

2018 FALL Semester Midterm Exam For General Chemistry I

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

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

Professor Name	Class	Student I.D. Number	Name

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

** This paper consists of 12 sheets with 10 problems (page 10 - 11: constants & periodic table, page 12: 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.

(채점 답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure

- 1) Return and Claim Period: **October 22 (Mon, 19:00 ~ 20:00 p.m.)**
- 2) **Location: Room for quiz session**
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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.

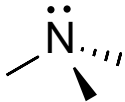
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2. Final Confirmation

- 1) Period: October 25 (Thu) – October 26 (Fri)
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** For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr.

1. (Total 15 pts) Give the steric number for each molecule in the table. Predict the geometry using the VSEPR method. For the geometry, provide a schematic drawing and describe the molecular shape in short words by choosing from “linear, trigonal planar, tetrahedral, trigonal bipyramidal, square pyramidal, octahedral, square planar, seesaw shape, and distorted T shape”. In each case, the central atom is listed first and the other atoms are all bonded directly to it. In the drawing, explicitly specify the locations of lone electron pairs based on the Lewis diagram. Follow the example of NH₃ below.

	NH₃ (example)	CBr₄	SO₃
Steric number	4		
Geometry			
	Trigonal pyramidal		
	I₃⁻	XeF₄	ICl₃
Steric number			
Geometry			

2. (total 5 pts) Write down the ground state electron configurations for the ions, Be⁺, C⁻, Ne²⁺, Mg⁺, P²⁺, Cl⁻, As⁺, and I⁻. Among these ions, which do you expect to be diamagnetic?

3. (total 10 pts) The non-normalized wavefunction of a particle in a one-dimensional box with the length L is $\psi(x) = \sin(n\pi x / L)$.

(a) Properly normalize this wavefunction.

(b) What is the probability that the particle will lie between $x = 0$ and $x = L/4$, if the particle is in its $n = 3$ state?

(c) What is the probability that the particle will lie between $x = 0$ and $x = L/2$, if the particle is in its $n = 20181017$ state?

(d) What is the probability that the particle will lie between $x = L/2$ and $x = L$, if the particle is in its $n = 20181018$ state?

4. (total 10 pts) Light with a wavelength of 525 nm strikes the surface of metallic rubidium in a photocell. The work function of rubidium is 2.09 eV.

(a) Convert the work function in the unit of J.

(b) Calculate the maximum velocity of the photoelectrons.

(c) Determine the longest wavelength of light that is capable of ejecting electrons from the surface of rubidium.

5. (total 9 pts) Which has the higher value in each pair below? Briefly explain the reason. IE = ionization energy.

(a) The 1st IE of Al or the 1st IE of Mg

(b) The 2nd IE of Al or the 2nd IE of Mg

(c) The 3rd IE of Al or the 3rd IE of Mg

6. (total 12 pts) One electronic wavefunction of a hydrogen atom is

$$\psi = r e^{-r/2a} \cos \theta$$

(a) Show that this satisfies the Schrödinger equation,

$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \psi = E\psi$$

and obtain the corresponding energy eigenvalue E in the unit of eV. To solve this problem, you will need $a = 4\pi\epsilon_0 \hbar^2 / (e^2 m_e)$, or equivalently $e^2 / (4\pi\epsilon_0) = \hbar^2 / (m_e a)$. Also, $h = 2\pi\hbar$.

(b) Sketch the 3-dimensional shape of this orbital, and designate its three quantum numbers (n, l, m).

(c) If the electron in this hydrogen atom radiates a photon to de-excite into a state described by the 1s orbital, what is the wavelength of this photon? Recall that $E_n \propto 1/n^2$.

7. (total 10 pts) The electronic wavefunction of a hydrogen atom can be written as $\psi_{n,l,m}(\mathbf{r}) = R_{n,l}(r)Y_{l,m}(\theta, \phi)$.

(a) Give all possible values of quantum numbers (l, m) with $n = 3$.

(b) Using the table below, write down the normalized form of the wavefunction with the lowest l value in (a).

Angular and Radial Parts of Wave Functions for One-Electron Atoms

Angular Part $Y(\theta, \phi)$

Radial Part $R_{n\ell}(r)$

$$\ell = 0 \left\{ Y_s = \left(\frac{1}{4\pi} \right)^{1/2} \right.$$

$$R_{1s} = 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp(-\sigma)$$

$$R_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \sigma) \exp(-\sigma/2)$$

$$R_{3s} = \frac{2}{81\sqrt{3}} \left(\frac{Z}{a_0} \right)^{3/2} (27 - 18\sigma + 2\sigma^2) \exp(-\sigma/3)$$

$$\sigma = \frac{Zr}{a_0} \quad a_0 = \frac{\epsilon_0 h^2}{\pi e^2 m_e} = 0.529 \times 10^{-10} \text{ m}$$

(c) By integrating over the angular part, derive the radial distribution function $P(r)$ for the wavefunction in (b). Namely, use $P(r)dr = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |\psi(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$ and obtain $P(r)$.

(d) Sketch both the wavefunction in (b) and the radial distribution function in (c) as functions of σ . Quantitatively specify the locations of radial nodes.

8. (total 6 pts) Noting $\lambda = \frac{h}{p}$ and $p = mv$, calculate the de Broglie wavelength for the following:

(a) an electron moving at a speed of 1.0 km s^{-1}

(b) a baseball with a mass of 145 g, moving at a speed of 75 km hr^{-1}

9. (total 8 pts) Consider an acetamide (CH_3CONH_2) molecule.

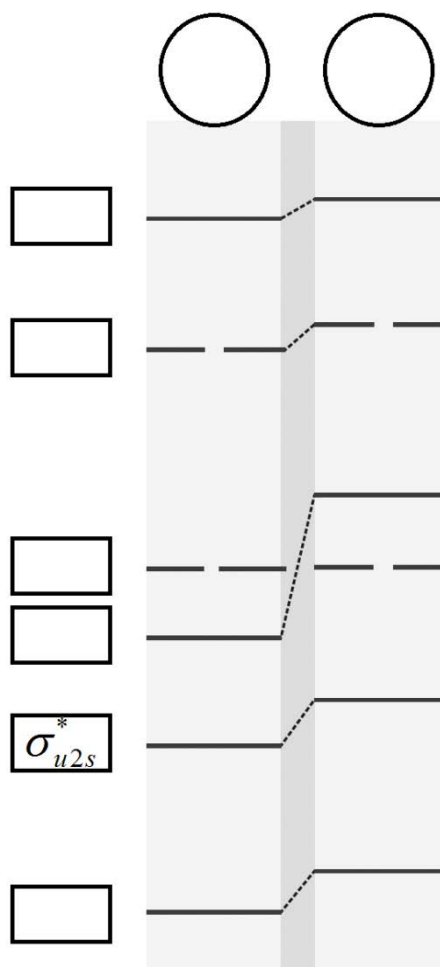
(a) Draw the Lewis diagram of this molecule with all possible resonance structures.

(b) What is the proper hybridization of each carbon atom?

(c) Based on the information that the three bonds around the N atom form a nearly planar triangle, sketch the shape of the energetically most stable π bonding molecular orbital.

10. (total 15 pts) The following diagram shows the molecular orbital energy levels for the homonuclear diatomics, N₂ and O₂.

(a) Fill in the boxes with appropriate molecular orbital notations as in the case of σ_{u2s}^* , based on the linear combination of atomic orbital (LCAO) scheme.



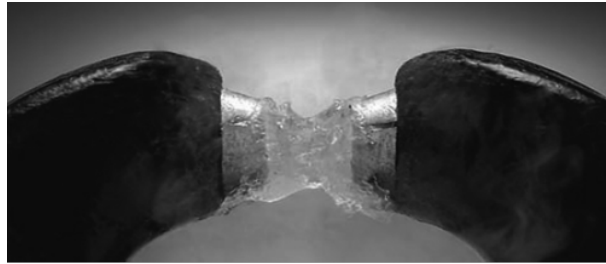
(b) In the two circles in the above diagram, designate which are N₂ and O₂, respectively. Fill the MO levels with arrows to represent the electronic structures of both molecules.

(c) The following data show that removing an electron from N₂ forms an ion with a weaker / longer bond than in the parent molecule, whereas the ion formed from O₂ has a stronger / shorter bond:

	N ₂	N ₂ ⁺	O ₂	O ₂ ⁺
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

Explain these facts with the above completed diagram together with the bond order concept.

(d) For liquefied nitrogen and oxygen, which will be attracted to the space between the poles of a magnet as in the following picture? Explain your reasoning with less than 30 words.



Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ \AA} = 5.2917720859 \times 10^{-11} \text{ m}$
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19} \text{ C}$
Faraday constant	$F = 96485.3399 \text{ C mol}^{-1}$
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	$m_p / m_e = 1836.15267247$
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	$1 \text{ \AA} = 10^{-10} \text{ m}$
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 form $E = mc^2$)
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.kkf-split.hr/periodic/en/>

GROUP	PERIOD																GROUP
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I A	II A	III B	IV B	V B	VI B	VII B	VIII B	VIII B	VIII B	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
GROUP NUMBERS IUPAC RECOMMENDATION (1985)																	
GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)																	
ATOMIC NUMBER — 5 — 10.811 — RELATIVE ATOMIC MASS (1)																	
SYMBOL — B																	
ELEMENT NAME — BORON — B																	
1 1.0079 H HYDROGEN	2 4.0026 He HELIUM	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM	5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM	13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTRITIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIObIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.80 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uu UNUNILIUM	111 (272) Uu UNUNUNIUM	112 (285) Uub UNUBIUM	114 (289) Uuq UNUNQUADIUM					

LANTHANIDE

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

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM
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(1) Pure Appl. Chem., 73, No. 4, 657-693 (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 (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Varshna (aditya@pnetlinux.com)

Claim Form for General Chemistry Examination

Page (/)

Class: _____, Professor Name: _____, I.D.# : _____, Name: _____

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

By Student		By TA	
Question #	Claims	Accepted? Yes(✓) or No(✓)	
		Yes: <input type="checkbox"/>	No: <input type="checkbox"/>
		Pts (+/-)	Reasons

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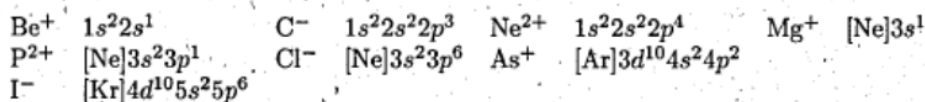
1. (Total 15 pts) Give the steric number for each molecule in the table. Predict the geometry using the VSEPR method. For the geometry, provide a schematic drawing and describe the molecular shape in short words by choosing from “linear, trigonal planar, tetrahedral, trigonal bipyramidal, square pyramidal, octahedral, square planar, seesaw shape, and distorted T shape”. In each case, the central atom is listed first and the other atoms are all bonded directly to it. In the drawing, explicitly specify the locations of lone electron pairs based on the Lewis diagram. Follow the example of NH₃ below.

	NH₃ (example)	CBr₄	SO₃
Steric number	4	4	3
Geometry			
	<u>Trigonal pyramidal</u>	Tetrahedral	Trigonal planar
	I₃⁻	XeF₄	ICl₃
Steric number	5	6	5
Geometry			
	Linear	Square planar	Distorted T

1 point for each correct answer. Not showing resonance in SO₃ is OK. For wrong distortion direction in ICl₃, 0 pt for the sketch.

2. (total 5 pts) Write down the ground state electron configurations for the ions, Be⁺, C⁻, Ne²⁺, Mg⁺, P²⁺, Cl⁻, As⁺, and I⁻. Among these ions, which do you expect to be diamagnetic?

The ground-state configuration of an ion derives from the ground-state configuration of the atom. In the case of a negative ion, add electrons to available orbitals in order of ascending energy. In the case of positive ions, remove electrons starting with the ones in the highest-energy orbitals



All of these electron configurations are ground-state (lowest energy) configurations. Be⁺, C⁻, Ne²⁺, Mg⁺, P²⁺ and As⁺ all have at least one unpaired electron (they have incomplete subshells) and should be paramagnetic. The Cl⁻ and I⁻ ions are diamagnetic; the others are paramagnetic.

-1 point for each wrong answer. 0 point for more than 4 wrong answers.

3. (total 10 pts) The non-normalized wavefunction of a particle in a one-dimensional box with the length L is $\psi(x) = \sin(n\pi x / L)$.

(a) Properly normalize this wavefunction.

Let $\psi = N \sin \frac{n\pi x}{L}$. The normalization condition is

$$\int_0^L |\psi|^2 dx = N^2 \int_0^L \frac{1}{2} \left(1 - \cos \frac{2n\pi x}{L} \right) dx = \frac{1}{2} LN^2 = 1$$

Thus, $N = \sqrt{2/L}$ and

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad 3 \text{ pt}$$

(b) What is the probability that the particle will lie between $x = 0$ and $x = L/4$, if the particle is in its $n = 3$ state?

$$P = \int_0^{L/4} |\psi|^2 dx = \frac{2}{L} \int_0^{L/4} \frac{1}{2} \left(1 - \cos \frac{6\pi x}{L} \right) dx = \frac{1}{L} \left(\frac{L}{4} - \frac{L}{6\pi} \sin \frac{6\pi x}{L} \Big|_0^{L/4} \right) = \frac{1}{4} + \frac{1}{6\pi} \quad 3\text{pt}$$

(c) What is the probability that the particle will lie between $x = 0$ and $x = L/2$, if the particle is in its $n = 20181017$ state?

Because the system is symmetric with respect to $x = L/2$, the two probabilities are 0.5 in both cases. (2pt)

(d) What is the probability that the particle will lie between $x = L/2$ and $x = L$, if the particle is in its $n = 20181018$ state?

Again, because the system is symmetric with respect to $x = L/2$, the two probabilities are 0.5 in both cases. (2pt)

4. (total 10 pts) Light with a wavelength of 525 nm strikes the surface of metallic rubidium in a photocell. The work function of rubidium is 2.09 eV.

(a) Convert the work function in the unit of J.

$$2.09 \text{ eV} = 2.09 \times 1.602 \times 10^{-19} \text{ C} \cdot \text{V} = 3.35 \times 10^{-19} \text{ J}$$

(2pt, no partial points)

(b) Calculate the maximum velocity of the photoelectrons.

525 nm photon energy:

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{525 \times 10^{-9} \text{ m}} = 3.79 \times 10^{-19} \text{ J} \quad (2\text{pt})$$

Letting $E_0 =$ work function, $E_k = \frac{1}{2}mv^2 = E - E_0 = (3.79 - 3.35) \times 10^{-19} \text{ J} = 4.4 \times 10^{-20} \text{ J}$

$$v = \sqrt{\frac{2E_k}{m_e}} = \sqrt{\frac{2 \times 4.4 \times 10^{-20} \text{ J}}{(9.11 \times 10^{-31} \text{ kg})}} = 3.11 \times 10^5 \text{ m s}^{-1} \quad (3\text{pt})$$

(c) Determine the longest wavelength of light that is capable of ejecting electrons from the surface of rubidium.

The longest wavelength to promote the photoelectric effect occurs when the light energy matches the work function, i.e. $h\nu_0 = E_0$, $E_0 = 3.35 \times 10^{-19} \text{ J} = h\nu_0 = \frac{hc}{\lambda_0}$.

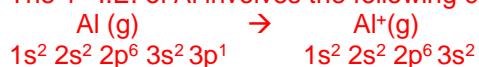
$$\lambda_0 = \frac{hc}{E_0} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m s}^{-1})}{3.35 \times 10^{-19} \text{ J}} = 5.93 \times 10^{-7} \text{ m} = 593 \text{ nm} \quad (3\text{pt})$$

5. (total 9 pts) Which has the higher value in each pair below? Briefly explain the reason. IE = ionization energy.

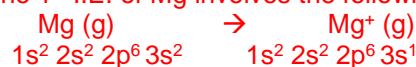
(a) The 1st IE of Al or the 1st IE of Mg

Mg ∴ electron is removed from lower energy orbital

The 1st I.E. of Al involves the following change.



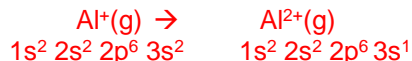
The 1st I.E. of Mg involves the following change.



(b) The 2nd IE of Al or the 2nd IE of Mg

Al ∴ larger effective nuclear charge

The 2nd I.E. of Al involves the following change.



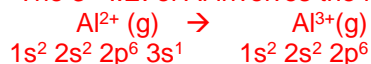
The 2nd I.E. of Mg involves the following change.



(c) The 3rd IE of Al or the 3rd IE of Mg

Mg ∴ electron is removed from lower energy orbital

The 3rd I.E. of Al involves the following change.



The 3rd I.E. of Mg involves the following change.



6. (total 12 pts) One electronic wavefunction of a hydrogen atom is

$$\psi = r e^{-r/2a} \cos \theta$$

(a) Show that this satisfies the Schrödinger equation,

$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \psi = E\psi$$

and obtain the corresponding energy eigenvalue E in the unit of eV. To solve this problem, you will need $a = 4\pi\epsilon_0 \hbar^2 / (e^2 m_e)$, or equivalently $e^2 / (4\pi\epsilon_0) = \hbar^2 / (m_e a)$. Also, $h = 2\pi\hbar$.

(7 pts) We can show that it is the solution by directly putting ψ back into the Schrödinger equation:

$$\begin{aligned} -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \psi &= -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \left(1 - \frac{r}{2a} \right) e^{-r/2a} \cos \theta \\ &= -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 - \frac{r^3}{2a} \right) e^{-r/2a} \cos \theta \\ &= -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \left[\left(2r - \frac{3r^2}{2a} \right) - \frac{1}{2a} \left(r^2 - \frac{r^3}{2a} \right) \right] e^{-r/2a} \cos \theta \\ &= -\frac{\hbar^2}{2m_e} \frac{1}{r} \left(2 - \frac{2r}{a} + \frac{r^2}{4a^2} \right) e^{-r/2a} \cos \theta \\ -\frac{\hbar^2}{2m_e} \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \psi &= -\frac{\hbar^2}{2m_e} \frac{1}{r^2 \sin \theta} r e^{-r/2a} \frac{\partial}{\partial \theta} (-\sin \theta \sin \theta) \\ &= \frac{\hbar^2}{2m_e} \frac{1}{r \sin \theta} e^{-r/2a} (2 \sin \theta \cos \theta) = \frac{\hbar^2}{2m_e} \frac{2}{r} e^{-r/2a} \cos \theta \\ -\frac{\hbar^2}{2m_e} \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \psi &= 0 \end{aligned}$$

By combining the above three, the term in the large bracket in the Schrödinger equation is:

$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r} \left(2 - \frac{2r}{a} + \frac{r^2}{4a^2} \right) \cos \theta - \frac{2}{r} \cos \theta \right] e^{-r/2a} = -\frac{\hbar^2}{2m_e} \left(-\frac{2}{a} + \frac{r}{4a^2} \right) \cos \theta e^{-r/2a}$$

Also, by using $\hbar^2 / (m_e a) = e^2 / (4\pi\epsilon_0)$, the last term of the left hand side of the SE becomes:

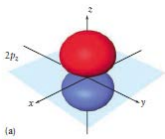
$$-\frac{\hbar^2}{m_e a} r e^{-r/2a} \cos \theta = -\frac{\hbar^2}{2m_e} \frac{2}{a} e^{-r/2a} \cos \theta$$

Therefore, the whole left term becomes:

$$-\frac{\hbar^2}{2m_e} \left(-\frac{2}{a} + \frac{r}{4a^2} \right) e^{-r/2a} \cos \theta - \frac{\hbar^2}{2m_e} \frac{2}{a} e^{-r/2a} \cos \theta = -\frac{\hbar^2}{8m_e a^2} r e^{-r/2a} \cos \theta = -\frac{\hbar^2}{8m_e a^2} \psi$$

$$\text{Thus, } E = -\frac{\hbar^2}{8m_e a^2} = -\frac{\hbar^2}{8m_e} \left(\frac{e^4 m_e^2}{16\pi^2 \epsilon_0^2 \hbar^4} \right) = -\frac{e^4 m_e}{32\epsilon_0^2 \hbar^2} = -5.45 \times 10^{-19} \text{ J} = -3.40 \text{ eV}$$

(b) Sketch the 3-dimensional shape of this orbital, and designate its three quantum numbers (n, l, m).



The wavefunction is 1 with $\theta = 0$, 0 with $\theta = \pi/2$, and -1 with $\theta = \pi$. \rightarrow p function, No radial node \rightarrow 2p, aligned along z-axis \rightarrow 2p_z. Thus, (n, l, m) = (2, 1, 0). (1 pt for the sketch, 1 pt for the quantum #'s)

(c) If the electron in this hydrogen atom radiates a photon to de-excite into a state described by the 1s orbital, what is the wavelength of this photon? Recall that $E_n \propto 1/n^2$.

$E_2 = -3.40 \text{ eV}$. Thus, $E_1 = -3.40 \text{ eV} \times 4 = -13.60 \text{ eV}$. Thus the transition energy is 10.20 eV . (2 pt)

$\lambda = hc / E = 121 \text{ nm}$. (1 pt)

7. (total 10 pts) The electronic wavefunction of a hydrogen atom can be written as $\psi_{n,l,m}(\mathbf{r}) = R_{n,l}(r)Y_{l,m}(\theta, \phi)$.

(a) Give all possible values of quantum numbers (l, m) with $n = 3$.

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

2pt total; If any one missing, -1 pt. 2 or more wrong answers will get no points.

(b) Using the table below, write down the normalized form of the wavefunction with the lowest l value in (a).

Angular and Radial Parts of Wave Functions for One-Electron Atoms

Angular Part $Y(\theta, \phi)$

Radial Part $R_{n\ell}(r)$

$$\ell = 0 \left\{ Y_s = \left(\frac{1}{4\pi} \right)^{1/2} \right.$$

$$R_{1s} = 2 \left(\frac{Z}{a_0} \right)^{3/2} \exp(-\sigma)$$

$$R_{2s} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \sigma) \exp(-\sigma/2)$$

$$R_{3s} = \frac{2}{81\sqrt{3}} \left(\frac{Z}{a_0} \right)^{3/2} (27 - 18\sigma + 2\sigma^2) \exp(-\sigma/3)$$

$$\sigma = \frac{Zr}{a_0}$$

$$a_0 = \frac{\epsilon_0 h^2}{\pi e^2 m_e} = 0.529 \times 10^{-10} \text{ m}$$

$$\psi = R_{3s} Y_s = \sqrt{\frac{1}{4\pi}} \frac{2}{81\sqrt{3}} \left(\frac{1}{a_0} \right)^{3/2} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}$$

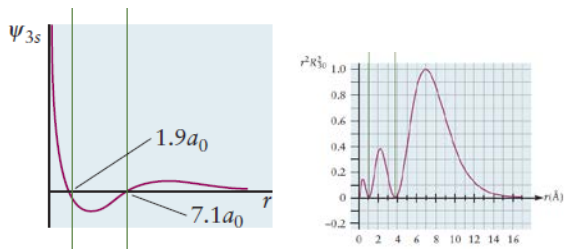
2pt. No partial credit.

(c) By integrating over the angular part, derive the radial distribution function $P(r)$ for the wavefunction in (b). Namely, use $P(r)dr = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |\psi(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$ and obtain $P(r)$.

$$\begin{aligned} P(r)dr &= \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |R_{3s}(r)|^2 r^2 \frac{1}{4\pi} \sin \theta dr d\theta d\phi = |R_{3s}(r)|^2 r^2 \frac{1}{4\pi} dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= [R_{3s}(r)]^2 r^2 dr \end{aligned} \quad (3\text{pt})$$

(d) Sketch both the wavefunction in (b) and the radial distribution function in (c) as functions of σ . Quantitatively specify the locations of radial nodes.

The wavefunction is zero when $\sigma = \frac{9 \pm \sqrt{27}}{2} = 7.09$ or 1.90 .



3pts in total. Deductions: If ψ goes to infinity at the origin, -2 pt; Wrong nodal points, -2 pt; non-zero $P(r)$ at the origin -2. (maximum deduction: -3 pts)

8. (total 6 pts) Noting $\lambda = \frac{h}{p}$ and $p = mv$, calculate the de Broglie wavelength for the following:

(a) an electron moving at a speed of 1.0 km s^{-1}

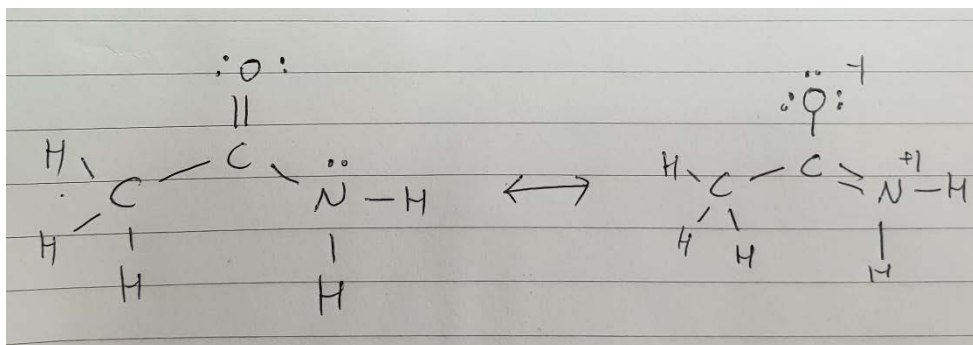
$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^3 \text{ m s}^{-1})} = 7.3 \times 10^{-7} \text{ m} = 7.3 \times 10^3 \text{ \AA}$$

(b) a baseball with a mass of 145 g, moving at a speed of 75 km hr^{-1}

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s}}{(0.145 \text{ kg})(75 \times 10^3 / 3600 \text{ m s}^{-1})} = 2.2 \times 10^{-34} \text{ m} = 2.2 \times 10^{-24} \text{ \AA}$$

9. (total 8 pts) Consider an acetamide (CH_3CONH_2) molecule.

(a) Draw the Lewis diagram of this molecule with all possible resonance structures.



(2pts; 1pt for each structure)

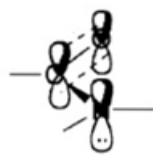
(b) What is the proper hybridization of each carbon atom?

sp^3 for $-\text{CH}_3$ carbon; sp^2 for the other carbon
2pts; 1 pt for each correct hybridization

(c) Based on the information that the three bonds around the N atom form a nearly planar triangle, state the most appropriate hybridization scheme for the N atom, and sketch the shape of the energetically most stable π bonding molecular orbital.

From the geometrical consideration, it should be sp^2 . (2 pts) Because $C=O$ also has a double bond character, p_z orbital should also participate the π bond. Thus, the MO will appear as

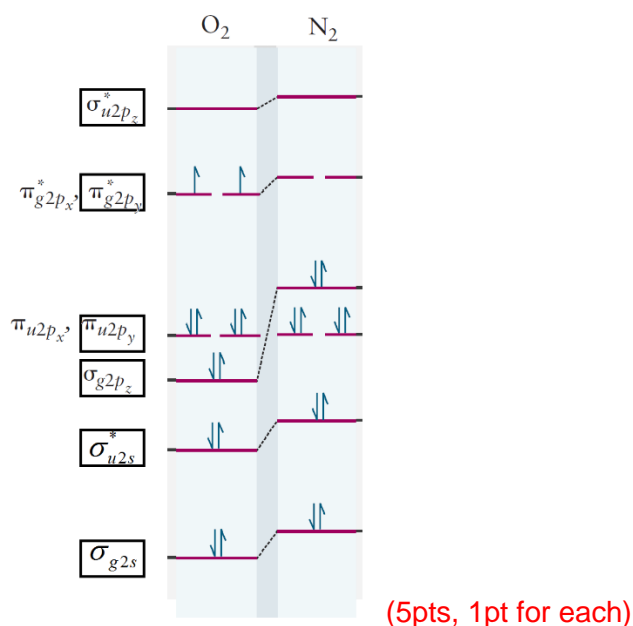
π bonds in $-\text{CONH}_2$



(2 pts)

10. (total 15 pts) The following diagram shows the molecular orbital energy levels for the homonuclear diatomics, N₂ and O₂.

(a) Fill in the boxes with appropriate molecular orbital notations as in the case of σ_{u2s}^* , based on the linear combination of atomic orbital (LCAO) scheme.



(b) In the two circles in the above diagram, designate which are N₂ and O₂, respectively. Fill the MO levels with arrows to represent the electronic structures of both molecules.

(4pts, 1pt for each right answer)

(c) The following data show that removing an electron from N₂ forms an ion with a weaker / longer bond than in the parent molecule, whereas the ion formed from O₂ has a stronger / shorter bond:

	N ₂	N ₂ ⁺	O ₂	O ₂ ⁺
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

Explain these facts with the above completed diagram together with the bond order concept.

N₂ has 10 valence electrons, so N₂⁺ has 9.

O₂ has 12 valence electrons, so O₂⁺ has 11.

N₂: bonding e⁻ removed, and bond order changes from 3 to 2.5

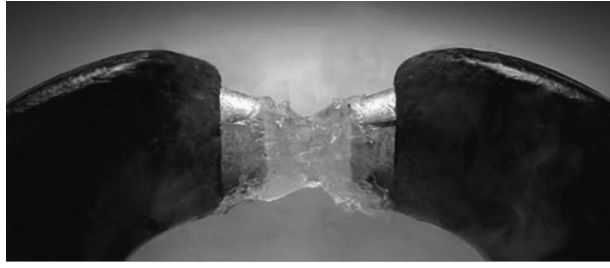
O₂: antibonding e⁻ removed, and bond order increased from 2 to 2.5.

(4pts total; 0pt when there is no explanation, 2pts only when)

(d) For liquefied nitrogen and oxygen, which will be attracted to the space between the poles of a magnet as in the following picture? Explain your reasoning with less than 30 words.

Because of the unpaired electrons in O₂, it is paramagnetic. Thus it is attracted to the magnetic field.

(2pts, no partial credit)



Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ \AA} = 5.2917720859 \times 10^{-11} \text{ m}$
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19} \text{ C}$
Faraday constant	$F = 96485.3399 \text{ C mol}^{-1}$
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	$m_p / m_e = 1836.15267247$
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	$1 \text{ \AA} = 10^{-10} \text{ m}$
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 form $E = mc^2$)
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.kjf-split.hr/periodic/en/>

GROUP	PERIOD																GROUP
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I A	II A	III B	IV B	V B	VI B	VII B	VIII B	IX B	X B	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H HYDROGEN	2 He HELIUM	3 Li LITHIUM	4 Be BERYLLIUM	5 B BORON	6 C CARBON	7 N NITROGEN	8 O OXYGEN	9 F FLUORINE	10 Ne NEON	11 Na SODIUM	12 Mg MAGNESIUM	13 Al ALUMINIUM	14 Si SILICON	15 P PHOSPHORUS	16 S SULPHUR	17 Cl CHLORINE	18 Ar ARGON
19 K POTASSIUM	20 Ca CALCIUM	21 Sc SCANDIUM	22 Ti TITANIUM	23 V VANADIUM	24 Cr CHROMIUM	25 Mn MANGANESE	26 Fe IRON	27 Co COBALT	28 Ni NICKEL	29 Cu COPPER	30 Zn ZINC	31 Ga GALLIUM	32 Ge GERMANIUM	33 As ARSENIC	34 Se SELENIUM	35 Br BROMINE	36 Kr KRYPTON
37 Rb RUBIDIUM	38 Sr STRONTIUM	39 Y YTRIVIUM	40 Zr ZIRCONIUM	41 Nb NIObIUM	42 Mo MOLYBDENUM	43 Tc TECHNETIUM	44 Ru RUTHENIUM	45 Rh RHODIUM	46 Pd PALLADIUM	47 Ag SILVER	48 Cd CADMIUM	49 In INDIUM	50 Sn TIN	51 Sb ANTIMONY	52 Te TELLURIUM	53 I IODINE	54 Xe XENON
55 Cs CAESIUM	56 Ba BARIUM	57-71 La-Lu LANTHANIDE	72 Hf HAFNIUM	73 Ta TANTALUM	74 W TUNGSTEN	75 Re RHENIUM	76 Os OSMIUM	77 Ir IRIDIUM	78 Pt PLATINUM	79 Au GOLD	80 Hg MERCURY	81 Tl THALLIUM	82 Pb LEAD	83 Bi BISMUTH	84 Po POLONIUM	85 At ASTATINE	86 Rn RADON
87 Fr FRANCIUM	88 Ra RADIUM	89-103 Ac-Lr ACTINIDE	104 Rf RUTHERFORDIUM	105 Dfb DUBNIUM	106 Sg SEABORGIUM	107 Bh BOHRVIUM	108 Hs HASSIUM	109 Mt MEITNERIUM	110 Uun UNUNNIUM	111 Uuu UNUNNIUM	112 Uub UNUNBIUM	114 Uuq UNUNQUADIUM					

LANTHANIDE

57 138.91 La	58 140.12 Ce	59 140.91 Pr	60 144.24 Nd	61 (145) Pm	62 150.36 Sm	63 151.96 Eu	64 157.25 Gd	65 158.93 Tb	66 162.50 Dy	67 164.93 Ho	68 167.26 Er	69 168.93 Tm	70 173.04 Yb	71 174.97 Lu
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ACTINIDE

89 (227) Ac	90 232.04 Th	91 231.04 Pa	92 238.03 U	93 (237) Np	94 (244) Pu	95 (243) Am	96 (247) Cm	97 (247) Bk	98 (251) Cf	99 (252) Es	100 (257) Fm	101 (258) Md	102 (259) No	103 (262) Lr
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(1) Pure Appl. Chem., 73, No. 4, 857-893 (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 (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.
 Editor: Aditya Varshan (aditya@pnetlinux.com)

Claim Form for General Chemistry Examination

Page (/)

Class: _____, Professor Name: _____, I.D.# : _____, Name: _____

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

By Student		By TA	
Question #	Claims	Accepted? Yes(✓) or No(✓)	
		Yes: <input type="checkbox"/>	No: <input type="checkbox"/>
		Pts (+/-)	Reasons

2018 FALL Semester Final Examination For General Chemistry I

Date: December 12 (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
1	/10	7	/8
2	/4	8	/11
3	/3	9	/13
4	/6	10	/13
5	/10	11	/13
6	/4	12	/5
/100			

** This paper consists of 13 sheets with 12 problem sets (pages 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 units in your answer when applicable. You will get 30% deduction for a missing unit.

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

(채점 답안지 분배 및 이의신청 일정)

1. Period, Location, and Procedure

- 1) Return and Claim Period: **December 14 (Fri, 12:00 ~ 14:00 p.m.)**
- 2) **Location: Room in Creative Learning Bldg. (E11)**

Class	Room	Class	Room	Class	Room
A	302	B	309	C	310

- 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)

(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 will be uploaded on **December 14** on the web.)

2. Final Confirmation

- 1) Period: December 15 (Sat) – December 16 (Sun)
- 2) Procedure: During this period, you can check the final score of the examination *on the website*.

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

1. (Total 10 pts)

Suppose that there are N molecules in a cubic box of a side length ℓ . Assume that each molecule with mass of m constantly collides elastically with the wall of the box with a speed of u . By using the ideal gas law, show that the average kinetic energy per molecule ($\bar{\epsilon}$) depends on the temperature. You should write down all the procedures to get the full points.

(Answer)

(1) **Force acted on the original wall by a molecule (+ 3 pts)**

$$\begin{aligned}\Delta p_{x,\text{mol}} &= m(-v_x) - mv_x = -2mv_x \\ \Delta p_{x,\text{wall}} &= 2mv_x \\ \Delta t &= 2\ell/v_x \\ f &= ma = m \frac{\Delta v}{\Delta t} = \frac{\Delta p_{x,\text{wall}}}{\Delta t} = \frac{mv_x^2}{\ell}\end{aligned}$$

(2) **Force acted on the original wall by N molecules (+ 1 pt)**

$$F = \frac{mv_{x1}^2}{\ell} + \frac{mv_{x2}^2}{\ell} + \frac{mv_{x3}^2}{\ell} + \dots + \frac{mv_{xN}^2}{\ell} = N \frac{m\overline{v_x^2}}{\ell}, \quad \text{where } \overline{v_x^2} = \frac{1}{N}(v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2)$$

(3) **Pressure on the original wall of area A (+ 1 pt)**

$$P = \frac{F}{A} = \frac{Nm}{A\ell} v_x^2 = \frac{Nm}{V} v_x^2$$

(4) **The mean-square speed of a molecule with no preferred direction (+ 1 pt)**

$$\begin{aligned}\overline{u^2} &= \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2} \\ PV &= Nm\overline{v_x^2} = \frac{1}{3}Nm\overline{u^2}\end{aligned}$$

(5) **Ideal gas law (+ 3 pts)**

$$nRT = \frac{1}{3}Nm\overline{u^2} \rightarrow RT = \frac{1}{3}N_A m\overline{u^2} \quad (\text{from the ideal gas law})$$

(6) **Average kinetic energy per molecule (+ 1 pt)**

$$\bar{E} = \frac{1}{2}N_A m\overline{u^2} \rightarrow \bar{\epsilon} = \frac{1}{2}m\overline{u^2} = \frac{1}{2}\left(\frac{3RT}{N_A}\right) = \frac{3}{2}k_B T$$

2. (Total 4 pts) The van der Waals equation is given as $\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$.

(a) List CH₄, H₂, N₂, and NH₃ in the increasing order in a with an explanation on your logic.

"a" constant depends on the strength of attractions between its component molecules



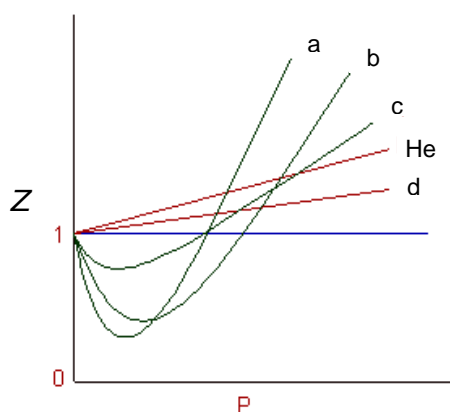
(b) List CH₄, H₂, N₂, and NH₃ in the increasing order in b with an explanation on your logic.

"b" constant reflects merely the actual volume of a mole of the molecules



3. (Total 3 pts)

The following five curves are sketches of the compressibility factors ($Z = PV / nRT$) for CH₄, CO₂, H₂, He, and NH₃ at varying pressures but at a constant temperature. The curve for He is explicitly designated for your information. For each of the remaining four curves marked with a – d, designate the gas by choosing from the remaining list (CH₄, CO₂, H₂, and NH₃).



a = NH₃ (hydrogen bonding and most deviating from ideality); b = CO₂ (larger dispersion than CH₄), c = CH₄; d = H₂ (closest to ideal)

→ 1pt for H₂, 1pt for NH₃, 1pt for getting CO₂ and CH₄ right.

4. (Total 6 pts)

State which attractive intermolecular force plays most dominantly in the following molecular pairs.

(a) Sodium ion – water : Ion – dipole force

(b) Hydroxide ion – water : Ion – dipole force

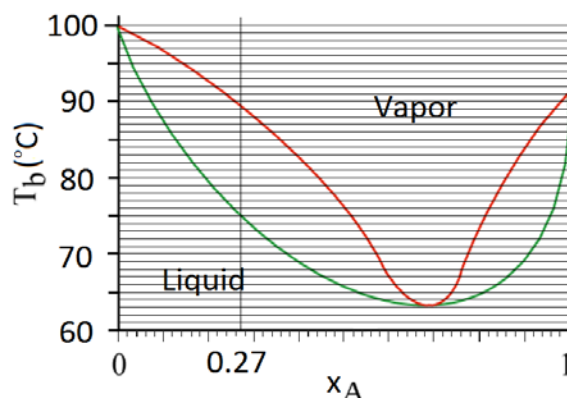
(c) Carbon dioxide gas – water : Induced dipole force (Dipole – induced dipole force)

(d) Methanol – ethanol : Hydrogen bonding

(e) Chloride ion – hexane (C₆H₁₄) : Ion – induced dipole / Charge – induced dipole force

(f) Octane (C₈H₁₈) – hexane (C₆H₁₄) : Induced dipole – induced dipole force (London dispersion force / Van der Waals force)

5. (Total 10 pts) Liquid A and B mix together as a non-ideal solution. Using the following phase diagram of boiling temperature at 1 atm as a function of the mole fraction of A (x_A), answer the following questions. (2pts each)



(a) Which of the two (namely, A or B) is more volatile at 1 atm?

Pure B boiling point: 100 deg; pure A boiling point: 91 deg → A is more volatile

(b) Estimate the boiling point of a solution with $x_A = 0.27$.

Just read it: 75 °C

(c) When an infinitesimally small amount of vapor is collected by boiling the solution in (b), what is the mole fraction of A in that vapor?

Follow the horizontal line, meet the vapor line, and then project to the x_A value: ~0.52

(d) If the vapor collected in (c) is condensed as liquid, what is its boiling point?

Do the same thing as in (b) with $x_A \sim 0.52$ to find 65 °C.

(e) Continuing the process of collecting vapor and then boiling again generates azeotrope. What is the mole fraction of A in this azeotrope?

0.68 (slight reading error is ok.)

6. (Total 4 pts: 1 pt for each right answer, -1 pt for each wrong one, and zero pt for not answering)

Answer whether the following statements are true or false. Just give the answer: no explanation is needed.

(a) When a system that is in thermal contact with a bath undergoes a spontaneous change, the entropy of the system always increases. **False, the entropy of the universe increases**

(b) The enthalpy of one mole of a monatomic ideal gas can be exactly known when its temperature but not its pressure is known. **True, $5/2 RT$**

(c) When a thermally isolated monatomic ideal gas expands freely against zero external pressure, its temperature always stays constant. **True, no work and no heat and its energy stays the same.**

(d) There is no inter-molecular interaction in an ideal solution in liquid phase. Namely, the molecules in an ideal solution do not attract or repel each other. **False, interactions are the same for each pair.**

7. (Total 8 pts) At 90°C, the vapor pressure of toluene (C₆H₅CH₃) is 0.534 atm and the vapor pressure of benzene (C₆H₆) is 1.34 atm. Now suppose that 0.400 mol of benzene is mixed with 0.900 mol of toluene to form an ideal solution at 90°C.

(a) Compute the mole fraction of benzene in the vapor that is in equilibrium with this solution.

$$P_{\text{toluene}} = x_{\text{toluene}} P_{\text{toluene}}^{\circ} = \frac{0.900}{0.400 + 0.900} \times 0.534 \text{ atm} = 0.370 \text{ atm}$$

$$P_{\text{benzene}} = x_{\text{benzene}} P_{\text{benzene}}^{\circ} = \frac{0.400}{0.400 + 0.900} \times 1.34 \text{ atm} = 0.412 \text{ atm}$$

The total pressure of the vapors above solution is 0.782 atm. Therefore, the mole fraction of benzene in the vapor is

$$x_{\text{benzene}} = \frac{0.412 \text{ atm}}{0.782 \text{ atm}} = 0.527$$

(b) Calculate the mole fraction of toluene in a mixture of benzene and toluene that boils at 90°C under atmospheric pressure.

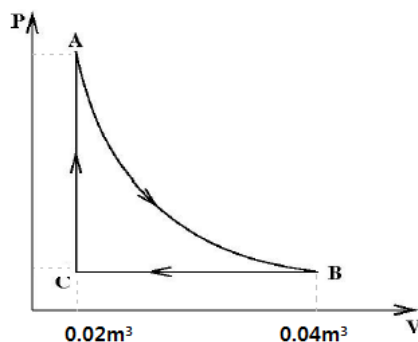
The vapor pressure of toluene is 0.534 atm at 90°C, and the vapor pressure of benzene is 1.34 atm. In order for the solution to boil, the total pressure above it must equal 1.00 atm. This total pressure is the sum of the pressures of the two components, each of which is given by Raoult's law. Letting the mole fraction of the toluene in solution as x_{toluene} , then the mole fraction of benzene is

$$x_{\text{benzene}} = 1 - x_{\text{toluene}}, \text{ and}$$

$$x_{\text{toluene}}(0.533 \text{ atm}) + (1 - x_{\text{toluene}})(0.533 \text{ atm}) = 1 \text{ atm}$$

Solving for x_{toluene} gives 0.42 as the answer.

8. (Total 11 pts) Four moles of a monatomic ideal gas goes through the cycle represented in the following figure. Process A → B is an isothermal expansion at a temperature $T_A = 300\text{K}$.



(a) Calculate P_A , P_B , and T_C , the pressures and temperature reached at A, B and C.

Process A → B is isothermal, so $T_A = T_B$

$$P_A = \frac{nRT_A}{V_A} = \frac{4 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.02 \text{ m}^3} = 4.988 \times 10^5 \text{ Pa} = 4.92 \text{ atm}$$

$$P_B = \frac{nRT_B}{V_B} = \frac{4 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.04 \text{ m}^3} = 2.494 \times 10^5 \text{ Pa} = 2.46 \text{ atm}$$

$$T_C = \frac{P_C V_C}{nR} = \frac{P_B V_A}{nR} = \frac{(2.494 \times 10^5 \text{ J m}^{-3}) \times (0.02 \text{ m}^3)}{4 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} = 150 \text{ K}$$

(b) (8 pts) Fill in the following table with numerical values in Joules.

Process	ΔU	q	w
A → B	0 J	6915 J	-6915 J
B → C	-7483 J	-12471 J	4988 J
C → A	7483 J	7483 J	0 J

(1) A → B

$$\Delta U_{AB} = q + w = 0 \text{ (isothermal)}, \text{ and } dq = -dw = PdV = \left(\frac{nRT}{V} \right) dV \rightarrow$$

$$q = \int_A^B dq = -\int_A^B dw = \int_A^B PdV = \int_A^B \left(\frac{nRT}{V} \right) dV = 4 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \ln \frac{0.04}{0.02} \text{ J} = 6915 \text{ J}$$

and w is equal to $-q = -6915 \text{ J}$

(2) B → C

$$w_{BC} = -P\Delta V = -(2.494 \times 10^5 \text{ J m}^{-3})(0.02 \text{ m}^3 - 0.04 \text{ m}^3) = +4988 \text{ J}$$

$$q_{BC} = nc_p \Delta T = (4 \text{ mol}) \left(\frac{5}{2} R \right) (150 - 300 \text{ K}) = -12471 \text{ J}$$

$$\Delta U_{BC} = q + w = -7483 \text{ J}$$

(3) C → A: Because U is a state function, $\Delta U_{CA} = -\Delta U_{AB} - \Delta U_{BC} = 7483 \text{ J} = q_{CA}$. Or equivalently,

$$q_{CA} = nc_v \Delta T = (4 \text{ mol}) \left(\frac{5}{2} R \right) (300 - 150 \text{ K}) = 7483 \text{ J} = \Delta U_{CA}$$

9. (Total 13 pts) The equipartition theorem allows you to estimate the molar heat capacity values for various species.

(a) (4 pts) Give the equipartition values of c_v in J/mol·K for the following species.



Ar has only 3 translational degrees of freedom, so its equipartition value is $3R/2$.

N₂ has 3 translational degrees of freedom, 2 rotational degrees of freedom (linear), and 1 vibrational degree of freedom ($3 \times 2 - 5 = 1$). Its equipartition value is $7R/2$.

CO₂ has 3 translational degrees of freedom, 2 rotational degrees of freedom (linear), and 4 vibrational degrees of freedom ($3 \times 3 - 5 = 4$). Its equipartition value is $13R/2$.

CH₄ has 3 translational degrees of freedom, 3 rotational degrees of freedom (nonlinear), and 9 vibrational degrees of freedom ($3 \times 5 - 6 = 9$). Its equipartition value is $24R/2$.

Therefore, for each atom or molecule,

$$c_v(\text{Ar}) = \frac{3}{2} \times 8.314 \text{ J/K} \cdot \text{mol} = 12.47 \text{ J/K} \cdot \text{mol}$$

$$c_v(\text{N}_2) = \frac{7}{2} \times 8.314 \text{ J/K} \cdot \text{mol} = 29.10 \text{ J/K} \cdot \text{mol}$$

$$c_v(\text{CO}_2) = \frac{13}{2} \times 8.314 \text{ J/K} \cdot \text{mol} = 54.04 \text{ J/K} \cdot \text{mol}$$

$$c_v(\text{CH}_4) = \frac{24}{2} \times 8.314 \text{ J/K} \cdot \text{mol} = 99.77 \text{ J/K} \cdot \text{mol}$$

+1 pt for each correct c_v value

If the values were not converted to J/K mol units, -1 pt maximum (NOT deducting -1 pt for each!)

(b) (3 pts) The equipartition theorem predicts c_p of methane (CH₄) at 298K to be 108.08 J/mol·K, but the experimental value of c_p is only 35.31 J/mol·K. Based on the assumption that translational and rotational motions of methane are fully activated, calculate the percent of the measured c_p value at 298K that arises from vibrational motion.

From (a), CH₄ has 9 vibrational degrees of freedom. Suppose these vibrational degrees of freedom have no contribution to c_p value. That gives

$$c_v = 3R, c_p = c_v + R = 4R = 33.25 \text{ J/K} \cdot \text{mol}$$

$$\therefore \text{The vibrational contribution} = (35.31 - 33.25) \text{ J K}^{-1} \text{ mol}^{-1} = 2.06 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{percent of } c_p \text{ due to vibration} = \left(\frac{2.06}{35.31} \right) \times 100\% = 5.83\%$$

+1 pt for the correct value of c_p value without vibrational contribution

+1 pt for the correct value of vibrational contribution

+1 pt for the correct answer

(c) (6 pts) Suppose 1.00 kJ of heat is transferred to 2.00 mol CH₄ at 298.0 K. During the heating process, the pressure is maintained constant at 1 atm. Calculate ΔU , q , w , ΔH , and the final temperature for this process. Use the measured value of c_p in (b). Toward calculating ΔU , assume that methane behaves with $PV = nRT$.

At constant pressure,

$$q_p = \Delta H = nc_p \Delta T = 1000 \text{ J}$$

$$1000 \text{ J} = (2.00 \text{ mol})(35.31 \text{ J K}^{-1} \text{ mol}^{-1}) \Delta T$$

$$\Delta T = 14.2 \text{ K}; \quad \therefore T_{\text{final}} = 298 + 14.2 = 312.2 \text{ K}$$

$$\Delta U = \Delta H - P\Delta V = \Delta H - nR\Delta T = 1000 \text{ J} - 2.00 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 14.2 \text{ K} = 764 \text{ J}$$

$$w = \Delta U - q = 764 \text{ J} - 1000 \text{ J} = -236 \text{ J}$$

+1 pt for each correct answers for q_p , ΔH , T , and w

+2 pt for ΔU

10. (Total 13 pts)

(a) Starting from the definition of the entropy change, $\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$, derive ΔS associated with the reversible expansion of n mol of an ideal monatomic gas, from volume V_1 to volume V_2 . Express your answer with the gas constant R together with n , V_1 , and V_2 .

$$\Delta S = \int_{V_1}^{V_2} \frac{PdV}{T} = \int_{V_1}^{V_2} \frac{nRdV}{V} = nR \ln \frac{V_2}{V_1} \quad (3\text{pts})$$

(b) Calculate the entropy change associated with the reversible expansion of 5.00 mol of an ideal monatomic gas at a constant temperature of 298.0 K from a pressure of 10.0 atm to 1.00 atm.

$$\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2} = (5.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 10 = 95.7 \text{ J K}^{-1} \quad (2\text{pts})$$

(c) Calculate the entropy change associated with the reversible adiabatic expansion of 5.00 mol of an ideal monatomic gas from a pressure of 10.0 atm to 1.00 atm.

For the adiabatic part of this path, $dq_{\text{rev}} = 0$ and entropy change is 0. (3pts)

(d) Based on the fact that the entropy is a state function, find the temperature of the expanded gas in (c). [Hint: You should use the fact that reversible heating of the gas at constant pressure back to 298.0 K will lead to the same state with the same entropy.]

Let us suppose that the temperature of the gas is T_2 , with $T_1 = 298.0$ K. For the reversible heating or cooling at constant pressure from T_2 to $T_1 = 298.0$ K, the entropy change is

$$\Delta S = \int_{T_2}^{T_1} \frac{nc_p dT}{T} = nc_p \ln \frac{T_1}{T_2} \quad (2\text{pts})$$

Because the entropy is a state function, this ΔS is the same as the entropy change in (b). Thus,

$$\Delta S = nc_p \ln \frac{T_1}{T_2} = (5.00 \text{ mol}) \left(\frac{5}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{T_1}{T_2} = 95.7 \text{ J K}^{-1}$$

$$\ln \frac{T_1}{T_2} = 0.921$$

$$\text{Thus, } T_2 = T_1 e^{-0.921} = 118.6 \text{ K. (3pts)}$$

[Note] -----

If $P_1 V_1^\gamma = P_2 V_2^\gamma$ and $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ are used to get $\left(\frac{P_1}{P_2} \right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{V_2}{V_1} \right)^{\gamma-1} = \frac{T_1}{T_2}$ and then to get

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{5/3-1}{5/3}} = 0.1^{0.4} \times 298.0 \text{ K} = 118.6 \text{ K, give only 3 pts.}$$

11. (Total 13 pts) For reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the Gibbs energy change can be expressed with the reaction quotient Q as

$$\Delta G = \Delta G^\circ + RT \ln Q$$

(a) By assuming that the reaction enthalpy ΔH° and the reaction entropy ΔS° does not depend on temperature, derive the van't Hoff equation that relates two equilibrium constants K_1 and K_2 at two different corresponding temperatures T_1 and T_2 .

Because the reaction free energy is zero when $Q = K$, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$. Thus,

$$\frac{\Delta H^\circ}{T} - \Delta S^\circ = -R \ln K \quad \text{and} \quad \Delta H^\circ \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = -R \ln \frac{K_2}{K_1}. \quad \text{Or equivalently,}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3\text{pts for correct derivation, 1pt for just writing down the equation})$$

(b) The equilibrium constant of the above reaction at 300°C is $K_1 = 11.5$. Calculate the equilibrium constant K_2 at 400°C. The standard enthalpies of formation (ΔH_f°) are -287.0 kJ/mol for $\text{PCl}_3(\text{g})$ and -374.9 kJ/mol for $\text{PCl}_5(\text{g})$ at 25°C.

Because the formation enthalpy of Cl_2 is zero, $\Delta H^\circ = 87.9$ kJ/mol.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = 2.74, \quad \text{and} \quad K_2 = 178. \quad (2 \text{ pts})$$

(c) Using the standard enthalpy of formation of $\text{Cl}(\text{g})$ given as $\Delta H_f^\circ[\text{Cl}(\text{g})] = 122$ kJ/mol, estimate the Cl-Cl bond enthalpy.

The bond enthalpy corresponds to the enthalpy change for one mole of bonds broken: $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$. Thus, $\Delta H^\circ = 244$ kJ/mol. (2pts; 0 pt for 122 kJ/mol or -244 kJ/mol)

(d) Estimate the average P-Cl bond enthalpy.

$$(d) \quad \Delta H^\circ \sim 5\Delta H^\circ(\text{P-Cl}) - 3\Delta H^\circ(\text{P-Cl}) - \Delta H^\circ(\text{Cl-Cl}) = 2x - 244 \text{ kJ/mol} = 87.9 \text{ kJ/mol}$$

$\rightarrow 166$ kJ/mol (1pt)

(e) A weighed quantity of solid PCl_5 is sealed in a 100.0 cm³ glass bulb to which a pressure gauge is attached. The bulb is heated to 300°C, and the gauge shows that the pressure in the bulb rises to 0.895 atm. Assuming that the contents of the bulb are at equilibrium with only the three gaseous compounds (PCl_5 , PCl_3 , and Cl_2), calculate the partial pressures of the three chemical species in the vessel. Also calculate the number of moles of the initially weighed solid PCl_5 .

Let us assume that the initial pressure with only PCl_5 is P_0 . The reaction can be considered as the

following:



initial	P_0		
change	$-x$	$+x$	$+x$
final	P_0-x	x	x

Thus, $K_1 = x^2 / (P_0 - x)$. Also, the final pressure is $P_T = 0.895 \text{ atm} = P_0 + x$. Therefore, $K_1 = x^2 / (P_T - 2x) = 11.2$. Solving this quadratic equation yields $x = 0.439$ as the only meaningful solution. Thus, $P(\text{PCl}_5) = P_T - 2x = 0.017 \text{ atm}$, $P(\text{PCl}_3) = P(\text{Cl}_2) = 0.439 \text{ atm}$. (3 pts)

Initially, there was 0.456 atm of PCl_5 . Thus, its number of moles is:

$$n = P_0V/RT = 0.456 \text{ atm} \times 0.100 \text{ L} / (0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 573.15 \text{ K}) = 0.970 \text{ mmol. (2pts)}$$

12. (Total 5 pts) There are two isomeric hydrocarbons with the formula C_4H_{10} , butane and isobutane, which we denote here as B and I. The standard enthalpies of formation for the gaseous species are: -124.7 kJ/mol for B, -131.3 kJ/mol for I. In addition, the standard Gibbs free energies of formation are -15.9 kJ/mol for B, -18.0 kJ/mol for I.

(a) Which isomer is more dominantly existing under the standard condition? Explain why.

Let us suppose a reaction: $\text{B} \rightarrow \text{I}$. $\Delta G^\circ = -18.0 \text{ kJ/mol} + 15.9 \text{ kJ/mol} = -2.1 \text{ kJ/mol}$.

Thus, I is more preferred.

(2 pts for correct answer and correct reasoning. 1pt for giving the answer without mentioning the reason)

(b) The following reaction can occur in the presence of a catalyst:



Calculate the equilibrium constant at 298 K for this conversion.

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{2.1 \times 10^3 \text{ J mol}^{-1}}{(8.31 \text{ J K}^{-1} \text{ mol}^{-1}) 298 \text{ K}} = 0.85 \quad K = 2.3$$

(1 pt)

(c) Calculate the mole fraction of B in the equilibrium mixture.

Let X be the fraction of B. Then $(1 - X)$ is the fraction of I. Then

$$K = \frac{1-X}{X} = 2.3 \quad 2.3X = 1 - X \quad X = \frac{1}{3.3} = 0.30$$

(2 pts)

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ \AA} = 5.2917720859 \times 10^{-11} \text{ m}$
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19} \text{ C}$
Faraday constant	$F = 96485.3399 \text{ C mol}^{-1}$
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	$1 \text{ \AA} = 10^{-10} \text{ m}$
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 form $E = mc^2$)
Calorie	$1 \text{ cal} = 4.184 \text{ J}$ (exactly)
Electron volt	$1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J} = 96.485335 \text{ kJ mol}^{-1}$
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	$1 \text{ Ry} = 2.17987197 \times 10^{-18} \text{ J} = 1312.7136 \text{ kJ mol}^{-1} = 13.60569193 \text{ eV}$
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	$1 \text{ torr} = 133.3224 \text{ Pa}$

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: <input type="checkbox"/>	No: <input type="checkbox"/>
		Pts (+/-)	Reasons