2017 SPRING Semester Midterm Examination
For General Chemistry I

Date: April 19 (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**	/4	
2	/8	**7**	/9	
3	/13	**8**	/12	**/100**
4	/11	**9**	/15	
5	/9	**10**	/11	

** 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: *April 24 (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.
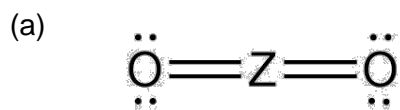
   (The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will

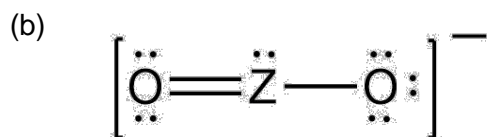   be uploaded on 4/25 on the web.)

 2. Final Confirmation

   1) Period: April 27 (Thu) – April 28 (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*.*
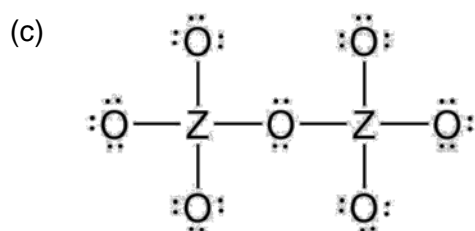
1. (total 8 pts) In each of the following Lewis diagrams, Z represents a main-group element. <u>Name the group</u> to which Z belongs in each case and <u>give an example</u> of such a compound or ion that actually exists.
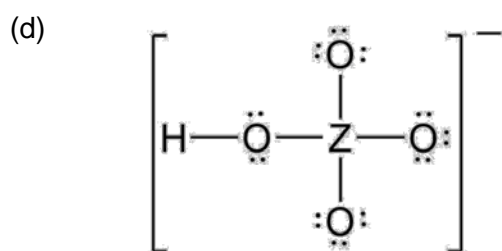
(a)

$$\ddot{O}=Z=\ddot{O}$$

(Answer)

(b)

$$\left[\ddot{O}=\ddot{Z}-\ddot{O}:\right]^{-}$$

(Answer)

(c)

$$:\!\ddot{O}-Z-\ddot{O}-Z-\ddot{O}:$$

(Answer)

(d)

$$\left[H-\ddot{O}-Z-\ddot{O}:\right]^{-}$$

(Answer)

2. (total 8 pts) Predict the geometry of the following molecules and ions precisely.

(a) ClO_3^+

   (Answer)

(b) ClO_2^+

   (Answer)

(c) SiH_4

   (Answer)

(d) IF_5

   (Answer)

3. (total 13 pts) A hydrogen atom that has the Balmer series in the visible region (Figure A; lines at 410.1, 434.1, 486.1, and 656.3 nm) was used for Franck-Hertz experiment (Figure B) and the following data in Figure C (note $V_{thr,1}$ = 10.2 V) were obtained.

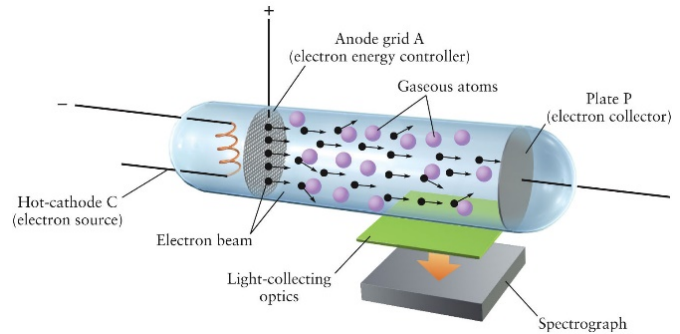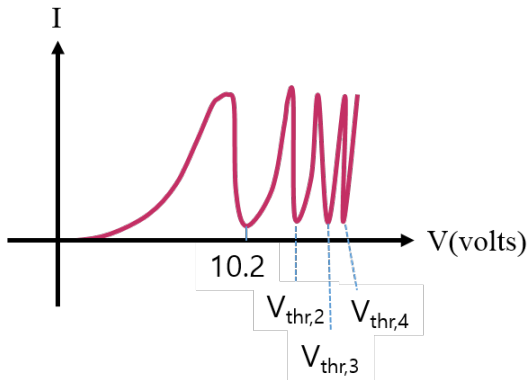Figure A   Figure B


Figure C

(a) Draw the electronic energy-level diagram for this atom and show the energy levels (with values) of excited states relative to the ground state in eV.

(Answer)

(b) Predict the higher voltage thresholds, $V_{thr,2}$, $V_{thr,3}$, and $V_{thr,4}$.

(Answer)

4. (total 11 pts) Cyclobutadiene, C_4H_4, is the hydrocarbon with the following cyclic structure. The electronic structure of π-system can be understood by particle-in-a-box.
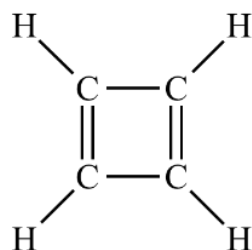
(a) One can assume that all C-C bond lengths are equal to L through resonance structure. Under this assumption, <u>draw the energy diagram</u> of π-system (Note that each state must be labeled by its energy and set of quantum numbers).
   (Answer)

(b) However, cyclobutadiene may not have resonance structure. In this case, one can assume a slight symmetry breaking so that carbon backbone has rectangular structure with bond length L and $L - \delta$ where δ is much smaller than L. Under this assumption, <u>draw the energy diagram</u> of π-system (Note that each state must be labeled by its energy and set of quantum numbers.)
   (Answer)

(c) <u>Calculate the energy differences</u> between <u>ground state</u> and <u>first excitation state</u> for (a) and (b). Which model requires lower energy for excitation? (You may use the approximation $(1 + x)^n \approx$

$1 + nx$ for $|x| \ll 1$ and integer n)

(Answer)

(d) Some experiments showed that cyclobutadiene is diamagnetic. <u>Can this result eliminate one model</u> out of two?

(Answer)

5. (total 9 pts) The first, second, and third ionization energies of phosphorus are 1011 KJ/mol, 1903 KJ/mol, and 2912 KJ/mol respectively.

(a) <u>Calculate the effective nuclear charge</u> (Z_{eff}) experienced by a 3p electron in phosphorus $[Ne]3s^2 3p^3$. Use the energy expression for the hydrogen atom $E_n = -R\frac{Z^2}{n^2}$ where the Rydberg constant R = 2.1799 x 10^{-18}J.

(Answer)

(b) Would it be expected that the minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment be <u>larger, smaller, or the same</u> as the 4th ionization energy (IE_4) of phosphorus? Briefly explain your answer.

(Answer)

(c) <u>Which experience less shielding</u>, 3s-electrons or 3p-electrons in phosphorus? Briefly explain why.

(Answer)

(d) <u>Calculate number of radial and angular nodes</u> for a phosphorus 3p orbital.

(Answer)

6. (total 4 pts) For H atom, the radial node of ψ_{2S} is located at $r = 2a_0$ where a_0 is the Bohr radius of 0.53 Å. <u>Predict the radial position</u> of the ψ_{2S} node for He$^+$ and Li^{2+}. Rationalize your answer (please give the reason or meaning for your answer).

(Answer)

7. (total 9 pts) Here we have one of solved wave functions of an electron in a hydrogen atom.

$$\frac{1}{4\sqrt{2\pi}}a_0^{-3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

(a) <u>What orbital</u> is this? And what are the orbitals that have <u>the same energy value</u>?

  (Answer)

(b) Please roughly draw <u>the radial wave function</u> of the above orbital plotted against distance from the nucleus, r. (don't' worry about scales but indicate radial node)

  (Answer)

(c) Please roughly draw <u>the radial probability density</u> of the above orbital plotted against distance from the nucleus, r. (don't' worry about scales but indicate radial node)

  (Answer)

8. (total 12 pts) Does each of the following set of quantum numbers describe a possible atomic orbital? <u>Answer with 'YES' or 'NO'</u>. If the answer is 'YES', <u>give the label</u> for this orbital. If the answer is 'NO',

<u>explain</u> why an electron with that set of quantum numbers isn't possible.

[Examples of how to answer: (Example_a) $n = 1$, $\ell = 0$, $m = 0$, $m_s = \frac{1}{2}$ (Ans. **YES**, 1s) ; (Example_b) $n = -1$, $\ell = 0$, $m = 0$, $m_s = 3/2$ (Ans. **NO**, n cannot be negative.)]

(a) $n = 4$, $\ell = 3$, $m = -3$, $m_s = +1/2$

   (Answer)

(b) $n = 1$, $\ell = 0$, $m = 0$, $\underline{m}_s = -1$

   (Answer)

(c) $n = 0$, $\ell = 0$, $m = 0$, $m_s = -1/2$

   (Answer)

(d) $n = 2$, $\ell = 3$, $m = 0$, $m_s = +1/2$

   (Answer)

(e) $n = 3$, $\ell = -2$, $m = 3$, $m_s = -1/2$

   (Answer)

(f) $n = 3$, $\ell = 2$, $m = 3$, $m_s = -1/2$

   (Answer)

9. (total 15 pts)

(a) The azide ion (N_3^-) is a weakly bound molecular ion. <u>Formulate its MO structure</u> for localized σ bonds and delocalized π bonds.

(Answer)

(b) Do you expect N_3 and N_3^+ <u>to be bound</u> as well? Which of the three species (N_3^-, N_3 and N_3^+) do you expect to be <u>paramagnetic</u>?

(Answer)

(c) Draw the <u>possible Lewis resonance diagrams</u> for the nitrite ion (NO_2^-). Use the VSEPR theory to determine <u>the steric number</u>, the <u>hybridization of the central nitrogen atom</u>, and the <u>geometry</u> of the ion.
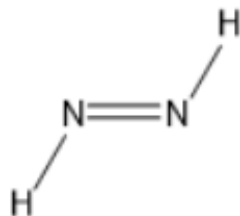
(Answer)

(d) Show how the use of resonance structures of the nitrite ion can be avoided by introducing a

delocalized π MO. What bond order does the MO model predict for the N-O bonds in the nitrite ion?

(Answer)

10. (total 11 pts) This is a molecule called *trans*-diazene (N_2H_2). Answer the following questions.

$$N{=}N$$

with H atoms: H on upper right N, H on lower left N

(a) Write hybridization for each nitrogen atom in *trans*-diazene.

(Answer)

(b) Draw <u>3D structure</u> of *trans*-diazene with <u>hybrid orbitals</u>. <u>Indicate lone pair</u> as well if it exists. <u>Mark for every bond</u> if it is σ or π bond.

(Answer)

(c) <u>Write a wavefunction</u> for the σ bond between nitrogen atoms using VB theory.

(Answer)

(d) Consider N_2 and N_2H_4 (Hydrazine) which are two other molecules containing two nitrogen atoms. <u>Expect the order of binding energy</u> of N-N among *trans*-N_2H_2, N_2, and N_2H_4.

(Answer)

Physical Constants

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

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

Conversion Factors

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

PERIODIC TABLE OF THE ELEMENTS

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

GROUP

PERIOD

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

GROUP NUMBERS
IUPAC RECOMMENDATION (1985)

GROUP NUMBERS
CHEMICAL ABSTRACT SERVICE (1986)

Period 1
- 1 IA — 1 1.0079 **H** HYDROGEN
- 18 VIIIA — 2 4.0026 **He** HELIUM

Period 2
- 3 6.941 **Li** LITHIUM
- 4 9.0122 **Be** BERYLLIUM
- 5 10.811 **B** BORON
- 6 12.011 **C** CARBON
- 7 14.007 **N** NITROGEN
- 8 15.999 **O** OXYGEN
- 9 18.998 **F** FLUORINE
- 10 20.180 **Ne** NEON

Period 3
- 11 22.990 **Na** SODIUM
- 12 24.305 **Mg** MAGNESIUM
- 13 26.982 **Al** ALUMINIUM
- 14 28.086 **Si** SILICON
- 15 30.974 **P** PHOSPHORUS
- 16 32.065 **S** SULPHUR
- 17 35.453 **Cl** CHLORINE
- 18 39.948 **Ar** ARGON

Period 4
- 19 39.098 **K** POTASSIUM
- 20 40.078 **Ca** CALCIUM
- 21 44.956 **Sc** SCANDIUM
- 22 47.867 **Ti** TITANIUM
- 23 50.942 **V** VANADIUM
- 24 51.996 **Cr** CHROMIUM
- 25 54.938 **Mn** MANGANESE
- 26 55.845 **Fe** IRON
- 27 58.933 **Co** COBALT
- 28 58.693 **Ni** NICKEL
- 29 63.546 **Cu** COPPER
- 30 65.39 **Zn** ZINC
- 31 69.723 **Ga** GALLIUM
- 32 72.64 **Ge** GERMANIUM
- 33 74.922 **As** ARSENIC
- 34 78.96 **Se** SELENIUM
- 35 79.904 **Br** BROMINE
- 36 83.80 **Kr** KRYPTON

Period 5
- 37 85.468 **Rb** RUBIDIUM
- 38 87.62 **Sr** STRONTIUM
- 39 88.906 **Y** YTTRIUM
- 40 91.224 **Zr** ZIRCONIUM
- 41 92.906 **Nb** NIOBIUM
- 42 95.94 **Mo** MOLYBDENUM
- 43 (98) **Tc** TECHNETIUM
- 44 101.07 **Ru** RUTHENIUM
- 45 102.91 **Rh** RHODIUM
- 46 106.42 **Pd** PALLADIUM
- 47 107.87 **Ag** SILVER
- 48 112.41 **Cd** CADMIUM
- 49 114.82 **In** INDIUM
- 50 118.71 **Sn** TIN
- 51 121.76 **Sb** ANTIMONY
- 52 127.60 **Te** TELLURIUM
- 53 126.90 **I** IODINE
- 54 131.29 **Xe** XENON

Period 6
- 55 132.91 **Cs** CAESIUM
- 56 137.33 **Ba** BARIUM
- 57-71 **La-Lu** Lanthanide
- 72 178.49 **Hf** HAFNIUM
- 73 180.95 **Ta** TANTALUM
- 74 183.84 **W** TUNGSTEN
- 75 186.21 **Re** RHENIUM
- 76 190.23 **Os** OSMIUM
- 77 192.22 **Ir** IRIDIUM
- 78 195.08 **Pt** PLATINUM
- 79 196.97 **Au** GOLD
- 80 200.59 **Hg** MERCURY
- 81 204.38 **Tl** THALLIUM
- 82 207.2 **Pb** LEAD
- 83 208.98 **Bi** BISMUTH
- 84 (209) **Po** POLONIUM
- 85 (210) **At** ASTATINE
- 86 (222) **Rn** RADON

Period 7
- 87 (223) **Fr** FRANCIUM
- 88 (226) **Ra** RADIUM
- 89-103 **Ac-Lr** Actinide
- 104 (261) **Rf** RUTHERFORDIUM
- 105 (262) **Db** DUBNIUM
- 106 (266) **Sg** SEABORGIUM
- 107 (264) **Bh** BOHRIUM
- 108 (277) **Hs** HASSIUM
- 109 (268) **Mt** METNERIUM
- 110 (281) **Uun** UNUNNILIUM
- 111 (272) **Uuu** UNUNUNIUM
- 112 (285) **Uub** UNUNBIUM
- 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** HOLMIUM
- 68 167.26 **Er** ERBIUM
- 69 168.93 **Tm** THULIUM
- 70 173.04 **Yb** YTTERBIUM
- 71 174.97 **Lu** LUTETIUM

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

(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

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	4x2/8	**6**	2+2/4	
2	4x2/8	**7**	3x3/9	
3	10+3/13	**8**	6x2/12	**/100**
4	3+3+3+2/11	**9**	5+2+4+4/15	
5	3+2+2+2/9	**10**	2+5+2+2/11	

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

1. (total 8 pts) Group # 1 pt, example 1 pt for each set

(a) (2 pts) In this structure of "ZO_2", the oxygen atoms both possess a formal charge of 0. Since there is no net charge on the molecule, Z must also have a f. c. of 0. Therefore, it has 4 valence electrons and belongs to **Group IV**. The compound **CO_2** (carbon dioxide) is an example.

(b) (2 pts) In "ZO_2^-", one of the oxygen atoms has a f. c. of zero but the other has f. c. -1. Since the species has a -1 net charge, Z must have f.c. of 0. Therefore, it comes from **Group V** (5 valence electrons). An example is **NO_2^-** (nitrite ion).

(c) (2 pts) In this Lewis structure of "Z_2O_7", each of the six peripheral O atoms has a formal charge of -1, but the bridging O atom has f.c. zero. Since the molecule has no net charge and is symmetrical, the f. c. on each Z is +3. Therefore, Z has 7 valence electrons and is in **Group VII**. An example is **Cl_2O_7** (dichlorineheptaoxide).

(d) (2 pts) In "$HOZO_3^-$", three of the O atoms have f.c. -1, and the other O atom and the H atom have f.c. zero. Since the ion has a -1 net charge, Z must have f.c. +2. Therefore, Z has 6 valence electrons and comes from **Group VI**. An example is **$HOSO_3^-$** (hydrogen sulfate ion).

2. (total 8 pts) 2 pts for each set, no description of angles -1 pt

(a) (2 pts) The central Cl atom has all of its valence electrons (six, because the ion has a net positive charge) involved in bonds to the surrounding three oxygen atoms and has no lone pairs. Its steric number is 3. In the molecular ion, the central Cl should be surrounded by the three O atoms arranged in a trigonal planar structure.

(b) (2 pts) The central Cl atom in this ion also has a steric number of 3, comprising two bonded atoms and a single lone pair. The predicted molecular geometry is a bent molecule with an angle somewhat less than 120°.

(c) (2 pts) The central Si atom has a steric number of 4 and no lone pairs. The molecular geometry should consist of the Si atom surrounded by a regular tetrahedron of H atoms.

(d) (2 pts) Iodine has seven valence electrons, of which five are shared in bonding pairs with F atoms. This leaves two electrons to form a lone pair, so the steric number is 5 (bonded atoms) 1 1 (lone pair) 5 6. The structure will be based on the octahedron of electron pairs from Figure 3.21, with five F atoms and one lone pair. The lone pair can be placed on any one of the six equivalent sites and will cause the four F atoms to bend away from it toward the fifth F atom, giving the distorted structure shown in Figure 3.24.
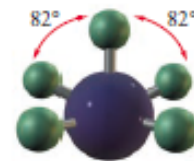
FIGURE 3.24 The structure of IF_5. Note the distortions of F—I—F bond angles from 90° because of the lone pair at the bottom (not shown).

3. (total 13 pts)

(a) (10 pts) Only energy level diagram 3 pts; Balmer series concept 3 pt; exact values 4 pts

The first voltage threshold is at 10.2 V.

$$\frac{hc}{\lambda} = eV_{thr}$$

Thus, the energy difference between the ground state (n = 1) and the first excited state (n = 2) is 10.2 eV. The lowest energy Balmer series 656.3 nm is for a transition of (n = 3 → n = 2). Thus, the 2nd excited state (n = 3) is higher in energy than the ground state by 10.2 eV + $\frac{hc}{(656.3\times10^{-9}\ m)(1.6022\times10^{-19}\ J/eV)}$. Other series lines represent (n = 4 → n = 2), (n = 5 → n = 2), and (n = 6 → n = 2) and thus their energy levels relative to the n = 2 can be obtained similarly.

(b) (3 pts) When the answers were wrong, correct concept (n = 1 to higher), 1 pt

V_{thr}'s appears for transitions from n = 1 to higher-energy excited states. Thus, $V_{thr,2}$ = 12.1 V, $V_{thr,3}$ = 12.8 V, and $V_{thr,4}$ = 13.1 V.

4. (total 11 pts)

(a) (3 pts) (-0.5 pt deduction for each improper labeling & electron assignment)

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

$$\overline{} \quad E_3 = \frac{h^2}{m_eL^2}$$
$$(2,2)$$

$$\underset{(2,1)}{\uparrow} \quad \underset{(1,2)}{\uparrow} \quad E_2 = \frac{5h^2}{8m_eL^2}$$

$$\underset{(1,1)}{\uparrow\downarrow} \quad E_1 = \frac{h^2}{4m_eL^2}$$

(b) (3 pts) (-0.5pt deduction for each improper labeling & electron assignment)

$$E_{n_x,n_y} = \frac{h^2}{8m_e}\left(\frac{n_x{}^2}{L^2} + \frac{n_y{}^2}{(L-\delta)^2}\right)$$

$$\underset{(1,2)}{\overline{}} \quad E_3 = \frac{h^2}{8m_e}\left(\frac{1}{L^2} + \frac{4}{(L-\delta)^2}\right)$$

$$\underset{(2,1)}{\uparrow\downarrow} \quad E_2 = \frac{h^2}{8m_e}\left(\frac{4}{L^2} + \frac{1}{(L-\delta)^2}\right)$$

$$\underset{(1,1)}{\uparrow\downarrow} \quad E_1 = \frac{h^2}{8m_e}\left(\frac{1}{L^2} + \frac{1}{(L-\delta)^2}\right)$$

(c) (3 pts) only for (a), 1 pt

$$\Delta E \ for \ (a) = \frac{3h^2}{8m_eL^2}$$

$$\Delta E \ for \ (b) = \frac{3h^2}{8m_e}\left(\frac{1}{(L-\delta)^2} - \frac{1}{L^2}\right) = \frac{3h^2}{8m_eL^2}\left(\left(1 - \frac{\delta}{L}\right)^{-2} - 1\right) \approx \frac{3h^2}{8m_eL^2} \cdot \frac{2\delta}{L}$$

Model of (b) requires lower energy than model of (a).
(1pt for each energy (approximation is not mandatory) / 1pt for correct comparison)

(d) (2 pts)
Yes. Model of (a) indicates cyclobutadiene is paramagnetic, whereas model of (b) indicates it is diamagnetic.
(No partial points)

5. (total 9 pts)

(a) (3 pts) IE= $-E_n = \frac{Z_{eff}{}^2 R}{n^2}$

$$Z_{eff} = \left[\frac{n^2 \ IE}{R}\right]^{\frac{1}{2}}$$

IE=$1011 KJ/mol$ x $\frac{1000J}{KJ}$ x $\frac{mol}{6.022\times10^{23}}$ = 1.6788 x 10^{-18}J

$$Z_{eff} = \left[\frac{(3)^2(1.6788\times10^{-18}J)}{2.1799\times10^{-18}J}\right]^{\frac{1}{2}} = (6.9311)^{\frac{1}{2}}$$
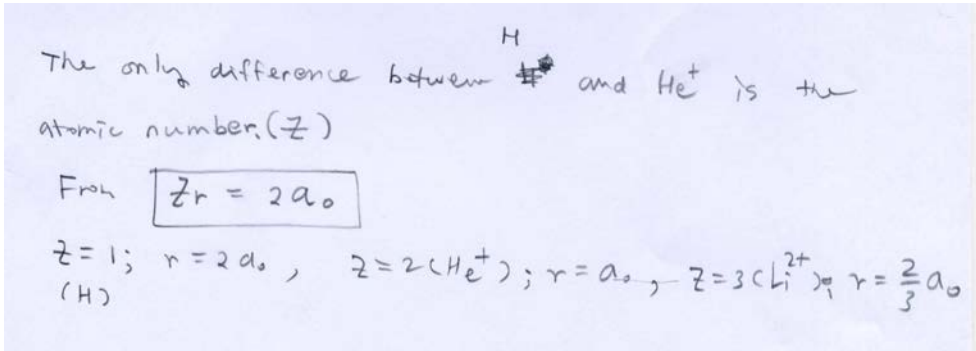
Z_{eff}=2.633

(b) (2 pts) [Ne] $3s^2 3p^3 \rightarrow$ [Ne]$3s^1 3p^3 + e^-$
The E to eject a 3s electron from P would be <u>smaller</u> than the 4th IE because there are more electrons in P, meaning more shielding and lower Z_{eff}.

(c) (2 pts) <u>3s</u>   3s electrons penetrate closer to the nucleus,
so z_{eff} avg. for 3s>Z_{eff} avg. for 3p.

(d) (2 pts) 3p orbital has a total of n-1=3-1=2 nodes. Of these, one is angular (l=1) and one is radial.
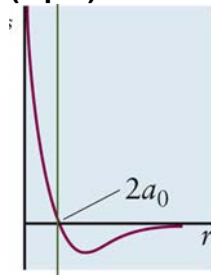
6. (total 4 pts) He⁺ and Li²⁺, 2 pts for each

The only difference between #ᴴ and He⁺ is the atomic number (Z)

From $Zr = 2a_0$

$Z = 1; r = 2a_0$, $Z = 2 (He^+); r = a_0$, $Z = 3 (Li^{2+}); r = \frac{2}{3}a_0$
(H)
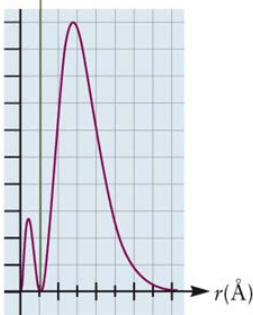
7. (total 9 pts)

(a) (3 pts) A: 2s
A: $2p_x, 2p_y, 2p_z$

(b) (3 pts)

A:

(c) (3 pts)

A:

8. (total 12 pts) 1 pt for YES or NO, 1 pt for labels and explanations, for each set

(a) $n = 4$, $\ell = 3$, $m = -3$, $\underline{m}_s = +1/2$ (YES, 4f)
(b) $n = 1$, $\ell = 0$, $m = 0$, $\underline{m}_s = -1$ (NO, $\underline{m}_s$ must be +1/2 or −1/2)
(c) $n = 0$, $\ell = 0$, $m = 0$, $\underline{m}_s = -1/2$ (NO, 'n cannot be zero.' or '$n = 1, 2, 3, ….$' or 'n must be positive integer.')
(d) $n = 2$, $\ell = 3$, $m = 0$, $\underline{m}_s = +1/2$ (NO, 'ℓ must be less than or equal to n–1.' or '$\ell = 0, 1, …, n$–1.')
(e) $n = 3$, $\ell = -2$, $m = 3$, $\underline{m}_s = -1/2$ (NO, 'ℓ cannot be negative.' or '$\ell = 0, 1, …, n$–1.')
(f) $n = 3$, $\ell = 2$, $m = 3$, $\underline{m}_s = -1/2$ (NO, '$|m|$ must be less than or equal to ℓ.' or '$m = -\ell , -\ell +1, …, \ell-1, \ell$.')

9. (total 15 pts)

(a) (5 pts) sigma bonds 2 pts, pi bonds 3 pts

The azide ion N_3^- is linear and has 16 valence electrons just like the CO_2 molecule, which is discussed in some detail on text page 288. Two N—N σ bonds result from overlap of sp hybrid orbitals on the central N atom with $2p_z$ orbitals on the two outer N atoms. These bonds use 4 electrons. Lone pairs in each of the $2s$ orbitals of the outer N atoms account for another 4 electrons. The remaining six p orbitals (two each on three atoms) overlap to form a π molecular orbital system to accommodate the remaining 8 valence electrons. The correlation diagram for CO_2 (text Figure 6.41) gives the relative energies of the MO's in this system. Four of the eight electrons thus go into the low-lying π_x and π_y orbitals. The remaining four go into the two π^{nb} orbitals. The π configuration is $(\pi)^4(\pi^{nb})^4$. This means a total of two π bonds and an overall bond order for the molecule of 4: (2 σ bonds plus 2 π bonds). The two N-to-N linkages are identical; each has bond order 2. All of the electrons are paired
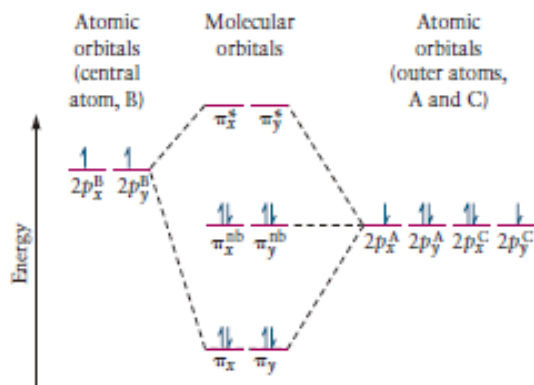

Figure 6.41

(b) (2 pts) N_3^- 1 pt, N_3 and N_3^+ 1 pt

bonds). The two N-to-N linkages are identical; each has bond order 2. All of the electrons are paired so the compound is $\boxed{\text{diamagnetic}}$.

The N_3 molecule has 15 valence electrons. It derives from N_3^- by the loss of an electron. The loss comes from the highest energy molecular orbital which is a nonbonding MO. N_3 is $\boxed{\text{bound}}$ with an overall bond order of 4, just like N_3^-. Unlike N_3^-, N_3 has an unpaired electron and is $\boxed{\text{paramagnetic}}$.

The N_3^+ ion has 14 valence-electrons. It derives from N_3^- by the loss of two nonbonding π electrons. The N_3^+ molecular ion is therefore $\boxed{\text{bound}}$ with bond order 4. There are two unpaired electrons in the set of π^{nb} MO's so N_3^+ is $\boxed{\text{paramagnetic}}$, too.

(c) (4 pts) Lewis diagram 2 pts, VSEPR 2 pts
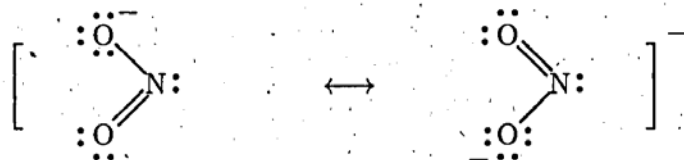
VSEPR theory assigns $\boxed{SN\ 3}$ to the central N. The O atoms occupy two of the three sites, and the lone pair the third. The molecular ion is therefore $\boxed{\text{bent}}$. The hybridization at the nitrogen atom is $\boxed{sp^2}$. Two of the three sp^2 hybrid orbitals form the σ bonds to the oxygen atoms, and the third accommodates the lone pair. The unhybridized $2p_z$ atomic orbital on the N atom is oriented

(d) (4 pts) pi MO 3 pts, bond order 1 pt

third accommodates the lone pair. The unhybridized $2p_z$ atomic orbital on the N atom is oriented perpendicular to the plane of the molecule. It overlaps with the $2p_z$ atomic orbitals of the two oxygen 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. 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. In a localized-orbital scheme, two resonance forms are necessary to represent the bonding in NO_2^-.
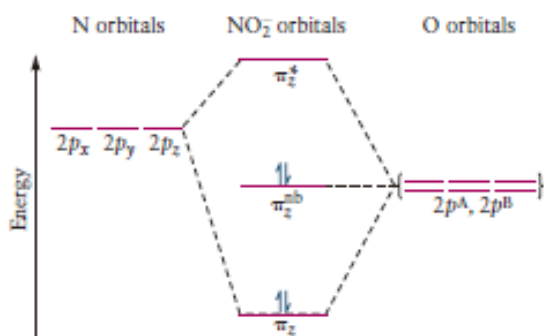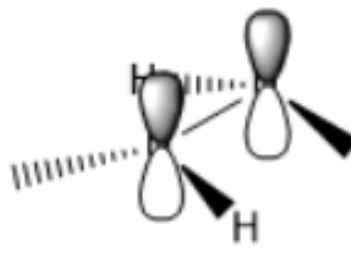

Figure 6.42

---

10. (total 11 pts)

(a) (2 pts) sp2, sp2 (No partial points)

(b) (5 pts)

σ bond framework and lone pairs (3 pts) π bond (2 pts)
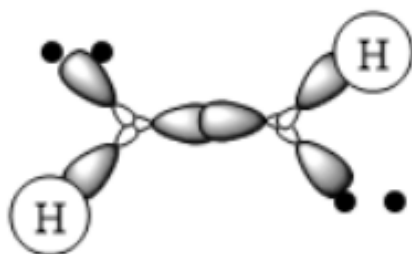
σ bond framework w/ sp2 hybrid orbitals (2 pts) and lone pairs (1 pts)
π bond only – (2 pts)

(c) (2 pts)
When sp² orbital of N^A is $\chi_1^A, \chi_2^A, \chi_3^A$,
$$\psi_\sigma^{Bond}(1,2) = C[\chi_1^A(1)\chi_1^B(2) + \chi_1^A(2)\chi_1^B(1)]$$

(d) (2 pts)
N_2 > *trans*-N_2H_2 > N_2H_4 (No partial points)

2017 SPRING Semester Final Examination
For General Chemistry I

Date: June 14 (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	/4	**7**	/6	
2	/6	**8**	/6	
3	/12	**9**	/9	
4	/9	**10**	/10	**/100**
5	/12	**11**	/8	
6	/10	**12**	/8	

** This paper consists of 14 sheets with 12 problem sets (pages 12 & 13: constants & periodic table, page 14: 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 16 (Friday, 12:00-14:00)*

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

Class	Room	Class	Class	Class	Room
A	**201**	**D**	**206**	**G**	**209**
B	**202**	**E**	**207**		
C	**203**	**F**	**208**		

　　3)　Claim Procedure:

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

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

(During the period, you can check the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it. The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 6/19 on the web.)

2. Final Confirmation

　　1) Period: *June 17(Sat) – 18(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. (4 pts) Assuming no temperature change, <u>determine the final pressure</u> inside the system below after all stopcocks are opened. Ignore the volume of the connecting tube and assume ideal gas behavior.

$N_2(g)$

$Ar(g)$

$O_2(g)$

| P = 2 atm | P = 2 atm | P = 4 atm |
| V = 4 L | V = 1 L | V = 5 L |
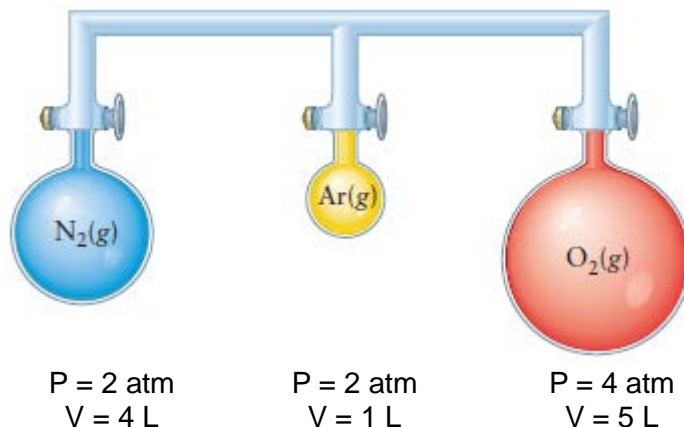
(Answer)

2. (6 pts) State <u>which attractive intermolecular force</u> does play the most dominant role in the following molecular pairs?
(a) Sodium ion - water
(Answer)

(b) Hydroxide ion - water
(Answer)

(c) Carbon dioxide gas - water
(Answer)

(d) Methanol - ethanol
(Answer)

(e) Chloride ion – hexane(C_6H_{14})
(Answer)

(f) Octane(C_8H_{18}) - hexane(C_6H_{14})
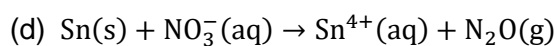**(Answer)**

3. (12 pts) <u>Balance</u> each equation.

(a) $\underline{MnO_4^-(aq)} + H_2S(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$

(Answer)

(b) $\underline{Zn(s)} + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + NH_4^+(aq)$

(Answer)

(c) $H_2O_2(aq) + \underline{MnO_4^-(aq)} \rightarrow O_2(g) + Mn^{2+}(aq)$

(Answer)

(d) $\underline{Sn(s)} + NO_3^-(aq) \rightarrow Sn^{4+}(aq) + N_2O(g)$

(Answer)

(e) $\underline{UO_2^{2+}(aq)} + Te(s) \rightarrow U^{4+}(aq) + TeO_4^{2-}(aq)$
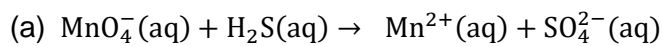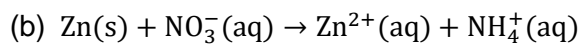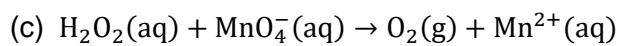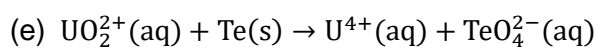
(Answer)

(f) The reactions, (a)-(e), began at the same acidic pH and then 1 mole of the substance underlined reacted completely. <u>Which reaction container</u> will have <u>the highest pH</u>?
(Answer)

4. (9 pts) Below we have graphs of solvent vapor pressure versus mole fraction of solvent in ideal and nonideal solutions with nonvolatile solute.
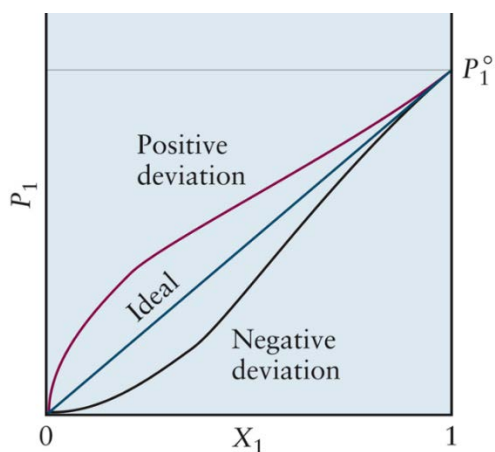
(a) Explain positive deviation and negative deviation with relative attraction forces between solvent and solute.

(Answer)

(b) Explain boiling-point elevation of solution with nonvolatile solute.

(Answer)

(c) Which nonideal solution (positive deviation or negative deviation) will have higher boiling-point elevation effect? Why?

(Answer)

5. (12 pts) Mixing 50.0 g of benzene(C_6H_6, MW = 78.11 g/mol) with 50.0 g of n-hexane(C_6H_{14}, MW = 86.18g/mol) gives a nearly ideal solution. The vapor pressure of pure benzene is 0.1355 atm and the vapor pressure of pure n-hexane is 0.2128 atm.

(a) Calculate the mole fraction of n-hexane in this solution.

(Answer)

(b) Calculate the mole fraction of n-hexane in the vapor in equilibrium with the solution.

(Answer)

(c) The vapor is removed and condensed to become liquid. Calculate the mole fraction of n-hexane in the vapor in equilibrium with this new solution.
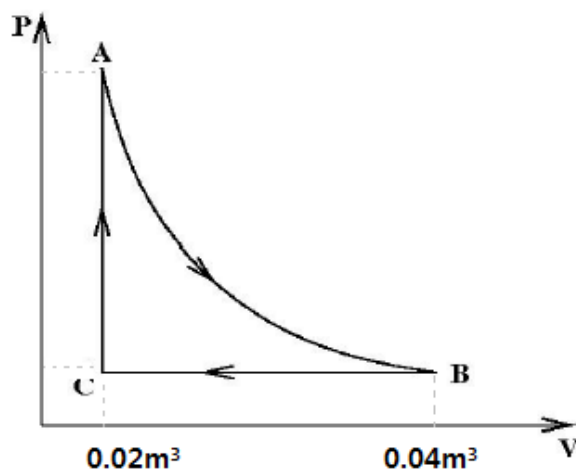
(Answer)

(d) In order for mole fraction of n-hexane in the solution to be more than 0.850, at least how many times of fractional distillation are needed from the starting solution?

(starting solution = 50.0 g benzene + 50.0 g n-hexane)

(Answer)

6. (10 pts) Four moles of monatomic ideal gas goes through the cycle represented in following figure. Process A → B is an isothermal expansion with temperature $T_A = 300K$.

0.02m³   0.04m³

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

(b) Fill the following table with <u>numerical values</u> <u>in Joules</u>.
(Answer)

Process	ΔU	q	w
A →B		6915 J	
B → C			
C → A			

7. (6 pts) Consider a system composed of one mole of liquid water at 25 ˚C placed in a cylinder with movable piston. In order words, the system includes liquid water plus the cylinder. This system is then heated under a constant external pressure of 1 atm until all the water evaporates and the final volume of the gas is 33.0 liter.

The change in state is

H_2O(liquid, 25 ˚C,1 atm) + Cylinder(25 ˚C) → H_2O(gas, T, 1 atm, 33 L) + Cylinder(T)
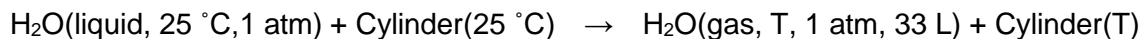
Calculate <u>the enthalpy of this change in state</u>. Assume that gaseous water is an ideal gas. C_p of liquid water and gaseous water is 75.3 $JK^{-1}mol^{-1}$ and 40.2 $JK^{-1}mol^{-1}$, respectively. C_p of cylinder is 1000 JK^{-1}. The heat of vaporization of water at 1 atm and 373 K is 40.6 $kJmol^{-1}$.

(Answer)

8. (6 pts) The equilibrium constant for the following reaction is 50.5 at 448 ℃.

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$
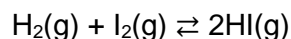
Suppose that a vessel at this temperature contains 5.0 M H_2, 3.0 M I_2, and 1.0 M HI.

(a) Determine <u>the concentrations of H_2, I_2 and HI</u> when the mixture comes to equilibrium.

(Answer)

(b) What would happen if the concentration of HI at equilibrium were suddenly increased to 10.0 M? Determine <u>the equilibrium concentrations of H_2, I_2 and HI</u>.

(Answer)

9. (9 pts) A young chemist buys an "one-lung" motorcycle but, before learning how to drive it, wants to understand the processes that occur in its engine. The manual says the cylinder has a radius of 5.00 cm, a piston stroke of 12.00 cm, and a (volume) compression ratio of 8:1. If a mixture of gasoline vapor (taken to be C_8H_{18}) and air in mole ratio 1 : 62.5 is drawn into the cylinder at 80 °C and 1.00 atm, calculate:

(a) Calculate <u>the volumes</u> inside the cylinder of the engine <u>before and after compression</u>.

(Answer)

(b) Calculate <u>the temperature of the compressed gases</u> just before the spark plug ignites them. (Assume the gases are ideal, the compression is adiabatic, and the average heat capacity of the mixture of gasoline vapor and air is $c_P = 35$ $JK^{-1}mol^{-1}$).

(Answer)

(c) Calculate <u>the volume of the compressed gases</u> just before ignition.

(Answer)

(d) Calculate <u>the pressure of the compressed gases</u> just before ignition.

(Answer)

10. (10 pts) Select <u>the alphabet</u> of the correct answer.

(a) In a spontaneous process, which of the following always increases?

A) the entropy of the system

B) the entropy of the surroundings

C) the entropy of the universe

D) the entropy of the system and the universe

E) the entropy of the system, surroundings and the universe

(b) Processes are always spontaneous, regardless of temperature, when _____ (H and S refer to the system).

A) $\Delta H > 0$ and $\Delta S < 0$ B) $\Delta H < 0$ and $\Delta S < 0$

C) $\Delta H > 0$ and $\Delta S > 0$ D) $\Delta H < 0$ and $\Delta S > 0$

E) None of these is true, as temperature must always be taken into account.

(c) The dissolution of ammonium nitrate in water is a spontaneous endothermic process. It is spontaneous because the system undergoes _____

A) a decrease in enthalpy.   B) an increase in entropy.

C) an increase in enthalpy   D) a decrease in entropy.
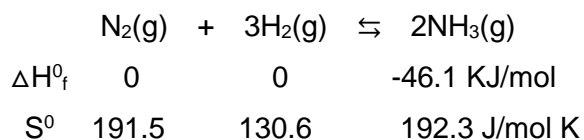
E) an increase in free energy.

(d) Any reaction will be spontaneous if _____

A) $\Delta G_{sys} > 0$ B) $\Delta G_{sys} < 0$

C) $\Delta S_{sys} > 0$ D) $\Delta S_{sys} < 0$

E) $\Delta H_{sys} < 0$

(e) The entropy of vaporization of water is 109.0 J/mol ·K. What is the enthalpy of vaporization of water at its normal boiling point of 100°C?

A) +10.90 kJ/mol

B) –40.66 kJ/mol

C) +3.42 kJ/mol

D) +40.66 kJ/mol

E) –10.90 kJ/mol

11. (8 pts) In the ammonia synthesis,

$$N_2(g) \ + \ 3H_2(g) \ \leftrightarrows \ 2NH_3(g)$$

	N_2	H_2	NH_3
ΔH^0_f	0	0	-46.1 KJ/mol
S^0	191.5	130.6	192.3 J/mol K

(a) Calculate <u>the change of the Gibbs free energy</u> of the reaction. Is the reaction <u>spontaneous in the forward direction</u> at 25℃?

(Answer)

(b) Estimate <u>the highest temperature</u> at which spontaneity is preserves, assuming that ΔH^0 and ΔS^0 remain constant throughout.
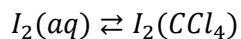
(Answer)

(c) Compute <u>the equilibrium constant</u> at 298 K.

(Answer)

(d) Suppose that hydrogen, nitrogen, and ammonia gas mixed together in a closed vessel, each component having a partial pressure of 4 atm. Is the mixture <u>in equilibrium</u> at 25 ℃?

(Answer)

12. (8 pts) At 25 °C the partition coefficient for the equilibrium

$$I_2(aq) \rightleftarrows I_2(CCl_4)$$

has the value K = 85. To 0.100 L of an aqueous solution, which is initially 2×10^{-3} M in I_2, we add 0.025 L of CCl_4. The mixture is shaken in a separatory funnel and allowed to separate into two phases, and the CCl_4 phase is withdrawn.

(a) Calculate the fraction of the I_2 remaining in the aqueous phase.

(Answer)

(b) Suppose the remaining aqueous phase is shaken with another 0.025 L of CCl_4 and again separated. What fraction of the I_2 from the original aqueous solution is *now in the aqueous phase*?

(Answer)

(c) Compare the above to the case where the same total amount of CCl_4 (0.050 L) was used in a *single* extraction. Which is the more efficient way to remove iodine from water?
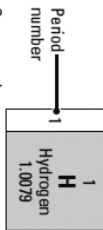
(Answer)

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^{-1}
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

KEY

79	
Au	Atomic number
Gold	Symbol
196.9665	Name
	Atomic weight

An element

- Main group metals
- Transition metals
- Metalloids
- Nonmetals, noble gases

Period number — 1
Group number, U.S. system — 1A (1)
Group number, IUPAC system — (1)

Numbers in parentheses are mass numbers of radioactive isotopes.

Main table

Period	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	8B (9)	8B (10)	1B (11)	2B (12)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 **H** Hydrogen 1.0079																	2 **He** Helium 4.0026
2	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.0122											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.0067	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984	10 **Ne** Neon 20.1797
3	11 **Na** Sodium 22.9898	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.9815	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.9738	16 **S** Sulfur 32.065	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
4	19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.9559	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.9380	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.9332	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.38	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.64	33 **As** Arsenic 74.9216	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.798
5	37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.9058	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.9064	42 **Mo** Molybdenum 95.96	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.9055	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.9045	54 **Xe** Xenon 131.293
6	55 **Cs** Cesium 132.9055	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.084	79 **Au** Gold 196.9666	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.9804	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (267)	105 **Db** Dubnium (268)	106 **Sg** Seaborgium (271)	107 **Bh** Bohrium (272)	108 **Hs** Hassium (277)	109 **Mt** Meitnerium (276)	110 **Ds** Darmstadtium (281)	111 **Rg** Roentgenium (280)	112 — (285)	113 — (284)	114 — (287)	115 — (288)	116 — (293)	— (—)	118 — (294)

Lanthanides (Period 6)

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.9076	60 **Nd** Neodymium 144.242	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.9254	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.9303	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.9342	70 **Yb** Ytterbium 173.054	71 **Lu** Lutetium 174.9668

Actinides (Period 7)

90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.0359	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

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*

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

sheet if you need more before use.

14

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	/4	**7**	1x4+2/6	
2	1x6/6	**8**	3+3/6	
3	2x6/12	**9**	2+3+2+2/9	
4	4+2+3/9	**10**	2x5/10	**/100**
5	2+3+3+4/12	**11**	2x4/8	
6	2+1x8/10	**12**	3+2+3/8	

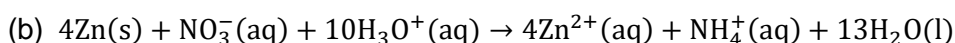**Missing units in the answer: -1 pt, "-1 pt" means "minus 1 point"**

1. (total 4 pts)

$n_{total}RT = 2 \times 4 + 2 \times 1 + 4 \times 5$; $P = n_{total}RT/V_{total} = 30/10 = $ **3 atm**

2. (total 6 pts) 1 pt for each

(a) **Ion – dipole force**

(b) **Ion – dipole force**

(c) **Induced dipole force (Dipole – induced dipole force)**

(d) **Hydrogen bonding**

(e) **Induced dipole force (Ion – induced dipole force)**

(f) **Induced dipole – Induced dipole force (London dispersion force or Van der waals force)**

3. (total 12 pts) 2 pts for each

(a) $\underline{8MnO_4^-(aq)} + 5H_2S(aq) + 14H_3O^+(aq) \rightarrow 8Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 26H_2O(l)$

(b) $4\underline{Zn(s)} + NO_3^-(aq) + 10H_3O^+(aq) \rightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 13H_2O(l)$

(c) $5H_2O_2(aq) + \underline{2MnO_4^-(aq)} + 6H_3O^+(aq) \rightarrow 5O_2(g) + 2Mn^{2+}(aq) + 14H_2O(l)$

(d) $2\underline{Sn(s)} + 2NO_3^-(aq) + 10H_3O^+(aq) \rightarrow 2Sn^{4+}(aq) + N_2O(g) + 15H_2O(l)$

(e) $3\underline{UO_2^{2+}(aq)} + Te(s) + 4H_3O^+(aq) \rightarrow U^{4+}(aq) + TeO_4^{2-}(aq) + 6H_2O(l)$
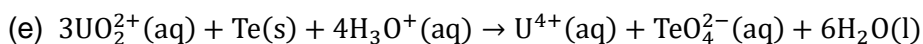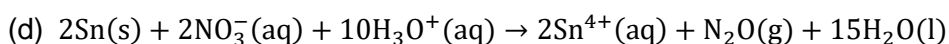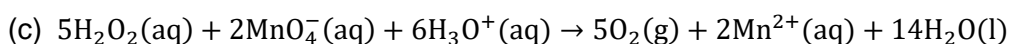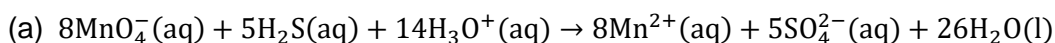
(f) **The reaction (d)** consumes the most proton (5 moles of protons/1 mole of the underlined substance) and thus results in the highest pH according to the balanced equations below.

4. (total 9 pts)

(a) (4 pts) Negative deviations
solute-solvent attractions > solvent-solvent attractions
Positive deviations
solute-solvent attractions < solvent-solvent attractions

(b) (2 pts) Because a dissolved solute reduces the vapor pressure, the temperature of the solution must be increased to make it boil.

(c) (3 pts) **Negative**: more vapor-pressure lowering → therefore more boiling point elevation

5. (total 12 pts)

(a) (2 pts)
$$\chi_{hexane} = \frac{50.0g/86.18g\cdot mol^{-1}}{50.0g/86.18g\cdot mol^{-1} + 50.0g/78.11g\cdot mol^{-1}} = \mathbf{0.475}$$

(b) (3 pts) calculation of each P, 1 pt
By Raoult's law, $P_{benzene} = \chi_{benzene} \cdot P^o_{benzene} = 0.525 \cdot 0.1355\ atm = 0.0711\ atm$
$P_{hexane} = \chi_{hexane} \cdot P^o_{hexane} = 0.475 \cdot 0.2128\ atm = 0.101\ atm$

Therefore, $\chi_{hexane,vapor} = \frac{0.101}{0.101 + 0.0711} = \mathbf{0.587}$

(c) (3 pts) calculation of each P, 1 pt
By Raoult's law, $P_{benzene} = \chi_{benzene} \cdot P^o_{benzene} = 0.413 \cdot 0.1355\ atm = 0.0560\ atm$
$P_{hexane} = \chi_{hexane} \cdot P^o_{hexane} = 0.587 \cdot 0.2128\ atm = 0.125\ atm$

Therefore, $\chi_{hexane,vapor} = \frac{0.125}{0.0560 + 0.125} = \mathbf{0.691}$

(d) (4 pts) without explanation, 1 pt

Let's say the mole fraction of n-hexane in the solution after n distillation, χ_n. Then,
$$\chi_n = \frac{0.2128 \cdot \chi_{n-1}}{0.2128 \cdot \chi_{n-1} + (1 - \chi_{n-1}) \cdot 0.1355} = \frac{0.2128 \cdot \chi_{n-1}}{0.1355 + 0.0773\chi_{n-1}}$$
If we start with $\chi_0 = 0.476$, then $\chi_1 = 0.587, \chi_2 = 0.691, \chi_3 = 0.773, \chi_4 = 0.842,\ \chi_5 = 0.893$

5 times need at least.

6. (total 10 pts)

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

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

$$P_A = \frac{nRT_A}{V_A} = \frac{4 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{ mol}^{-1} \times 300 \text{ K}}{0.04 \text{ m}^3} = 2.494 \times 10^5 \text{ J m}^{-3} = 2.494 \times 10^5 \text{ Pa (2.46 atm)}$$

And $P_B = P_C$ and $V_C = V_A$,

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

(b) (8 pts) for each value, 1 pt

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

1) A → B
Because of A → B Process is isothermal, $\Delta U_{AB} = 0$
So , $\Delta U_{AB} = q + w = 0$.

$$dq = -dw = PdV = \left(\frac{nRT}{V}\right)dV$$

$$q = \int_A^B dq = -\int_A^B dw = \int_A^B PdV = \int_A^B \left(\frac{nRT}{V}\right)dV$$

$$= 4 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{ mol}^{-1} \times 300 \text{ K} \times \ln\frac{0.04}{0.02} \text{ J}$$

$$= 6915 \text{ J}$$

and work is equal to $-q$, so **w = −6915 J**

2) B → C

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

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

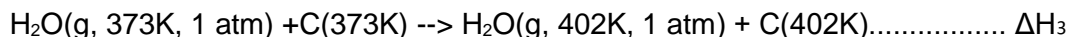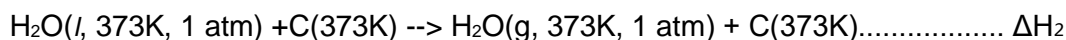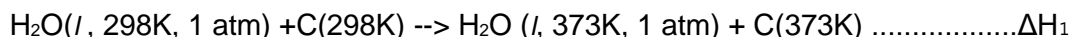Since $\Delta U_{AB} = q + w$, $\Delta U_{AB} = -12471 \text{ J} + 4988 \text{ J} = -7483 \text{ J}$

3) C → A

$$w_{BC} = -P\Delta V = 0 \text{ J}$$

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

7. (6 pts)

Calculating T = 402 K

$H_2O(l, 298K, 1\ atm) + C(298K) \rightarrow H_2O\ (l, 373K, 1\ atm) + C(373K)$ ....ΔH_1

$H_2O(l, 373K, 1\ atm) + C(373K) \rightarrow H_2O(g, 373K, 1\ atm) + C(373K)$................. ΔH_2

$H_2O(g, 373K, 1\ atm) + C(373K) \rightarrow H_2O(g, 402K, 1\ atm) + C(402K)$................ ΔH_3

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$
= 75.3 (373-298) + 1000 (373-298) + 40600
+40.2 (402-373) + 1000 (402-373)
= 5647.5 + 75000+ 40600+ 1165.8 +29000
= 151413.3J = **151.4 kJ**

8. (6 pts)
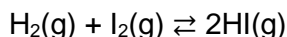
(a) (3 pts)
$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$
5.0M   3.0M   1.0M
    -x   -x   +2x
Equilibrium 5.0-x   3.0-x   1.0+2x

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0+2x)^5}{(5.0-x)(3.0-x)} = 50.5$$
$$46.5x^2 - 408x + 756.5 = 0$$
$$x = \frac{408 \pm 160.48}{93.0} = 2.66M$$
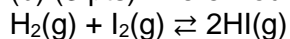$$[H_2] = 5.0 - 2.66 = 2.34M$$
$$[I_2] = 3.0 - 2.66 = 0.34M$$
$$[H\dot{I}] = 1.0 + 2 \times 2.66 = 6.32M$$

(b) (3 pts) There would be a move toward a new equilibrium
$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$
2.34M 0.34M 10.0M
at equilibrium 2.34+x 0.34+x 10.0-2x

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(10.0-2x)^2}{(2.34+x)(0.34+x)} = 50.5$$
$$x = 0.315$$
$$[H_2] = 2.34 + x = 2.66M$$
$$[I_2] = 0.34 + x = 0.66M$$
$$[H\dot{I}] = 10 - 2x = 9.37M$$

The stress of having too much HI is relieved.

9. (9 pts)

(a) (2 pts)

a) The gases trapped inside the cylinder of the "one-lung" engine have volume V_1 when the piston is fully withdrawn but a smaller volume V_2 when the piston is thrust home. The compression ratio is 8 : 1 so $V_1 = 8V_2$. The area of the base of the engine's cylinder is πr^2, where r is the radius of the base. The volume of a cylinder is the area of its base times its height h.

$$V_1 = Ah \quad \text{and} \quad V_2 = A(h - 12.00 \text{ cm})$$

which employs the (given) fact that full compression shortens h by 12.00 cm. Because r is 5.00 cm, the area A is 78.54 cm^2. Substituting for V_1 and V_2 in terms of A and h gives

$$Ah = 8A(h - 12.00 \text{ cm})$$

The A's cancel, allowing solution for h. The result is 13.714 cm. Once h is known, it is easy to compute V_1 and V_2, which equal 1.077 L and 0.1347 L respectively.

(b) (3 pts)

The temperature and pressure of the air-fuel mixture are 353 K (80°C) and 1.00 atm when the mixture enters the cylinder with fully withdrawn piston (V_1). Assuming the air-fuel mixture is an ideal gas

$$n_{\text{mixture}} = \frac{(1.00 \text{ atm})(1.077 \text{ L})}{(0.08206 \text{ L atm mol}^{-1}\text{K}^{-1})(353 \text{ K})} = 0.0372 \text{ mol}$$

The molar ratio of air to fuel (C_8H_{18}) is 62.5 to 1, so $n_{\text{air}} = 62.5\, n_{\text{fuel}}$. and it follows that at the start the cylinder contains 0.0366 mol of air and 5.86×10^{-4} mol of octane fuel.

During the compression stroke, the system undergoes an irreversible adiabatic compression to one-eighth of its initial volume. None of the relationships that govern *reversible* adiabatic processes applies. Assume however, as advised in the problem, that the compression is near to reversible. If it is, and if the mixture of gases in the cylinder is approximately ideal, then

$$T_1 V_1^{\gamma-1} \approx T_2 V_2^{\gamma-1} \quad \text{where } \gamma = \frac{c_P}{c_V} = \frac{c_P}{c_P - R} = \frac{35 \text{ J K}^{-1}\text{mol}^{-1}}{(35 - 8.315) \text{ J K}^{-1}\text{mol}^{-1}} = 1.31$$

The temperature after the compression stroke is

$$T_2 \approx T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} = (353 \text{ K}) \left(\frac{1.077 \text{ L}}{0.1347 \text{ L}}\right)^{0.31} = (353 \text{ K})(8)^{0.31} = \boxed{673 \text{ K}}$$

(c) (2 pts)

The compressed gases occupy a volume of **0.135 L** just before they are ignited, as calculated in (a).

(d) (2 pts)

c) The pressure of the compressed air-fuel mixture just before ignition is P_2. Compute it by applying the ideal-gas equation to the system with $T_2 = 673$ K, $V_2 = 0.1347$ L, and $n = 0.0372$ mol.

$$P_2 \approx \frac{nRT_2}{V_2} = \frac{0.0372 \text{ mol}(0.082057 \text{ L atm mol}^{-1}\text{K}^{-1})(673 \text{ K})}{0.1347 \text{ L}} = \boxed{15.3 \text{ atm}}$$

Alternatively, estimate P_2 using the formula for a reversible adiabatic change

$$P_2 \approx P_1 \left(\frac{V_1}{V_2}\right)^{\gamma} = 1.00 \text{ atm} \left(\frac{1.077}{0.1347}\right)^{1.31} = \boxed{15.3 \text{ atm}}$$

10. (10 pts) 2 pts for each set

(a) C (page 592)
(b) D (page 597)
(c) B (page 597)
(d) B (page 594)
(e) D (page 582)

11. (8 pts) 2 pts for each set

(a) $\triangle H^0$ = (2mol) (46.kJ mol^{-1})-0-3(0)= -92.2kJ

$\triangle S^0$ = 2mol × $\dfrac{192.3J}{molk}$ -1mol x $\dfrac{191 \cdot SJ}{molk}$ - 3mol × $\dfrac{130 \cdot 6J}{molk}$
= -198.7 J·K-1 = -0.1987 kJ·K-1

$\triangle G^0$ = $\triangle H^0$-T$\triangle S^0$ =-92.2kJ - (298K) (-0.1987 kJ/K)
= -92.2kJ + 59.24kJ = **-33.0 kJ**

The reaction is spontaneous.

(b) The crossover ($\triangle G^0$=0)is reached when $\triangle H^0$ = T$\triangle S^0$

T= $\dfrac{\triangle H^0}{\triangle S^0}$ = $\dfrac{-92 \cdot 2kJ}{0 \cdot 1987 \, kJK^{-1}}$ = **464K**

(c) K= exp(- $\dfrac{\triangle G^0}{RT}$)
= exp(- $\dfrac{-33 \cdot 0kJ}{(8 \cdot 3145 J/K)(298K)}$ x $\dfrac{1000J}{kJ}$)
= exp(13.32)
= 6.1 x 10^5

(d) Q = $\dfrac{p_{NH_3}^2}{p_{N_2}p_{H_2}^3}$ = $\dfrac{(4 \cdot 0)^2}{(4 \cdot 0)(4 \cdot 0)^3}$ = 0.0625

Q differs substantially from K (=6.1 x 10^5)
The mixture is not yet at equilibrium.

12. (8 pts)
(a) (3 pts)

a) The chemical amount of I_2 initially in the 0.100 L of aqueous solution is

$$n_{I_2} = 0.100 \text{ L} \times \left(\frac{2 \times 10^{-3} \text{ mol } I_2}{1.00 \text{ L}} \right) = 2 \times 10^{-4} \text{ mol } I_2$$

Shaking this solution with 0.025 L of CCl_4 in a separatory funnel allows the I_2 to distribute itself between the two phases. When the partition of the I_2 between the phases comes to equilibrium at 25°C, y mol of I_2 has moved into the CCl_4 phase, and $(2 \times 10^{-4} - y)$ mol remains in the aqueous phase. Assume that the two solvents are perfectly immiscible—that no water dissolves in the CCl_4 and that no CCl_4 dissolves in the water. Then the volumes of the two solvents remain unchanged and the concentrations of the solute in the two phases are

$$[I_2]_{(aq)} = \left(\frac{2 \times 10^{-4} - y}{0.100} \right) \text{ mol L}^{-1} \quad \text{and} \quad [I_2]_{(CCl_4)} = \left(\frac{y}{0.025} \right) \text{ mol L}^{-1}$$

The mass-action expression for this system is

$$\frac{[I_2]_{(CCl_4)}}{[I_2]_{(aq)}} = K = 85 \quad \text{from which} \quad \frac{y/0.025}{(2 \times 10^{-4} - y)/0.100} = 85$$

The last equation is easily solved for y, which equals 1.91×10^{-4} mol. Remember that y is the amount of I_2 that transfers to the CCl_4, and not a concentration. By subtraction, the amount remaining in the water is 0.09×10^{-4} mol. The fraction remaining equals the amount remaining divided by the original amount

$$f = \frac{0.09 \times 10^{-4}}{2 \times 10^{-4}} = 0.045 = \boxed{0.04}$$

(b) (2 pts)

b) The first extraction with 0.025 L of CCl_4 leaves only 0.045 (4.5%) of the I_2 in the water. Another extraction with a fresh 0.025 L of CCl_4 will leave only 0.045 of that 0.045. The fraction remaining after these successive treatments is

$$f = 0.045 \times 0.045 = \boxed{0.0020}$$

(c) (3 pts) no reason: 1 pts, calculation for 0.023: all 3 pts

c) From text Example 14.18, the fraction of I_2 remaining in the water after a single 0.050 L extraction is 0.023, which is substantially larger than 0.0020.

Tip. It is about 11 times more efficient to extract the iodine with two half-sized portions of CCl_4 rather than one large portion. In general, it is more efficient to use several smaller portions of solvent, rather than one or two portions in performing separations by extraction.