2016 SPRING Semester Midterm Examination
For General Chemistry I

Date: April 20 (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	/8	**6**	/12	
2	/9	**7**	/8	
3	/6	**8**	/15	**/100**
4	/8	**9**	/16	
5	/8	**10**	/10	

** This paper consists of 15 sheets with 10 problems (page 13 - 14: constants & periodic table, page 15: 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: *May 2 (Mon, 19: 00 ~ 20:00 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 5/2 on the web.)

2. Final Confirmation

 1) Period: May 4 (Wed) – May 6 (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. (total 8 pts)

Which atom or ion in each pair has the <u>smaller radius</u>?

(a) Li, Li$^+$

   (Answer)

(b) F, F$^-$

   (Answer)

(c) O^{2-}, F$^-$

   (Answer)

(d) Na$^+$, Mg^{2+}

   (Answer)

Which atom or ion in each pair has the <u>larger ionization energy</u>?

(e) C, N

   (Answer)

(f) N, O

   (Answer)

(g) O, S

   (Answer)

(h) Na, Na$^+$

   (Answer)

2. (total 9 pts)

Draw the Lewis structures for the molecules below. Be sure to show formal charges of each atom and all lone pairs. Only one resonance structure needs to be shown.

(a) PI_3

   (Answer)

(b) O_3

   (Answer)

(c) $[ClF_4]^+$ (Cl = chlorine)

   (Answer)

(d) Use the VSEPR model to sketch the correct geometries of CH_3^+ and NH_2^+. Include all lone pairs. Which molecule will have the smaller H–X–H angle (where X = C or N)? Explain your answer.

   (Answer)

3. (total 6 pts)

Neutron diffractometer is used to visualize structures of hydrogens in complex compounds such as proteins. Mass of a neutron equals to 1.675×10^{-24} g.

(a) <u>How fast</u> the neutron have to be accelerated to attain 1 angstrom resolution?

  (Answer)

(b) <u>How much energy</u> (thermal energy) should be supplied to the neutron to attain the wavelength?

  (Answer)

4. (total 8 pts)

A particle of mass m is placed in a three-dimensional rectangular box with edge lengths $2L$, L, and L. Inside the box the potential energy is zero, and outside it is infinite; therefore, the wave function goes smoothly to zero at the sides of the box. <u>Calculate the energies and give the quantum numbers of the ground state and the first five excited states</u> (or sets of states of equal energy) for the particle in the box.

  (Answer)

5. (total 8 pts)

Use the energy expression for the hydrogen atom.

$$E_n = -\frac{Z^2 e^4 m_e}{8 h^2 \varepsilon_0^2 n^2} = -R\frac{Z^2}{n^2}$$

where the Rydberg constant R = 2.1799 X 10^{-18} J.

(a) Ionization energy is the energy required to remove an electron from an atom or a molecule. Calculate the ratio between the first and n-th ionization energies for a hydrogen atom.
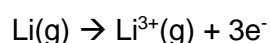
  (Answer)

(b) The formula for a hydrogen like ion cannot be used for many-electron atoms. One way to approximate it is to replace Z with Z - s (Z minus s), where s is a positive dimensionless quantity called the shielding constant. Z - s is often called the "effective nuclear charge". Consider a He atom. Calculate the value of s if the first ionization energy of helium is 3.94 X 10^{-18} J per atom.

  (Answer)

(c) The energy needed for the following process is 1.96 X 10^4 kJ mol^{-1}

  Li(g) → Li^{3+}(g) + 3e⁻

If the first ionization energy of Li is 520 kJ mol^{-1}, calculate the second ionization energy of Li.

  (Answer)

6. (total 12 pts)

(a) Give all values of <u>quantum numbers</u> (ℓ, m_l) with $n = 3$ for one-electron atoms.

 (Answer)

(b) Give the <u>names of all the orbitals</u>.

 (Answer)

(c) Plot <u>radial probability densities</u> $(r^2[R_{nl}(r)]^2)$ on distance from the nucleus for each one-electron orbital.

 (Answer)

(d) <u>How many radial nodes and how many angular nodes</u> do each of the orbitals?

(Answer)

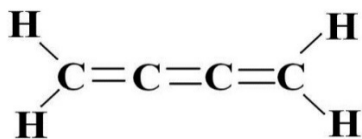(e) Draw <u>the shapes of all orbitals</u> and <u>identify</u> them.

(Answer)

(f) <u>Compare the energy-level diagrams</u> for all orbitals for one-electron atom to a many-electron atom.

(Answer)

7. (total 8 pts)

(a) Use hybridization theory to <u>label the hybridization</u> made for each of the carbon atoms in the molecule buta-1,2,3,-triene.

$$\begin{array}{c} H \\ \diagdown \\ H \end{array} C{=}C{=}C{=}C \begin{array}{c} H \\ \diagup \\ H \end{array}$$

(Answer)

(b) Sketch the <u>sigma framework</u> and <u>π-bonds</u> for this structure.

(Answer)

8. (total 15 pts)

(a) Draw <u>Lewis diagrams</u> of IO_3^-, IO_6^{5-} and IO_4^-.

 (Answer)

(b) Give the <u>steric numbers</u> and identify the <u>geometries</u> using VSEPR for IO_3^-, IO_6^{5-} and IO_4^-.

 (Answer)

(c) Predict the relative I–O <u>bond length order</u> for IO_3^-, IO_6^{5-} and IO_4^- from bond orders.

 (Answer)

(d) Give the <u>ground-state electron configuration</u> of the valence electrons of iodine <u>molecules</u> (I_2). Is iodine <u>paramagnetic or diamagnetic</u>?

 (Answer)

(e) Give the <u>electron configuration</u> of the I_2^+ molecular ion and <u>bond order</u>. Is its bond <u>stronger or weaker</u> than that in I_2?

 (Answer)

9. (total 16 pts)

(a) Construct the <u>correlation diagram</u> for NO and <u>label</u> the molecular orbitals (MOs). (The correlation diagram should include MOs from 1s orbitals), and predict which atom would <u>contribute to σ_{2pz}-more</u> (In which atom the electron in σ_{2pz} orbital would spend more time)?

 (Answer)

(b) Give the ground-state electron configurations of NO, NO$^+$, and NO$^-$.

 (Answer)

(c) Give the bond orders of chemical species in (b).

 (Answer)

(d) Rank the bond energies and bond lengths of chemical species in (b).

 (Answer)

(e) Predict whether the chemical species in (b) are paramagnetic or diamagnetic.

 (Answer)

10. (total 10 pts) Discuss the nature of the bonding in sulfur dioxide (SO_2).

(a) Draw the possible Lewis resonance diagrams for this molecule.

 (Answer)

(b) Use the VSEPR theory to determine the steric number, the hybridization of the central sulfur atom, and the geometry of the molecule.

 (Answer)

(c) Draw a correlation diagram to show how the use of resonance structures can be avoided by introducing a delocalized π MO. Consider only the π bondings.

 (Answer)

(d) What bond order does the MO model predict for the S-O bonds in the sulfur dioxide molecule?

 (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/

Editor: Aditya Vardhan (adivar@netlinx.com)

(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.

PERIOD	GROUP

Legend:
- GROUP NUMBERS IUPAC RECOMMENDATION (1985) → 13
- GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986) → IIIA
- ATOMIC NUMBER → 5
- SYMBOL → B
- RELATIVE ATOMIC MASS (1) → 10.811
- ELEMENT NAME → BORON

Periodic Table

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

LANTHANIDE

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

ACTINIDE

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

Claim Form for General Chemistry Examination

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

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	1x8/8	**6**	2+1+2+2+3+2/ 12	
2	2+2+2+3/9	**7**	4+4/8	
3	3+3/6	**8**	3+3+3+3+3/15	
4	2+3+3/8	**9**	4+3+3+3+3/16	**/100**
5	3+3+2/8	**10**	2+3+3+2/10	

단순히 계산이 틀리거나 **unit** 이 맞지 않지만 내용이 모두 맞았을 때 **– 1 pt**

1. (total 8 pts) 1 pt per each

(a) Cation is smaller than its parent atom (Z-1) negative charges are attracted more strongly by the Z protons, Li^+ is smaller than Li.

(b) Atom and anion. F is smaller than F^-.

(c) Isoelectronic, each with 8 valence electrons O nucleus has 8 protons, F nucleus has 9. F^- has the smaller radius.

(d) Mg^{2+} is smaller than Na^+

(e) Nitrogen, the smaller atom, has the higher effective nuclear charge and hence the higher ionization energy.

(f) Nitrogen has the larger ionization energy. Oxygen's paired p electrons bring them additional repulsions, leaving the oxygen atom more loosely bound and therefore easier to ionize than nitrogen.

(g) Oxygen is situated just above sulfur. It is smaller and more difficult to ionize.

(h) Na^+ enjoys the special stability of a neon configuration. The Na^+ is far harder to ionize than sodium atom.

2. (total 9 pts)

(a) (2 pts) PI_3
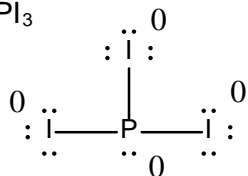
(b) (2 pts) O_3
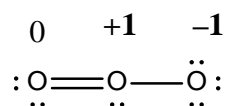
(c) (2 pts) $[ClF_4]^+$
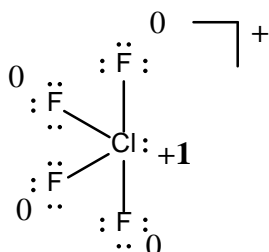
(d) (3 pts) 2 pts for structures, 1 pt for explanation

CH_3^+ is perfectly trigonal planar. Each H–C–H bond angle is 120º. There are only bond-pair–bond-pair repulsions.

NH_2^+ has a lone pair in the "trigonal planar" geometry: a bent structure. A lone pair exerts more repulsion on a bond-pair than just another bond-pair. That means the H's are pushed closer together forming a slightly smaller H–N–H bond angle.
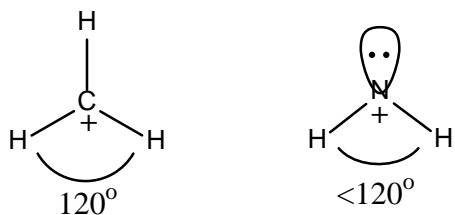
3. (total 6 pts)

(a) (3 pts)

$$v = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\, J \cdot s}{1.675 \times 10^{-27}\, kg \times 10^{-10}\, m} = 3.956 \times 10^3 \text{ m/s}$$

(b) (3 pts)

$$E = \frac{1}{2}mv^2 = \frac{1}{2} \times 1.675 \times 10^{-27}\, kg \times (3956\, m/s)^2 = 1.310 \times 10^{-20}\, J$$

4. (total 8 pts) 2 pts, correct equation; 3 pts, correct quantum numbers, 3 pts, energies

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{(2L)^2} + \frac{n_y^2}{L^2} + \frac{n_z^2}{L^2}\right]$$

$$E_{111} = \frac{h^2}{8\,mL^2}\left(1/4+1+1\right) = \frac{9}{4}\frac{h^2}{8mL^2}$$

$$E_{311} = \frac{h^2}{8\,mL^2}\left(9/4+1+1\right) = \frac{17}{4}\frac{h^2}{8mL^2}$$

$$E_{411} = E_{221} = E_{212} = \frac{h^2}{8\,mL^2}\left(6\right) = \frac{24}{4}\frac{h^2}{8mL^2}$$

$$E_{211} = \frac{h^2}{8\,mL^2}\left(4/4+1+1\right) = \frac{12}{4}\frac{h^2}{8mL^2}$$

$$E_{112} = E_{121} = \frac{h^2}{8\,mL^2}\left(1/4+4+1\right) = \frac{21}{4}\frac{h^2}{8mL^2}$$

$$E_{321} = E_{312} = \frac{h^2}{8\,mL^2}\left(9/4+4+1\right) = \frac{29}{4}\frac{h^2}{8mL^2}$$

The (111) state is the ground state; the others are excited states. Note the double degeneracy of two of the excited states and the triple degeneracy of a third.

5. (total 8 pts)

(a) (3 pts)

The n-th ionization energy (IE) for H (Z=1) can be calculated using

$$IE_n = R\left\{\frac{1}{n^2} - \frac{1}{n_f^2}\right\} = \frac{R}{n^2}$$

because n_f goes to infinity.
Therefore, the ratio is given by

$$\frac{IE_n}{IE_1} = \frac{1}{n^2}$$

(b) (3 pts)

The n-th ionization energy for He can be calculated by using

$$IE_n = R\left\{\frac{(Z-s)^2}{n^2} - \frac{(Z-s)^2}{n_f^2}\right\} = \frac{R(Z-s)^2}{n^2}$$

The experimental first IE is used to determine s as follows.

$$IE_1 = \frac{R(Z-s)^2}{1^2} = (2.1799\times10^{-18}\,J)(2-s)^2 = 3.94 \text{ x } 10^{-18}\text{ J}$$

Finally, s = 0.656.

(c) (2 pts)
The overall process is a sum of the following three processes:

Li(g) → Li⁺(g) + e⁻ IE_1;   Li⁺(g) → Li²⁺(g) + e⁻ IE_2;   Li²⁺(g) → Li³⁺(g) + e⁻ IE_3
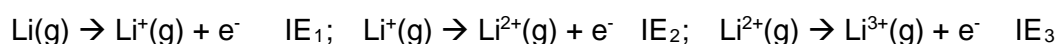
Therefore, IE = IE_1+IE_2+IE_3 = 1.96 X 10⁴ kJ mol⁻¹, which gives

IE_2 = IE − IE_1 − IE_3 = 1.96 X 10⁴ kJ mol⁻¹ − 520 kJ mol⁻¹ − IE_3.

IE_3 can be calculated from the formula in (a) when Z = 3.

$$IE_3 = (2.1799 \times 10^{-18} J) \frac{3^2}{1^2} = 1.96191 \times 10^{-17} J$$

or $IE_3 = (1.96191 \times 10^{-17} J) \times \dfrac{6.022 \times 10^{23}}{1\text{mol}} = 1.1815 \times 10^4 \, kJ\text{mol}^{-1}$

Therefore, $IE_2 = 1.96 \times 10^4$ kJ mol^{-1} – 520 kJ mol^{-1} – IE_3 = **7.3 X 10^3 kJ mol^{-1}**

6. (total 12 pts)
(a) (2 pt)

n	3		
ℓ	0	1	2
m_l	0	-1, 0, +1	-2, -1, 0, +1, +2

(b) (1 pt) *3s, 3p, 3d*

(c) (2 pts) 하나라도 그리면 1 pt, 모두 그리면 2 pts
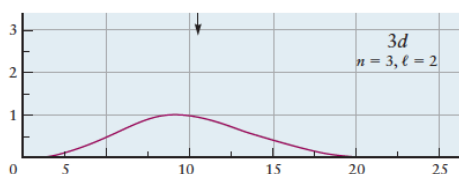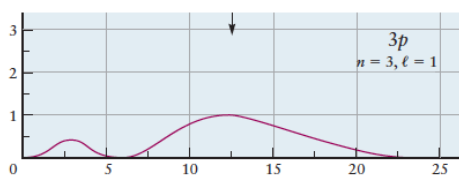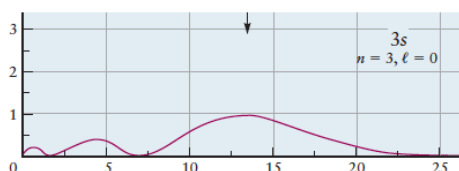
(d) (2 pts)
 3s: 2 radial and 0 angular   *3p*: 1 radial and 1 angular   *3d*: 0 radial and 2 angular
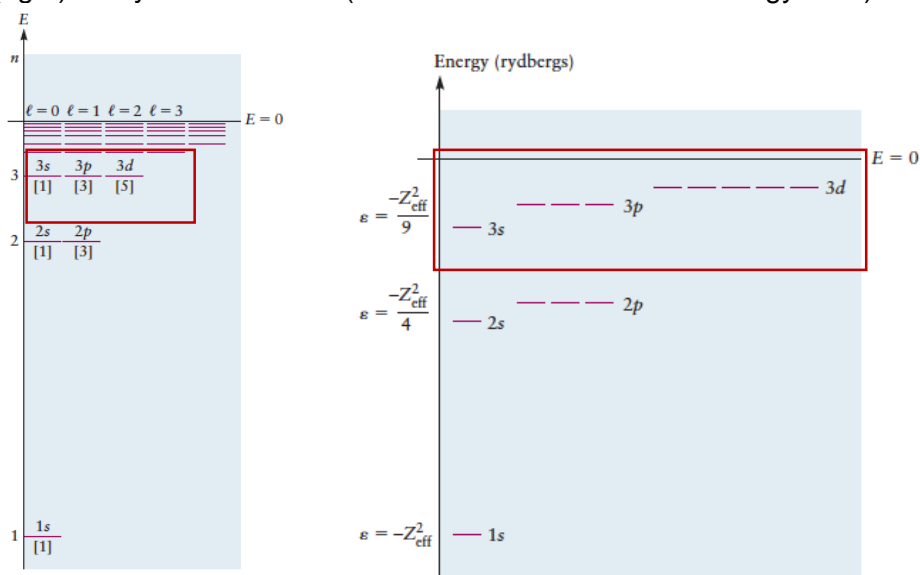
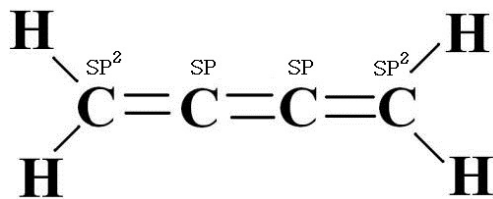(e) (3 pts) 1 pt, s and p orbitals; 2 pts, d orbitals
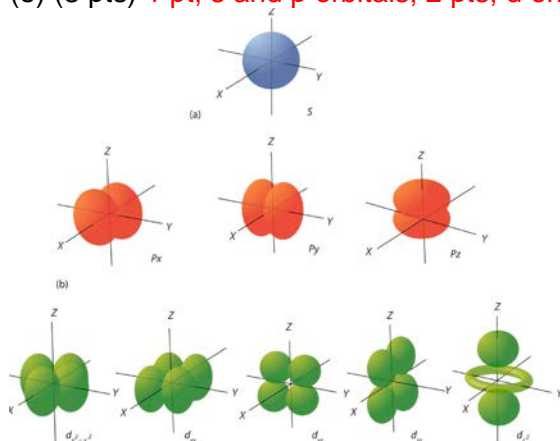
(f) (2 pts)
(left) one-electron atom (contribution of n for energy level)
(right) many-electron atom (contribution of $n \; and \; \ell$ for energy level)
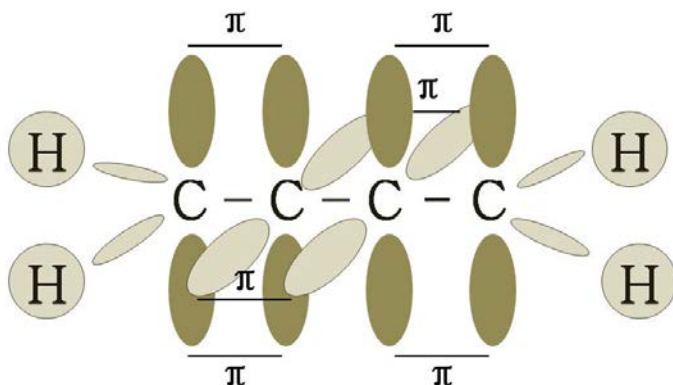

7. (total 8 pts)
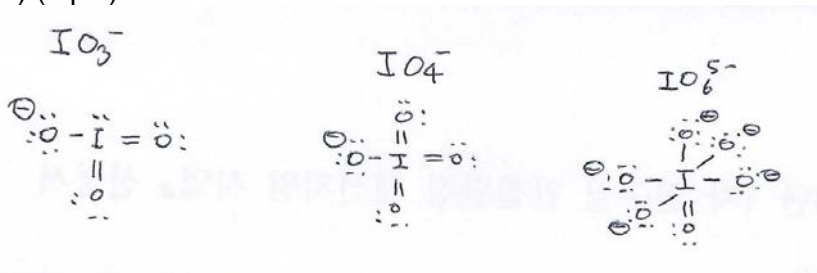
(a) (4 pts) 1 pt for each carbon

(b) (4 pts)
    1 pt, sigma bonding; 1 pt, two outer π bondings; 2 pts, a center π bonding perpendicular to the other two π bondings

When the carbon atoms are named as C1, C2, C3, and C4 from left to right, the π bonding of C2-C3 must be perpendicular to those of C1-C2 and C3-C4.

8. (total 15 pts)

(a) (3 pts)

(b) (3 pts)

IO_3^-: $SN = 4$, structure is pyramidal; IO_6^{5-}: $SN = 6$, structure is octahedral; IO_4^-: $SN = 4$, structure is tetrahedral.

(c) (3 pts)

IO_4^- (a bond order of 1(2/3)), IO_3^- (1(3/4)), IO_6^{5-} (1(1/6))

Bond length order: $IO_4^- < IO_3^- < IO_6^{5-}$

(d) (3 pts) 2 pts, e configuration; 1 pt, diamagnetic

$(\sigma_{g5s})^2(\sigma_{u5s}^*)^2(\sigma_{g5p_z})^2(\pi_{u5p_x}\pi_{u5p_y})^4(\pi_{g5p_x}^*\pi_{g5p_y}^*)^4$; iodine is diamagnetic.
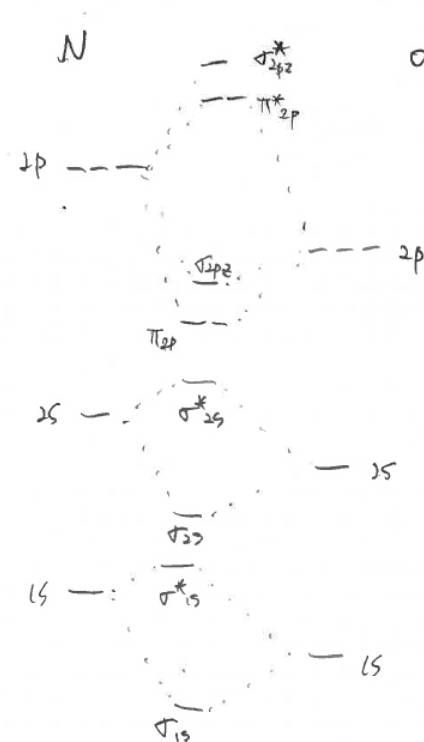
(e) (3 pts) 2 pts, e configuration; 1 pt, bond order

$(\sigma_{g5s})^2(\sigma_{u5s}^*)^2(\sigma_{g5p_z})^2(\pi_{u5p_x}\pi_{u5p_y})^4(\pi_{g5p_x}^*\pi_{g5p_y}^*)^3$; the bond is stronger; bond order is 3/2 versus 1.

9. (total 16 pts)

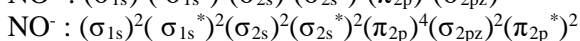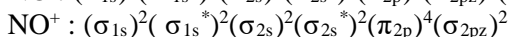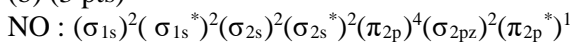### (a) (4 pts) 3 pts, correlation diagram; 1 pt, notation (no g nor u !!)

Correlation diagram for NO is shown below .(The MO labeling system in textbook for heteronuclear diatomic molecule, ignore the (u, g) notation part)

Oxygen atom would contribute to σ_{2pz} more, because the energy of σ_{2pz} is closer to the energy of p orbitals of oxygen atom

(b) (3 pts)
NO : $(\sigma_{1s})^2(\sigma_{1s}{}^*)^2(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2pz})^2(\pi_{2p}{}^*)^1$
NO^+ : $(\sigma_{1s})^2(\sigma_{1s}{}^*)^2(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2pz})^2$
NO^- : $(\sigma_{1s})^2(\sigma_{1s}{}^*)^2(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2pz})^2(\pi_{2p}{}^*)^2$

(c) (3 pts)
NO : $(6-1)/2 = 2.5$
NO^+ : $(6-0)/2 = 3$
NO^- : $(6-2)/2 = 2$

(d) (3 pts)
Bond energy : $NO^+ > NO > NO^-$
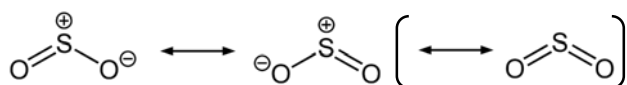Bond length : $NO^+ < NO < NO^-$

(e) (3 pts)
NO has an unpaired electron, therefore it is paramagnetic.
NO^+ has no unpaired electrons, therefore it is diamagnetic.
NO^- has two unpaired electrons, therefore it is paramagnetic.
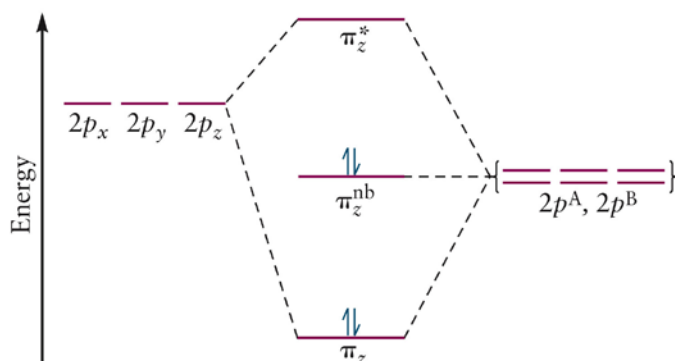

10. (total 10 pts)

(a) (2 pts) 괄호 내 구조는 안 써도 됨

(b) (3 pts)

VSEPR theory assigns $\boxed{SN\ 3}$ to the central S. The O atoms occupy two of the three sites, and the lone pair the third. The molecular ion is therefore $\boxed{\text{bent}}$. The hybridization at the nitrogen atom is $\boxed{sp^2}$.

(c) (3 pts) p_x, p_y 는 안 써도 됨.

Two of the three sp^2 hybrid orbitals form the σ bonds to the oxygen atoms, and the third accommodates the lone pair. The unhybridized $2p_z$ atomic orbital on the S atom is oriented perpendicular to the plane of the molecule. It overlaps with the $2p_z$ atomic orbitals of the two oxygens to form a π system. See text Figure 16.42. Two electrons occupy the bonding π orbital in this system and two electrons occupy the nonbonding (π^{nb}) orbital. The antibonding (π^*) orbital remains empty.

(d) (2 pts)

Two electrons occupy the bonding π orbital in this system and two electrons occupy the nonbonding (π^{nb}) orbital. The antibonding (π^*) orbital remains empty. Adding the σ MO's to the bonding contributed by the π system gives an overall bond order of 3, which amounts to $\boxed{\frac{3}{2}}$ for each bond.

2016 SPRING Semester Final Examination
For General Chemistry I

Date: June 15 (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	**7**	/8	
2	/7	**8**	/8	
3	/10	**9**	/10	
4	/8	**10**	/10	**/100**
5	/9	**11**	/6	
6	/12			

** This paper consists of 15 sheets with 10 problem sets (pages 13 & 14: constants & periodic table, page 15: 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.

   1. Period, Location and Procedure

   1)   Return and Claim Period: *June 17 (Friday, 12:00-14:00)*

   2)   *Location: Creative Learning Bldg.(E11)*

Class	Room	Class	Class	Class	Room
A	**203**	**D**	**207**	**G**	**210**
B	**205**	**E**	**208**		
C	**206**	**F**	**209**		

   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 6/18 on the web.)

   2. Final Confirmation

   1) Period: *June 18(Sat) – 19(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. (12 pts) One mole of liquid water is allowed to equilibrate with its vapor inside a one-liter vessel. The vapor pressure at 20 °C is then found to be 17.5 torr.

(a) <u>How many moles of water</u> exist in the vapor state? Assume ideal behavior.

(Answer)

(b) Suppose that the volume of the vessel is doubled to 2 L. What is the <u>new vapor pressure</u>?

(Answer)

(c) <u>How many moles of water vapor</u> are present in the larger container?

(Answer)

(d) Water's vapor pressure falls from 17.5 torr at 20 °C to 9.2 torr at 10 °C. If equilibrium is first established at 20 °C in a volume of 1 L, then approximately <u>how many mL of water will condense</u> when the temperature is lowered to 10 °C? Assume that liquid water has a density of 1 g/mL.

(Answer)

(e) The vapor pressure of water/sucrose solution ($C_{11}H_{22}O_{11}$, table sugar) is found to be 16.1 torr at 20 °C, lower by 1.4 torr compared with pure water. The solution, presumed to be ideal, contains 500 g of water. Compute the molality.

(Answer)

2. (7 pts)

(a) Using the ideal gas law, calculate the pressure exerted by 50.0 g carbon dioxide in a 1.00 L vessel at 25 °C.

(Answer)

(b) Using the van der Waals equation, calculate the pressure under the above condition. For CO_2, a = 3.592 atm L^2 mol^{-2} and b = 0.04267 L mol^{-1}.

(Answer)

(c) Do attractive or repulsive forces dominate in CO_2?

(Answer)

3. (10 pts) In this problem, we will consider following intermolecular interaction:

① Ion-Ion interaction, ② Ion-Dipole interaction, ③ Dipole-Dipole interaction, ③ Dipole-Induced dipole interaction, ⑤ London force.

(a) We can say that potential energy (E_P) of above interactions is **proportional to $-r^{-n}$** where r is distance between molecules. Specify <u>the value of n for each interaction</u>.
ex) n = 9 for Ion-Ion interaction (Not correct)
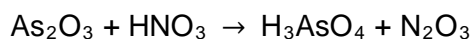**(Answer)**

(b) Specify the most <u>predominant intermolecular interaction</u> for Ne, CaF_2, CH_4, He, PH_3, H_2S, KCl (7 species).
(Answer)

(c) Predict <u>the order of increasing normal boiling point</u> for Ne, CaF_2, CH_4, He, PH_3, H_2S, KCl (7 species).
(Answer)

4. (8 pts) Nitric acid is one of the well-known oxidant, and can react with many metals. Here is the reaction of nitric acid with arsenic oxide without any stoichiometry.

$$As_2O_3 + HNO_3 \rightarrow H_3AsO_4 + N_2O_3$$

(a) Balance the stoichiometry of the total reaction.

(Answer)

(b) N_2O_3 goes through further reaction with oxygen to make NO_2. Write down the reaction of N_2O_3 with oxygen in the air with the correct stoichiometry.

(Answer)

(c) A scientist has unknown amount of As_2O_3. The scientist titrated As_2O_3 with excess amount of HNO_3. After this reaction finished, all the product of titration is oxidized by the oxygen in the air. Finally, the scientist could obtain 0.2 g of NO_2. Calculate the amount of As_2O_3 the scientist has at first in gram unit.

(Answer)

5. (9 pts)

(a) The vapor pressure of solid acetylene at -84.0 °C is 760 Torr. Does <u>the triple-point temperature</u> lie above or below -84.0 °C? <u>Explain</u>.

(Answer)

(b) Suppose a sample of solid acetylene is held under an external pressure of 0.80 atm and heated from 10 to 300 K. What <u>phase change(s)</u>, if any, will occur?

(Answer)

(c) At 20 °C, the vapor pressure of toluene is 0.0289 atm and the vapor pressure of benzene is 0.0987 atm. Equal numbers of moles of toluene and benzene are mixed and form an ideal solution. Compute <u>the mole fraction of benzene in the vapor</u> in equilibrium with this solution.

(Answer)

6. (12 pts) One mole of an ideal monatomic gas initially at 300 K and a pressure of 15.0 atm expands to a final pressure of 1.00 atm. The expansion can occur via any one of four different paths: (a) isothermal and reversible, (b) isothermal and irreversible, (c) adiabatic and reversible. In irreversible processes, the expansion occurs against an external pressure of 1.00 atm. For each case, <u>calculate the values of q, w, ΔU, and ΔH</u>.

(a) isothermal and reversible

(Answer)

(b) isothermal and irreversible

(Answer)

(c) adiabatic and reversible

(Answer)

7. (8 pts)

(a) <u>Calculate change in the entropy</u> for the free expansion of an ideal gas into vacuum from V_1 to V_2 using Boltzmann's statistical definition of entropy.

(Answer)

(b) <u>Show that the entropy of mixing</u> in the system below is $\Delta_{mix}S = 2R\ln 2$.
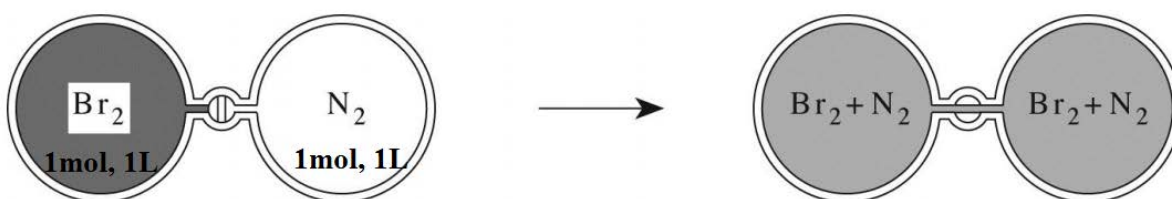
(Answer)

(c) When both sides are filled with N_2 of 1 mole at each, <u>calculate the entropy of mixing</u>. Does the result equal to the answer in (b)? <u>Justify your answer</u>.

(Answer)

8. (8 pts) The protein lysozyme unfolds at a transition temperature of 75.5 °C, and the standard enthalpy of transition is 509 kJ mol^{-1}. The difference in the constant-pressure heat capacities on unfolding is 6.28 kJ K^{-1} mol^{-1} and can be assumed to be independent of temperature.

(a) <u>Calculate the entropy of unfolding</u> of lysozyme at the transition temperature.

(Answer)

(b) <u>Calculate the entropy of unfolding</u> of lysozyme at 25.0 °C.

(Answer)

9. (10 pts) Ethanol's enthalpy of vaporization is 38.7 kJ mol^{-1} at its normal boiling point, 78 ^{o}C. Calculate *q, w,* ΔU, ΔS_{sys}, and ΔG when 1.00 mol ethanol is vaporized reversibly at 78 ^{o}C and 1 atm. Assume that the vapor is an ideal gas and neglect the volume of liquid ethanol relative to that of its vapor.

(Answer)

10. (10 pts) Photosynthesis can be represented by

$$6CO_2 \text{ (g)} + 6\ H_2O(l) \rightarrow C_6H_{12}O_6 \text{ (s)} + 6O_2 \text{ (g)}$$
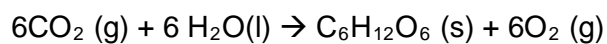
Explain how the equilibrium would be affected by the following changes using the following equation.

$$\Delta G = RT \ln (Q/K)$$

(a) the partial pressure of CO_2 is increased.

(Answer)

(b) O_2 is removed from the mixture.

(Answer)

(c) $C_6H_{12}O_6$ is removed from the mixture.

(Answer)

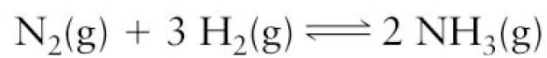(d) more water is added.

(Answer)

(e) more sunlight shines on the plants.

(Answer)

11. (6 pts)

The equilibrium constant K for the synthesis of ammonia is 6.8 x 10^5 at 298 K and the heat of formation of ammonia $\Delta H_f^0(NH_3(g))$ = -46.11 kJ mol^{-1}.

$$N_2(g) + 3\, H_2(g) \rightleftharpoons 2\, NH_3(g)$$

At <u>which temperature</u> will the equilibrium constant be equal to 1?

Physical Constants

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

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

Conversion Factors

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

PERIODIC TABLE OF THE ELEMENTS

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

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

LANTHANIDE

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

ACTINIDE

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

Legend

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

GROUP NUMBERS IUPAC RECOMMENDATION (1985)
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

(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

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

15

<The Answers>

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

Missing units in the answer: -1 pt, "-1 pt" means "minus 1 point"

1. (total 12 pts)

(a) (2 pts)

$P = 17.5 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.023 \text{ atm}$

$V = 1L$

$T = 20°C = 293 \text{ K}$

$R = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$

$n = \frac{PV}{RT} =$ **9.57 X 10^{-4} mol**

(b) (2 pts)

The same as in a 1L container: **17.5 torr**
The vapor pressure depends only on temperature.

(c) (2 pts)

Since the volume doubles, so must the number of moles.

9.57×10^{-4} moles $\times 2 =$ **1.91 X 10^{-3}mol**

(d) (3 pts)

$P = 9.2 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.012 \text{ atm}$

$V = 1L$

$T = 10°C = 283 \text{ K}$

$n = \frac{PV}{RT} = \frac{0.012 \times 1}{0.082 \times 283} = 5.2 \times 10^{-4} \text{ mol}$

$9.57 \times 10^{-4} \text{ mol} - 5.2 \times 10^{-4} \text{ mol} = 4.4 \times 10^{-4} \text{ mol}$

The difference, 4.4×10^{-4} mol, condensate

$4.4 \times 10^{-4} \text{ mol} \times \frac{18g}{\text{mol}} \times \frac{1 \text{mL}}{1g} =$ **7.9 X 10^{-3} mL**

(e) (3 pts)

$n_1 = 500g \ H_2O \times \frac{1 \text{ mol}}{18g} = 27.8 \text{ mol } H_2O$

$X_1 = \dfrac{n_1}{n_1 + n_2}$ $X_1(n_1 + n_2) = n_1$

$n_2 = \dfrac{n_1(1 - X_1)}{X_1}$

$P_1 = X_1 P_1{}^0$

$X_1 = \dfrac{P_1}{P_1{}^0} = \dfrac{16.1 \text{ torr}}{17.5 \text{ torr}} = 0.92$

$n_2 = \dfrac{n_1(1 - X_1)}{X_1} = \dfrac{(27.8)(1 - 0.92)}{0.92} = 2.417 \text{ mol}$

molality $= \dfrac{2.417 \text{mol sucrose}}{0.5 \text{kg } H_2O} = $ **4.83 mol/kg**

2. (total 7 pts)

The problem provides a comparison between the ideal-gas pressure and the van der Waals pressure of a typical gas under ordinary conditions. The data for this sample of CO_2 are

$$n = 50.0 \text{ g}/44.0 \text{ g mol}^{-1} = 1.136 \text{ mol} \qquad T = 298.15 \text{ K} \qquad V = 1.00 \text{ L}$$

(a) (2 pts)

Solve the ideal-gas equation for P and substitute

$$P = \dfrac{(1.136 \text{ mol})(0.08206 \text{ L atm mol}^{-1}K^{-1})(298.15 \text{ K})}{1.00 \text{ L}} = \boxed{27.8 \text{ atm}}$$

(b) (3 pts)

b) The van der Waals equation includes terms (a and b) that depend on the identity of the gas. For CO_2, $a = 3.592$ atm L^2mol^{-2} and $b = 0.04267$ L mol^{-1}.^{6}. Solve the van der Waals equation for P and substitute

$$P = \dfrac{nRT}{V - nb} - a\dfrac{n^2}{V^2} = \dfrac{(1.136 \text{ mol})(0.08206 \text{ L atm mol}^{-1}K^{-1})(298.15 \text{ K})}{1.00 \text{ L} - (1.136 \text{ mol})(0.04267 \text{ L mol}^{-1})} - a\dfrac{n^2}{V^2}$$

$$= 29.2 \text{ atm} - (3.592 \text{ atm L}^2\text{mol}^{-2})\left(\dfrac{(1.136)^2 \text{ mol}^2}{(1.00)^2 \text{ L}^2}\right) = 29.2 \text{ atm} - 4.64 \text{ atm} = \boxed{24.6 \text{ atm}}$$

(c) (2 pts)

The van der Waals P is less than the ideal-gas P. The effect of the b term in the van der Waals equation was to increase P from 27.8 to 29.2 atm; the effect of a was to decrease P by 4.64 atm. The a term in this case is more influential than the b term. That is, $\boxed{\text{attractive forces dominate}}$.

3. (total 10 pts)

(a) (3 pts) Ion-ion, ion-dipole 1 pt; dipole-dipole, dipole-induced dipole 1 pt; London 1 pt

n = 1 for Ion-Ion interaction, n = 2 for Ion-Dipole interaction, n = 3 for Dipole-Dipole interaction, n = 6 for Dipole-Induced dipole interaction, n = 6 for London force

(b) (3 pts) He, Ne, CH_4: 1 pt; PH_3, H_2S: 1 pt;   KCl, CaF_2: 1 pt

He, Ne, CH_4: London force
PH_3, H_2S: Dipole-Dipole interaction
KCl, CaF_2: Ion-Ion interaction

(c) (4 pts)   He < Ne < CH_4 1 pt; PH_3 < H_2S 1 pt;   KCl < CaF_2 1 pt;   entire 1 pt

He < Ne < CH_4 < PH_3 < H_2S < KCl < CaF_2

4. (total 8 pts)

(a) (3 pts)

$$As_2O_3 + 2\ HNO_3 + 2H_2O \rightarrow 2\ H_3AsO_4 + N_2O_3$$

(b) (2 pts)
N_2O_3 goes through further reaction with oxygen to make NO_2. Write down the reaction of N_2O_3 with oxygen in the air.

$$2N_2O_3 + O_2 \rightarrow 4NO_2$$

(c) (3 pts)
 A scientist has unknown amount of As_2O_3. The scientist titrated As_2O_3 with excess amount of HNO_3. After this reaction finished, all the product of titration is oxidized by the oxygen in the air. Finally, the scientist could obtain 0.2(g) of NO_2. Calculate the amount of As_2O_3 the scientist has at first in gram unit.

$$\text{Amount of } NO_2 = \frac{0.2}{14+32} = 4.348 \times 10^{-3}(mol)$$
$$\text{Ratio between } As_2O_3 \text{ and } N_2O_3 = 1:1$$
$$\text{Ratio between } N_2O_3 \text{ and } NO_2 = 1:2$$
$$\text{Therefore, the amount of } As_2O_3 = \frac{1}{2} \times 4.348 \times 10^{-3}(mol) = \textbf{0.43(g)}$$

5. (total 9 pts)

(a) (2 pts)
a) The temperature of the triple point of acetylene $\boxed{\text{lies above}}$ $-84.0°C$. For a pure substance, T's at which liquid and gas are in equilibrium equal or exceed T's at which liquid and solid are in equilibrium.

(b) (2 pts)
b) Note that 0.8 atm is *less* than 760 torr, which is the vapor pressure of solid acetylene at $-84°C$. If solid acetylene is heated at $P = 0.8$ atm, it therefore passes directly into the vaporous (gaseous) state without ever existing as a liquid. It $\boxed{\text{sublimes}}$ at some temperature below $-84.0°C$.

(c) (5 pts) Partial P, 2 pts;   final mole fraction, 3 pts
Write Raoult's law for both the benzene and toluene

$$P_{benz} = X_{benz} P_{benz}^{\circ} \quad \text{and} \quad P_{tol} = X_{tol} P_{tol}^{\circ}.$$

Since equal numbers of moles of benzene and toluene were mixed, $X_{benz} = X_{tol} = 0.500$. Use these mole fractions and the vapor pressures of the pure substances to compute the partial pressure of each substance above the mixture

$$P_{benz} = 0.500(0.0987 \text{ atm}) = 0.04935 \text{ atm}$$
$$P_{tol} = 0.500(0.0289 \text{ atm}) = 0.01445 \text{ atm}$$

The number of moles of a particular gas in an ideal gaseous mixture is directly proportional to its partial pressure. Assume ideality. Then

$$n_{benz} = P_{benz} \frac{V}{RT} \quad \text{and} \quad n_{tol} = P_{tol} \frac{V}{RT}$$

The mole fraction of benzene in the vapor is

$$X_{benz,vap} = \frac{n_{benz}}{n_{benz} + n_{tol}} = \frac{P_{benz}(V/RT)}{P_{benz}(V/RT) + P_{tol}(V/RT)} = \frac{P_{benz}}{P_{benz} + P_{tol}}$$
$$= \frac{0.04935 \text{ atm}}{(0.04935 + 0.01445) \text{ atm}} = \boxed{0.774}$$

6. (total 12 pts)

(a) (4 pts)   for each, 1 pt

(a) When an ideal gas undergoes an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -nRT \ln \frac{P_1}{P_2} = - (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (300 \text{ K}) \ln \frac{15.0 \text{ atm}}{1.00 \text{ atm}} = -6.75 \times 10^3 \text{ J}$$

$$q = \Delta U - w = -w = 6.75 \times 10^3 \text{ J}$$

(b) (4 pts)   for each, 1 pt

(b) When an ideal gas undergoes an isothermal process, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -P_{\text{ex}} \left(V_2 - V_1 \right)$$

V_1 and V_2 can be determined using the ideal gas law:

$$V_1 = \frac{nRT}{P_1} = \frac{(1 \text{ mol}) \left(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \right) (300 \text{ K})}{15.0 \text{ atm}} = 1.641 \text{ L}$$

$$V_2 = \frac{nRT}{P_2} = \frac{(1 \text{ mol}) \left(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \right) (300 \text{ K})}{1.00 \text{ atm}} = 24.62 \text{ L}$$

Therefore,

$$w = - (1.00 \text{ atm}) (24.62 \text{ L} - 1.641 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -2.33 \times 10^3 \text{ J}$$

and

$$q = \Delta U - w = -w = 2.33 \times 10^3 \text{ J}$$

(c) (4 pts)   for each, 1 pt

(c) $q = 0$ for an adiabatic process.

To determine ΔU and ΔH, T_2 needs to be calculated.

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} = (300 \text{ K}) \left(\frac{1.00 \text{ atm}}{15.0 \text{ atm}} \right)^{\left(\frac{5}{3} - 1 \right)/\frac{5}{3}} = 101.6 \text{ K}$$

Now the rest of the quantities can be calculated:

$$\Delta U = C_V \Delta T = \frac{3}{2} (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (101.6 \text{ K} - 300 \text{ K}) = -2.47 \times 10^3 \text{ J}$$

$$w = \Delta U - q = \Delta U = -2.47 \times 10^3 \text{ J}$$

$$\Delta H = C_P \Delta T = \frac{5}{2} (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) (101.6 \text{ K} - 300 \text{ K}) = -4.12 \times 10^3 \text{ J}$$

7. (total 8 pts)

(a) (3 pts)

Number of states available per molecule = cV

Number of states available for N-molecules system = $\Omega = (cV)^N$

Entropy by definition $\Rightarrow S = k_B \ln \Omega$

$$\Delta S = N_0 k_B \ln (cV_2) - N_0 k_B \ln (cV_1) = N_0 k_B \ln (V_2/V_1) = nR \ln (V_2/V_1)$$

(b) (3 pts)

$\Delta_{mix}S = \Delta S(Br_2) + \Delta S(N_2) = n_1 R \ln V_2/V_1 + n_2 R \ln V_2/V_1$,

and n=2mol, n_1=n_2=1mol, V_2 = 2L, V_1 =1L.

Therefore, $\Delta_{mix}S = 2R\ln2$

(c) (2 pts)

Since the molecules at both sides are identical, the mixing process does not change the state of the system. Therefore, $\Delta S = 0$ in this case. This is called the Gibb's paradox.

8. (total 8 pts)

(a) (2 pts)

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$
$$= \frac{509,000 \text{ J mol}^{-1}}{348.5 \text{ K}}$$
$$= 1,460 \text{ J K}^{-1} \text{ mol}^{-1}$$

(b) (6 pts) heating 2 pts; cooling 2 pts; total sum 2 pts

the transition at 25.0°C occurs in three steps:

(i) heating of the folded protein from 25.0°C to the transition temperature,

$$\Delta S_{heating} = C_{p,m}^{folded} \ln \frac{348.5 \text{ K}}{298 \text{ K}}$$

(ii) unfolding at the transition temperature, See problem 8(a).

(iii) cooling of the unfolded protein to 25.0°C.

$$\Delta S_{cooling} = C_{p,m}^{unfolded} \ln \frac{298 \text{ K}}{348.5 \text{ K}}$$

(iv) Entire process

$$\Delta S = \Delta S_{heating} + \Delta S_{trans} + \Delta S_{cooling} = C_{p,m}^{folded} \ln \frac{348.5 \text{ K}}{298 \text{ K}} + 1,460 \, JK^{-1}mol^{-1} + C_{p,m}^{unfolded} \ln \frac{298 \text{ K}}{348.5 \text{ K}}$$

$$= 1,460 \, JK^{-1}mol^{-1} + [C_{p,m}^{unfolded} - C_{p,m}^{folded}] \ln \frac{298 \text{ K}}{348.5 \text{ K}}$$

$$= 1,460 \, JK^{-1}mol^{-1} + 6,280 \, JK^{-1}mol^{-1} \ln \frac{298 \text{ K}}{348.5 \text{ K}} = 477 \, JK^{-1}mol^{-1}$$

9. (total 10 pts) for each, 2 pts

$C_2H_6O(l) \leftrightarrow C_2H_6O(g)$ at 351.1 K

At constant pressure, $q = \Delta H = 38.7$ kJ when 1.00 mol of ethanol is vaporized.

$\Delta S = \dfrac{q_{rev}}{T} = \dfrac{38.7\ kJ}{351.1\ K} = 110\ J\ K^{-1}$

$\Delta G = \Delta H - T\Delta S = 38.7\ kJ - (351.15\ K)(0.110\ kJ\ K^{-1}) = 0\ kJ$

$\Delta U = \Delta H - \Delta(PV) = \Delta H - P(V_2 - V_1)$

V_2: the volume of one more of vaporous ethanol at 351.1 K, V_1 the volume of one mole of liquid ethanol at 351.1 K.

$V_2 = \dfrac{nRT}{P} = \dfrac{(1.00\ mol)(0.08206\ L\ atm\ mol^{-1}K^{-1})(351.15\ K)}{1.00\ atm} = 28.8\ L$

Because V_1 is negligible, $P(V_2 - V_1) = (1.00\ atm)(28.8L) = 2.92\ kJ$

$\therefore \Delta U = 38.7\ kJ - 2.92\ KJ = 35.8\ kJ$

By expanding against a constant pressure, the system performs +2.92 kJ of pressure-volume work on its surroundings. The work done by the surroundings on the system is the negative of the work done by the system on the surroundings: w = –2.92 kJ.

10. (total 10 pts)

$Q = [O_2]^6/[CO_2]^6$, since H_2O and $C_6H_{12}O_6$ are liquid and solid.

(a) (2 pts) The increase in the partial pressure of CO_2 results in Q < K and thus ΔG < 0. Therefore, the forward reaction is spontaneous or the equilibrium shifts from left to right.

(b) (2 pts) The decrease in the partial pressure of O_2 results in Q < K and thus ΔG < 0. Therefore, the forward reaction is spontaneous or the equilibrium shifts from left to right.

(c) (2 pts) The change in $[C_6H_{12}O_6]$ does not affect Q and thus the equilibrium.

(d) (2 pts) The change in $[H_2O]$ does not affect Q and thus the equilibrium.

> (아래의 경우에도 맞게 해줄 것
>
> CO_2 is more soluble in water, thus the CO_2 pressure decreases. Then, the equilibrium shifts from right to left.)

(e) (2 pts) More sunlight may enhance the concentration of activated CO_2, giving rise to Q < K and thus ΔG < 0. Therefore, the forward reaction is spontaneous or the equilibrium shifts from left to right.

11. (total 6 pts) ΔH 2 pts; Final equation 4 pts

$\Delta H_r^\circ = 2\Delta H_f^\circ(NH_3, g) = 2(-46.11\ kJ \cdot mol^{-1})$
$\qquad = -92.22\ kJ \cdot mol^{-1}\ or\ -92.22 \times 10^3\ J \cdot mol^{-1}$

K_1 at 298 K = 6.8 x 10^5

K_2 at x K = 1

$\ln K_1 - \ln K_2 = -\dfrac{\Delta H_r^\circ}{R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\} = \dfrac{9.222 \times 10^4\ J \cdot mol^{-1}}{8.3145\ J \cdot K^{-1} \cdot mol^{-1}} \times \left\{\dfrac{1}{298\ K} - \dfrac{1}{X}\right\}$

x = 466 K