

2013 SPRING Semester Midterm Examination For General Chemistry I

Date: April 24 (Wed), Time Limit: 7:00 ~ 9:00 p.m.

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	/100
2	/10	7	/10	
3	/10	8	/11	
4	/8	9	/11	
5	/9	10	/15	

** This paper consists of 13 sheets with 10 problems (page 11 & 12: constants & periodic table, page 13: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the Answer 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: *April 29 (Mon, 6: 30 ~ 7:00 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.

(The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 4/27 on the web.)

2. Final Confirmation

- 1) Period: May 2 (Thu) – 3 (Fri)
- 2) Procedure: During this period, you can check final score of the examination *on the website* again.

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

1. (6 pts in total) Take note that ionization energies for the 1s element of the second-row atoms are :

Li	4,820	Be	10,600	B	18,300	C	27,000
N	38,600	O	51,000	F	66,600		kJ mol^{-1}

Now suppose that a certain substance is bombarded by X-rays having a wavelength of 0.989 nm. If photoelectrons with kinetic energies of (a) $94,000 \text{ kJ mol}^{-1}$ and (b) $69,900 \text{ kJ mol}^{-1}$ are ejected from the material, which of the elements listed above must be present in the sample?

(Answer)

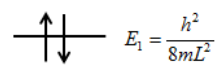
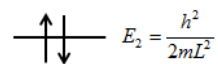
2. (10 pts in total) In the 1D-particle-in-a-box problem, the energy of a particle is given by the formula, $E = n^2 h^2 / (8mL^2)$ [$n = 1, 2, 3, \dots$; L : the length of the box].

(a) What is the energy of a particle, if we extend it to the 2D-particle-in-a-box problem? Each side of the 2D box has the length of L .

(Answer)

(b) Let's try to fill energy levels obtained in (a) with 4 electrons. Assume that though energy levels are not altered by the repulsive potential between electrons, all the other properties of an electron (e.g., Pauli exclusion principle and Hund's rule) should be considered. Draw the ground state electronic configuration as shown in the following example.

Example) In the case of 1D with 4 electrons,

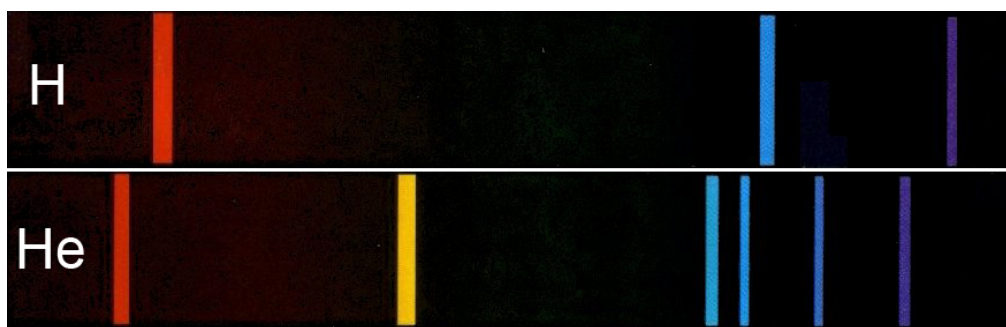


(Answer)

(c) What would be the lowest excitation energy in the case of (b)?

(Answer)

3. (10 pts in total) While the atomic spectrum of hydrogen shows mainly 3 lines in the visible range (420~700 nm), the spectrum of helium shows mainly 6 lines.



(a) Calculate the wavelengths (nm) of three distinct lines of hydrogen and assign them with the orbital energy levels.

(Answer)

(b) Why does the spectrum double the number of lines in helium?

(Answer)

(c) Draw the orbital energy levels of helium based on the above observation.

(Answer)

4. (8 pts in total)

(a) Iridium (Ir) is predicted by the building-up principle to have three unpaired electrons in its ground state outer configuration, but in fact has only one. Write the predicted and actual full electron configurations that explain this fact. You may use short hand noble gas configurations for core electrons.

(Answer)

(b) Write the electron configuration of Sc and Sc⁺, given that they are both paramagnetic. You may use short hand noble gas configurations for core electrons.

(Answer)

(c) Identify the element of period 2 that possesses the ionization energies (I in kJ mol⁻¹) in the table below.

I_1	I_2	I_3	I_4	I_5	I_6
1090	2350	4610	6220	37800	47000

(Answer)

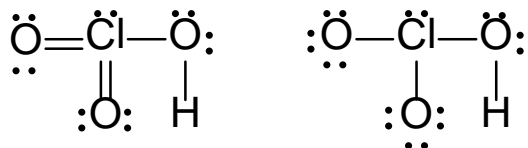
5. (9 pts in total)

(a) In the P_4 molecule, each atom has a complete octet. Figure out the structure of P_4 .

(Answer)

Determine the formal charge on each atom in the following molecules. Identify the structure of lower energy in each pair.

(b)



(c)



(d)



6. (10 pts in total)

For each pair, determine which compound has bonds with greater ionic character:

(a) HCl or HI

(b) CH_4 or CF_4

(c) CO_2 or CS_2

(d) Arrange the anions Cl^- , Br^- , N^{3-} , and O^{2-} in order of increasing polarizability and give reasons for your decisions.

7. (10 pts in total) Predict the geometry of the following molecules, using the VSEPR method.

(a) SF_4

(b) BF_3

(c) ClF_3 (Cl = chlorine)

(d) XeF_2

(e) C_2H_2

(f) Acrylonitrile, CH_2CHCN , is used in the synthesis of acrylic fibers (polyacrylonitriles), such as Orlon. Write the Lewis structure of acrylonitrile and describe the hybrid orbitals on each carbon atom. What are the approximate values of the bond angles?

8. (11 pts in total) To explain molecular geometries of a water molecule, H₂O,

(a) Write the electron configurations of H and O atoms.

(Answer)

(b) Use the VSEPR theory to sketch and name the molecular geometry of H₂O.

(Answer)

(c) Use the valence bond (VB) theory to predict the hybridization of atomic orbitals of the oxygen atom. Give the number and name of hybridized orbitals, occupied electrons, and bonding electrons.

(Answer)

(d) How many molecular orbitals (MOs) do we need to explain electron spreading over a water molecule?

(Answer)

9. (11 pts in total)

(a) On the basis of the configuration of the neutral molecule F_2 , write the molecular orbital configuration of the valence molecular orbitals for (1) F_2^- ; (2) F_2^+ ; (3) F_2^{2-} .

(b) For each species, give the expected bond order.

(c) Which are paramagnetic, if any?

(d) Is the highest-energy orbital that contains an electron σ or π in character?

10. (15 pts in total)

(a) Suggest two Lewis structures that contribute equally to the resonance structure for sulfur dioxide, SO_2 molecule.

(b) Use a valence bond approach to describe the geometry, hybridization, and bonding.

(c) Construct three molecular orbitals using the p orbitals of O and S atoms perpendicular to the plane of the molecule.

(d) Among the three molecular orbitals, which one is HOMO?

FUNDAMENTAL CONSTANTS

Name	Symbol	Value
Atomic mass constant	m_u	$1.660\ 54 \times 10^{-27}$ kg
Avogadro's constant	N_A	$6.022\ 14 \times 10^{23}$ mol ⁻¹
Boltzmann's constant	k	$1.380\ 65 \times 10^{-23}$ J·K ⁻¹
Fundamental charge	e	$1.602\ 18 \times 10^{-19}$ C
Faraday's constant	$F = N_A e$	$9.648\ 53 \times 10^4$ C·mol ⁻¹
Gas constant	$R = N_A k$	$8.314\ 47$ J·K ⁻¹ ·mol ⁻¹ $8.314\ 47$ L·kPa·K ⁻¹ ·mol ⁻¹ $8.205\ 74 \times 10^{-2}$ L·atm·K ⁻¹ ·mol ⁻¹ $62.36\ 37$ L·Torr·K ⁻¹ ·mol ⁻¹ $8.314\ 47 \times 10^{-2}$ L·bar·K ⁻¹ ·mol ⁻¹
Mass of electron	m_e	$9.109\ 38 \times 10^{-31}$ kg
Mass of neutron	m_n	$1.674\ 93 \times 10^{-27}$ kg
Mass of proton	m_p	$1.672\ 62 \times 10^{-27}$ kg
Planck's constant	h	$6.626\ 08 \times 10^{-34}$ J·s
	$\hbar = h/2\pi$	$1.054\ 57 \times 10^{-34}$ J·s
Rydberg constant	\mathcal{R}	$3.289\ 84 \times 10^{15}$ Hz
Speed of light	c	$2.997\ 92 \times 10^8$ m·s ⁻¹
Standard acceleration of free fall	g	$9.806\ 65$ m·s ⁻²
Vacuum permittivity	ϵ_0	$8.854\ 19 \times 10^{-12}$ J ⁻¹ ·C ² ·m ⁻¹

RELATIONS BETWEEN UNITS*

Property	Common unit	SI unit
Mass	2.205 lb (lb = pound)	1.000 kg
	1.000 lb	453.6 g
	1.000 oz (oz = ounce)	28.35 g
	1.000 ton (= 2000 lb)	907.2 kg
	1 t (t = tonne, metric ton)	10 ³ kg
Length	1.094 yd (yd = yard)	1.000 m
	0.3937 in. (in. = inch)	1.000 cm
	0.6214 mi (mi = mile)	1.000 km
	1 in.	2.54 cm
	1 ft (ft = foot)	30.48 cm
	1.000 yd	0.9144 m
	1 Å (Å = ångström)	10 ⁻¹⁰ m
Volume	1 L (L = liter)	10 ³ cm ³ , 1 dm ³
	1.000 gal (gal = gallon) [†]	3.785 dm ³ (3.785 L)
	1.00 ft ³ (ft ³ = cubic foot)	2.83×10^{-2} m ³ (28.3 L)
	1.00 qt (qt = quart) [†]	9.46×10^{-2} m ³ (0.946 L)
Time	1 min (min = minute)	60 s
	1 h (h = hour)	3600 s
	1 day	86 400 s
Pressure	1 atm (atm = atmosphere)	$1.013\ 25 \times 10^5$ Pa
	1.000 Torr or 1.000 mmHg	133.3 Pa
	1.000 psi (psi = pounds per square inch)	6.895 kPa
	1 bar	10 ⁵ Pa
Energy	1 cal	4.184 J
	1 eV	1.60218×10^{-19} J; 96.485 kJ·mol ⁻¹
	1 C·V	1 J
	1 kWh (kWh = kilowatt hour)	3.600×10^3 kJ
	1 L·atm	101.325 J
Temperature conversions	(Fahrenheit temperature)/°F = $\frac{9}{5} \times$ (Celsius temperature)/°C + 32 (Celsius temperature)/°C = $\frac{5}{9} + \{$ (Fahrenheit temperature)/°F - 32} (Kelvin temperature)/K = (Celsius temperature)/°C + 273.15	

*Entries in boldface type are exact.

[†]The European and Canadian Imperial quart and gallon are 1.201 times as large.

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	3+3/6	6	2+2+2+4/10	/100
2	3+3+4/10	7	1×5+5/10	
3	3+4+3/10	8	2+2+4+3/11	
4	3+3+2/8	9	5+2+2+2/11	
5	3+2+2+2/9	10	3+5+5+2/15	

1. (6 pts in total)

(a) (3 pts)

$$E = h\nu = \frac{hc}{\lambda}$$

part of which plays for ionization (I), while the rest goes into the kinetic energy of the ejected photoelectron.

$$E = I + \frac{1}{2}mv^2$$

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ ms}^{-1})}{0.989 \times 10^{-9} \text{ m}} \times \frac{6.02 \times 10^{23}}{\text{mol}}$$
$$= 1.21 \times 10^5 \text{ kJ/mol}$$

For 94,000 kJ/mol

$$I = E - \frac{1}{2}mv^2 = (1.21 - 0.94) \times 10^5 \text{ kJ/mol}$$
$$= 2.7 \times 10^4 \text{ kJ/mol}$$

attribute to carbon atom

(b) (3 pts)

For 69,900 kJ/mol

$$I = E - \frac{1}{2}mv^2 = (1.21 - 0.699) \times 10^5 \text{ kJ/mol}$$
$$= 5.11 \times 10^4 \text{ kJ/mol}$$

attribute to oxygen atom

2. (10 pts in total)

(a) (3 pts) Hamiltonian for a particle in the 2D box can exactly be decomposed by two independent Hamiltonian for the corresponding 1D problem: $H = H_1 + H_2$. Therefore, the energy of a particle in 2D is simply the sum of energies for the H_1 and H_2 . Consequently,

$$E_{n_1, n_2} = \frac{h^2}{8mL^2} (n_1^2 + n_2^2), \text{ where } n_1 = 1, 2, 3, \dots \text{ and } n_2 = 1, 2, 3, \dots$$

(b) (3 pts)

$$E_{2,1} = E_{1,2} = \frac{5h^2}{8mL^2}$$

$$E_{1,1} = \frac{h^2}{4mL^2}$$

(c) (4 pts)

$$E_{2,1} = E_{1,2} = \frac{5h^2}{8mL^2}$$

$$E_{1,1} = \frac{h^2}{4mL^2}$$

or

$$E_{2,1} = E_{1,2} = \frac{5h^2}{8mL^2}$$

$$E_{1,1} = \frac{h^2}{4mL^2}$$

Excitation energy = $E_{2,1}$ (or $E_{1,2}$) - $E_{1,1} = (3h^2)/(8mL^2)$

3. (10 pts in total)

(a) (3 pts) $\Delta E = hc/\lambda = -hR(1/n^2 - 1/2^2)$

$$\lambda = c/\{R(1/2^2 - 1/n^2)\} = (2.998 \times 10^8 \text{ ms}^{-1}) / (3.29 \times 10^{15} \text{ s}^{-1}) \times 1 / (1/n^2 - 1/2^2)$$

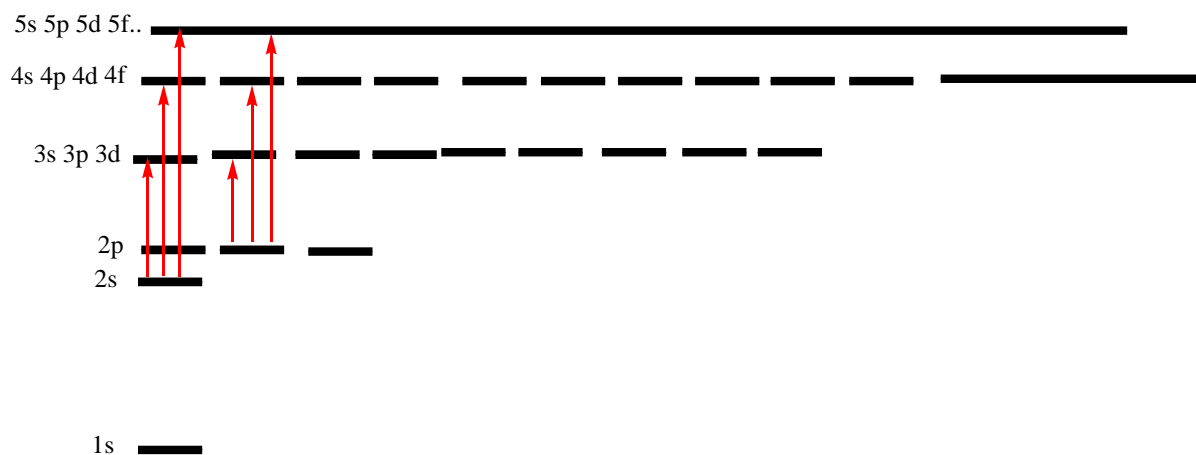
$$\lambda_1 = 36c/5R = 657 \text{ nm}; \quad (n=3; 3s, 3p, 3d) \rightarrow (n=2; 2s, 2p)$$

$$\lambda_1 = 16c/3R = 486 \text{ nm}; \quad (n=4; 4s, 4p, 4d, 4f) \rightarrow (n=2; 2s, 2p)$$

$$\lambda_1 = 100c/21R = 434 \text{ nm}; \quad (n=5; 5s, 5p, 5d, 5f) \rightarrow (n=2; 2s, 2p)$$

(b) (4 pts) With two electrons in helium, subshell orbitals do not have the same energy level from $n=2$. Doubling of the lines means only the orbitals with $n=2$ quantum number have significantly different energy levels and thus the Balmer series has energy transfers from 2s and 2p energy levels.

(c) (3 pts)



4. (8 pts in total)

(a) (3 pts) Predicted electronic configuration of Ir ($Z = 77$) is $[\text{Xe}]4f^{14}5d^76s^2$. Actual electronic configuration is $[\text{Xe}]4f^{14}5d^9$

(b) (3 pts) Sc ($Z = 21$) is $[\text{Ar}]3d^14s^2$ (paramagnetic)

Sc^+ is $[\text{Ar}]3d^14s^1$ (paramagnetic)

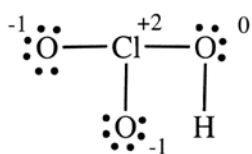
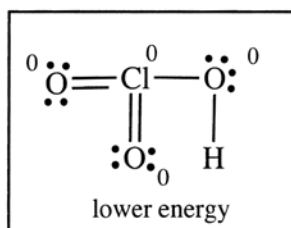
(c) (2 pts) Carbon (C)

5. (9 pts in total)

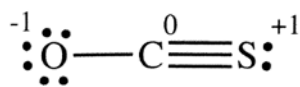
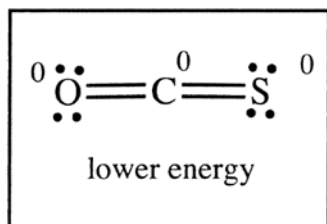
(a) (3 pts) tetrahedral



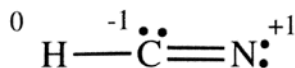
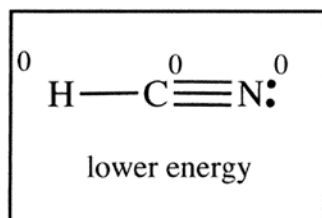
(b) (2 pts)



(c) (2 pts)



(d) (2 pts)



6. (10 pts in total)

(a-c) (each 2 pts) × 3

(a) The bond in HCl would be more ionic. The electronegativity difference is greater between H and Cl than between H and I, making the H—Cl bond more ionic.

(b) The bonds in CF₄ would be more ionic. The electronegativity difference is greater between C and F than between C and H, making the C—F bonds more ionic.

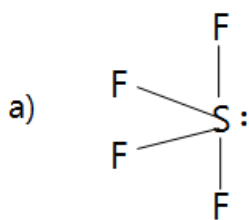
(c) C and S have nearly identical electronegativities, so the C—S bonds would be expected to be almost completely covalent, whereas the C—O bonds would be more ionic.

(d) (4 pts)

$\text{O}^{2-} < \text{N}^{3-} < \text{Cl}^- < \text{Br}^-$; the polarizability increases as the ion gets larger and less electronegative. The ionic radii for these species are 140 pm, 171 pm, 181 pm, 196 pm, respectively.

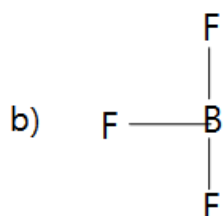
7. (10 pts in total)

(a-e) (each 1 pt) × 5

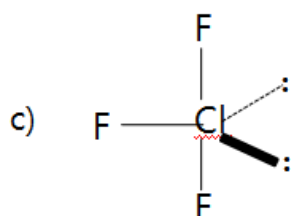


5 electron pairs about sulfur should have a trigonal bipyramidal arrangement

lone pairs occupy equatorial position

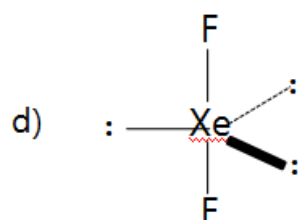


3 electron pairs about Boron have a Trigonal planar arrangement



5 electron pairs about chlorine have a trigonal bipyramidal arrangement

2 lone pairs occupy equatorial position

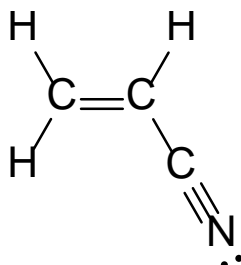


5 electron pairs about Xe have a trigonal bipyramidal arrangement

3 lone pairs occupy equatorial position



(f) (5 pts)



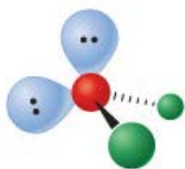
The first two carbons (CH_2 and CH) are sp^2 hybridized with $\text{H}-\text{C}-\text{H}$ and $\text{C}-\text{C}-\text{H}$ angles of 120° . The third carbon (bonded to N) is sp hybridized with a $\text{C}-\text{C}-\text{N}$ angle of 180° .

8. (11 pts in total)

(a) (2 pts) H, $1s^1$

O, $1s^2 2s^2 2p^4$

(b) (2 pts)



Bent

bent or angular

(c) (4 pts)

- Four sp^3 hybrid orbitals
- Two of sp^3 hybrid orbitals occupied by two lone pair electrons
- Two of sp^3 hybrid orbitals with an unpaired electron forming O-H σ bonds

(d) (3 pts) six MOs from two hydrogen 1s orbitals and one 2s, three 2p oxygen orbitals

9. (11 pts in total)

(a) (5 pts)

(b-d) (each 2 pt) $\times 3$

$$(a) (1) (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^2 (\sigma_{2p}^*)^1$$

$$(2) (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^1$$

$$(3) (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^2 (\sigma_{2p}^*)^2$$

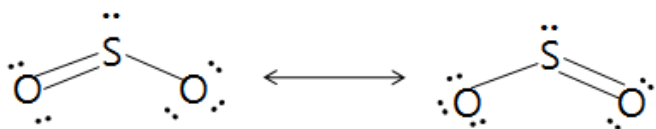
(b) (1) 0.5; (2) 1.5; (3) 0

(c) (1) and (2) are paramagnetic, with one unpaired electron each

(d) σ for (1) and (3), π for (2).

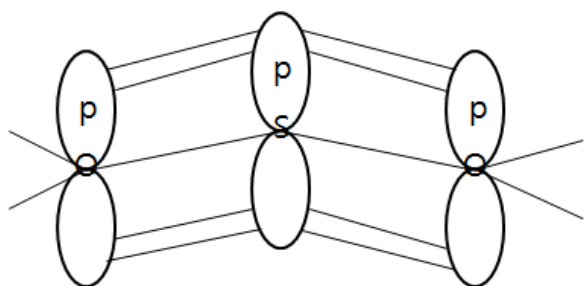
10. (15 pts in total)

(a) (3 pts)



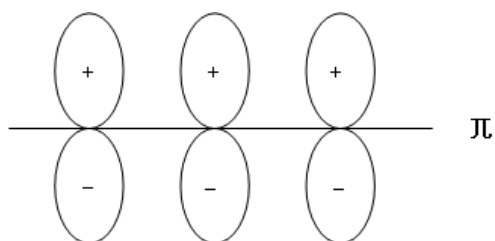
(b) (5 pts)

Each atom uses sp^2 hybrid orbital (planar 120° network of S-O sigma bond).
The overlap of a hybrid orbital from sulfur with one from oxygen gives an S-O σ bond.
Four of the 18 electrons go into the 2 S-O bonds, while 10 go into the 5 lone pairs.
Four electrons and three unhybridized p orbital remain.
Perpendicular to the plane, these three p orbitals then combine to make a delocalized π orbitals for the last 4 electrons.

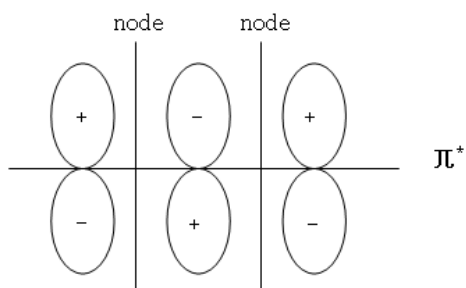


(c) (5 pts)

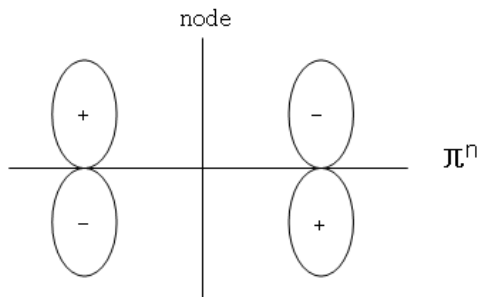
Three atomic p orbitals mix themselves into 3 π molecular orbitals.
They mix constructively to produce π bonding combination with no nodes.



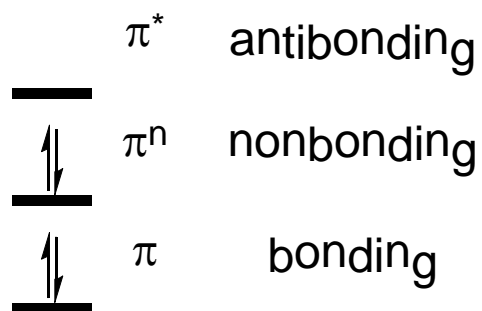
They mix destructively to produce π antibonding combination with two nodes



And they mix indifferently to produce a π nonbonding combination with one node.



4 π electrons therefore manage to lower the energy of the molecule.



(d) (2 pts)

π^n is HOMO (Highest Occupied Molecular Orbital).

2013 SPRING Semester Final Examination For General Chemistry I

Date: June 19 (Wed), **Time Limit:** 7:00 ~ 9:00 p.m.

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	/18	6	/7	/100
2	/6	7	/10	
3	/8	8	/6	
4	/11	9	/10	
5	/8	10	/16	

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

1. Period, Location and Procedure

- 1) Return and Claim Period: **June 22 (Saturday, 11:00 ~ 13:00, 2 hours)**
- 2) **Location: Creative Learning Bldg.(E11)**

Class	Room	Class	Room
A	205	E	209
B	206	F	210
C	207	G	211
D	208		

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)

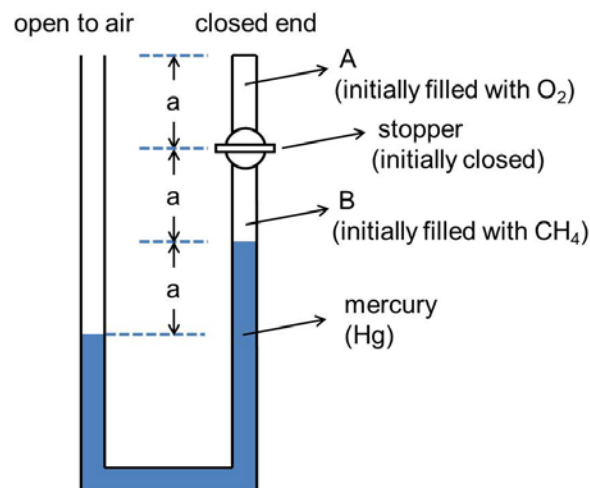
(During the period, you can check the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it.)

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

2. Final Confirmation

- 1) Period: **June 25 (Tuesday, 24 hours)**
- 2) Procedure: During this period, you can check the final score of the examination *on the website* again.

1. (18 points) Consider the following open-tube manometer filled with mercury. The temperature is maintained constant all the time. The left end is open to the atmosphere and the right end is closed. The atmospheric pressure is 760 Torr. The part A is initially filled with 0.2 mol O_2 gas and the part B is filled with 0.1 mol CH_4 gas. The parts A and B are initially separated by a stopcock. Initially the value of a is 200 mm. In other words, the right side of mercury is higher than the left side by 200 mm, and the initial volume of A is the same as that of B. Assume that the volume occupied by the stopcock is zero.



(a) What is the initial pressure of CH_4 gas? What is the initial pressure of O_2 gas?

(Answer)

(b) The stopper is rotated and the parts A and B are connected so that CH_4 and O_2 gases are mixed. Then the right side of mercury level would go up or down? Explain your answer. (Hint: Consider the pressure of A+B when the volumes of A and B momentarily do not change)

(Answer)

(c) Eventually what would be the new pressure of this mixed gas? (Hint: It would help you if you first know which side (left or right) would be eventually higher. For this purpose, consider the pressure of A+B by assuming both sides would have equal height.)

(Answer)

(d) The gas mixture is considered to be our system of interest. In this mixing process, what are the internal energy change (ΔU) and the entropy change (ΔS) of the system?

(Answer)

(e) Then a spark was given in the mixture of CH_4 and O_2 gas so that CH_4 undergoes a combustion reaction. Write down the chemical equation of the combustion reaction of CH_4 gas.

(Answer)

(f) If the combustion reaction goes until no more CH_4 is left, the right side of mercury level would go up or down? Explain your answer. (Hint: Consider the pressure of the gas mixture when the volumes of the gas mixture momentarily does not change)

(Answer)

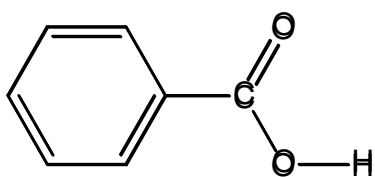
2. (6 points) A 1.00-L flask contains nitrogen gas at a temperature of 15 °C and a pressure of 0.50 bar. 0.10 mol O₂(g) is added to the flask and allowed to mix. Then a stopcock is opened to allow 0.020 mol of molecules to escape. What is the partial pressure of oxygen in the final mixture?

(Answer)

3. (8 points) (a) N₂H₄ is used as a reducing agent and in the manufacture of rocket fuels. How do you expect its boiling point to compare with that of C₂H₂?

(Answer)

(b) Benzoic acid is able to form dimers (dimeric molecules) in the gas phase and in nonpolar solvents, such as tetrachloromethane.



Sketch one unit of benzoic acid dimer, showing clearly and naming the major intermolecular force responsible for dimerization.

Would such dimers be present in ethanol?

(Answer)

4. (11 points) A sample consists of 8.00 kg of gaseous nitrogen and fills a 100 L flask at 300 °C.

The molar mass of N₂ gas is 28 g mol⁻¹, and R = 0.08206 L atm mol⁻¹ K⁻¹.

The van der Waals constants of N₂ gas, *a* and *b*, are *a* = 1.390 atm L² mol⁻², *b* = 0.03913 L mol⁻¹.

(a) What is the pressure of the gas using the van der Waals equation?

(Answer)

(b) What is the compressibility factor ($Z = PV/nRT$) using the van der Waals equation?

(Answer)

(c) Obtain Boyle temperature (T_b) of the gas using the van der Waals equation. Note that $Z = 1$ at T_b .

(Answer)

5. (8 points) What fraction of the total space in a body-centered cubic unit cell is unoccupied? Assume that the central atom touches each of the eight corner atoms of the cube.

(Answer)

6. (7 points) Calculate the work for each of the following processes beginning with ideal gas sample in a piston assembly with $T = 305 \text{ K}$, $P = 1.79 \text{ atm}$, and $V = 4.29 \text{ L}$;

(a) irreversible expansion against a constant external pressure of 1.00 atm to a final volume of 6.52 L ;

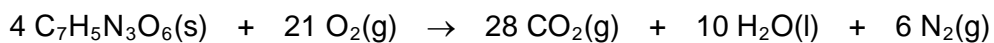
(Answer)

(b) isothermal, reversible expansion to a final volume of 6.52 L .

(Answer)

7. (10 points)

(a) The enthalpy of formation of trinitrotoluene (TNT) is -67 kJ mol^{-1} , and the density of TNT is 1.65 g cm^{-3} . In principle, it could be used as a rocket fuel, with the gases resulting from its decomposition streaming out of the rocket to give the required thrust. In practice, of course, it would be extremely dangerous as a fuel because it is sensitive to shock. Explore its potential as a rocket fuel by calculating its enthalpy density (enthalpy released per liter) for the reaction:



(Standard enthalpies of formation (kJ mol^{-1}): $\text{CO}_2(\text{g}) -393.51$; $\text{H}_2\text{O}(\text{l}) -241.82$)

(Answer)

(b) Benzene (C_6H_6) is more stable than is predicted by its Kekule structure. Estimate this difference of molar energy if the standard enthalpy of formation of benzene liquid is $+49.0 \text{ kJ mol}^{-1}$ and the mean standard bond enthalpies (kJ mol^{-1}) of a Kekule structure are $+412$ (C-H); $+348$ (C-C) and $+612$ (C=C). The standard bond enthalpy of $\text{H}_2(\text{g})$ is $+436 \text{ kJ mol}^{-1}$ and of $\text{C}(\text{s}, \text{graphite})$ is $+717 \text{ kJ mol}^{-1}$.

(Answer)

8. (6 points) If SO_2F_2 adopts a disordered arrangement in its crystal form, what would its residual molar entropy be?

(Answer)

9. (10 points) Calculate the standard entropy of vaporization of water at 85 °C, given that its standard entropy of vaporization at 100 °C is $109.0 \text{ J K}^{-1} \text{ mol}^{-1}$ and the molar heat capacities at constant pressure of liquid water and water vapor are $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $33.6 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively, in this range.

(Answer)

10. (16 points)

For the two processes below (a and b), calculate the entropy change associated with the expansion of 5.00 mol of an ideal monatomic gas, at 298.0 K, from a pressure of 10.0 atm to 1.00 atm.

(a) Reversibly, at a constant temperature of 298.0 K. (4 points)

(Answer)

(b) Reversibly and adiabatically, so that the system temperature drops to 118.6 K, followed by reversible heating of the gas at constant pressure back to 298.0 K.

(Answer)

The standard enthalpy (ΔH°) and entropy (ΔS°) of vaporization of chloroform (CHCl_3) are +31.4 kJ mol⁻¹ and +93.8 J mol⁻¹ K⁻¹, respectively.

(c) Calculate the standard Gibbs free energy change of vaporization (ΔG°) of 1 mol of chloroform at 0 °C and comment on whether the process is favorable at this temperature.

(Answer)

(d) Calculate the boiling point (in °C) of chloroform.

(Answer)

FUNDAMENTAL CONSTANTS

Name	Symbol	Value
Atomic mass constant	m_u	$1.660\ 54 \times 10^{-27}$ kg
Avogadro's constant	N_A	$6.022\ 14 \times 10^{23}$ mol ⁻¹
Boltzmann's constant	k	$1.380\ 65 \times 10^{-23}$ J·K ⁻¹
Fundamental charge	e	$1.602\ 18 \times 10^{-19}$ C
Faraday's constant	$F = N_A e$	$9.648\ 53 \times 10^4$ C·mol ⁻¹
Gas constant	$R = N_A k$	$8.314\ 47$ J·K ⁻¹ ·mol ⁻¹ $8.314\ 47$ L·kPa·K ⁻¹ ·mol ⁻¹ $8.205\ 74 \times 10^{-2}$ L·atm·K ⁻¹ ·mol ⁻¹ $62.36\ 37$ L·Torr·K ⁻¹ ·mol ⁻¹ $8.314\ 47 \times 10^{-2}$ L·bar·K ⁻¹ ·mol ⁻¹
Mass of electron	m_e	$9.109\ 38 \times 10^{-31}$ kg
Mass of neutron	m_n	$1.674\ 93 \times 10^{-27}$ kg
Mass of proton	m_p	$1.672\ 62 \times 10^{-27}$ kg
Planck's constant	h	$6.626\ 08 \times 10^{-34}$ J·s
	$\hbar = h/2\pi$	$1.054\ 57 \times 10^{-34}$ J·s
Rydberg constant	\mathcal{R}	$3.289\ 84 \times 10^{15}$ Hz
Speed of light	c	$2.997\ 92 \times 10^8$ m·s ⁻¹
Standard acceleration of free fall	g	$9.806\ 65$ m·s ⁻²
Vacuum permittivity	ϵ_0	$8.854\ 19 \times 10^{-12}$ J ⁻¹ ·C ² ·m ⁻¹

RELATIONS BETWEEN UNITS*

Property	Common unit	SI unit
Mass	2.205 lb (lb = pound)	1.000 kg
	1.000 lb	453.6 g
	1.000 oz (oz = ounce)	28.35 g
	1.000 ton (= 2000 lb)	907.2 kg
	1 t (t = tonne, metric ton)	10 ³ kg
Length	1.094 yd (yd = yard)	1.000 m
	0.3937 in. (in. = inch)	1.000 cm
	0.6214 mi (mi = mile)	1.000 km
	1 in.	2.54 cm
	1 ft (ft = foot)	30.48 cm
	1.000 yd	0.9144 m
	1 Å (Å = ångström)	10 ⁻¹⁰ m
Volume	1 L (L = liter)	10 ³ cm ³ , 1 dm ³
	1.000 gal (gal = gallon) [†]	3.785 dm ³ (3.785 L)
	1.00 ft ³ (ft ³ = cubic foot)	2.83×10^{-2} m ³ (28.3 L)
	1.00 qt (qt = quart) [†]	9.46×10^2 cm ³ (0.946 L)
Time	1 min (min = minute)	60 s
	1 h (h = hour)	3600 s
	1 day	86 400 s
Pressure	1 atm (atm = atmosphere)	$1.013\ 25 \times 10^5$ Pa
	1.000 Torr or 1.000 mmHg	133.3 Pa
	1.000 psi (psi = pounds per square inch)	6.895 kPa
	1 bar	10 ⁵ Pa
Energy	1 cal	4.184 J
	1 eV	1.60218×10^{-19} J; 96.485 kJ·mol ⁻¹
	1 C·V	1 J
	1 kWh (kWh = kilowatt hour)	3.600×10^3 kJ
	1 L·atm	101.325 J
Temperature conversions	(Fahrenheit temperature)/°F = $\frac{9}{5} \times$ (Celsius temperature)/°C + 32 (Celsius temperature)/°C = $\frac{5}{9} + \{$ (Fahrenheit temperature)/°F - 32} (Kelvin temperature)/K = (Celsius temperature)/°C + 273.15	

*Entries in boldface type are exact.

[†]The European and Canadian Imperial quart and gallon are 1.201 times as large.

PERIODIC TABLE OF THE ELEMENTS

<http://www.kcf-spl.it/hr/periodic/en/>

GROUP	PERIOD																GROUP																																																			
1	2		3										4		5	6	7	8	9	10	11	12	13	14	15	16	17	18																																								
IA	IIA		IIIB										IVB		VB		VIB		VIIB		VIII		IB		IIB		IIIA	IVA	VA	VIA	VIIA	VIIIA																																				
1	2		3										4		5		6		7		8		9		10		11		12		13	14	15	16	17	18																																
H	He		Li										Be		B		C		N		O		F		Ne		Na	Mg	Al										Si		P		S		Cl		Ar																					
1.0079	4.0026		6.941										9.0122		10.811		12.011		14.007		15.999		18.998		20.180		22.990	24.305	26.982										28.086		30.974		32.065		35.453		39.948																					
HYDROGEN	HELIUM		LITHIUM										BERYLLIUM		BORON		CARBON		NITROGEN		OXYGEN		FLUORINE		NEON		SODIUM	MAGNESIUM	ALUMINIUM										SILICON		PHOSPHORUS		SULPHUR		CHLORINE		ARGON																					
3	4		5										6		7		8		9		10		11		12		13	14	15	16	17	18																																				
6.941	9.0122		11										12		13		14		15		16		17		18		19	20	21										22		23		24		25		26																					
Li	Be		Na										Mg		Al		Si		P		S		Cl		Ar		K	Ca	Sc										Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
Li	Be		Na										Mg		Al		Si		P		S		Cl		Ar		K	Ca	Sc										Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
6.941	9.0122		22.990										24.305		26.982		28.086		30.974		32.065		35.453		39.948		39.098	40.078	44.956										47.867		50.942		51.996		54.938		55.845		58.933		58.693		63.546		65.39		69.723		72.64		74.922		78.96		79.904		83.80	
POTASSIUM	CALCIUM		RUBIDIUM										STRONTIUM		YTRBIUM		ZIRCONIUM		NIOBIUM		MOLYBDENUM		TECHNETIUM		RUTHENIUM		RHODIUM		PALLADIUM		SILVER		CADMIUM		INDIUM		TIN		ANTIMONY		TELLURIUM		IODINE		XENON																							
37	38		39										40		41		42		43		44		45		46		47		48		49		50		51		52		53		54																											
Rb	Sr		Cs										Ba		La-Lu		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn																							
85.468	87.62		132.91										137.33		175.1		178.49		180.95		183.84		186.21		190.23		192.22		195.08		196.97		200.59		204.38		207.2		208.98		209		210		222																							
Rb	Sr		Cs										Ba		La-Lu		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn																							
85.468	87.62		132.91										137.33		175.1		178.49		180.95		183.84		186.21		190.23		192.22		195.08		196.97		200.59		204.38		207.2		208.98		209		210		222																							
Caesium	Barium		Francium										Radium		Actinide		Rf		Db		Sg		Bh		Hs		Mt		Uu		Uub		Uuq		Uuq		Uuq		Uuq		Uuq																											
87	88		89										90		91		92		93		94		95		96		97		98		99		100		101		102		103																													
Fr	Ra		Ac-Lr										Ac-Lr		Rf		Db		Sg		Bh		Hs		Mt		Uu		Uub		Uuq		Uuq		Uuq		Uuq		Uuq																													
Fr	Ra		Ac-Lr										Ac-Lr		Rf		Db		Sg		Bh		Hs		Mt		Uu		Uub		Uuq		Uuq		Uuq		Uuq		Uuq																													
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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
 Relative atomic mass, is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
 However three such elements (Tl, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adive@netlix.com)

LANTHANIDE																ACTINIDE															
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		
138.91	140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97	(227)	232.04	231.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(262)		
Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lavrencium		

Class: _____, Professor Name: _____, Student 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: <input type="checkbox"/>	No: <input type="checkbox"/>
		Pts (+/-)	Reasons

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	2+3+4+4+2+3 /18	6	3+4 /7	/100
2	6 /6	7	5+5 /10	
3	2+6/8	8	6 /6	
4	3+4+4 /11	9	4+2+4+2/10	
5	8 /8	10	4+4+4+4/16	

Missing units in the answer: -1 pt

“-1 pt” means “minus 1 point”

1. (total 18 points)

(a) **(2 pts)** The pressure of CH₄ gas = 760 Torr - 200 Torr = **560 Torr**.

The temperature and volume are the same for A and B. On the other hand, A has two times more molecules than B. Therefore, the pressure should be also two times larger.

The pressure of O₂ gas = 2 × 560 Torr = **1120 Torr**.

각 1 pt

(b) **(3 pts)** It would be easier if we consider the situation where the volume remains unchanged.

In this case, if we set V = initial volume of B, then the final volume of A+B is 2V.

The initial pressure of A = P_A = 0.2RT/V.

The initial pressure of B = P_B = 0.1RT/V.

The final pressure of A+B = P = 0.3RT/(2V) = (P_A + P_B)/2 = (560 Torr + 1220 Torr)/2 = 840 Torr.

Since this is higher than the atmospheric pressure (760 Torr), **the right side of mercury should go down.**

설명 없이 down 만 썼을 경우 1 pt

(c) **(4 pts)** If both sides have the same height, that means that the right side moved down by $a/2$ ($=100$ mm) and the left side moved up by 100 mm. Then the new volume of A+B = $2.5V$.

Therefore $P \times 2.5V = 840 \text{ Torr} \times 2V$. $P = 672 \text{ Torr}$. This is now lower than the atmospheric pressure (760 Torr). This means that the right side would not go down this much. In other words, the right side would be still higher.

P_f = final pressure of A+B. V_f = final volume of A+B. If the right side moves down by b mm with respect to the initial position (at which the right side is higher by 200 mm), then the right side would be higher than the left side by $200 \text{ mm} - 2b$.

In addition $V_f = 2V \times (400 + b)/400$.

$P_f V_f = 840 \text{ Torr} \times 2V$.

$P_f \times 2V \times (400 + b)/400 = 840 \text{ Torr} \times 2V$ (eq 1)

In addition, the left side and right side pressure should balance. Therefore

$760 \text{ Torr} = P_f + 200 - 2b$ (eq 2)

Solving eqs 1 and 2 gives $b = 74.26 \text{ mm}$, **$P_f = 708.5 \text{ Torr}$** .

논리적이지만 답만 틀릴 경우 -1 pt

(d) **(4 pts)** Since the temperature is maintained constant, $\Delta T = 0$. Thus **$\Delta U = 0$** .

For the 0.2 mol O_2 gas, $\Delta S = nR \ln(V_2/V_1) = 0.2R \ln((200+200+74.26)/(200)) = 0.17R$

For the 0.1 CH_4 gas, $\Delta S = nR \ln(V_2/V_1) = 0.1R \ln((200+200+74.26)/(200)) = 0.086R$

Thus **$\Delta S = 0.17R + 0.086R = 0.259R = 2.15 \text{ J/K}$**

ΔU 1 pt; ΔS 2 pts

(e) **(2 pts)** A combustion reaction is the reaction with O_2 gas to give $CO_2(g)$ and $H_2O(l)$.

Therefore, **$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$** .

Stoichiometry 틀릴 경우 -1 pt

(f) **(3 pts)** Due to the reaction, 3 gas molecules are reduced to 1 gas molecule. So if the volume does not change, the pressure would go down by three times and the new pressure would be momentarily $615/3 \text{ Torr} = \text{205 Torr}$. **The right side of mercury level would go up.**

설명이 없이 up 만 썼을 경우 1 pt

2. (total 6 points)

$$n_{\text{total}} = n_{\text{N}_2} + n_{\text{O}_2}; n_{\text{N}_2} = \frac{PV}{RT} = \frac{(0.50 \text{ bar}) \times \left(\frac{1 \text{ atm}}{1.01325 \text{ bar}}\right) \times (1.00 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \times (288 \text{ K})}$$
$$= 0.021 \text{ mol}$$

$$n_{\text{total}} = 0.021 + 0.10 = 0.12 \text{ mol}; x_{\text{nitrogen}} = \left(\frac{0.021}{0.12}\right) = 0.18; x_{\text{oxygen}} = 0.82$$

If 0.020 mol were released, then

$$n_{\text{left}} = 0.10 \text{ mol and } n_{\text{oxygen}} = (0.82) \times (0.10 \text{ mol}) = 0.082 \text{ mol}$$

$$P_{\text{O}_2} = \frac{nRT}{V} = \frac{(0.082 \text{ mol}) \times (0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \times (288 \text{ K})}{1.00 \text{ L}}$$
$$= 1.9 \text{ atm}$$

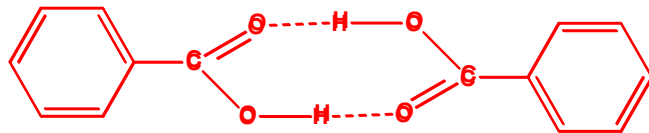
전개가 다 맞으나 계산만 틀린 경우 -1 pt

Mole fraction 까지만 맞은 경우 2 pts

3. (total 8 points)

(a) (2 pts) The boiling point of N_2H_4 would be higher than that of C_2H_4 because N-H...N hydrogen bonds are present in N_2H_4 but not in C_2H_4 .

(b) (6 pts)



----- Hydrogen bonding

No, this dimer would not form much in ethanol solution because of the strong competition from ethanol for hydrogen bonding

그림 4 pts, 한 hydrogen bonding 만 그릴 경우 2 pts

Ethanol 조건에 대한 description 2 pts

4. (11 points)

$$a) P = \frac{nRT}{V-nb} - a\frac{n^2}{V^2}$$

$$= \frac{(286)(0.082)(573)}{100 - (286)(0.03913)} - (1.390) \left(\frac{286}{100}\right)$$

$$= 139.94 \text{ atm} \approx 140 \text{ atm} \quad (3 \text{ pts})$$

$$b) Z \cong 1 + \left(b - \frac{a}{RT}\right) \left(\frac{n}{V}\right) + \dots$$

$$= 1 + \left(0.03913 - \frac{1.390}{0.082 \times 573}\right) \left(\frac{286}{100}\right)$$

$$= 1.0273 \quad (4 \text{ pts})$$

$$c) T_B = \frac{a}{Rb} = \frac{1.390}{0.08206 \times 0.03913} = 432.88 \quad (4 \text{ pts})$$

식은 맞되 계산만 틀릴 경우 -1 pt

5. (total 8 points)

of atoms in unit cube = (1/8 atom/corner X 8 corners) + 1atom (in center) = 2 atoms

Volume of 2 atoms = 2 X 4/3 π = 8.38

The radius of atoms is taken to be 1.

Volume of the cube = (4/ $\sqrt{3}$)³ = 12.32

Volume of space = Volume of cube - Volume of spheres = 12.32 - 8.38 = 3.94

percentage of cube taken by space = 3.94 / 12.32 x 100 = 32%

답만 맞을 경우 5 pts, 전개과정은 맞되 답만 틀린 경우 -1 pt

6. (total 7 points)

(a) The irreversible work of expansion against a constant opposing pressure is given by

$$w = -P_{\text{ex}} \Delta V$$

$$w = -(1.00 \text{ atm})(6.52 \text{ L} - 4.29 \text{ L})$$

$$= -2.23 \text{ L} \cdot \text{atm}$$

$$= -2.23 \text{ L} \cdot \text{atm} \times 101.325 \text{ J} \cdot \text{L}^{-1} \cdot \text{atm}^{-1} = -226 \text{ J}$$

(3 pts)

부호 틀린 경우 -1 pt

(b) An isothermal expansion will be given by

$$w = -nRT \ln \frac{V_2}{V_1}$$

n is calculated from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(1.79 \text{ atm})(4.29 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(305 \text{ K})} = 0.307 \text{ mol}$$

$$w = -(0.307 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(305 \text{ K}) \ln \frac{6.52}{4.29}$$

$$= -326 \text{ J}$$

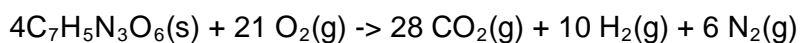
(4 pts)

부호 틀린 경우 -1 pt

7. (total 10 points)

(a) (5 pts)

The enthalpy of reaction for the reaction



May be found using enthalpies of formation:

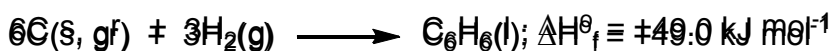
$$28(-393.51\text{ kJ/mol}) + 10(-241.82\text{ kJ/mol}) - 4(+67\text{ kJ/mol}) = \mathbf{-13704\text{ kJ/mol}}$$

This is the energy released per mole of reaction as written. One fourth of this amount of energy or **3426 kJ/mol** will be released per mole of TNT consumed. The energy density in kJ per L may be found by dividing this amount of energy with the mass of one mole of TNT and then by multiplying with the density of TNT:

$$\{(3426\text{ kJ/mol}) / 227.14\text{ g/mol}\} (1.65\text{ g/cm}^3) (10^3\text{ cm}^3 / 1\text{L}) = \mathbf{+ 24.9 \times 10^3\text{ kJ/L}}$$

3426 kJ/mol 까지만 쓴 경우 **2 pts**

(b) (5 pts)



Bonds broken (in kJ)

$$6 \times +717 + 3 \times +436 \equiv +5610\text{ kJ}$$

Bonds made (in kJ), assuming 3 isolated C=C and 3 isolated C-C of Kekule structure

$$3 \times -612 + 3 \times -348 + 6 \times -412 \equiv -5352\text{ kJ}$$



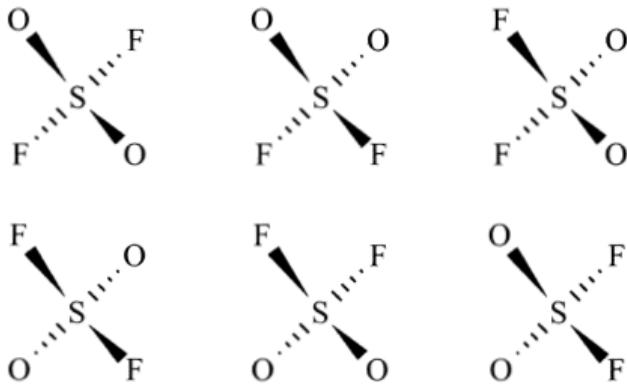
This gives $\Delta H_f^\ominus \equiv +258\text{ kJ mol}^{-1}$

The real benzene molecule is thus more stable than Kekule structure by 209 kJ mol^{-1}

부호 -1 pt

8. (total 6 points)

There are six orientations of an SO_2F_2 molecule as shown below:



$$S = k \ln 6^{6.02 \times 10^{23}} = (1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}) \ln 6^{6.02 \times 10^{23}}$$

$$S = 14.9 \text{ J} \cdot \text{K}^{-1}$$

Orientation 개수가 틀려 답이 틀린 경우 -4 pts

9. (total 10 points)

The entropy of vaporization of water at 85 °C may be carried out through a series of three reversible steps. Namely, reversibly heating the reactants to 100 °C, carrying out the phase change at this temperature, and finally cooling the products back to 85 °C. The sum of the ΔS 's for these three steps will be equivalent to vaporizing water at 85 °C in one irreversible step.

Step 1, heating the reactants to 100 °C :

$$\Delta S_1 = C_{p,m} \ln\left(\frac{T_2}{T_1}\right) = (75.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln\left(\frac{373 \text{ K}}{358 \text{ K}}\right) = 3.09 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Step 2, the entropy of vaporization of H₂O at 100 °C is 109.0 J · K⁻¹ · mol⁻¹

Step 3, cooling the products to 85 °C :

$$\Delta S_3 = C_{p,m} \ln\left(\frac{T_2}{T_1}\right) = (33.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln\left(\frac{358 \text{ K}}{373 \text{ K}}\right) = -1.38 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Therefore, the molar entropy of vaporization is H₂O at 85 °C is:

$$\Delta S_{v,m} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 111 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

ΔS_1 3 pts; ΔS_2 2 pts; ΔS_3 3 pts; sum 2 pts

10. (total 16 points)

(a) (4 pts) At constant temperature, the entropy change is given by

$$\begin{aligned}\Delta S &= nR \ln(V_2/V_1) = nR \ln(P_1/P_2) = (5.00 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 10 \\ &= \underline{\underline{+95.7 \text{ J K}^{-1}}}\end{aligned}$$

부호 -1 pt

(b) (4 pts) For the adiabatic part of this path, entropy change is 0. For the reversible heating at constant pressure from 118.6 K to 298.0 K, the entropy change is

$$\begin{aligned}\Delta S &= nC_p \ln(T_2/T_1) = (5.00 \text{ mol})(5/2 \times 8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(298.0 \text{ K} / 118.6 \text{ K}) \\ &= \underline{\underline{+95.7 \text{ J K}^{-1}}}\end{aligned}$$

부호 -1 pt

(c) (4 pts) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$$\equiv 31400 \text{ J/mol} - (233 \text{ K})(93.8 \text{ J/K mol})$$

$$\equiv \underline{\underline{+5793 \text{ J mol}^{-1}}}$$

Because $\Delta G^\ominus > 0$, vaporization of chloroform at 0 °C (273 K) is NOT spontaneous

부호 -1 pt, no comments -1 pt

(d) (4 pts) At the equilibrium between chloroform vapor and liquid (at the boiling point, T_b , of chloroform), $\Delta G = 0$

Hence $\Delta H^\ominus = T_b \Delta S^\ominus$ (assuming negligible variations of ΔH^\ominus and ΔS^\ominus with T)

$$T_b = \frac{\Delta H^\ominus}{\Delta S^\ominus} = \frac{31400 \text{ J/mol}}{93.8 \text{ J/K mol}} = \underline{\underline{334.6 \text{ K or } 61.6 \text{ }^\circ\text{C}}}$$