2015 SPRING Semester Midterm Examination
For General Chemistry I

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

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

Professor Name	Class	Student I.D. Number	Name

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

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

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

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

 1. Period, Location, and Procedure

   1)   Return and Claim Period: *April 27 (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 4/27 on the web.)

 2. Final Confirmation

   1) Period: April 30 (Thu) – May 1 (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 9 pts)

(a) Draw the <u>Lewis diagram</u> and predict <u>the structure</u> of the N_2O molecule by the VSEPR theory.

   (Answer)

(b) The N_2O molecule has a small dipole moment. <u>Which end of the molecule</u> is more likely to be the positive end, based only on electronegativity?

   (Answer)

(c) The molecules of a certain compound contain one atom each of nitrogen, fluorine and oxygen. Two possible structures are NOF (O as central atom) and ONF (N as central atom). Does the information that the molecule is bent <u>limit the choice</u> to one of these two possibilities? <u>Explain</u>.

   (Answer)

2. (total 10 pts; 1 pt deduction for each incorrect answer) Answer only in T (true) or F (false) for the following questions.

(a) The energy of a free electron is quantized.

(Answer)

(b) de Broglie matter wave of a particle means the probability density distribution of finding the particle.

(Answer)

(c) The energy of a photon is proportional to both its wavelength and intensity.

(Answer)

(d) The energy of an electron in a box with size L is quantized, while that of a proton is continuous, because the proton is much heavier than the electron.

(Answer)

(e) For a hydrogen atom, the 3d orbital has more nodes than the 3s.

(Answer)

(f) The relative energy order of atomic orbitals follows … <3s < 3p < 3d < 4s < 4p < 4d ….

(Answer)

(g) Only one-electron wave functions are called molecular orbitals.

(Answer)

(h) Hartree orbitals are not the solutions of Schrödinger equation.

(Answer)

(i) Molecular orbital theory provides the exact solutions of Schrödinger equation.

(Answer)

(j) Valence orbital theory obeys both Pauli exclusion and aufbau principles.

(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.
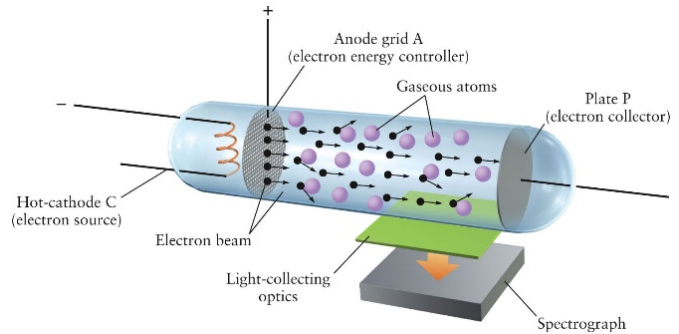
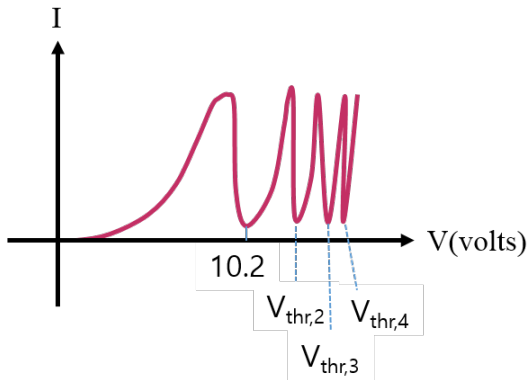Figure A   Figure B

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 8 pts) A particle of mass m is placed in a 3D rectangular box with edge lengths $2L$, L, and L. Inside the box the potential energy is zero, and outside it is infinite; therefore, the wave function goes smoothly to zero at the sides of the box. Calculate <u>the energies</u> and give <u>the quantum numbers of the ground state and the first five excited states</u> (or sets of states of equal energy) for the particle in the box.

(*Hint:* The energy of the 1D particle in a box is given as $E_n = n^2h^2/8mL^2$)

(Answer)

5. (total 12 pts) Below the X-ray photoelectron spectra of CuO (top) and Cu_2O (bottom) in two different energy ranges are given. The spectra were obtained using a 0.834 nm X-ray beam. The peaks on the left are from the 3d orbital, while those on the right are from the 3s orbital.
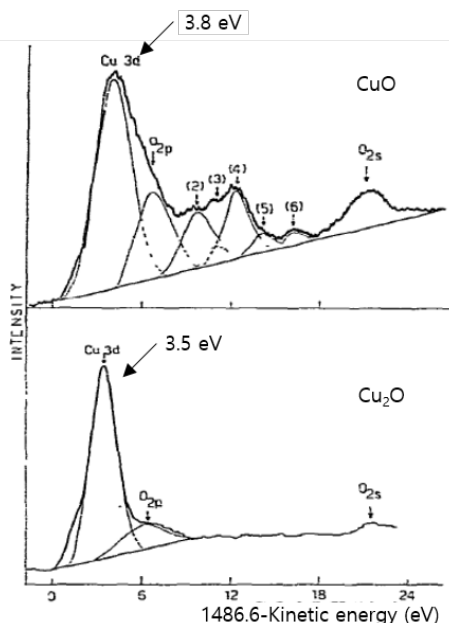

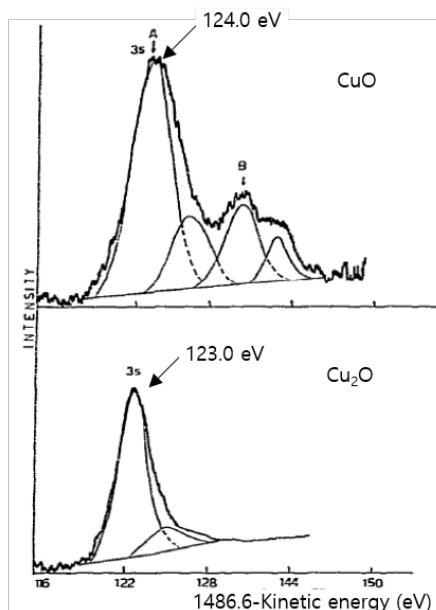Fig. 2. X-ray photoelectron spectra for the valence band in CuO and Cu_2O.

Fig. 4. X-ray photoelectron spectra of Cu_{3s} level in CuO and Cu_2O.

(a) Obtain the effective nuclear charges (Z_{eff}'s) for Cu 3d and 3s orbitals in CuO and Cu_2O, respectively. Use 1 Ry = 13.606 eV.

(Answer)

species	orbital	Binding Energy	Z_{eff}
CuO	3d		
	3s		
Cu_2O	3d		
	3s		

(b) Compare Z_{eff} of Cu 3d vs. Z_{eff} of Cu 3s (in the same compound) and explain why the difference exists.

(Answer)

(c) Compare Z_{eff} of Cu 3d in CuO vs. Z_{eff} of Cu 3d in Cu_2O and explain why the difference exists.

(Answer)

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

$$\psi_{210}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\ a_0^{-3/2}\ \frac{r}{a_0}\ e^{-r/2a_0}\ \cos\theta$$

(a) <u>What orbital</u> is this?

(Answer)

(b) <u>What are the orbitals</u> that have the energy values identical to the energy of this orbital?

(Answer)

(c) <u>How many</u> and <u>what kind of nodes</u> in this wave function?

(Answer)

(d) Say that the energy value of this electron is -1/4 (Rydberg) in a hydrogen atom. If we put this electron with above wave function to a <u>He atom</u> (with effective nuclear charge 1.69), <u>what is the energy value of the electron</u> (<u>higher or lower</u> than that in hydrogen atom)?

(Answer)

7. (total 6 pts)

(a) Suppose that the spin quantum number did not exist, and therefore only one electron could occupy each orbital of a many-electron atom. Give <u>the atomic numbers of the first three noble-gas atoms</u> in this case.

(Answer)

(b) Suppose that the spin quantum number had three allowed values (m_s = 0, +1/2, -1/2). Give <u>the atomic numbers of the first three noble-gas atoms</u> in this case.

(Answer)

8. (total 13 pts) Consider the allyl cation, $CH_2CHCH_2^+$.

Assumptions:

1) The eight atoms lie in a single plane.

2) The H-C-H and central C-C-C bond angles are all nearly 120°.

3) Both C-C bond lengths are the same, falling between the usual values for C-C single and C=C double bonds.

(a) Construct <u>the molecular orbital form</u> (<u>correlation diagram and molecular orbital shapes</u>) of the 2p atomic orbitals <u>perpendicular to</u> the plane of the carbon atoms.

(Answer)

(b) Indicate whether the ion is <u>paramagnetic or diamagnetic</u>.

(Answer)

9. (total 12 pts) Suppose an unknown substance A. Elemental analysis shows its mass per cent composition to be 30.43% nitrogen and 69.57% oxygen. Its density at 1 atm pressure and 300 K is 1.87 g/L. Use the following atomic mass information: N = 14 g/mol and O = 16 g/mol.

(a) Determine the <u>molecular formula</u> of the substance A.

  (Answer)

(b) Draw the <u>Lewis diagram</u> of the substance A.

  (Answer)

(c) Determine the <u>bond orders</u> of NO bonds using the <u>molecular orbital theory</u> and the <u>hybridization scheme</u> for the <u>cation state, $[A]^{\pm}$.</u>

  (Answer)

10. (total 10 pts) The following figure shows the schematic potential energy curves for the dissociation of H_2 as a function of internuclear distance R_{H-H}. The dotted and dashed lines correspond to the results from the molecular orbital theory (MOT) and the valence bond theory (VBT), respectively.
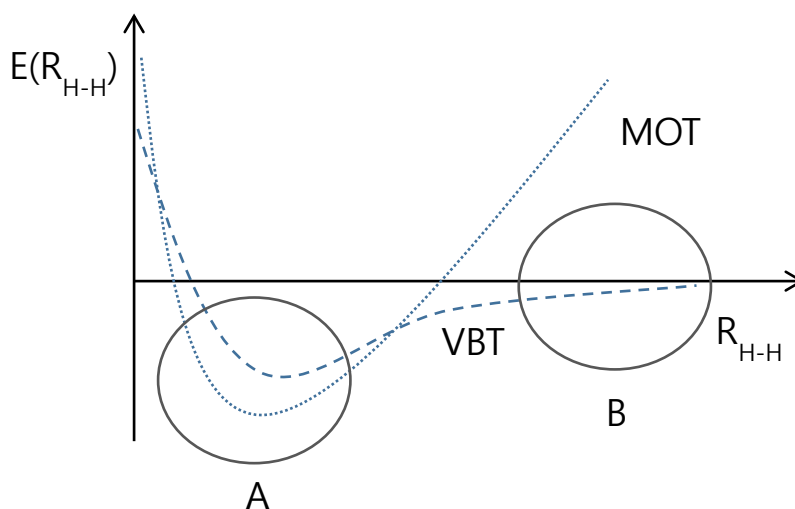
(a) Around the equilibrium bond distance (region A), the MOT gives lower energy than the VBT, whereas at the dissociation limit (region B), the former gives much higher energy than the latter. <u>Explain it through comparison</u> of the wave functions from MOT and VBT.

(Answer)

(b) In order to improve the potential energy curve, one may combine MOT and VBT as follows.

$$\psi_{improved} = \psi_{VB} + \lambda \psi_{ionic}$$

Draw an <u>estimated potential energy curve</u> from the above wave function and estimate <u>the λ values</u> at the regions A and B, respectively.

(Answer)

Physical Constants

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

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

Conversion Factors

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

PERIODIC TABLE OF THE ELEMENTS

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

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

LANTHANIDE

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

GROUP NUMBERS IUPAC RECOMMENDATION (1985)

GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

ATOMIC NUMBER — 5 — 13 IIIA
SYMBOL — B
BORON — 10.811 — RELATIVE ATOMIC MASS (1)
ELEMENT NAME

(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@netlinx.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

Problem	points	Problem	points	TOTAL pts
1	3+2+4/9	**6**	1+2+2+2/7	
2	1x10/10	**7**	3+3/6	
3	10+3/13	**8**	10+3/13	
4	2+1x6/8	**9**	2+4+6/12	/100
5	8+2+2/12	**10**	5+5/10	

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

1. (total 9 pts)

(a) (3 pts) Lewis Dot 2 pts; VSEPR 1 pt

a) The resonance structures

$$\left[:\!\ddot{N}\!=\!N\!=\!\ddot{O}: \longleftrightarrow :N\!\equiv\!N\!-\!\ddot{\underset{..}{O}}: \right]$$
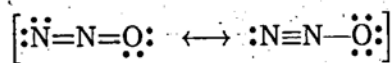
can be written for the NNO molecule. When either is considered, the *SN* of the central nitrogen atom equals two. The predicted molecular geometry is | linear |.

(b) (2 pts)

b) The linear geometry in NNO would cause the N—O and N—N bond dipoles to add vectorially to zero if they were equal in magnitude. The observed net dipole moment means that the two bond dipoles differ in magnitude. The N—O bond should be more polar than the N—N bond because O is more electronegative than N. The | N end | of the molecule is therefore expected to have the positive partial charge.

(c) (4 pts) Only the answer -3 pts; without describing both molecules -2 pts

No, because VSEPR theory predicts a steric number of 3 and a bent molecule in both cases.
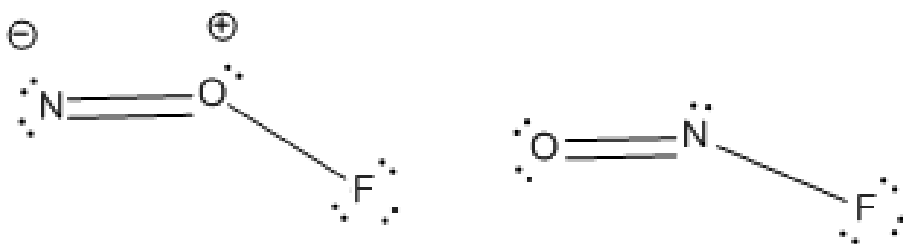
2. (total 10 pts; 1 pt deduction for each incorrect answer)

(a) F

(b) F

(c) F

(d) F

(e) F

(f) F

(g) T

(h) T

(i) F

(j) F

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.

$$\frac{hc}{\lambda} = eV_{thr}$$
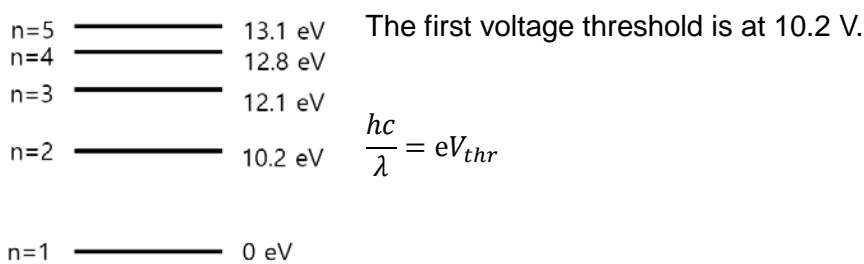
Thus, the energy difference between the ground state (n=1) and the first excited state (n=2) is 10.2 eV. The lowest energy Balmer series 656.3 nm is for a transition of (n=3→n=2). Thus, the 2nd excited state (n=3) is higher in energy than the ground state by 10.2 eV + $\frac{hc}{(656.3\times10^{-9}\ m)(1.6022\times10^{-19}\ J/eV)}$.

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) **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 8 pts) 1D box 의 경우 2 pts; 식 2 pts + 각 값 1 pt X 6

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

$$E_{111} = \frac{h^2}{8\,mL^2}\left(1/4+1+1\right) = \frac{9}{4}\frac{h^2}{8mL^2} \qquad E_{211} = \frac{h^2}{8\,mL^2}\left(4/4+1+1\right) = \frac{12}{4}\frac{h^2}{8mL^2}$$

$$E_{311} = \frac{h^2}{8\,mL^2}\left(9/4+1+1\right) = \frac{17}{4}\frac{h^2}{8mL^2} \qquad E_{112} = E_{121} = \frac{h^2}{8\,mL^2}\left(1/4+4+1\right) = \frac{21}{4}\frac{h^2}{8mL^2}$$

$$E_{411} = E_{221} = E_{212} = \frac{h^2}{8\,mL^2}\left(6\right) = \frac{24}{4}\frac{h^2}{8mL^2} \qquad E_{321} = E_{312} = \frac{h^2}{8\,mL^2}\left(9/4+4+1\right) = \frac{29}{4}\frac{h^2}{8mL^2}$$

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

5. (total 12 pts)

(a) (8 pts) For each species (4 pts), BE, 1 pt + Z_{eff}, 3 pts

species	orbital	Binding Energy $=(Z_{eff})^2/3^2$	Z_{eff}
CuO	3d	3.8 eV = 0.28 Ry	1.6
	3s	124 eV = 9.11 Ry	9.05
Cu_2O	3d	3.5 eV = 0.26 Ry	1.5
	3s	123 eV = 9.04 Ry	9.02

(b) (2 pts) Z_{eff} of 3d < Z_{eff} of 3s, because s electrons can penetrate into the nucleus, while d electrons cannot.

(c) (2 pts) Z_{eff} of 3d in Cu^{2+} > Z_{eff} of 3d in Cu^+, due to less screening effect in Cu^{2+}.

6. (total 7 pts)

(a) (1 pt) $2p_z$ or $2p_0$

(b) (2 pts) $2s$, $2p_x$, $2p_y$

(c) (2 pts) one angular node (or nodal plane)

(d) (2 pts) $-(1.69)^2/4$ (higher)

7. (total 6 pts)

(a) (3 pts) for each, 1 pt

If only one electron could occupy each orbital in many-electron atoms, then the configurations $1s^1$ and $1s^1 2s^1 2p^3$ and $1s^1 2s^1 2p^3 3s^1 3p^3$ would be closed-shell electron configurations. Atoms with $Z = \boxed{1, 5, 9}$ respectively would have these ground-state electron configurations.

(b) (3 pts) for each, 1 pt

The three noble-gas atoms would have $Z = 3$ (which corresponds to "$1s^3$"), $Z = 15\left("1s^3 2s^3 2p^9"\right)$, and $Z = 27\left("1s^3 2s^3 2p^9 3s^3 3p^9"\right)$.

8. (total 13 pts)

(a) (10 pts) for MO shapes, 6 pts; correlation diagram 3 pts, electron 1 pts

120° angles, atoms in a plane, and carbon-carbon bonds intermediate between single and double **-**

$$[CH_2 \text{------} CH \text{------} CH_2]^+$$
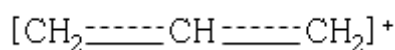
its sounds like benzene. We represent the allyl cation as a delocalized structures.

From sp^2 hybridized carbon atom, the planar 120° network of C-C and C-H sigma bonds come. Three unhybridized p orbital remain. Perpendicular to the plane, these three p orbitals combine constructively to make a delocalized π bonding combination with no nodes.
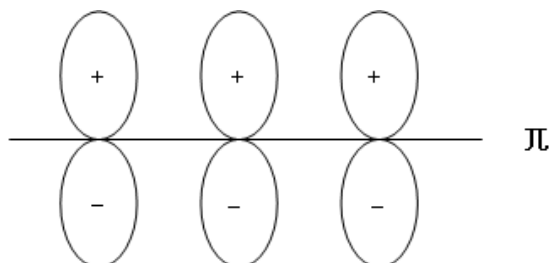

They mix destructively, all three out of phase, to produce a π antibonding combination with two nodes.

node   node

π^*
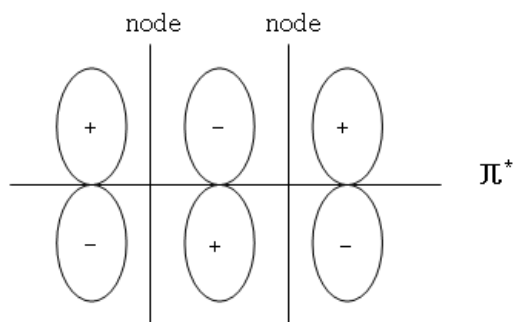
And they mix indifferently, excluding the middle, to produce a π nonbonding combination with one node.

node

π^n
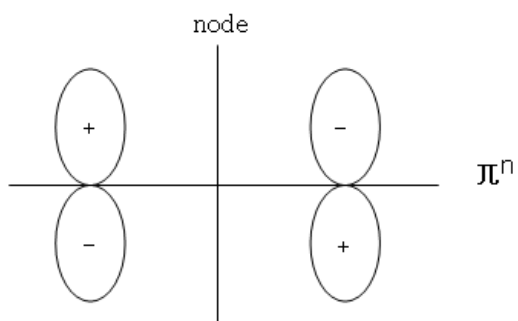
Ten of the 16 electrons go into the five C-H bonds, 4 go into the two C-C sigma bonds. Two electrons remain. Therefore the two electrons go into lower π bonding orbital.

π^* ——

π^n ——

π ⥮
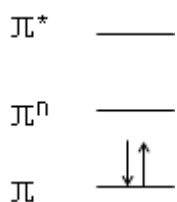
(b) (3 pts)

The structure is stable, diamagnetic, and symmetric. The two carbon-carbon distances are the same.

9. (total 12 pts)

(a) (2 pts)

N: 30.43 g / 14 gmol^{-1} =2.17 mol; O: 69.57 g / 16 gmol^{-1} = 4.35 mol

Thus, ratio between N and O = 1:2 ➜ Empirical formula of A is NO_2.

From the ideal gas law,

M = ρRT/P = (1.87 gL^{-1})(0.0821 L atm mol^{-1} K^{-1})(300K)/(1 atm) = 46.06 g/mol

Since the molar mass from the empirical formula is almost the same with the molar mass, the molecular formula should be NO_2.

(b) (4 pts) each resonance formula, 1 pt; no formal charge, -1 pt

$$\left[\overset{0}{\ddot{O}}=\overset{+1}{\dot{N}}-\overset{-1}{\ddot{O}} \longleftrightarrow \overset{-1}{:\ddot{O}}-\overset{+1}{\dot{N}}=\overset{0}{\ddot{O}} \longleftrightarrow \overset{0}{\cdot\ddot{O}}-\overset{0}{\dot{N}}=\overset{0}{\ddot{O}} \longleftrightarrow \overset{0}{\ddot{O}}=\overset{0}{\dot{N}}-\overset{0}{\ddot{O}}\cdot \right]$$
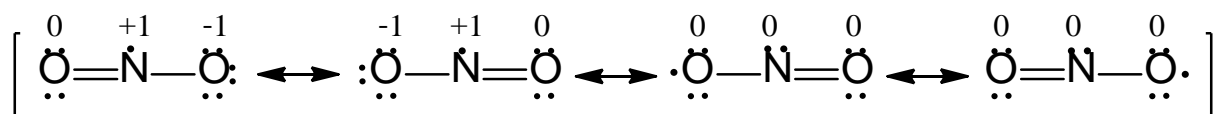
(c) (6 pts) no use MO, only answers, 1 pt; σ-bonds 2 pts + π-bonds 2 pts + BO 1 pt + sp 1 pt

The total number of valence electrons = (5 of N + 2 X 6 of O − 1)=16. Two 2s electrons from each oxygen do not involve in forming chemical bonds. The number of the remaining electrons is 12. Since $[NO_2]^+$ has a linear structure as $[O=N=O]^+$, the hybridization of N should be sp. Therefore,

For the σ-bonds of $[NO_2]^+$,
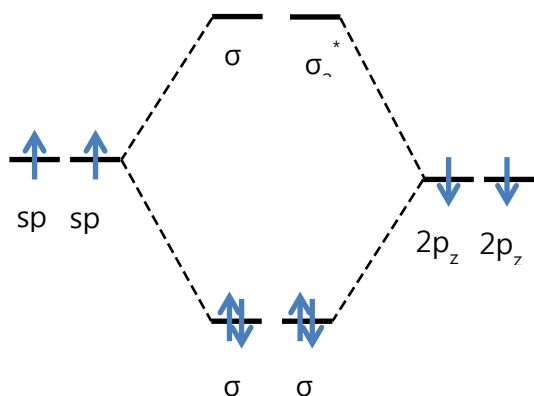
For the π-bonds of $[NO_2]^+$
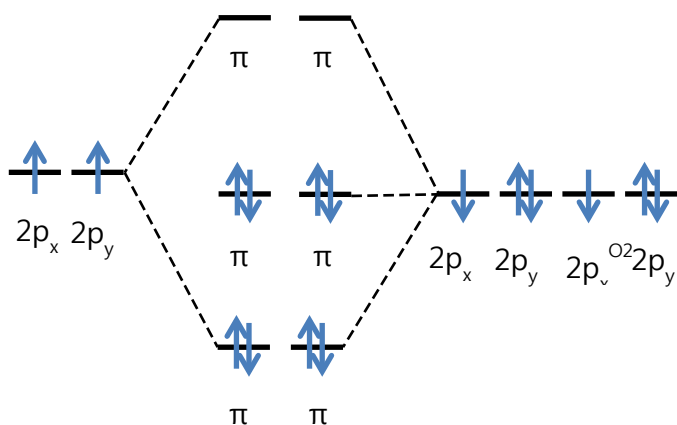
Thus, the total bond order = (4 from the σ-bonds + 4 from the σ-bonds)/2 = 4. The bond order of each NO is 2.

10. (total 10 pts)

(a) (5 pts) VBT and MO description, 1 pts + region A, 2 pts + region B, 2 pts

The wave function from VBT is given by

$$\psi_{VB}^{el}(r_{1A}, r_{2B}) = c_1\varphi_A(r_{1A})\varphi_B(r_{2B}) + c_2\varphi_A(r_{2A})\varphi_B(r_{1B}) \rightarrow \psi_{VB}^{el} = 1s^A(1)1s^B(2) + 1s^A(2)1s^B(1)$$

The wave function from MOT is

$$\psi_{MO}^{el} = \underbrace{[1s^A(1)1s^B(2) + 1s^A(2)1s^B(1)]}_{\psi_{VB}^{el}} + \underbrace{[1s^A(1)1s^A(2) + 1s^B(1)1s^B(2)]}_{\psi_{ionic}}$$

purely covalent structure   mixture of ionic states,
H–H $H_A^-H_B^+$ and $H_A^+H_B^-$

At the region A, due to the ionic contribution of the wave function from MOT, electrons can be more delocalized, resulting in the lower energy compared to the energy of the wave function from VBT that has only the covalent character. However, at the region B, the ionic character from MOT causes very repulsive interactions between two electrons residing on the same atom, leading to such high energy.

(b) (5 pts) curve 1 pts + region A 2 pts + region B 2 pts

At the region A, λ is close to 1 so that the wave function is similar to the one from MOT. At the region B, however, λ will be zero and thus the wave function becomes the one from VBT. As a result, the improved potential energy curve will look like the solid line in the figure below.
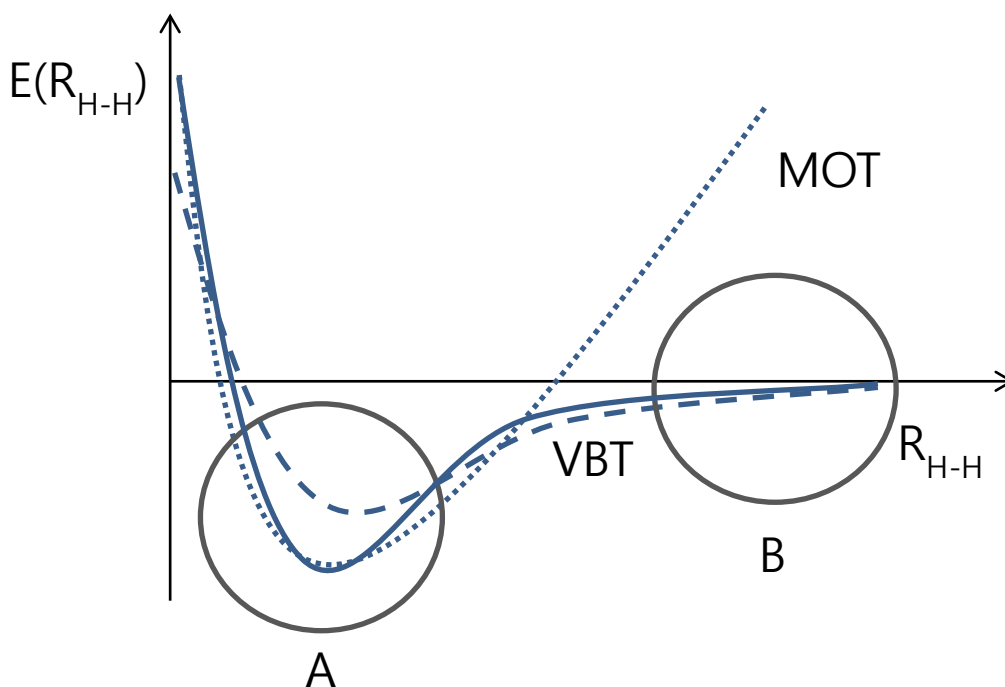
2015 SPRING Semester Final Examination
For General Chemistry I

Date: June 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	/7	**6**	/11	
2	/12	**7**	/12	
3	/10	**8**	/10	**/100**
4	/9	**9**	/8	
5	/8	**10**	/13	

** This paper consists of 14 sheets with 10 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 19 (Friday, 12:00-14:00)*

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

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

  3)   Claim Procedure:

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

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

  (During the period, you can check the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it. The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 6/20 on the web.)

2. Final Confirmation

  1) Period: *June 20(Sat) – 21(Sun)*

  2) Procedure: During this period, you can check the final score of the examination *on the website* again.

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

1. (7 points) A diver who had been working 300 meters below the sea level ascended fast up to the sea level and suffered from decompression sickness (also known as divers' disease, aeroembolism, or caisson disease).

(a) Calculate the pressure exerted on the diver at the depth of 300 m under the water.

(water density = 1 g/ml).

(Answer)

(b) Assume that the pressure of air that the diver inhaled from the air tank was the same as the answer above. Use Henry's law constant of N_2 = 1640 atm/M and calculate the volume (at the sea level) of N_2 bubble generated upon the diver's ascent. On average, humans have ~5 liters of blood and the body temperature of 37 °C. Assume here N_2 is ideal gas.

(Answer)

2. (12 points)

(a) Assume that the molecular weight of a cold virus is 5×10^6 and that it behaves like an ideal gas. <u>Calculate its root-mean-square speed</u> at 27 °C.

(Answer)

(b) What are the <u>root-mean-square speeds of ideal N_2 and O_2 at 27 °C?</u>

(Answer)

(c) For the atmosphere that consists of the ideal N_2 and O_2 gas, <u>calculate the number density of air gas molecules</u> in unit of m^{-3} at 27 °C. <u>Estimate the average distance</u> amongst the gas molecules.

(Answer)

(d) Round up the root-mean-square speeds of N_2 and O_2 to have one significant digit and use it to <u>calculate the</u> $u_{rms,air}$-$u_{rms,virus}$. Use this relative speed and the answer of (a)-(c) to <u>estimate how frequently the virus molecule collides</u> with air molecules.

(Answer)

3. (10 points) On the right side, we have plots of z against pressure for four different gases.

(a) <u>Define the equation</u> to describe the compressibility factor z.

(Answer)

(b) What are the <u>kinds of intermolecular forces</u> that these gases (NH_3, C_2H_4, CH_4, H_2) can have?

(Answer)
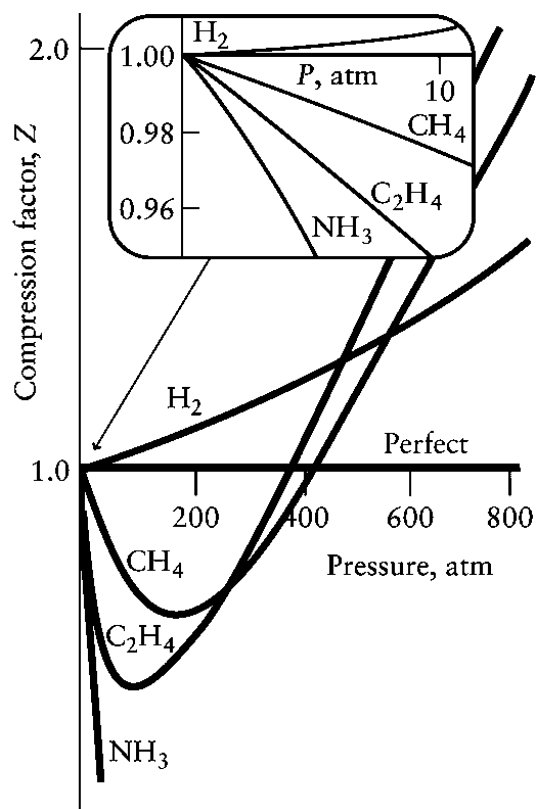
(c) <u>How do these forces determine relative z values</u> of these gases at ~10 atm ($NH_3 < C_2H_4 < CH_4 < 1 < H_2$)?
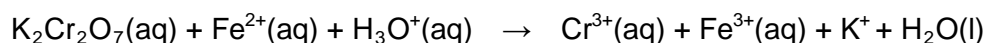
(Answer)

(d) <u>Why</u> does NH_3 has a particularly <u>small z value</u>?

(Answer)

4. (9 points) Potassium dichromate in acidic solution is used to titrate a solution of iron(II) ions.

(a) <u>Balance the following equation</u>, and <u>write the oxidation number</u> above the symbol of potassium dichromate.

$$K_2Cr_2O_7(aq) + Fe^{2+}(aq) + H_3O^+(aq) \rightarrow Cr^{3+}(aq) + Fe^{3+}(aq) + K^+ + H_2O(l)$$

(Answer)

(b) If 40.00 mL of the 100 mM Fe^{2+} solution was found to be equivalent to 25.00 mL of the potassium dichromate solution, <u>calculate the mass</u> of potassium dichromate.

(Answer)

(c) <u>How much does the water volume</u> need to make 100 mL potassium dichromate solution to 100 mM in (b)?

(Answer)

5. (8 points) At 90 °C, the vapor pressure of toluene is 0.534 atm and the vapor pressure of benzene is 1.34 atm. Benzene (0.400 mol) is mixed with toluene (0.900 mol) to form an ideal solution.

(a) <u>Compute the mole fraction of benzene in the vapor</u> in equilibrium with this solution.

(Answer)

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

(Answer)

6. (11 points, 1 point deduction for each incorrect answer) Answer only in T (true) or F (false) for the following questions.

(a) In real gases, attractive interaction reduces pressure with respect to the ideal case, while repulsive interaction increases volume.

(Answer)

(b) Among molecular isomers, one with spherical shape has stronger intermolecular interactions than a rod-shaped one.

(Answer)

(c) Ideal molecules (no intermolecular interactions) do not show boiling-point elevation or freezing-point depression.

(Answer)

(d) According to the Henry's law, one can fully separate two or more components of a liquid solution using fractional distillation.

(Answer)

(e) Heat capacity due to the vibrational degrees of freedom is triggered at higher temperature than that due to the rotational degrees of freedom.

(Answer)

(f) When chemical reaction is in an equilibrium state, it is said to be reversible.

(Answer)

(g) Gibbs free energy always determines the direction of chemical reactions.

(Answer)

(h) Heat from chemical reactions is always equivalent to the change in enthalpy.

(Answer)

(i) The entropy of a pure substance in its thermodynamically most stable form is zero at the absolute zero of temperature, independent of pressure.

(Answer)

(j) Le Châtelier's principle implies that equilibrium constant is a function of pressure, concentration, and temperature.

(Answer)

(k) The reason why Haber-Bosch process is performed at high temperature is because the ammonia formation reaction is endothermic.

(Answer)

7. (12 points) The figure in the right side shows two different processes between the states A and B for ideal gases.

(a) <u>Calculate the work, heat, and change in the internal energy</u> along the path, A → C → B.

(Answer)
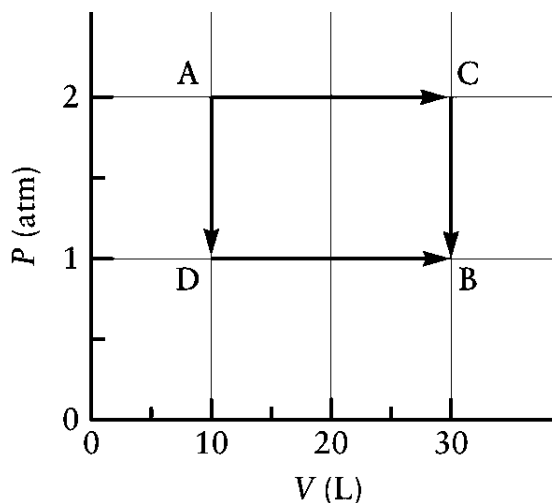
(b) <u>Calculate the work, heat, and change in the internal energy</u> along the path, A → D → B, and confirm that change in the internal energy is independent of paths.

(Answer)

(c) Real gases have typically larger heat capacity than ideal gases. Arrange the following molecules in <u>an increasing order of the heat capacity as T goes to zero or infinity</u>, respectively, and justify your answer. Assume that the molecules remain intact and in the gas phase at any temperature.

(Ar, N_2, O_2, H_2O, C_6H_6)

(Answer)

8. (10 points) The molar enthalpy of fusion of solid ammonia is 5.65 kJ mol^{-1}, and the molar entropy of fusion is 28.9 J K^{-1} mol^{-1}.

(a) <u>Calculate the Gibbs free energy change</u> for the melting of 1.00 mol ammonia at 170 K.

(Answer)

(b) <u>Calculate the Gibbs free energy change</u> for the conversion of 3.60 mol solid ammonia to liquid ammonia at 170 K.

(Answer)

(c) Will ammonia <u>melt spontaneously</u> at 170 K?

(Answer)

(d) <u>At what temperature</u> are solid and liquid ammonia in equilibrium at a pressure of 1 atm?

(Answer)

9. (8 points) Calculate the entropy change, ΔS for the following process

$$H_2O \text{ (l, 120 °C, 1 atm)} \rightarrow H_2O \text{ (g, 120 °C, 1 atm)}$$
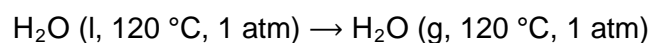
The enthalpy of vaporization of H_2O(l) at 100 °C is 40,580 J mol^{-1} and heat capacity of H_2O(l) is 75.3 J K^{-1} mol^{-1}. The heat capacity of H_2O(g) is 36.0 + (0.013)T J K^{-1} mol^{-1}, where T is absolute temperature.

(Answer)

10. (13 points)

(a) <u>Calculate ΔH^0, ΔS^0, and ΔG^0</u> for the following reaction.

$$N_2 \text{ (g)} \ + \ 3 H_2 \text{ (g)} \ \rightleftarrows \ 2 NH_3 \text{ (g)}$$
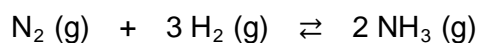
<u>Is this reaction spontaneous</u> in the forward direction at 25 °C?

Substance	ΔH_f^0 (kJ/mol)	S^0 (J/mol·K)
N_2 (g)	0	191.5
H_2 (g)	0	130.6
NH_3 (g)	-46.1	192.3

(Answer)

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

(Answer)

(c) <u>Compute the equilibrium constant</u> at 25 °C.

(Answer)

(d) Suppose that hydrogen, nitrogen, and ammonia gas are mixed together in a closed vessel, each component having a partial pressure of 4.0 atm. <u>Is the mixture in equilibrium</u> at 25 °C?

(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/

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

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

LANTHANIDE

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

ACTINIDE

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

Claim Form for General Chemistry Examination

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

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

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

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	3+4/7	**6**	1x11/11	
2	2+2+4+4/12	**7**	3+3+6/12	
3	2+4+2+2/10	**8**	3+2+2+3/10	
4	3+3+3/9	**9**	2+2+2+2/8	**/100**
5	4+4/8	**10**	6+3+2+2/13	

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

1. (total 7 points)

(a) (3 points) No addition of P_0, -1 pt

    Pressure at the sea level = P_0 = 1 atm = 101 kPa

    Pressure at the depth of 300m below the sea level = P_{300} = P_0 + ρgh

    = 101 kPa + (1000 kg/m^3)(9.8 m/s^2)(300 m)

    = 101 kPa + 2940 kPa = 3041 kPa = **30.1 atm**

(b) (4 points) P_{300}, +1 pt; P_0, +1 pt; Final calculation, +2 pts

    The concentration of N_2 in the blood at P_{300} = (0.80 * 30.1 atm)/(1640 atm/M) =

        0.0147 M

    The concentration of N_2 in the blood at P_0 = (0.80 atm)/(1640 atm/M) = 0.000488 M

    Thus, $V_{N_2} = \dfrac{n_{N_2}RT}{P_{N_2}} = \dfrac{((0.0147-0.0005)mol/l*5l)(0.082\frac{l \cdot atm}{mol \cdot K})(310\ K)}{0.80\ atm}$=**2.3 liters**

2. (total 12 points)

(a) (2 points)

$$u_{rms,virus} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.3145\frac{J}{K\,mol})(300\ K)}{5\times10^3 kg/mol}} = \mathbf{1.2\ m/s}$$

(b) (2 points) for each, +1 pt

$$u_{rms,N2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\left(8.3145\frac{J}{K\,mol}\right)(300\ K)}{28\times\frac{10^{-3}kg}{mol}}} = \mathbf{517\frac{m}{s}}$$

$$u_{rms,O2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.3145\frac{J}{K\,mol})(300\ K)}{32\times10^{-3}kg/mol}} = \mathbf{484\ m/s}$$

(c) (4 points) for each, +2 pts

$$\frac{n}{V} = \frac{P}{RT} = \frac{1\ atm}{(0.082\frac{atm\,l}{mol\,K})(300\ K)}\frac{6.02\times10^{23}}{1mol}\frac{1\ l}{10^{-3}m^3} = \mathbf{2.4\times10^{25}\ m^{-3}}$$

Average distance d; $d^3 \sim \frac{1m^3}{2.4\times10^{25}}$; then d~**3.5×10^{-9} m**

(d) (4 points) for each, +2 pts

$u_{rms,air}$-$u_{rms,virus}$ = 500 m/s − 1 m/s ≈ **500 m/s**

(3.5*10^{-9} m)/(500 m/s) = 7 * 10^{-12} s; that is, **every 7 ps**, the virus molecule is hit by air molecules.

3. (total 10 points)

(a) (2 points)

$$Z = \frac{V_m}{V_m^{ideal}} = \frac{V_m}{RT/P} = \frac{PV_m}{RT}$$

or z = PV/nRT

(b) (4 points) NH_3, +3 pts; others, +1 pt

NH_3: London (dispersion) forces, dipole-dipole, hydrogen bonding

C_2H_4: London forces

CH_4: London forces

H_2: London forces

(c) (2 points)

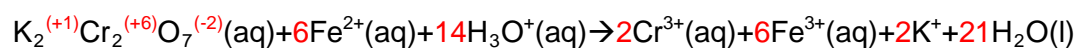**Relative z values can be explained by relative attractive forces**

$NH_3 > C_2H_4 > CH_4 > H_2$

(d) (2 points)

NH_3 with hydrogen bonding has particularly high attractive forces, leading to the lowest z value.

4. (total 9 points)

(a) (3 points)

$$K_2^{(+1)}Cr_2^{(+6)}O_7^{(-2)}(aq)+6Fe^{2+}(aq)+14H_3O^+(aq)\rightarrow 2Cr^{3+}(aq)+6Fe^{3+}(aq)+2K^++21H_2O(l)$$

(b) (3 points)

40.00mL x 100 mM = 25.00mL x X mM x 6

Concentration of potassium dichromate = X = 26.7mM

Mass of potassium dichromate = Mw x X x V=294.1846 x 0.0267M x 0.025mL= **0.196 g**

(c) (3 points)

No solution: all 3 points

5. (total 8 points)

(a) (4 points)

11.62 The vapor pressure of a component in this ideal case is simply the vapor pressure that the pure component would have multiplied by its mole fraction in the solution. Therefore, the vapor pressure of the toluene above this solution is

$$P_{toluene} = X_{toluene} \, P^{\circ}_{toluene} = \left(\frac{0.900}{0.400 + 0.900} \right)(0.534 \text{ atm}) = 0.370 \text{ atm}$$

at this temperature, and the vapor pressure of the benzene is 0.412 atm, by a similar calculation. The total pressure of the vapors above the solution is 0.782 atm, which is the sum of the partial pressures of the two volatile components of the solution. The mole fraction of benzene in the vapor is

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

(b) (4 points)

11.84 According to problem 11.62, 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. Let the mole fraction of the toluene in solution equal X_{tol} Then the mole fraction of the benzene is $1 - X_{tol}$, and

$$(0.534 \text{ atm})X_{tol} + (1.34 \text{ atm})(1 - X_{tol}) = 1.00 \text{ atm}$$

Solving for X_{tol} gives 0.42 as the answer

6. (11 points, 1 point deduction for each incorrect answer)

(a) T

(b) F

(c) F

(d) F

(e) T

(f) T

(g) F

(h) F

(i) T

(j) F

(k) F

7. (total 12 points)

(a) (3 points) each w, q, ΔU, +1 pt

Along the path $A \rightarrow C \rightarrow B$:

$$w_{AC} = -P_{ext}\Delta V = -P_A(V_B - V_A)$$

$$w_{CB} = 0 \; (V_C = V_B)$$

$$q_{AC} = q_P = nc_P\Delta T = (5/2)nR(T_C - T_A)$$
$$= (5/2)(P_C V_C - P_A V_A)$$

$$q_{CB} = q_V = nc_V\Delta T = (3/2)nR(T_B - T_C)$$
$$= (3/2)(P_B V_B - P_C V_C)$$

$$w_{ACB} = w_{AC} + w_{CB} = -P_A(V_B - V_A)$$
$$= -40.0 \text{ L atm} = -4050 \text{ J}$$

$$q_{ACB} = q_{AC} + q_{CB}$$
$$= (5/2)(P_C V_C - P_A V_A) + (3/2)(P_B V_B - P_C V_C)$$
$$= (5/2)P_A(V_B - V_A) + (3/2)V_B(P_B - P_A) = 5570 \text{ J}$$

$$\Delta U = q_{ACB} + w_{ACB} = 1520 \text{ J}$$

(b) (3 points) each w, q, ΔU, +1 pt

Similarly, along the path $A \rightarrow D \rightarrow B$:

$$W_{ADB} = -2030 \text{ J}, \; q_{ADB} = 3550 \text{ J} \rightarrow \Delta U = q_{ADB} + w_{ADB} = 1520 \text{ J}$$

Changes in the internal energy along both paths are identical to each other, meaning that ΔU is independent of paths.

(c) (6 points) for T = 0, 3 pts; for T = infinity, 3 pts

As T → 0, Ar = N$_2$ = O$_2$ = H$_2$O = C$_6$H$_6$, because only the translational modes will be available that is 3/2 R according to the equipartition theorem.

As T → infinity, Ar < N$_2$ = O$_2$ < H$_2$O < C$_6$H$_6$, because the heat capacity of gas molecules at high temperature is proportional to the number of degrees of freedom due to the equipartition theorem.

8. (total 10 points)

(a) (3 points)

13.29 **a)** Solid ammonia is held at a constant temperature of 170 K. It is implied that the pressure is a constant 1 atm. The molar Gibbs energy of fusion is

$$\Delta G_{fus} = \Delta H_{fus} - T\Delta S_{fus} = 5.65 \text{ kJ mol}^{-1} - (170 \text{ K})(0.0289 \text{ kJ K}^{-1}\text{mol}^{-1}) = 0.74 \text{ kJ mol}^{-1}$$

(b) (2 points)

b) This case differs from part **a)** only in the amount of ammonia. Multiply the molar Gibbs energy of fusion by 3.60 mol, the amount of NH_3 that melts. The result is $\boxed{2.65 \text{ kJ}}$.
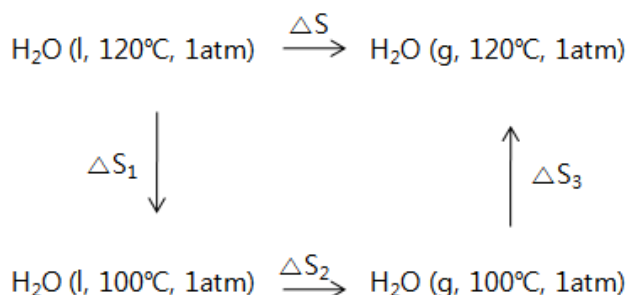
(c) (2 points)

c) At 170 K, $\Delta G > 0$. Hence the melting of ammonia is $\boxed{\text{not spontaneous}}$ at 170 K (and 1 atm pressure).

(d) (3 points)

d) If solid and liquid NH_3 are in equilibrium, then ΔG equals zero for the fusion process, which is solid $\rightleftharpoons$ liquid. Calculate the T that makes this true. Use the molar enthalpy of fusion and the molar entropy of fusion that are quoted in the problem

$$\text{If } \Delta G = \Delta H_{fus} - T\Delta S_{fus} = 0 \quad \text{then} \quad T_{fus} = \frac{\Delta H_{fus}}{\Delta S_{fus}} = \frac{5.65 \times 10^3 \text{ J mol}^{-1}}{28.9 \text{ J K}^{-1}\text{mol}^{-1}} = \boxed{196 \text{ K}}$$

9. (total 8 points) for each ΔS_x, +2 pts

$$H_2O \text{ (l, 120°C, 1atm)} \xrightarrow{\Delta S} H_2O \text{ (g, 120°C, 1atm)}$$

$$\downarrow \Delta S_1 \qquad\qquad\qquad \uparrow \Delta S_3$$

$$H_2O \text{ (l, 100°C, 1atm)} \xrightarrow{\Delta S_2} H_2O \text{ (g, 100°C, 1atm)}$$

$$\Delta S_1 = \int_{393}^{373} \frac{C_{p,l}}{T} dT = 75.3 \ln\frac{373}{393} = -3.93 \text{ J/Kmol}$$

$$\Delta S_2 = \frac{\Delta H_{vap}}{T} = \frac{40580}{373} = 108.83 \text{ J/Kmol}$$

$$\Delta S_3 = \int_{373}^{393} \frac{C_{p,g}}{T} dT = \int_{373}^{393} \frac{36 + 0.013 \, T}{T} dT = 2.14 \text{ J/Kmol}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = \textbf{107.04 J/Kmol}$$

10. (total 13 points)

(a) (6 points) for each value, +2 pts

$\Delta H^0 = 2 \Delta H_f^0 [NH_3 (g)] - \Delta H_f^0 [N_2 (g)] - 3\Delta H_f^0 [H_2 (g)]$

$= (2 \text{ mol})(-46.1 \text{ kJ/mol}) - 0 - 3 \times (0) = \textbf{-92.2 kJ}$

$\Delta S^0 = 2 S^0 [NH_3 (g)] - S^0 [N_2 (g)] - 3 S^0 [H_2 (g)]$

$= 2 \text{ mol} \times \dfrac{192.3 J}{mol \cdot K} - 1 \text{ mol} \times \dfrac{191.5 J}{mol \cdot K} - 3 \text{ mol} \times \dfrac{130.6 J}{mol \cdot K}$

$= \text{-198.7 J/K}$

$= \textbf{-0.1987 kJ/K}$

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = \text{-92.2 kJ} - (298.15K) (\text{-0.1987kJ/K})$

$= \text{-92.2 kJ} + 59.24 \text{ kJ} = \textbf{-33.0 kJ}$

The negative sign shows that **the reaction is spontaneous**.

(b) (3 points)

$T_{max} = \Delta H^0/\Delta S^0 = \text{-92.2 kJ} / \text{-0.1987 kJ/K} = \textbf{464 K} = \textbf{191 °C}$

(c) (2 points) $K = \exp (-\dfrac{\Delta G^0}{RT})$

$= \exp \left[(-\dfrac{-33.0 \text{ kJ}}{\left(8.3145 \,^{J}/_{K}\right)(298 \text{ K})}) \times \dfrac{1000 \text{ J}}{kJ} \right]$

$= \textbf{6.1 x 10}^{\textbf{5}}$

(d) (2 points) No explanation, 0 pt

$Q = \dfrac{P^2_{NH3}}{P_{N2}P^3_{H2}} = \dfrac{(4.0)^2}{(4.0) (4.0)^3} = 0.0625$

This differs substantially from the equilibrium constant at 25 ℃ (K= 6.1 x 10^5 **). The mixture is not**

yet at equilibrium. There are still too many reactants and too few products.