2010 SPRING Semester Mid-Term Examination
For General Chemistry I (CHEM101)

Date: March 24 (Wed), 2010,   Time Limit: 7:00 ~ 9:00 p.m.

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

Professor Name	Class	Student I.D.	Name

Problem	points	Problem	points	TOTAL pts
1	/15	**8**	/5	**/100**
2	/5	**9**	/5	
3	/10	**10**	/5	
4	/5	**11**	/10	
5	/5	**12**	/10	
6	/10	**13**	/5	
7	/5	**14**	/5	

**** This paper consists of 12 sheets with 14 problems. Please check all page numbers before taking the exam. Write down your work and answers in the (Answer) space below each question. And take a good use of the reference materials (page 11, 12), which include Fundamental Constants, Conversion Factors, and Periodic Table with atomic weights.**

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: ***March 29 (Mon, 6: 00 p.m.) ~ 30 (Tue, 9: 00 a.m.)***
   2) ***Location: Lobby (1st floor), GoongNi lab Bldg.***
   3) Procedure: During the period, you can take your mid-term paper scored. If you have any claims on it, you can submit a claim paper with your opinion. After writing your opinions on any paper you can get easily, **attach it with a stapler to your paper scored** (Please, write your name, professor, and class.). Put them into a paper box in front of elevator. The papers with the claims will be re-examined by TA.

The claim is permitted only on the period. Keep that in mind**!**

(A solution file with answers will be uploaded on 3/28 at the web.)

2. Final Confirmation
   1) Period: **April 1 (Thur) ~ 2 (Fri)**
   2) Procedure: During this period, you can check final score of the examination *on the website* again.

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

CHEM 101: General Chemistry I
Mid-Term Examination (100 points): Answers

1. (1) $E_n = n^2h^2/8mL^2$ (page739-741)
(2) n = 2 $\rightarrow$ n = 3
$\Delta E = 9.02\times10^{-19}$ J, $\upsilon = 4.54\times10^{4}$ cm^{-1}
(3) (2,1,1) *vs.* (1,1,1)
$\Delta E = 2.8\times10^{-40}$ J = 1.7×10^{-19} kJ/mol

2. $HF + H_2O \rightarrow H_3O^+ + F^-$
$HF + H_2O \rightarrow H_2F^+ + OH^-$
F is more electronegative than O and less readily donates its electrons; F-H bond is more polar than O-H, making HF more susceptible to nucleophilic attack
.

3. (a) (2,0,0) 1 and 0
(b) (2,1,1) 0 and 1 (or -1)
(c) (3,0,0) 2 and 0
(d) (3,1,0) 1 and 1
(e) (3,2,0) 0 and 2

4. $\Delta E = E_{bound} - E_{free} = -RZ^2/n^2 - 1/2mv^2$
$= -2.64\times10^{-18}$ J

5. A
IE(Na) - EA(Cl): (ionization energy of Na) - (electron affinity of Cl)

6. 3 and 1:2:1 (↑↑:↑↓ and ↓↑:↓↓)
The ambuquity was found in the interpretation of question 6 in the mid-term exam; therefore, in addition to the announced answer (3 peaks), " 1 peak" will be credited as an answer.

7. Oxidation half equation: $(COOH)_2 \rightarrow 2CO_2 + 2H^+ + 2e^-$
Reduction half equation: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
Full ionic redox equation (after dropping counter ions):
$5(COOH)_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

8. $IE = E(He^+) - E(He)$
$= 4E_H - 2\times(1.6875)^2\times(-13.60) = 23.06$ eV

9. 5.52

52. Writing the equation in ionic form and cancelling spectators,

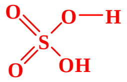
$$2Na^+(aq) + S^{2-}(aq) + Cd^{2+}(aq) + 2Cl^-(aq) \rightarrow CdS(s) + 2Na^+(aq) + 2Cl^-(aq)$$

$$\underset{\text{base}}{S^{2-}(aq)} + \underset{\text{acid}}{Cd^{2+}(aq)} \rightarrow \underset{\text{adduct}}{CdS(s)}$$

The identification of S^{2-} as the Lewis base follows from its four lone pairs and negative charge.

10.

HOCa—O—H X(Ca) < X(H), so ionization to Ca^{2+} and $2OH^-$ is favored, hence basic character.



X(S) > X(H), so ionization to HSO_4^- and H^+ (etc) is favored, hence acidic character.

11. (a) F, (b) T, (c) F, (d) F, (e) T

12. ε_{photon} = hc/λ = [(6.6261 x 10^{-34} Js)(2.9979 x 10^8 ms^{-1})]/(0.9890 x 10^{-10} m)(1.6022 x 10^{-19} JeV^{-1})]
= **12536 eV**
Because BE = $h\nu_{photon} - (1/2)m_e v^2_{electron}$
Therefore, BE for 383.4 eV → **12161.3 eV or 1.947 X 10^{-15} J**
BE for 1205.2 eV → **11339.5 eV or 1.815 X 10^{-15} J**
BE for 1232.0 eV → **11312.7 eV or 1.811 X 10^{-15} J**

13. example 3.3
$\Delta p = h/(4\pi\,\Delta x) = 6.63\times10^{-34}\ \mathrm{J\,s} / [(4\,\pi)(1.0\times10^{-3}\ \mathrm{m})]$
$= 5.28\times10^{-32}\ \mathrm{kg\,m\,s^{-1}}$
$p = (0.140\ \mathrm{kg})\,(92\ \mathrm{mph})\,(1609\ \mathrm{m/mi})(1\mathrm{hr}/3600\ \mathrm{s})$
$= 5.76\ \mathrm{kg\,m\,s^{-1}}$

14. 5.48

48. See the text key for the balanced titration equations; from these and the titration data we have

$$n_{ClO^-} = (17.32\,\mathrm{mL})(0.1000\,\mathrm{M}\,S_2O_3^{2-})\left(\frac{1\,\mathrm{mmol}\,I_2}{2\,\mathrm{mmol}\,S_2O_3^{2-}}\right)\left(\frac{1\,\mathrm{mmol}\,ClO^-}{1\,\mathrm{mmol}\,I_2}\right) = 0.8660\,\mathrm{mmol}$$

and a molarity $[ClO^-]$ = 0.8660 mmol / 1.000 mL = 0.8660M.

1. (5 pt each)
(a) Derive the allowed energies having the quantum number of *n* for the one-dimensional particle-in-a-box problem.

(Answer)

(b) The 4 pi electrons of butadiene, $H_2C{=}CHCH{=}CH_2$, are assumed to be confined in a straight line the length of which is equal to the sum of two C=C bond-lengths (135 pm per bond), one C-C bond (154 pm), and two carbon-radii at the end (77.0 pm per carbon). Calculate the adsorption band, in wavenumber, which corresponds to the electronic transition to the first excited state ($m_e = 9.11\times10^{-31}$ kg; $h = 6.626\times10^{-34}$ Js; $c = 2.9979 \times 10^{8}$ ms^{-1}).

(Answer)

(c) A helium atom is confined in a cube having a side-length of 30 cm. Calculate the energy difference between the ground and the first excited state in kJ/mol.

(Answer)

2. (5 pt) HF, in principle, can react with water in two different ways (as an electrophile or a nucleophile). Write down the two possible reactions, and explain why one reaction is favored over the other.

(Answer)

3. (2 pt each) Give the value of quantum numbers (*n*, *l*, and *m*) and the number of radial nodes and angular nodes for each of the following hydrogen atomic orbitals ($\rho = r/a_0$).

(a) $\Psi = (32\pi)^{-1/2}a_0^{-3/2}(2 - \rho)e^{-\rho/2}$
(Answer)

(b) $\Psi = (32\pi)^{-1/2}a_0^{-3/2}\rho e^{-\rho/2}\sin\theta\cos\phi$
(Answer)

(c) $\Psi = 81^{-1}(3\pi)^{-1/2}a_0^{-3/2}(27 - 18\rho + 2\rho^2)e^{-\rho/3}$
(Answer)

(d) $\Psi = 81^{-1}(2/\pi)^{1/2}a_0^{-3/2}(6 - \rho)\rho e^{-\rho/3}\cos\theta$
(Answer)

(e) $\Psi = 81^{-1}(6\pi)^{-1/2}a_0^{-3/2}\rho^2 e^{-\rho/3}(3\cos^2\theta - 1)$
(Answer)

4. (5 pt) A free electron moves with velocity (*v*) of 1.00×10^{6} m/s before being captured by a hydrogen nucleus, and eventually lands in the 1*s* orbital. What is the energy change in joule?
[R (Rydberg constant) = 2.18×10^{-18} J]

(Answer)

5. (5 pt) We have two atomic systems, $Na^+ + Cl^-$ (system **A**) and Na + Cl (system **B**), where all the particles are separated in the infinite distance. Which system (**A** or **B**) is higher in the energy? Describe the energy difference of the two systems by the ionization energy and the electron affinity.

(Answer)

6. (10 pt) Uhlenbeck and Goudsmit explained nicely the doublet of Na-D line by introducing the concept of "spin". One year later (1926), Stern and Gerlach successfully confirmed this postulation by measuring the magnetic properties of a single state of Na atom. They observed that two deflected beams of Na vapor were deposited onto a collector plate with a ratio of 1:1. When the same experiment was performed with a helium atom instead of Na, <u>how many deflection patterns</u> and <u>what ratio of each deflected patterns</u> can you expect theoretically on the basis of the modern electron configuration?

(Answer)

7. (5 pt) Oxalic acid, $(COOH)_2$, reacts with potassium permanganate in acid solution according to the *unbalanced* neutral equation below. Write a fully balanced **ionic** redox equation for this reaction, using oxidation and reduction half equations.

$(COOH)_2(aq) + KMnO_4(aq) + H_2SO_4(aq) \rightarrow CO_2(g) + MnSO_4(aq) + H_2O(l)$

(Answer)

8. (5 pt) The Hartree wavefunction for the ground state of He (Ψ_{He}) is a product of two identical one-electron orbitals, which are hydrogen 1*s*-like ones. Calculate the first ionization energy of He in eV based on the Hartree's approximation ($E_H = -e^2/2a_0 = -13.60$ eV; $Z_{eff}^{He} = 1.6875$).

(Answer)

9. (5 pt) A test used for aqueous cadmium ion analysis is sulfide precipitation to give the yellow CdS(*s*):
$Na_2S(aq) + CdCl_2(aq) \rightarrow CdS(s) + 2NaCl(aq)$. Write the equation in ionic form, and identify the Lewis acid and base.

(Answer)

10. (5 pt) Use Lewis structures and electronegativities to compare the acid-base character of $Ca(OH)_2$ and H_2SO_4 (= $O_2S(OH)_2$). For convenience, assume both are covalent.

(Answer)

11. (+2 pt per correct answer; -1 pt per incorrect one; 0 pt per unanswered one)
Determine whether the following statements are true or false.

(a) The Hartree's orbital approximation says that each electron moves in an effective field created by the nucleus and all the other electrons, and the effective field for the electron has angular dependency.

(Answer)

(b) Without electron-electron repulsion, the Hamiltonian for He splits into two He^+ Hamiltonians.

(Answer)

(c) Lewis electron-dot structures were proposed based on the electronic configurations of quantum mechanics.

(Answer)

(d) The first IE is greater than $-E_{HOAO}$.

(Answer)

(e) The boundary conditions yield quantum numbers.

(Answer)

12. (10 pt) The photoelectron spectrum for Ne, excited by X-ray with wavelength of 9.890 x 10^{-11} m, showed three peaks with kinetic energy of 383.4 eV, 1205.2 eV, and 1232.0 eV, respectively. Calculate the binding energies for the three observed peaks, and provide the name of each orbital that corresponds to the calculated binding energy level (1 eV = 1.6022 x 10^{-19} J).

(Answer)

13. (5 pt) To hit a baseball squarely, a batter must locate the 140-g ball (by eye) within about 1 mm. Find the uncertainty in momentum of the ball, and compare this to the total momentum of a 92-mph fastball (1 mile = 1609 meters).

(Answer)

14. (5 pt) For analysis of hypochlorite (ClO^-), the active ingredient in laundry bleach, the unbalanced ionic reactions are: $ClO^- + I^- \rightarrow Cl^- + I_2$ and $S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + I^-$. After balancing these reactions, determine the molarity of ClO^- in bleach if 1.000 mL of bleach required 17.32 mL of 0.1000 M $Na_2S_2O_3$ to titrate the I_2 produced by it.

(Answer)

2010 SPRING Semester Final Examination
For General Chemistry I (CHEM101)

Date: May 19 (Wed), 2010,   Time Limit: 7:00 ~ 9:00 p.m.

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

Professor Name	Class	Student I.D.	Name

Problem	points	Problem	points	TOTAL pts
1	/10	**7**	/5	
2	/20	**8**	/5	
3	/5	**9**	/5	
4	/5	**10**	/10	
5	/10	**11**	/20	**/100**
6	/5			

**** This paper consists of 12 sheets with 11 problems. Please check all page numbers before taking the exam. Write down your work and answers in the (Answer) space below each question.**
And take a good use of:
Page 10 and 11- Fundamental Constants, Conversion Factors, and Periodic Table with atomic weights, Page 12- a claim form.

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

1. Period, Location and Procedure
   1) Return and Claim Period: ***May 24 (Mon, 11: 00 a.m.) ~ 25 (Tue, 13: 00 p.m.)***
   2) ***Location: Lobby (1st floor), GoongNi Lab Bldg.***
   3) Claim Procedure:
   (During the period, you can take the final exam paper and submit a form for claims if you have any claims on it.)
   After writing your claims on *the form (Page 12),* attach it to the top of the final paper with a stapler. Put them into a paper box in front of elevator. Only final papers with the formally written claims will be re-examined by TA.

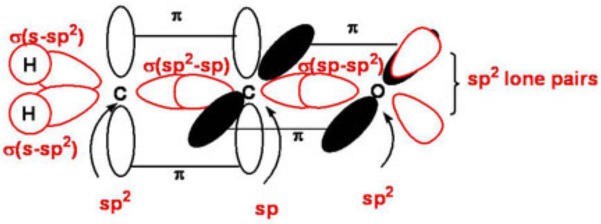
The claim is permitted only on the period. Keep that in mind!
(A solution file with answers will be uploaded on 5/24 at the web.)

2. Final Confirmation
   1) Period: **May 26 (Wed)**
   2) Procedure: During this period, you can check final score of the examination *on the website* again.

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

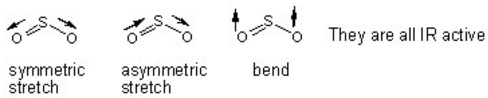
CHEM 101: General Chemistry I
Final Examination (100 points): Answers

1. (a) The carbon in the $–CCl_3$ group is hybridized as sp^3, consistent with four σ bonds arranged tetrahedrally. The carbons in the C≡C triple bond (one σ bond plus two π bonds) are hybridized as sp, consistent with a 180 angle (linear).
(b)



2. (a-1) the same
(a-1) the two terminal carbons
(b) The electron is removed from the antibonding orbital.
(c) The bond length increases, because the additional electron goes to the antibonding orbital.

3.



4. to be increased, because the interaction between HOMO and LUMO increases due to the decreased energy level of LUMO caused by the electronegative atom/moiety.

5. a)

$\mu = (m_{Na} \cdot m_H)/(m_{Na} + m_H) = 0.9655$ amu $= 1.603\text{x}10^{-27}$ kg

$\Delta E_{rot} = h\nu = hc/\lambda = [(6.626\text{x}10^{-34}\text{Js}) \cdot (2.998\text{x}10^8 \text{m/s})]/(1.02\text{x}10\text{-}3\ \text{m}) = 1.95\text{x}10^{-22}\text{J}$

$= (h^2/8\pi^2 I)[1\cdot 2 - 0\cdot 1] = h^2/4\pi^2\ I$

$I = h^2/(4\pi^2\ \Delta E_{rot}) = 5.70\text{x}10^{-47}$ kg·m^2

$r^2 = I/\ \mu = 3.56\text{x}10^{-20}$ m^2

$r = 1.89\text{x}10^{-10}$ m $= 1.89$ Å

b)

vibrational frequency is

$\nu = c/\lambda = 2.998\text{x}10^8\ \text{ms}^{-1}/8.53\text{x}10^{-6}\ \text{m} = 3.515\text{x}10^{13}\ \text{s}^{-1} = (1/2\pi)\cdot\ (k/\mu)^{1/2}$

$k = \mu(2\pi\ \nu)^2 = 78.2\ \text{kg}\cdot\text{s}^{-2} = 78.2\ \text{J}\cdot\text{m}^{-2}$

6. (~)162 atm

7. $(\sigma_{1s})^2(\sigma^*_{1s})^2$
Bond order: 0
Should be unstable.

8. Figure 7.18

9. Figure 7.13

10. (a) It would correspond to the largest moment of inertia. $^7Li^{37}Cl$
(b) The lowest frequency line will be J = 0 → J = 1 .
The 3 of the next 4 lines should correspond to the J = 0 → J = 1 transition in the other isotopic species. The

last one should be the J = 1 → J = 2 transition in $^{7}Li^{37}Cl$.

37727, 42620, 42961, and 74776 MHz

$$\frac{\nu}{\nu_o} = \frac{I_o}{I} = \frac{\mu_0 r^2}{\mu r^2} = \frac{\mu_0}{\mu}$$

$$\nu = \frac{\mu_o \nu_o}{\mu}$$

For $^{7}Li^{35}Cl$

$$\mu = 9.705 \times 10^{-24} g$$

$$\nu = 37388 \times \frac{9.793 \times 10^{-24}}{9.705 \times 10^{-24}} = 37727 \text{ MH}_z$$

For $^{6}Li^{37}Cl$

$$\mu = 8.591 \times 10^{-24} g$$

$$\nu = 37388 \times \frac{9.793 \times 10^{-24}}{8.591 \times 10^{-24}} = 42620 \text{ MH}_z$$

For $^{6}Li^{35}Cl^{-}$

$$\mu = \frac{6.016 \times 34.98}{6.016 + 34.98} \times \frac{1}{6.023 \times 10^{23}} = 8.523 \times 10^{-24} g$$

$$\nu = 37388 \times \frac{9.793 \times 10^{-24}}{8.523 \times 10^{-24}} = 42961 \text{ MH}_z$$

$\nu_{1\to 2} 2\nu_{0\to 1}$= = 2 (373388) MH_z

= 74776 MH_z

11. (a) F, (b) F, (c) T, (d) T, (e) T, (f) F, (g) T, (h) T, (i) F, (j) F

1. (5 pt each) (a) Describe the geometries and hybridizations for C (sp, sp^2, and sp^3), and bonding characters (single, double, triple, σ, and π) of CCl_3CCH, based on the valence bond approach.

(Answer)

(b) Sketch the overlapping and lone pair orbitals of the molecule ketene ($H_2C{=}C{=}O$), indicating clearly the kinds of bonds (σ, π) present and the hybridization of the carbon and oxygen atoms.

(Answer)

2. (5 pt each)

(a-1) Which one do you expect to be the most stable among allyl cation ($CH_2CHCH_2^+$), allyl radical ($CH_2CHCH_2^\bullet$), and allyl anion ($CH_2CHCH_2^-$), based on the π MO model.

(Answer)

(a-2) Among the three carbon atoms in allyl cation, which carbon has the highest probability of the positive charge?

(Answer)

(b) Using MO configurations or energy levels, explain why the O_2^+ ion is more stable than the O_2 molecule.

(Answer)

(c) Decide what would happen to the O-F bond length if one electron were added to OF (i.e. to produce OF^-).

(Answer)

3. (5 pt) Sketch the vibrations associated with the SO_2 molecule and indicate which are infrared active.

(Answer)

4. (5 pt) Suppose that HOMO of butadiene (CH_2=CH-CH=CH_2) interacts with LUMO of ethylene (CH_2=CH_2) to form a cyclic compound called cyclohexene in Diels-Alder reactions. When one of the hydrogen atoms in ethylene is replaced by an electronegative atom/moiety, do you expect the reaction rate to be increased or decreased? Explain your answer with the FMO model.

(Answer)

5. (10 pt) The spectrum of gaseous $^{23}Na^{1}H$ was obtained by absorption spectroscopy. The wavelength of light required to excite the molecule rotationally from the state J = 0 to J = 1 was measured to be 1.02×10^{-3} m, and the wavelength needed to excite it vibrationally from the state $v = 0$ to $v = 1$ was 8.53×10^{-6} m. Calculate (a) the bond length and (b) the vibrational force constant of the NaH molecule
(h = 6.626×10^{-34} J s; c = 2.998×10^{8} m s^{-1}; m_{Na} = 22.9898 amu; m_H = 1.0078 amu).

(Answer)

6. (5 pt) An oxygen cylinder has an internal volume of 28.0 L and contains 6.80 kg of oxygen. Use the van der Waals equation to calculate the pressure inside such a cylinder at 20 ^{o}C. Express it in atm (R = 0.08206 L atm K^{-1} mol^{-1}; m_O = 15.9994 amu; a = 1.360 atm L^2 mol^{-2}; b = 0.03183 L mol^{-1}).

(Answer)

7. (5 pt) What would be the electron configuration for the HeH^- molecular ion? What bond order would you predict? How stable should such a species be?

(Answer)

8. (5 pt) Using the frontier orbital idea, explain why the donation of a pair of electrons to the water molecule always results in the breaking of one O-H bond. Draw a frontier orbital picture of the reaction and indicate the Lewis acid and Lewis base.

(Answer)

9. (5 pt) Construct the LCAO-MO energy levels and sketch the boundary surfaces of the MOs for the HF molecule.

(Answer)

10. (10 pt) Lithium and chlorine each have two naturally occurring isotopes, whose abundances and atomic masses are listed below

Isotope	Abundance	Atomic Mass
^{6}Li	8%	6.016
^{7}Li	92%	7.018
^{35}Cl	75%	34.98
^{37}Cl	25%	36.98

Naturally occurring LiCl consists of a mixture of the four possible isotopic combinations. A sample of natural LiCl is vaporized at 1500 K and a microwave spectrum is obtained. The lowest frequency line is found at 37388 MH_z (1 $MH_z = 10^6\ s^{-1}$).

(a) To which isotopic combination does this lowest frequency line correspond?
(b) Assuming that the bond distance is independent of isotopic substitution and rotation state, calculate the frequency of the next 4 lines seen in the spectrum (i.e., 2nd - 5th lines). To what transition does each correspond?

(Answer)

11. (+2 pt per correct answer; -1 pt per incorrect one; 0 pt per unanswered one) Determine whether the following statements are true or false.

(a) While the VB-VSEPR model fails to explain the magnetism of O_2 and N_2, it provides a description of the energy levels and associated orbitals for molecules.

(Answer)

(b) Rotational transitions do not accompany transitions in the vibrational and electronic degrees of freedom, since they are all independent.

(Answer)

(c) In the van der Waals equation of state, the "b" values correlate generally with the size of the molecules, and the magnitudes of the "a" closely parallel the boiling points.

(Answer)

(d) At a fixed temperature and pressure, CH_4 will have a higher most probable velocity than N_2.

(Answer)

(e) The energy of an ideal gas monatomic gas depends solely on the temperature.

(Answer)

(f) The VB model overemphasizes the ionic character of bonding.

(Answer)

(g) As the size of the conjugated molecules (the molecules with alternating double bonds) increases, the energy gap decreases.

(Answer)

(h) The rate of effusion of a gas is inversely proportional to the square root of its density.

(Answer)

(i) The most probable velocity for a gas at a fixed temperature is higher than the root mean square velocity.

(Answer)

(j) The bond order of nitric oxide (NO) is 2.

(Answer)