration will the rate of decomposition be 30% of that calculated in part (a)?
(Answer)

6. (7 pts) Following figure is a pure rotational spectrum for HCl. The line positions of the fourth, fifth, and sixth lines of the spectrum shown in the figure are $\tilde{\nu}_4$ = 83.03 cm^{-1}, $\tilde{\nu}_5$ = 103.8 cm^{-1}, and $\tilde{\nu}_6$ = 124.3 cm^{-1}. Find <u>the equilibrium bond length</u> r_e for HCl. Note that $\tilde{B} = \left(\frac{h}{8\pi^2 cI}\right)$.

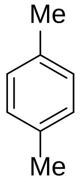
(m_H = 1.00, m_{Cl} = 35.00)



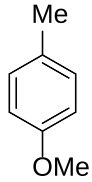
(Answer)

7. (Total 12 pts)

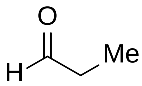
(a) <u>Predict the number of peaks</u> (set of peaks generated by spin-spin coupling is counted as one peak) in the proton NMR spectrum of the following compounds.



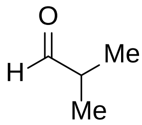
___



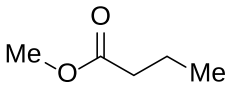
___



___

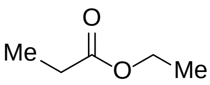


___

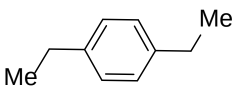


___

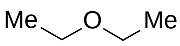
(b) Below are the ^{1}H NMR spectra (DMSO-d_6, 300 MHz) of five different compounds. <u>Assign the spectra to each compounds</u>. Refer the ^{1}H NMR chemical shift chart.



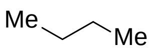
______



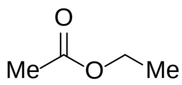
______



______

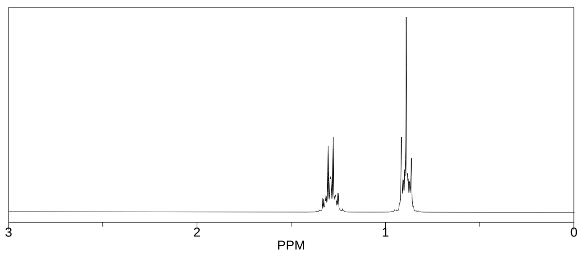


______

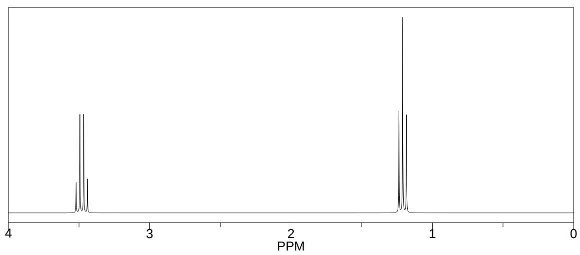


______

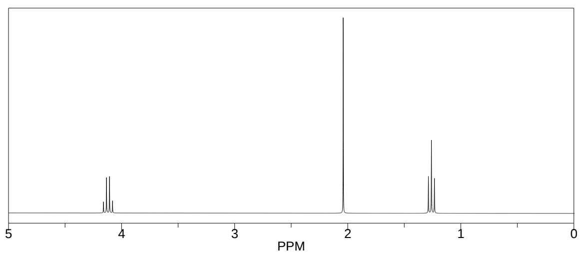
A



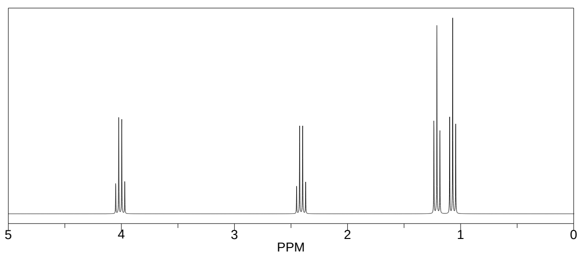
B



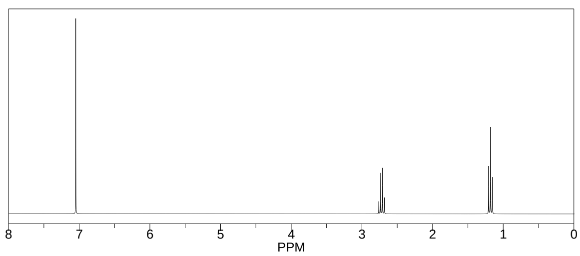
C



D



E



8. (Total 14 pts) Classify each of the following statements as 'True' (T) or 'False' (F). You will get 2 pts for a correct answer and -1 pt for a wrong answer.

(a) If an ethylene molecule gains an additional electron to give the $C_2H_4^-$ ion, the bond order of the carbon-carbon bond will increase.

(Answer)

(b) If an electron in the π orbital of C_2H_4 is excited by a photon to the π^* orbital, the vibrational frequency in the excited state will be higher than in the ground state.

(Answer)

(c) The structure of the molecules cyclohexene and benzene are shown below.

cyclohexene benzene

The absorption of ultraviolet light by benzene occurs at shorter wavelength.

(Answer)

(d) Intersystem crossing is enhanced between states of different orbital configurations for organic molecules containing only the lighter elements.

(Answer)

(e) Φ_p's are small for molecules that have rapid $S_1 \rightarrow T_n$ intersystem crossing rates.

(Answer)

(f) Bacteria have a single photosynthetic system that absorbs longer wavelengths than plants and does not produce holes sufficiently oxidizing to oxidize water.

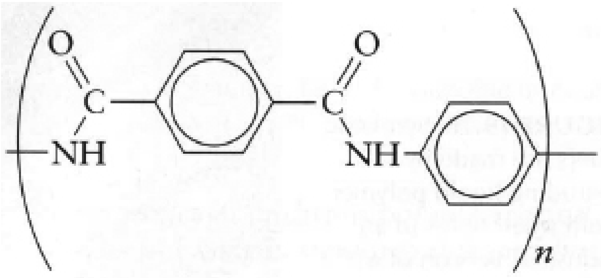
(Answer)

(g) A strong absorption observed in the ultraviolet region of the spectrum of formaldehyde is attributed to an $n \rightarrow \pi^*$ transition.

(Answer)

9. (Total 8 pts)

(a) The following structure is the repeating unit of Kevlar, a mechanically strong fiber used to make bulletproof vests. Draw two monomer chemical structures for Kevlar.



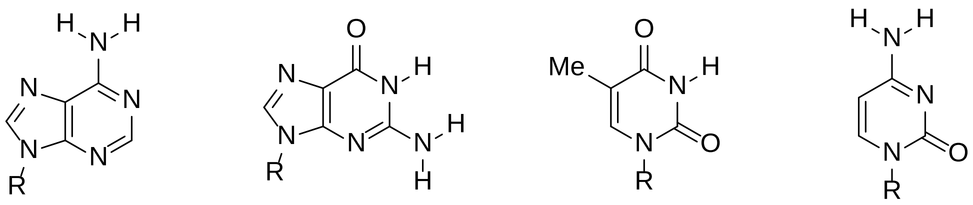
(Answer)

(b) Draw the repeating unit of the polymer which is formed when peroxides are added to $CH_3CH_2CH=CH_2$ at a high temperature and pressure.

(Answer)

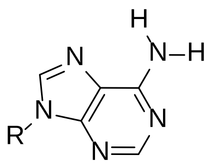
10. (Total 10 pts)

(a) The primary genetic material of biological systems is DNA. DNA is made up of four types of nucleotides which have different bases. Those are adenine, thymine, guanine and cytosine. Below are the structures of four bases. Write the name of each base below the structure.



adenine ________ ________ ________

(b) Adenine and thymine can form two intermolecular hydrogen bonding which enable the formation of DNA double helix. Indicate these two hydrogen bonds from the molecular structure of these two bases.



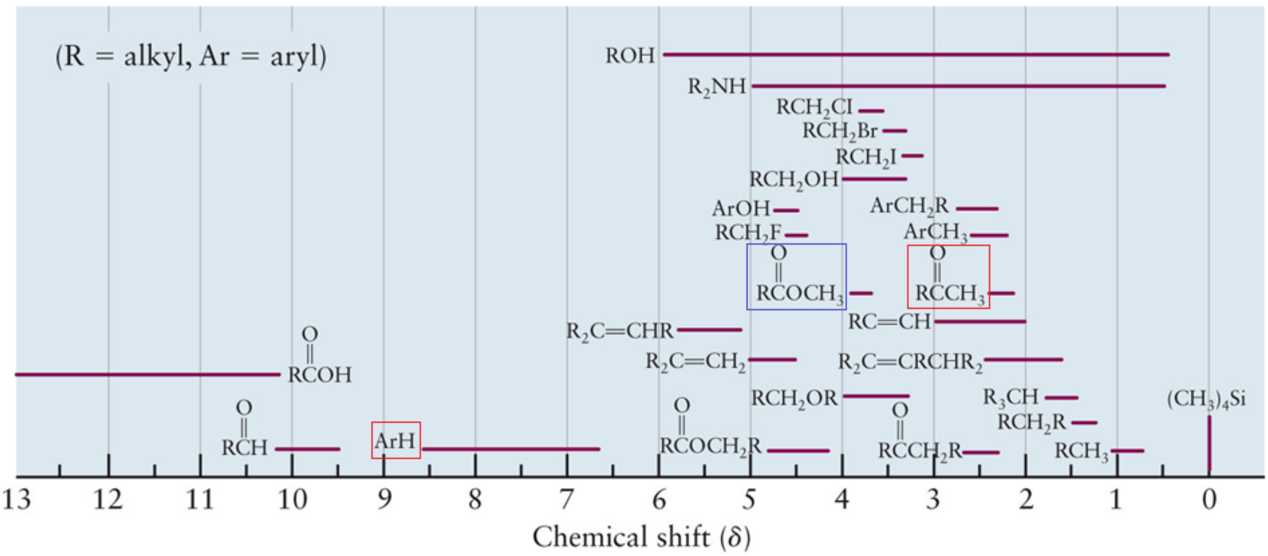
adenine thymine

(c) Guanine and cytosine can form three intermolecular hydrogen bonding which enable the formation of DNA double helix. Indicate these three hydrogen bonds from the molecular structure of these two bases.

guanine cytosine

<Standard Reduction Potentials at 25 °C and [1]H NMR chemical shifts>

Half-Reaction	$E°$ (volts)	Half-Reaction	$E°$ (volts)
$F_2(g) + 2\,e^- \rightarrow 2\,F^-$	2.87	$Cu^{2+} + e^- \rightarrow Cu^+$	0.158
$H_2O_2 + 2\,H_3O^+ + 2\,e^- \rightarrow 4\,H_2O$	1.776	$S_4O_6^{2-} + 2\,e^- \rightarrow 2\,S_2O_3^{2-}$	0.0895
$Au^+ + e^- \rightarrow Au(s)$	1.68	$NO_3^- + H_2O + 2\,e^- \rightarrow NO_2^- + 2\,OH^-$	0.01
$MnO_4^- + 4\,H_3O^+ + 3\,e^- \rightarrow MnO_2(s) + 6\,H_2O$	1.679	$2\,H_3O^+ + 2\,e^- \rightarrow H_2(g) + 2\,H_2O(\ell)$	0.000 exactly
$HClO_2 + 2\,H_3O^+ + 2\,e^- \rightarrow HClO + 3\,H_2O$	1.64	$Pb^{2+} + 2\,e^- \rightarrow Pb(s)$	−0.1263
$HClO + H_3O^+ + e^- \rightarrow Cl_2(g) + 2\,H_2O$	1.63	$Sn^{2+} + 2\,e^- \rightarrow Sn(s)$	−0.1364
$Ce^{4+} + e^- \rightarrow Ce^{3+}$ (1 M HNO_3 solution)	1.61	$Ni^{2+} + 2\,e^- \rightarrow Ni(s)$	−0.23
$2\,NO(g) + 2\,H_3O^+ + 2\,e^- \rightarrow N_2O(g) + 3\,H_2O$	1.59	$Co^{2+} + 2\,e^- \rightarrow Co(s)$	−0.28
$BrO_3^- + 6\,H_3O^+ + 5\,e^- \rightarrow Br_2(\ell) + 9\,H_2O$	1.52	$PbSO_4(s) + 2\,e^- \rightarrow Pb(s) + SO_4^{2-}$	−0.356
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	1.51	$Mn(OH)_3(s) + e^- \rightarrow Mn(OH)_2(s) + OH^-$	−0.40
$MnO_4^- + 8\,H_3O^+ + 5\,e^- \rightarrow Mn^{2+} + 12\,H_2O$	1.491	$Cd^{2+} + 2\,e^- \rightarrow Cd(s)$	−0.4026
$ClO_3^- + 6\,H_3O^+ + 5\,e^- \rightarrow Cl_2(g) + 9\,H_2O$	1.47	$Fe^{2+} + 2\,e^- \rightarrow Fe(s)$	−0.409
$PbO_2(s) + 4\,H_3O^+ + 2\,e^- \rightarrow Pb^{2+} + 6\,H_2O$	1.46	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.424
$Au^{3+} + 3\,e^- \rightarrow Au(s)$	1.42	$Fe(OH)_3(s) + e^- \rightarrow Fe(OH)_2(s) + OH^-$	−0.56
$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-$	1.3583	$PbO(s) + H_2O + 2\,e^- \rightarrow Pb(s) + 2\,OH^-$	−0.576
$Cr_2O_7^{2-} + 14\,H_3O^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 21\,H_2O$	1.33	$2\,SO_3^{2-} + 3\,H_2O + 4\,e^- \rightarrow S_2O_3^{2-} + 6\,OH^-$	−0.58
$O_3(g) + H_2O + 2\,e^- \rightarrow O_2 + 2\,OH^-$	1.24	$Ni(OH)_2(s) + 2\,e^- \rightarrow Ni(s) + 2\,OH^-$	−0.66
$O_2(g) + 4\,H_3O^+ + 4\,e^- \rightarrow 6\,H_2O$	1.229	$Co(OH)_2(s) + 2\,e^- \rightarrow Co(s) + 2\,OH^-$	−0.73
$MnO_2(s) + 4\,H_3O^+ + 2\,e^- \rightarrow Mn^{2+} + 6\,H_2O$	1.208	$Cr^{3+} + 3\,e^- \rightarrow Cr(s)$	−0.74
$ClO_4^- + 2\,H_3O^+ + 2\,e^- \rightarrow ClO_3 + 3\,H_2O$	1.19	$Zn^{2+} + 2\,e^- \rightarrow Zn(s)$	−0.7628
$Br_2(\ell) + 2\,e^- \rightarrow 2\,Br^-$	1.065	$2\,H_2O + 2\,e^- \rightarrow H_2(g) + 2\,OH^-$	−0.8277
$NO_3^- + 4\,H_3O^+ + 3\,e^- \rightarrow NO(g) + 6\,H_2O$	0.96	$Cr^{2+} + 2\,e^- \rightarrow Cr(s)$	−0.905
$2\,Hg^{2+} + 2\,e^- \rightarrow Hg_2^{2+}$	0.905	$SO_4^{2-} + H_2O + 2\,e^- \rightarrow SO_3^{2-} + 2\,OH^-$	−0.92
$Ag^+ + e^- \rightarrow Ag(s)$	0.7996	$Mn^{2+} + 2\,e^- \rightarrow Mn(s)$	−1.029
$Hg_2^{2+} + 2\,e^- \rightarrow 2\,Hg(\ell)$	0.7961	$Mn(OH)_2(s) + 2\,e^- \rightarrow Mn(s) + 2\,OH^-$	−1.47
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.770	$Al^{3+} + 3\,e^- \rightarrow Al(s)$	−1.706
$O_2(g) + 2\,H_3O^+ + 2\,e^- \rightarrow H_2O_2 + 2\,H_2O$	0.682	$Sc^{3+} + 3\,e^- \rightarrow Sc(s)$	−2.08
$BrO_3^- + 3\,H_2O + 6\,e^- \rightarrow Br^- + 6\,OH^-$	0.61	$Ce^{3+} + 3\,e^- \rightarrow Ce(s)$	−2.335
$MnO_4^- + 2\,H_2O + 3\,e^- \rightarrow MnO_2(s) + 4\,OH^-$	0.588	$La^{3+} + 3\,e^- \rightarrow La(s)$	−2.37
$I_2(s) + 2\,e^- \rightarrow 2\,I^-$	0.535	$Mg^{2+} + 2\,e^- \rightarrow Mg(s)$	−2.375
$Cu^+ + e^- \rightarrow Cu(s)$	0.522	$Mg(OH)_2(s) + 2\,e^- \rightarrow Mg(s) + 2\,OH^-$	−2.69
$O_2(g) + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^-$	0.401	$Na^+ + e^- \rightarrow Na(s)$	−2.7109
$Cu^{2+} + 2\,e^- \rightarrow Cu(s)$	0.3402	$Ca^{2+} + 2\,e^- \rightarrow Ca(s)$	−2.76
$PbO_2(s) + H_2O + 2\,e^- \rightarrow PbO(s) + 2\,OH^-$	0.28	$Ba^{2+} + 2\,e^- \rightarrow Ba(s)$	−2.90
$Hg_2Cl_2(s) + 2\,e^- \rightarrow 2\,Hg(\ell) + 2\,Cl^-$	0.2682	$K^+ + e^- \rightarrow K(s)$	−2.925
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	0.2223	$Li^+ + e^- \rightarrow Li(s)$	−3.045
$SO_4^{2-} + 4\,H_3O^+ + 2\,e^- \rightarrow H_2SO_3 + 5\,H_2O$	0.20		



Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23}\ \mathrm{mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859$ Å $= 5.2917720859 \times 10^{-11}$ m
Boltzmann's constant	$k_B = 1.3806504 \times 10^{-23}\ \mathrm{J\ K}^{-1}$
Electron charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96{,}485.3399\ \mathrm{C\ mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31}$ kg
Proton	$m_p = 1.672621637 \times 10^{-27}$ kg
Neutron	$m_n = 1.674927211 \times 10^{-27}$ kg
Permittivity of vacuum	$\epsilon_0 = 8.854187817 \times 10^{-12}\ \mathrm{C}^{-2}\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}$
Planck's constant	$h = 6.62606896 \times 10^{-34}$ J s
Ratio of proton mass to electron mass	$m_p/m_e = 1836.15267247$
Speed of light in a vacuum	$c = 2.99792458 \times 10^{8}\ \mathrm{m\ s}^{-1}$ (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665\ \mathrm{m\ s}^{-2}$ (exactly)
Universal gas constant	$R = 8.314472\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$
	$= 0.0820574\ \mathrm{L\ atm\ mol}^{-1}\ \mathrm{K}^{-1}$

Values are taken from the 2006 CODATA recommended values,
as listed by the National Institute of Standards and Technology.

Conversion Factors

Ångström 1	Å $= 10^{-10}$ m
Atomic mass unit	1 u $= 1.660538782 \times 10^{-27}$ kg
	1 u $= 1.492417830 \times 10^{-10}$ J $= 931.494028$ MeV (energy equivalent from $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV $= 1.602177 \times 10^{-19}$ J
	= 96.485335 kJ mol
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U.S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	1 L $= 10^{-3}\ \mathrm{m}^{-3} = 10^{3}\ \mathrm{cm}^{3}$ (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 t = 1000 kg (exactly)
Pound	1 lb = 16 oz 0.4539237 kg (exactly)
Rydberg	1 Ry $= 2.17987197 \times 10^{-18}$ J
	= 1312.7136 kJ mol
	= 13.60569193 eV
Standard atmosphere	1 atm $= 1.01325 \times 10^{5}$ Pa
	$= 1.01325 \times 10^{5}\ \mathrm{kg\ m}^{-1}\ \mathrm{s}^{-2}$ (exactly)
Torr	1 torr = 133.3224 Pa

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985): 13
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986): IIIA

ATOMIC NUMBER: 5 — RELATIVE ATOMIC MASS (1): 10.811 — SYMBOL: B — ELEMENT NAME: BORON

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** Actinide	104 (261) **Rf** RUTHERFORDIUM	105 (262) **Db** DUBNIUM	106 (266) **Sg** SEABORGIUM	107 (264) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (268) **Mt** MEITNERIUM	110 (281) **Uun** UNUNNILIUM	111 (272) **Uuu** UNUNUNIUM	112 (285) **Uub** UNUNBIUM		114 (289) **Uuq** UNUNQUADIUM				

LANTHANIDE

6	57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

7	89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., **73**, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@nettlinx.com)

Claim Form for General Chemistry Examination

Page (/)

Class:__________, Professor Name:___________, I.D.# :_____________, Name:______________________

If you have any claims on the marked paper, please write down them on this form and ***submit this with your paper in the assigned place***. (And this form should be attached ***on the top of the marked paper with a stapler***.) Please, ***copy this sheet if you need more before use***.

By Student		By TA	
Question #	Claims	Accepted? Yes(√) or No(√)	
		Yes: □	No: □
		Pts (+/-)	Reasons

2014 FALL Semester Midterm Examination
For General Chemistry II (CH103)

Date: October 22 (Wed), ***Time Limit: 19:00 ~ 21:00***

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/6	**6**	/10	
2	/10	**7**	/13	
3	/8	**8**	/10	
4	/11	**9**	/12	**/100**
5	/14	**10**	/6	

** This paper consists of 14 sheets with 10 problems (page 12: fundamental constants, page 13: periodic table, page 14: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the sheet.

Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.
(채점답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure
   1) Return and Claim Period: ***October 27 (Mon, 6:30 ~ 7:30 p.m.)***
   2) ***Location: Room for quiz session***
   3) Procedure:
      Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)
      Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

   If you have any claims on it, you can submit the claim paper with your opinion. After writing your opinions on the claim form, attach it to your mid-term paper with a stapler. Give them to TA.

2. Final Confirmation
   1) Period: October 30 (Thu) – October 31 (Fri)
   2) Procedure: During this period, you can check the final score of the examination *on the website*.

***** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr.***

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	6/6	**6**	3+4+3/10	
2	2x5/10	**7**	2x3+3+2+2/13	
3	4+4/8	**8**	2+2+4+2/10	
4	8+3/11	**9**	10+2/12	**/100**
5	2+2+5+3+2/14	**10**	6/6	

전체 기준: 계산 문제 위주이므로 부분 점수를 최소한으로 줄 것.

전개과정은 맞으나 답이나 unit 이 틀리면 -1

답은 맞으나 전개과정이 약간 틀렸을 때 -1

식을 전혀 쓰지 않고 (혹은 흔적이 전혀 없고) 답만 맞았을 때 -1 (3 pts), -2 (4 pts 이상)

1. (Total 6 pts) Kirchhoff's law 적용 4 pts, Cp 2 pts

$\bar{C}^\circ_{p,\,rxn} = \sum_{products} \nu_P \bar{C}^\circ_P - \sum_{reactants} \nu_R \bar{C}^\circ_P$

$= 2\bar{C}^\circ_P[H_2O\ (l)] - 2\bar{C}^\circ_P[H_2\ (g)] - \bar{C}^\circ_P[O_2\ (g)]$

$= 2(75.3\ \mathrm{J\ mol^{-1}\ K^{-1}}) - 2(28.8\ \mathrm{J\ mol^{-1}\ K^{-1}}) - 29.4\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$= 63.6\ \mathrm{J\ mol^{-1}\ K^{-1}}$

Using Kirchhoff's law gives

$\Delta H^\circ_{rxn}(T_2) = \Delta H^\circ_{rxn}(T_1) + \bar{C}^\circ_{p,\,rxn}\,\Delta T$

$= -571.6\ \mathrm{kJ\ mol^{-1}} + (63.6\ \mathrm{J\ mol^{-1}\ K^{-1}})(373.15\ \mathrm{K} - 298.15\ \mathrm{K})(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}})$

$=$ **$-566.8\ \mathrm{kJ\ mol^{-1}}$**

(Heat capacities are generally given in units of J mol^{-1} K^{-1}, whereas enthalpies are usually in units of kJ mol^{-1} so we must always be careful to include the conversion from joules to kilojoules in these types of calculations.)

2. (Total 10 pts) 각각 맞으면 1pt 씩, 틀리면 -0.5 pt

(a) **F** (an isolated system.)

(b) **T**

(c) **F** (only for an isolated system)

(d) **T**

(e) **F** ((3/2)(1+1+2*(N-2))R = (3/2)(2N-2)R)

(f) **F** (i.e. phase change)

(g) **T**

(h) **F** (for pure substance)

(i) **F** (opposite to the 2nd thermodynamic law)

(j) **T**

3. (Total 8 pts)

(a) (4 pts) **2 pts for each**

$\Delta H_{Fe} = nC_P\Delta T$ = (1.00 mol)(25.1 J K^{-1}mol^{-1})(273.15 - 373.15 K) = **-2510 J**

$\Delta S_{Fe} = nC_P \ln \frac{T_f}{T_i}$ = (1.00 mol)(25.1 J K^{-1}mol^{-1}) $\ln\frac{273.15}{373.15}$ = **-7.83 J K^{-1}**

(b) (4 pts) **2 pts for each**

The entropy S is a function of state, and the initial and final states of the piece of iron are the same as in part **a)**. Therefore **ΔS_{Fe} = -7.83 J K^{-1}**. The reservoir of water gains the 2510 J of heat from the piece of iron at a constant temperature of 273.15 K.

Therefore **ΔS_{water} = 2510 J /273.15 K = +9.19 J K^{-1}.**

$\Delta S_{total} = \Delta S_{Fe} + \Delta S_{water}$ = **1.36 J K^{-1}**

4. (Total 11 pts)

(a) (8 pts) **2 pts for each**

$q = \Delta H_{vap} + nCp\Delta T$

= 2.00 mol × 23.4 kJ/mol + 2 mol × 38 J/molK × 58 K = **51.2 kJ**

$w = -P\Delta V = -P \times \frac{nRT}{P} = -nRT$

= –2.00 mol × 8.315 J/molK × 298 K = **–4.96 kJ**

$\Delta U = q + w$

=51208 J – 4955.7 J = **46.2 kJ**

The reaction is conducted at constant pressure of 1 atm. Hence, $\Delta H = q$.

ΔH = **51.2 kJ**

(b) (3 pts)

$\Delta S_{vap} = q_{rev}/T = \Delta H_{vap}/T$ = (23.4 × 10^3 J/mol) / 240 K = **97.5 J mol^{-1} K^{-1}**

5. (Total 14 pts)

(a) (2 pts)

$[PCl_5]$ = 3.00 mol/L, $[PCl_3]$ = 6.00 mol/L, $[Cl_2]$ = 1.00 mol/L,

$Q = \frac{[PCl_5]}{[PCl_3][Cl_2]}$ = 3.00/6.00*1.00 = 0.5

Q ≠ K, hence the reaction is not at equilibrium.

(b) (2 pts)

Q < K, hence the reaction will proceed to **the right direction to form PCl_5**.

(c) (5 pts) **2^{nd} order equation까지 세웠으나 약간 틀렸을 경우 2 pts**

	PCl_3 +	Cl_2	$\rightleftharpoons$	PCl_5
initial conc (mol/L)	6.00	1.00		3.00
change in conc (mol/L)	-x	-x		+x
equilibrium conc (mol/L)	6-x	1-x		3+x

$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]}$ = (3+x)/[(6-x)(1-x)] = 0.56

Hence

$0.56x^2 - 4.92x + 0.36 = 0$

Solve the quadratic equation to get

x = 9.2 or 0.07. 9.2 is physically nonsensical. x=0.07

Hence,

$[PCl_5]$ = 3.07 mol L^{-1}, $[PCl_3]$ = 5.93 mol L^{-1}, $[Cl_2]$ = 0.93 mol L^{-1} at equilibrium

(d) (3 pts) **ΔH° 구하지 않고 정성적인 답만 썼을 경우 1 pt**

ΔH_f° (PCl_3(g)) = –287.0 kJ/mol. ΔH_f° (PCl_5(g)) = –374.9 kJ/mol.

Hence, the enthalpy of reaction

$\Delta H^\circ = \Delta H_f^\circ (PCl_5(g)) - (\Delta H_f^\circ (PCl_3(g)) + \Delta H_f^\circ (Cl_2(g)))$

= –374.9 + 287.0 = –87.9 kJ/mol (Exothermic reaction)

If the temperature is increased, **PCl_5 will be consumed** to form more chlorine gas (Le Chatelier's principle).

(e) (2 pts)

If the volume is decreased, **chlorine will be consumed** to form more PCl_5 (Le Chatelier's principle).

6. (Total 10 pts)

(a) (3 pts)

From van't Hoff equation applied in the vapor pressure case,

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$\ln(4.23/0.4034) = -\Delta H_{vap}/(8.315\ \text{J/molK})[1/273.5\ \text{K} - 1/223.15]$

$\therefore \Delta H_{vap}$ = **23.82 kJ mol^{-1}**

(b) (4 pts)

$$-\mathrm{RTlnK} = \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

In vaporization case $P_{NH3(g)} = K$

$$-\mathrm{RTlnP} = \Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$$ (equation 1)

$$\Delta S_{vap} = \frac{(\Delta H_{vap} + RTlnP)}{T}$$
$$= \frac{23.82 \times 10^3\ J/mol + 8.315\ J/molK\ \times 273.15\ K\ \times ln4.230}{273.15\ K}$$
$$= 99.20\ J/mol\,K$$

(c) (3 pts)

Normal boiling point is temperature where vapor pressure is 1 atm.

From equation 1,

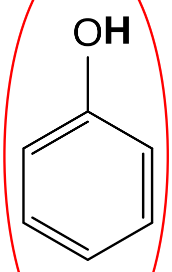
$T = \Delta H_{vap} / (\Delta S_{vap} - \mathrm{RlnP})$

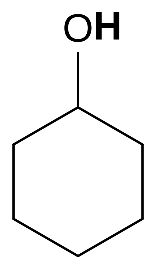
$= (23820\ \text{J/mol}) / (99.20\ \text{J/molK} - 8.315\ \text{J/molK} \times \ln 1)$

= **240.1 K**

7. (Total 13 pts) **2 pts for (a-c, e, f); 3 pts for (d), circle 1 pt + reason 1 pt;**

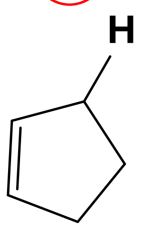
(a) (2 pts)

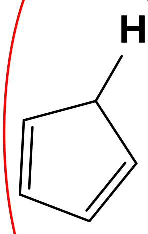




Conjugate base has more resonance structures.

(b) (2 pts)



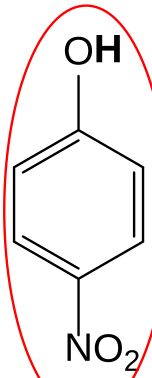


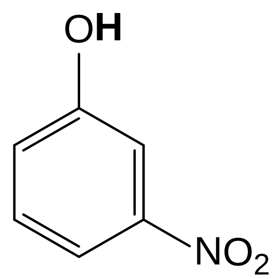
Conjugate base has more resonance structures.

(c) (2 pts) CF_3COOH CCl_3COOH

F is more electronegative than Cl.

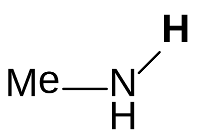
(d) **(3 pts)**

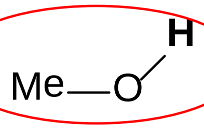




Conjugate base has more resonance structures over the nitro group.

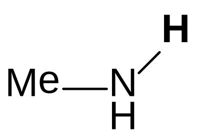
(e) (2 pts)

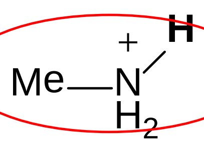




O is more electronegative than N.

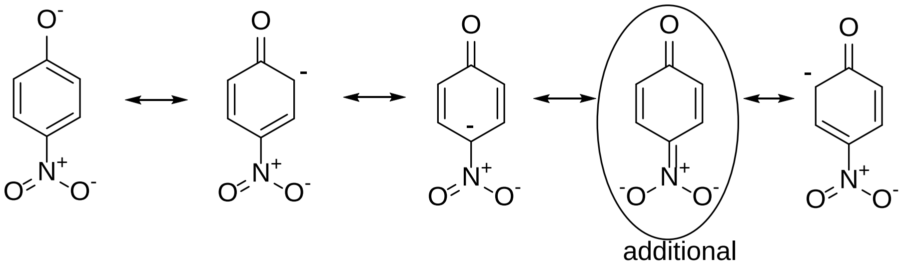
(f) (2 pts)





Protonated amine is more acidic.

For (d),



8. (Total 10 pts)

(a) (2 pts)

In applying the Henderson-Hasselbalch equation,

n_{HA} = n_{NaA} = 0.010 mol, and pH = pK_a =**4.75**

(b) (2 pts)

n_{HA} = 0.005 mol, n_{NaA} = 0.015 mol; pH = 4.75 + $\log_{10}$(0.015/0.005) = **5.23**

(c) (4 pts) **2 pts for each**

Note that solution (b), which contains more salt, has a higher pH as expected since the salt is basic. The added strong base will react stoichiometrically with HA, thereby reducing the amount n_{HA}, and increasing n_{NaA}.

For (a), n_{HA} = 0.010 – 0.002 = 0.008 mol; n_{NaA} = 0.010 + 0.002 = 0.012 mol

pH= 4.75 + $\log_{10}$(0.012/0.008) = **4.93, an increase of 0.18**

For (b), n_{HA} = 0.005 – 0.002 = 0.003 mol; n_{NaA} = 0.015 + 0.002 = 0.017 mol

pH= 4.75 + $\log_{10}$(0.017/0.003) = **5.50, an increase of 0.27**

(d) (2 pts)

If the solution is unbuffered, the acid present to yield pH = 4.75 is negligible compared to the added base, and the pH is determined entirely by the NaOH: pOH = -$\log_{10}$(0.002 mol/0.1L) = 1.70 and **pH 12.30, an increase of pH 7.55.**

9. (Total 12 pts)

(a) (10 pts) **the second equation 4 pts, the first equation 6 pts**

Very high formation constant indicates that most of the Cu^{2+} would exist as a complex-ion with the cyanide anion upon mixing. Limiting reagent is $CuCl_2$. Hence,

Initial $Cu(CN)_4^{2-}$ concentration: 0.02 M

Initial CN^- concentration: $0.1 - 4 \times 0.02 = 0.02$ M.

CN^- hydrolyzes water

$CN^- + H_2O \rightleftharpoons HCN + OH^-$

	CN^- + H_2O	$\rightleftharpoons$	OH^-	HCN
initial conc (M)	0.02		~0	0
change in conc (M)	-x		+x	+x
equilibrium conc (M)	0.02-x		x	x

$[HCN][OH^-]/[CN^-] = x^2/(0.02-x) = K_b = K_w/K_a = 10^{-14}/(6.166 \times 10^{-10}) = 1.62 \times 10^{-5}$

Solving the quadratic equation for x gives,

$x = 5.61 \times 10^{-4}$

$[CN^-] = 0.02 - 5.61\times10^{-4} = 0.0194$ M

$Cu(CN)_4^{2-}(aq) \rightleftharpoons Cu^{2+}(aq) + 4CN^-(aq) \quad K = 1/K_f = 5 \times 10^{-31}$

	$Cu(CN)_4^{2-}$	$\rightleftharpoons$	Cu^{2+}	$4CN^-$
initial conc (M)	0.02		~0	0.0194
change in conc (M)	-x		+x	+4x
equilibrium conc (M)	0.02-x		x	0.0194+4x

$[Cu^{2+}][CN^-]^4/[Cu(CN)_4^{2-}] = [x*(0.0194+4x)^4]/(0.02-x) \fallingdotseq (x*0.0194^4)/(0.02) = K = 5 \times 10^{-31}$

$x = [Cu^{2+}] =$ **7.06×10^{-26} M**

(b) (2 pts)

$[OH^-] = 5.61 \text{ X } 10^{-4}$

$[H_3O^+] = K_w/[OH^-] = 10^{-14} / (5.61 \times 10^{-4}) = 1.78 \times 10^{-11}$

pH = **10.7**

10. (Total 6 pts) K_{sp} of $CaCO_3$ 2 pts

Use the letter C to refer to $CaCO_3$ and B to refer to $BaCO_3$. For $CaCO_3$:

$S_C = 7 \times 10^{-3}$ g $L^{-1} \times \frac{1\ \text{mol}}{100\ \text{g}} = 7 \times 10^{-5}$ mol L^{-1} so that $K_{sp,C} = S^2_C = 5 \times 10^{-9}$

Write the K_{sp} expressions for dissolution of the two carbonates and divide one by the other:

$$\frac{[Ba^{2+}][CO_3{}^{2-}]}{[Ca^{2+}][CO_3{}^{2-}]} = \frac{K_{sp,B}}{K_{sp,C}}$$

Just after the precipitation of $CaCO_3$ has begun, both dissolution reactions are at equilibrium, and the concentration of Ba^{2+} has been reduced to 0.10 of what it was originally. Therefore

$$\frac{[Ba^{2+}]}{[Ca^{2+}]} = \frac{(0.10)[Ca^{2+}]}{[Ca^{2+}]} = \frac{K_{sp,B}}{K_{sp,C}}$$

$K_{sp,B} = (0.10)\ K_{sp,C} = 0.10\ (5 \times 10^{-9}) = 5 \times 10^{-10}$

1. (Total 6 pts) The standard enthalpy change for the reaction

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$$

is -571.6 kJ mol^{-1} at 25 ^oC. Calculate the value of ΔH°_{rxn} at 100 ^oC, assuming that all $\bar{C}_p^o$ values are independent of temperature. ($\bar{C}_p^o$ is 29.4, 28.8, and 75.3 J mol^{-1} K^{-1} for $O_2(g)$, $H_2(g)$, and $H_2O(l)$, respectively.)

(Answer)

2. (Total 10 pts) Classify each of the following statements as 'True' (T) or 'False' (F). You will get 1 pt for a correct answer, and -0.5 pt for a wrong answer.

(a) A bomb calorimeter in which benzene is burned is a thermodynamically closed system.

(Answer)

(b) V (volume) and S (entropy) are both state functions and extensive properties.

(Answer)

(c) The total energy of a system is always conserved.

(Answer)

(d) The constant-pressure heat capacity is always larger than the constant-volume heat capacity.
(Answer)

(e) According to the equipartition theorem of energy, a nonlinear ideal gas molecule containing N atoms has 3N degree of freedom and thus can contribute (3/2)NR to C_v.
(Answer)

(f) Enthalpy change is always stored as bond energies.
(Answer)

(g) Entropy of the isolated system always increases in any spontaneous processes.
(Answer)

(h) Entropy approaches to zero as temperature decreases to 0 K for any substance in its equilibrium.
(Answer)

(i) There is a device that can transfer heat withdrawn from a reservoir completely into work with no other effect.
(Answer)

(j) NO_2 has the higher molar heat capacity than NO.
(Answer)

3. (Total 8 pts) Iron has a heat capacity of 25.1 J $K^{-1}mol^{-1}$, approximately independent of temperature between 0 ^oC and 100 ^oC.

(a) Calculate the enthalpy and entropy change of 1.00 mol iron as it is cooled at atmospheric pressure from 100 ^oC to 0 ^oC.

(Answer)

(b) A piece of iron weighting 55.85 g and at 100 ^oC is placed in a large reservoir of water held at 0 ^oC. It cools irreversibly until its temperature equals that of the water. Assuming the water reservoir is large enough that its temperature remains close to 0 ^oC, calculate the entropy changes for the iron and the water and the total entropy change in this process.

(Answer)

4. (Total 11 pts)

(a) Calculate *q, w, ΔH, and ΔU* for the following reaction. (Assume that the gas behaves ideally and that the volume occupied by the liquid is negligible.)

$$2.00 \text{ mol } NH_3\ (l, 1 \text{ atm}, 240 \text{ K}) \rightarrow 2.00 \text{ mol } NH_3\ (g, 1 \text{ atm}, 298 \text{ K})$$

- Normal boiling point of liquid ammonia: 240 K
- Enthalpy of vaporization at 240 K: 23.4 kJ mol^{-1}
- C_p of ammonia: 38 J $K^{-1}mol^{-1}$

(Answer)

(b) Calculate the entropy of vaporization of ammonia at 240 K.

(Answer)

5. (Total 14 pts) In the following reaction,

$$PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5\ (g) \quad K = 0.56\ (\text{L mol}^{-1}) \text{ at } 250\ °\text{C}$$

1.50 mol PCl_5, 3.00 mol PCl_3, 0.50 mol Cl_2 are present in a 0.500 L reaction vessel at 250 °C (ΔH_f° ($PCl_3(g)$) = –287.0 kJ mol^{-1}, ΔH_f° ($PCl_5(g)$) = –374.9 kJ mol^{-1}).

(a) Is the reaction at equilibrium? Write the reason for your statement.

(Answer)

(b) If not, in which direction is it proceeding?

(Answer)

(c) What are the equilibrium compositions (mol L^{-1}) of all chemical substances?

(Answer)

(d) Once the equilibrium is reached, if the temperature is increased to 300 °C, do you expect more chlorine gas to be consumed or generated?

(Answer)

(e) Once the equilibrium is reached, if you compress the vessel to half the volume, do you expect more chlorine gas to be consumed or generated?

(Answer)

6. (Total 10 pts) The vapor pressure of ammonia at –50 °C is 0.4034 atm. At 0 °C, it is 4.230 atm. Assume that ΔH_{vap} and ΔS_{vap} are approximately independent of temperature.

(a) Calculate the molar enthalpy of vaporization of ammonia.

(Answer)

(b) Calculate the molar entropy of vaporization of ammonia.

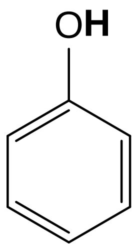
(Answer)

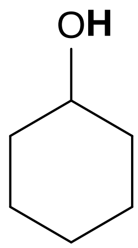
(c) Calculate the normal boiling temperature of ammonia liquid.

(Answer)

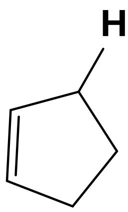
7. (Total 13 pts) Between two chemical structures shown below, circle the substances with a more acidic proton (evaluate the acidity of the "**bold**" protons, a-f), and briefly explain the reason.

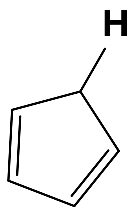
(a)





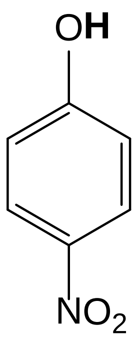
(b)

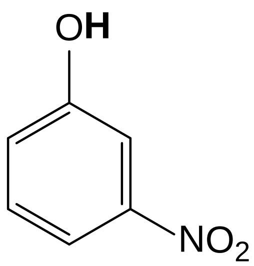




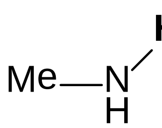
(c) $CF_3COO\mathbf{H}$ $CCl_3COO\mathbf{H}$

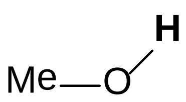
(d)



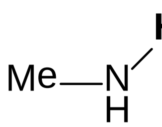


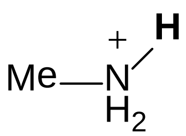
(e)





(f)





8. (Total 10 pts)

Find the pH of acetic acid (HA)/ sodium acetate (NaA) buffer solutions made from

(a) 50 mL 0.20 M HA and 50 mL 0.20 M NaA

(Answer)

(b) 25 mL 0.20 M HA and 75 mL 0.20 M NaA.

(Answer)

(c) Calculate the change in pH when 80 mg NaOH (s) is added to each of these solutions (a and b).

(Answer)

(d) Compare the results with adding the same amount of NaOH to an unbuffered solution of the same pH and volume as solution (a). Neglect the change in volume on adding NaOH (s) (pK_a of HA is 4.75).

(Answer)

9. (Total 12 pts)

(a) Calculate the concentration of Cu^{2+} (aq) in an aqueous solution that contains 0.020 ml of $CuCl_2$ and 0.1 mol of NaCN in 1.0 L (pK_a of HCN is 9.21).

$$Cu^{2+}(aq) + 4CN^{-}(aq) \rightleftarrows Cu(CN)_4^{2-}(aq) \qquad K_f = 2.0 \text{ X } 10^{30}$$

(Answer)

(b) What is the pH of the resulting solution?

(Answer)

10. (Total 6 pts) The solubility of $CaCO_3$ in water is about 7 mg L^{-1}. Show how one can calculate the solubility product of $BaCO_3$ from this information and from the fact that when sodium carbonate solution is added slowly to a solution containing equimolar concentrations of Ca^{2+} and Ba^{2+}, no $CaCO_3$ is formed until about 90% of the Ba^{2+} has been precipitated as $BaCO_3$.

(Answer)

Physical Constants	
Avogadro's number	$N_A = 6.02214179 \times 10^{23}\ mol^{-1}$
Bohr radius	$a_0 = 0.52917720859$ Å $= 5.2917720859 \times 10^{-11}$ m
Boltzmann's constant	$k_B = 1.3806504 \times 10^{-23}\ J\ K^{-1}$
Electron charge	$e = 1.602176487 \times 10^{-19}$ C
Faraday constant	$F = 96{,}485.3399\ C\ mol^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31}$ kg
Proton	$m_p = 1.672621637 \times 10^{-27}$ kg
Neutron	$m_n = 1.674927211 \times 10^{-27}$ kg
Permittivity of vacuum	$\epsilon_0 = 8.854187817 \times 10^{-12}\ C^{-2}\ J^{-1}\ m^{-1}$
Planck's constant	$h = 6.62606896 \times 10^{-34}$ J s
Ratio of proton mass to electron mass	$m_p/m_e = 1836.15267247$
Speed of light in a vacuum	$c = 2.99792458 \times 10^{8}\ m\ s^{-1}$ (exactly)
Standard acceleration of terrestrial gravity	$g = 9.80665\ m\ s^{-2}$ (exactly)
Universal gas constant	$R = 8.314472\ J\ mol^{-1}\ K^{-1}$
	$= 0.0820574\ L\ atm\ mol^{-1}\ K^{-1}$

Values are taken from the 2006 CODATA recommended values, as listed by the National Institute of Standards and Technology.

Conversion Factors	
Ångström 1	Å $= 10^{-10}$ m
Atomic mass unit	$1\ u = 1.660538782 \times 10^{-27}$ kg
	$1\ u = 1.492417830 \times 10^{-10}\ J = 931.494028$ MeV (energy equivalent from $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	$1\ eV = 1.602177 \times 10^{-19}$ J
	= 96.485335 kJ mol
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U.S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	$1\ L = 10^{-3}\ m^{-3} = 10^{3}\ cm^{3}$ (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 t = 1000 kg (exactly)
Pound	1 lb = 16 oz 0.4539237 kg (exactly)
Rydberg	$1\ Ry = 2.17987197 \times 10^{-18}$ J
	= 1312.7136 kJ mol
	= 13.60569193 eV
Standard atmosphere	$1\ atm = 1.01325 \times 10^{5}$ Pa
	$= 1.01325 \times 10^{5}\ kg\ m^{-1}\ s^{-2}$ (exactly)
Torr	1 torr = 133.3224 Pa

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985): 13 — GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986): IIIA

ATOMIC NUMBER: 5 — RELATIVE ATOMIC MASS (1): 10.811

SYMBOL: B — ELEMENT NAME: BORON

PERIOD	GROUP 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.941 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.811 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.086 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.065 **S** SULPHUR	17 35.453 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.39 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.96 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.80 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.94 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** Actinide	104 (261) **Rf** RUTHERFORDIUM	105 (262) **Db** DUBNIUM	106 (266) **Sg** SEABORGIUM	107 (264) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (268) **Mt** MEITNERIUM	110 (281) **Uun** UNUNNILIUM	111 (272) **Uuu** UNUNUNIUM	112 (285) **Uub** UNUNBIUM		114 (289) **Uuq** UNUNQUADIUM				

LANTHANIDE

6	57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.04 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

7	89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

(1) Pure Appl. Chem., **73**, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@nettlinx.com)

Claim Form for General Chemistry Examination

Page (/)

Class:___________, Professor Name:____________, I.D.# :______________, Name:________________________

If you have any claims on the marked paper, please write down them on this form and ***submit this with your paper in the assigned place***. (And this form should be attached ***on the top of the marked paper with a stapler***.) Please, ***copy this sheet if you need more before use***.

By Student		By TA	
Question #	Claims	Accepted? Yes(√) or No(√)	
		Yes: ☐	No: ☐
		Pts (+/-)	Reasons