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

* Both equations/procedures and answers should be correct to get the point; otherwise, no point is given.

Double-check your calculations.

1. (2 pt each; 10 pt in total) 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 ($\rho = r/a_0$).

nodes and angular nodes for each of the form (a) $\Psi = (32\pi)^{-1/2} a_0^{-3/2} (2 - \rho) e^{-\rho/2}$ (b) $\Psi = (64\pi)^{-1/2} a_0^{-3/2} \rho e^{-\rho/2} \sin \theta e^{+i\phi}$ (c) $\Psi = 81^{-1} (3\pi)^{-1/2} a_0^{-3/2} (27 - 18\rho + 2\rho^2) e^{-\rho/3}$ (d) $\Psi = 81^{-1} (2/\pi)^{1/2} a_0^{-3/2} (6 - \rho) \rho e^{-\rho/3} \cos \theta$ (e) $\Psi = 81^{-1} (6\pi)^{-1/2} a_0^{-3/2} \rho^2 e^{-\rho/3} (3\cos^2\theta - 1)$

2. (+2 pt if correct; -1 pt if incorrect; 0 pt for no answer; 20 pt in total) Determine whether the following statements are true (T) or false (F).

(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.

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

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

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

(e) The boundary conditions yield quantum numbers.

(f) The transition elements of the 6th period (Hf-Hg) have somewhat higher first ionization energies than those of the 5th period, due to prior filling of the 4*f* orbitals, which are less effective at screening the outer electrons from the nuclear charge than d orbitals.

(g) There are 15 electron-electron repulsion potential energy terms in the Hamiltonian operator for the carbon atom.

(h) For the lithium atom, the principal quantum number completely defines the energy of a given electron.

(i) The 4th ionization energy of AI is much greater than the 3rd ionization energy.

(i) The ground state electronic configuration of Cu is $[Ar]4s^23d^9$.

3. (4 pt) Compute the de Broglie wavelength of a photoelectron, when cesium is irradiated by a photon with wavelength of 525 nm (the work function of metallic cesium: 3.43 X 10⁻¹⁹ J; the mass of electron: 9.11 X 10⁻³¹ kg; Planck constant: 6.626 X 10⁻³⁴ Js; speed of light: 2.998 X 10⁸ m/s).

4. (6 pt in total) Consider the one-electron species, H, He^+ , and Li^{2+} , in their ground states.

(a) (1 pt) Which one has the smallest radius?

(b) (3 pt) Compute the first ionization energy (IE) for each in J

 $[e^{2}/(2a_{0}) = 2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV}, a_{0}$ Bohr radius]

(c) (2 pt) Without attempting a detailed calculation, determine the lowest and highest first IE values possible for a ground-state helium atom in J.

5. (7 pt in total) According to the Hartree's orbital approximation, the total energy of the He atom is predicted to be the sum of the energies of the individual, screened electrons, $E_{He} = E_1 + E_2$, and, in accord of the Bohr model, the two 1s electrons contribute the identical energies. The total energy of hydrogen-like atom, He⁺ ion, is given by Bohr model.

(a) (2 pt) When $E_{He} = -77.5 \text{ eV}$, calculate Z_{eff} .

(b) (3 pt) Calculate the first IE of He.

(c) (2 pt) Predict the second IE of He.

6. (10 pt in total) In the 1D-particle-in-a-box problem, the energy of a particle is given by the formula, $E = n^2 h^2 / (8mL^2)$ [n = 1, 2, 3, ...; L: the length of the box].

(a) (3 pt) What is the energy of a particle, if we extend it to the 2D-particle-in-a-box problem? Each side of the 2D box has the length of L. Use the above equation, when you derive an energy formula (Note that the calculation of wavefunctions corresponding to the energy formula is not necessary). (b) (3 pt) Let's try to fill energy levels obtained in (a) with 4 electrons. Assume that though energy

levels are not altered by the repulsive potential between electrons, all the other properties of an electron (e.g., Pauli exclusion principle and Hund's rule) should be considered. Draw the ground state electronic configuration as shown in the following example.

Example) In the case of 1D with 4 electrons,

$$E_2 = \frac{h^2}{2mL^2}$$

$$E_1 = \frac{h^2}{8mL^2}$$

(c) (4 pt) What would be the lowest excitation energy in the case of (b)? Draw the electronic configuration of the excited states and calculate the excitation energy.

7. (3 pt) When you pass AI (Z = 13) atoms and Al¹²⁺ ion beams through the inhomogeneous magnetic field, respectively, as Stern and Gerlach did experiment in1926, predict which beam(s) will split?

8. (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.

9. (5 pt) Rewrite the equation below as an ionic equation and rationalize it in terms of electron transfer and Lewis (electron dot) structures. Indicate the electrophilic and nucleophilic center in the reactants. NaOH(aq) + Cl₂(g) \rightarrow HOCI(aq) + NaCI(aq)

10. (1 pt each; 4 pt in total) Determine the oxidation number of (a) C in $(COOH)_2$ (oxalic acid), (b) O in H_2O_2 , (c) Fe in Fe $(CN)_6^{3^2}$, (d) N in N_2H_4 (hydrazine)

11. (6 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.

 $(\text{COOH})_2(aq) + \text{KMnO}_4(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CO}_2(g) + \text{MnSO}_4(aq) + \text{H}_2\text{O}(l)$

12. (10 pt in total) When a gas-phase atom is irradiated with light of a sufficiently short wavelength, it will ionize. This is analogous to the photoelectric effect and is called photoionization. Einstein's photoelectric equation can be applied to the gas ionization, with the work function *W* replaced by the atom's IE.

(a) (3 pt) When Na vapor is irradiated by Lyman- α (λ = 121.568 nm), electrons of kinetic energy 5.060 eV are produced. Find the IE of Na in electron-volts.

(b) (2 pt) Na D-line consists of two closely spaced lines (a doublet) of λ_a =589.158 and λ_b =589.755 nm, assuming that the light absorptions are due to electronic transitions from the common 3s ground state (E₁) to two different 3*p* states (corresponding energies = E_a and E_b, respectively). Calculate the energy level spacings ($\Delta E_a = E_a - E_1$, and $\Delta E_b = E_b - E_1$) in electron-volts between the stationary states involved.

(c) (2 pt) Assuming that the IE you obtained in (a) was for the photoionization from the 3s state, find the energies of the two 3p states.

(d) (3 pt) Draw the energy-level diagram to include the ionization continuum above E = 0 and indicates the observed transitions by upward arrows.

13. (5 pt in total) Chlorine oxide (Cl_2O_7) reacts with water to produce perchloric acid, which is one of the strongest inorganic acids.

(a) (2 pt) Complete and balance the reaction.

(b) (3 pt) Draw the Lewis structures of chlorine oxide and perchloric acid.

14. (5 pt) Draw the Lewis electron-dot formula for the molecules N_2H_4 , N_2 , and N_2F_2 . Which molecule has the longest nitrogen-nitrogen bond?

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

1. (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

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

3. <u>2.6X10⁻⁹ m</u>

(a) E = h ν = $\frac{hc}{\lambda} = \frac{(6.626 X 10^{-34} J_{\rm S})(2.998 X 10^8 m s^{-1})}{525 X 10^{-9} m}$

= 3.78 X
$$10^{-19}$$
J
E = $\frac{1}{2}$ m v^2 = E - E₀ = (3.78-3.43) X 10^{-19} J = 3.5 X 10^{-20} J

$$\upsilon = \sqrt{\frac{2Ek}{m}} = \sqrt{\frac{2X3.5X10^{-20}kgm^2s^{-2}}{9.11X10^{-31}kg}} = 2.8X10^5 ms^{-1}$$

$$\lambda = \frac{h}{m\upsilon} = \frac{6.626 X 10^{-34}}{9.11 X 10^{-31} X 2.8 X 10^5} = 2.6 X 10^{-9} m$$

4. (a) Li²⁺

(a) In Li^{2^+} , three protons attract one electron. Li^{2^+} is the smallest atom of the three

(b) To ionize the atom, we must supply sufficient energy to promote the electron from n=1 to n= ∞

$$E_n = -\frac{e^2}{2a_0} \frac{Z^2}{n^2} = -(2.18 \times 10^{-18} J) \frac{Z^2}{n^2}$$

The ionization energy is therefore

 $E_{\infty} - E_1 = -(2.18 \times 10^{-18} J) Z^2 (\frac{1}{\infty^2} - \frac{1}{1^2})$ $= 2.18 \times 10^{-18} J (Z^2)$ H (Z=1) : 2.18 X 10⁻¹⁸ J He^+ (Z=2) : 4 X 2.18 X 10^{-18} J = 8.72 X 10^{-18} J Li^{2+} (Z=3) : 9 X 2.18 X 10⁻¹⁸ J = 1.96 X 10⁻¹⁷ J (C) Helium has two $1s^2$ electrons, attracted to a nucleus containing two protons (Z=2) Competing for the same nuclear charge, the electrons screen one another. Lower limit : Each 1s electron screens the other completely. Effective nuclear change Z_{eff} =2-1=1 Upper limit : No screening at all. Each electron interacts with the full nuclear change so are to make Zeff=2 Heliums' first ionization energy thus falls between 2.18 x 10^{-18} J x (1^2) and 2.18 x 10^{-18} J x (2^2) lower limit : 2.18 X 10⁻¹⁸ J upper limit : 8.72 X 10⁻¹⁸ J **5.** (a) $Z_{eff} = (77.5/2x13.6)^{1/2} = 1.69$ (b) $E[He^+] = -13.6 \cdot Z^2/n^2$ (eV)= $-13.6 \cdot x 2^2/1^2 = -54.4$ eV First IE = E(He+) - E(He) = -54.4 - (-77.5) = 23.1 eV(c) Total Energy = first IE + 2nd IE

 2^{nd} IE = 77.5 - 23.1 = **54.4 eV**

6. (a) Hamiltonian for a particle in the 2D box can exactly be decomposed by two independent Hamiltonian for the corresponding 1D problem: $H = H_1 + H_2$. Therefore, the energy of a particle in 2D is simply the sum of energies for the H_1 and H_2 . Consequently,

$$E_{n_1,n_2} = \frac{h^2}{8mL^2} (n_1^2 + n_2^2)$$
, where n₁ = 1, 2, 3, ... and n₂ = 1, 2, 3,

(b)





Excitation energy = $E_{2,1}$ (or $E_{1,2}$) – $E_{1,1} = (3h^2)/(8mL^2)$

7. <u>Both</u>

AI $\overline{(Z=13, [Ne]3s^23p^1)}$ atom and Al⁺¹² (1s¹)

8. HF + H₂O \rightarrow H₃O⁺ + F⁻ (Favored) HF + H₂O \rightarrow H₂F⁺ + 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.

9.

(ii) $OH^{-}(aq) + Cl_{2}(g) \longrightarrow HOCl(aq) + Cl^{-}(aq)$

Nucleophile Electrophile

11. 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): $5(COOH)_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(I)$

12. (a) The rounding is accepted.

$$IE = \frac{hc}{\lambda} - K$$

= $\frac{1239.842 \text{ eV nm}}{121.568 \text{ nm}} - 5.060 \text{ eV}$
= $10.199 - 5.060 = 5.139 \text{ eV}$
and $E_1 = -IE = -5.139 \text{ eV}$.

(b)

$$E(eV) = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(2.998 \times 10^8 \text{ m/s})}{(1.602 \times 10^{-19} \text{ J/eV})(10^{-9} \text{ m/nm}) \lambda(\text{nm})}$$
$$= \frac{1240 \text{ eV nm}}{\lambda(\text{nm})}$$
By this formula, we can obtain

 $\Delta E_a = 2.10470 \text{ eV}$ $\Delta E_b = 2.10257 \text{ eV}$

(c) The energies of the upper pair of states may then be obtained by adding the ΔE of (b) to E1, yielding E2 = -5.139 + 2.102 = -3.037 eV and likewise E3 = -3.035 eV



13. $CI_2O_7 + H_2O \rightarrow 2HCIO_4$ Cl_2O_7

















14.

Lewis formulas



The nitrogen-nitrogen bond should be the longest in, N_2H_4 , where it is a single bond

(d)

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

Both equations/procedures and answers should be correct to get the point; otherwise, no point is given. Double-check your calculations.

Date: May 25 (Wed), 2011, 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	6	/10	
2-1	/5	7	/12	
2-2	/5	8	/10	
3	/4	9	/15	/100
4	/10	10	/15	/100
5	/4			

** This paper consists of 10 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. *Page 9: A CLAIM FORM is attached on last page for claims on the marked exam paper later*) Page10: Periodic Table

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 31 (Tue, 11:00 a.m. ~ 13:00 p.m.)
- 2) Location: Room assigned to each class below

Class	Room (E11)	Class	Room (E11)
A	401	F	406
В	402	G	407
С	403	Н	408
D	404	Ι	409
E	405	J	410

3) Claim Procedure:

(During the period, you can take the marked exam paper from your TA and should hand in a FORM for claims if you have any claims on it.)

To get more information and the procedure, visit the website at <u>www.gencheminkaist.pe.kr</u>.

- 2. Final Confirmation
 - 1) Period: June 2 (Thu)

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

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



(b) NO_2 : sp² (1 pt); NO_3 : sp²(1 pt)

(c) NO₂: bent (1 pt) (The center N atom has one lone pair and two O atoms (steric number SN=3).

NO₃⁻: trigonal planar (1 pt) (The center N atom has 3 atoms (steric number SN=3).

(d) NO₂: yes ($\mu \neq 0$) (1 pt); NO₃: no ($\mu = 0$) (1 pt)

(e) NO_2^- (2 pts) (bond order of NO_2^- =1.5; bond order of NO_3^- =1(1/3). As the bond order increases, the force constant increases)

2-1. (a) A (3 pts)

Reduced mass: $\mu(\mathbf{A})(35/36=0.9722) < \mu(\mathbf{B})(70/37=1.892)$ Spectral line spacing = 2B; B ~ 1/I ~ 1/ μ (b) **A** (2 pts) $\nu = (1/2\pi)(k/\mu)^{1/2}$, $\nu ~ (1/\mu)^{1/2}$

2-2. (a) $O_2^{-}: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^3 (1 \text{ pt})$ $O_2: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^2 (1 \text{ pt})$ $O_2^{+}: (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi_{2p}^*)^1 (1 \text{ pt})$ (b) $O_2^{+} (O_2^{+} \text{ has stronger bond than } O_2 \text{ and than } O_2^{-}) (2 \text{ pts})$

3. (a) SO₂: bent(1 pt); CO₂: linear(1 pt) (b) paramagnetic $[(\sigma_{2s})^2(\sigma_{2p})^2(n\pi_{2p})^1]$ (2 pts)

4. (a) (8 pts)



(b) Diamagnetic (2 pts)

5. Bond order: 3, $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p})^2$ (2 pts) ; diamagnetic (2 pts)

6. (a) (4 pts)1903 N/m μ (¹²CO) = 1.139 x 10-26 kg $k = 4\pi^2 \mu c^2 \overline{\nu}^2$ (b) (6 pts)2122 cm⁻¹

$$\frac{\overline{v}_1}{\overline{v}_2} = \sqrt{\frac{\mu_2}{\mu_1}}$$

7. (a) Acrylonitrile: sp^2 , sp^2 , and sp from the left to right carbons (3 pts) Methyl methacrylate: sp^2 , sp^2 , sp^3 , sp^2 , and sp^3 from the left to right carbons(3 pts) (b) Acrylonitrile: σ bonds = 6, π bonds = 3(3 pts) Methyl methacrylate: σ bonds = 14, π bonds = 2(3 pts)

8. (a) T (b) T (c) T (d) F (e) F



Additional answers: Lewis structures that satisfy the octet rule and have correct geometry for (a) and (c).

10. (a) $(\sigma_{3s})^2(\sigma_{3p})^2(n_{3p})^4$ or $(n_{3s})^2(\sigma_{3p})^2(n_{3p})^4$ (**10 pts) additional answers:** $(n_{3s})^2(\sigma_{3p})^2(n_{\pi_{3p}})^4$ (b) HOMO of the SH⁻ ion; n_{3p} or $n_{\pi_{3p}}$ (**5pts**) Refer to Figure 7.13 in the textbook; replace F, 2s, 2p with S, 3s, 3p in the MO diagram of HF.

- 1. (2 pt each; 10 pt in total) Consider the two ions, NO₂⁻ and NO₃⁻.
- (a) Draw the Lewis electron-dot structures of these ions. (Answer)

(b) What type of hybridization do you expect for the center N atom of these ions? (Answer)

(c) Based on the VSEPR model, expect the geometry of these ions. (Answer)

(d) Tell whether these ions can show pure rotational microwave spectra (Answer)

(e) Which ion has the higher force constant of the N-O bond? (Answer)

- **2-1.** (5 pt in total) Consider the isotopes of ${}^{1}H^{35}CI$ (**A**) and ${}^{2}H^{35}CI$ (**B**)
- (a) (3 pt) Which isotope has larger spacing between spectral lines observed in the microwave spectra? (Answer)

(b) (2 pt) Which isotope has higher vibrational frequency? (Answer)

2-2. (5 pt in total) (a) (3 pt) Write the molecular electronic configuration for O_2^- , O_2 , and O_2^+ . (Answer)

(b) (2 pt) Which one would show the highest oxygen-oxygen stretching vibrational frequency? (Answer)

3. (2 pt each; 4 pt in total)

(a) Predict the geometries of SO_2 and CO_2 using the VSEPR model. (Answer)

(b) Predict the magnetic property of the CH radical. (Answer)

4. (10 pt in total) Consider the allyl cation, $CH_2CHCH_2^+$.

Assumptions:

(a) The eight atoms lie in a single plane.

(b) The bond angles of H-C-H and C-C-C are all nearly 120° .

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

(a) (8 pt) Construct the molecular orbital form of the 2p atomic orbitals perpendicular to the plane of the carbon atoms.

(Answer)

(b) (2 pt) Indicate whether the ion is paramagnetic or diamagnetic.

(Answer)

5. (4 pt) Acetylene (C_2H_2) can be produced from the reaction of calcium carbide (CaC_2) with water. Use the MO theory to describe the bond order (2 pt) and magnetic property (2 pt) of the acetylide anion (C_2^{-2}).

6. (10 pt in total) The IR spectrum of ¹²CO shows a vibrational absorption peak at 2170 cm⁻¹.

(a) (4 pt) What is the force constant (unit: N/m) for the CO bond? (Answer)

(b) (6 pt) At what wavenumber would the corresponding peak for ¹³CO occur? Assuming both force constants of ¹²CO and ¹³CO are the same. [¹²C: 12 amu; ¹³C: 13 amu; O: 16 amu; $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$; speed of light = 2.998 x 10⁸ m/s; 1 N = 1 kg m/s²]

(Answer)

7. (12 pt in total) Many important compounds in the chemical industry are derivatives of ethylene (C_2H_4). Two of them are acrylonitrile ($CH_2=CH-CN$) and methyl methacrylate ($CH_2=C(CH_3)-COOCH_3$).

 $\begin{array}{c} & \circ \\ {}_{H_2C=} c - \overset{||}{C} - och_3 \\ {}_{CH_3} \end{array}$

(a) (3 pt each) Give the hybridization of all carbon atoms for the two molecules. (Answer)

(b) (3 pt each) How many σ bonds and how many π bonds are there in acrylonitrile and methyl methacrylate? (Answer)

8. (2 pt for each correct answer; -1 pt for each incorrect answer; 0 pt for no answer) Determine whether the following statements are true (T) or false (F).

(a) 1,2,3-butatriene $[CH_2=C=C=CH_2]$ is a planar molecule with sp and sp² hybridized carbon atoms. (Answer)

(b) Addition of an electron to C_2 leads to increased stability (higher bond energy), according to the LCAO-MO theory.

(Answer)

(c) The ion HHe⁻ has a bond order of zero, according to the LCAO-MO theory and hence should be unstable. (Answer)

(d) A "C-D bond" (D= deuterium, ²H) will stretch at a higher wavenumber than a corresponding C-H bond. (Answer)

(e) The vibrational energy of the vibrational ground state is zero. (\mbox{Answer})

9. (5 pt each; 15 pt in total) Write the Lewis structure and predict the shape of (a) SO_2Cl_2 , (b) $OCCl_2$, (c) IO_2F_2 . The atom in boldface type is the central atom. [structure: 3 pt; shape: 2 pt]

10. (15 pt in total) Consider the SH⁻ ion having 8 valence electrons (S: $3s^23p^4$, H: $1s^1$)

(a) (10 pt) Write the electronic configuration for the ground state SH^{-} ion. (Answer)

(b) (5 pt) Identify the frontier orbital(s) of SH⁻ involved in the simplest form of the Arrehnius acid-base reaction, $H^+ + SH^- \rightarrow H_2S$.

(Answer)