2008 SPRING Semester Mid-term Examination
For General Chemistry I

Time Limit: 7:00 ~ 9:00 p.m.

Professor Name	Class	Student Number	Name

Problem No.	Scores (points)	Problem No.	Scores (points)	TOTAL
1	/12	**5**	/10	
2	/10	**6**	/15	
3	/10	**7**	/10	
4	/15	**8**	/8	**/100**
		9	/10	

** This paper consists of 12 sheets with 9 problems. Please check all page numbers before taking the exam.

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NOTICE: SCHEDULES on DISTRIBUTION and CORRECTION of Mid-term PAPER SCORED.
(채점답안지 분배 및 정정 일정)

 1. Period, and Procedure

   1) Distribution and Correction Period: *April 7 (Monday), Practice Hours; 7: 00 ~ 9:45*

   2) Procedure: During the practice hours, 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 to your mid-term paper scored (Please, write your name, professor, and class.). Submit them to your TA. The papers with the claims will be re-examined by TA.

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

2. Final Confirmation

   1) Period: April 14 (Monday)-April 15 (Tuesday), 2 days

   2) Procedure: During the period, you can check your score of the mid-term examination *on the website* again.

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

[1] (12 pts) Complete and balance the following reactions. Then, classify each of the following reactions as either acid-base reaction or reduction-oxidation reaction. In the case of reduction-oxidation reaction, specify which species is reduced and which species is oxidized. In the case of acid-base reaction, specify which species is acid and which species is base. Also specify whether it is Arrhenius acid and base, Bronsted-Lowry acid and base, or Lewis acid and base (Please provide the most specific (narrowest) definition. For example, for the reaction $OH^- + H^+ \rightarrow H_2O$, H^+ can be considered as Arrhenius acid, but also as Bronsted-Lowry acid and Lewis acid. However the most specific definition is Arrhenius acid.) Each problem is given 3 pts; 1 pt for correct balancing, 1 pt for correct classification, and 1 pt for correct indication of reduced and oxidized species or acid and base.

(a) $SO_2(g) + O_2(g) \rightarrow SO_3(g)$

Answer)

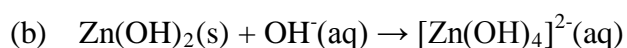(a) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
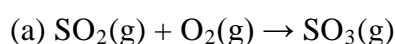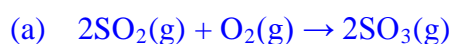
redox process

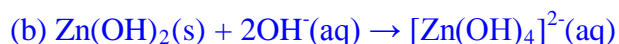Oxygen gains electrons (reduction: oxidation state of oxygen $0 \rightarrow -2$)

Sulfur is oxidized (oxidation from S^{4+} to S^{6+} in SO_3)

Sulfur supplies the electrons.

O_2 is reduced and SO_2 is oxidized.

(b) $Zn(OH)_2(s) + OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$

Answer)

(b) $Zn(OH)_2(s) + 2OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$
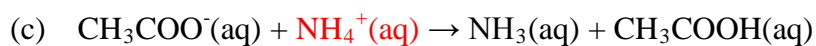
acid-base reaction

There is no change of oxidation number.

$Zn(OH)_2$ is dissolved in basic solution, and gives complex anion $[Zn(OH)_4]^{2-}$.

Zn^{2+} ion or $Zn(OH)_2$: (Lewis) acid (takes a pair of electrons)

OH^- ion : (Lewis) base (gives a pair of electrons)

(c) $CH_3COO^-(aq) + NH_4^+(aq) \rightarrow NH_3(aq) + CH_3COOH(aq)$

Answer)

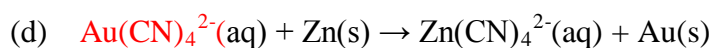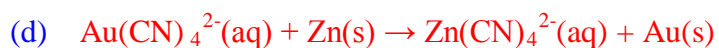(c) $CH_3COO^-(aq) + NH_4^+(aq) \rightarrow NH_3(aq) + CH_3COOH(aq)$
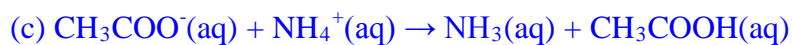
acid-base reaction

There is no change of oxidation number.

NH^{4+} (Bronsted-Lowry acid) gives a proton to electron-rich CH_3COO^- anion and CH_3COO^- (Bronsted-Lowry base) receives the proton.

(d) $Au(CN)_4^{2-}(aq) + Zn(s) \rightarrow Zn(CN)_4^{2-}(aq) + Au(s)$

Answer)

(d) $Au(CN)_4^{2-}(aq) + Zn(s) \rightarrow Zn(CN)_4^{2-}(aq) + Au(s)$

redox reaction

$Zn : Zn^0 \rightarrow Zn^{2+}$ (gives the electrons), Zn is oxidized.

$Au : Au^{2+} \rightarrow Au^0$ (takes the electrons), Au or $Au(CN)_4^{2-}(aq)$ is reduced.

[2] (10 pts) Consider the formation of an ionic molecule, AB, by the donation of an electron from atom A to atom B. The ionization energy (IE) of A is 5.5 eV and the electron affinity (EA) of B is 1.5 eV. If A and B is brought together and the distance between A and B is reduced from infinity, the electron from A will be transferred to B at a certain distance to form ionic bonding character between A^+ and B^-. Calculate this electron-transfer distance (8 pts). 2 pts will be given for correct concept (writing down a correct equation). 4 pts will be given for correct values in the equation. 2 pts will be given to a final correct numerical value. At this specific distance (electron-transfer distance), if the ion B^- has a radius of 0.20 nm, what is the radius of A^+ (2 pts)?

(Hint: electron-proton potential energy is expressed $V(eV) = 14.4q_1q_2/r(Å)$ where the charge are expressed in units of e.)

Answer)

When A ionizes to A^+, it absorbs 5.5 eV of energy. When B accepts an electron to form B^-, it gives up 1.5 eV of energy. Hence, a total energy of V (eV) = 5.5 eV - 1.5 eV = 4.0 eV goes into the formation of the AB ionic bond.

$$14.4(eV)\frac{e^2}{r} = 4.0\,eV \qquad\qquad 14.4\frac{(1)^2}{r} = 4.0$$

$$r = \frac{14.4}{4.0}\,(\text{Å})$$

$$= 3.6\,\text{Å} = 0.36\,nm$$

Hence, the nucleus of A is separated from the nucleus of B by 0.36 nm.

The maximum radius of A^+ is 0.36 nm - 0.20 nm = **0.16 nm**

[3] (10 pts)

(6 pts) Arrange the following elements in order of increasing ionization energy. Atomic number is given in the parenthesis. You only have to write down the final answer. No explanation is necessary. A correct answer will get a full credit, and an incorrect answer will get zero points.

a) (2 pts) F (9)   Ba (56)   Ga (31)   Ne (10)   S (16)

   Answer) Ba<Ga<S<F<Ne

b) (2 pts) Te (52)   I (53)   Br (35)   Cl (17)   Ar (18)

   Answer) Te<I<Br<Cl<Ar

c) (2 pts) N (7)   Si (14)   Al (13)   Mg (12)   Cs (55)

   Answer) Cs<Al<Mg<Si<N

(4 pts) Which one of the following pairs of atoms has the higher IE? Atomic number is given in the parenthesis. You only have to write down the final answer. No explanation is necessary. A correct answer will get a full credit, and an incorrect answer will get zero point.

d) (1 pt) Hg (80)   Cd (48)

   Answer)   Hg

e) (1 pt) Cu (29)   Zn (30)

   Answer) Zn

f) (1 pt) P (15)   S (16)

   Answer) P

g) (1 pt) Ga (31)   Ca (20)

   Answer) Ca

[4] (15 pts)

(a) (3 pts) Suggest the electron configuration of Cu atom (Z = 29) (For Li, the electron configuration is $1s^2 2s^1$). Please note that this belongs to Anomalous Configurations. A correct answer considering anomalous scattering will get 3 pts. An answer without this consideration will get 1 pt. You only have to write down the final answer. No explanation is necessary.

Answer)

(a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$ or [Ar] $4s^1\ 3d^{10}$

(b) (3 pts) A copper species in oxidation state of +1 (e.g. CuI) shows the diamagnetic property that does not react with an external magnetic field. Based on this observation, please provide the electron configuration of Cu^+ ion. A correct answer will get 3 pts, and incorrect answers will basically get zero point. You only have to write down the final answer. No explanation is necessary.

Answer)

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ or [Ar] $3d^{10}$

(c) (4 pts) If electron spin can have 3 values of +1/2, 0, and -1/2 instead of the usual 2 values of +1/2 and -1/2, what will be the electron configuration of the Cu atom? Please assume that the Pauli exclusion principle and the Aufbau principle are still valid and the ordering of the orbitals are the same (in other words, 1s < 2s < 2p < 3s and so on). You only have to write down the final answer. No explanation is necessary. A correct answer will get 4 pts, and incorrect answers will basically get zero point.

Answer)

Now an orbital can hold up to 3 electrons instead of 2, so **$1s^3\ 2s^3\ 2p^9\ 3s^3\ 3p^9\ 4s^2$**

(d) (5 pts) If you write down the Hamiltonian for the Cu atom, how many kinetic energy terms does the Hamiltonian have (1 pt)? How many electron-nucleus attraction terms does the Hamiltonian have (1 pt)? How many electron-electron repulsion terms does the Hamiltonian have (1 pt)? Write down the electron-nucleus attraction term for the first electron of the Cu atom (1 pt) (hint: The electron-nucleus attraction term for the first electron of He is $-2e^2/r_1$). Write down the electron-electron repulsion term between the first and second electrons for the Cu atom (1 pt) (hint: The electron-electron repulsion term between the first and second electrons for the He atom is $+e^2/r_{12}$.). You only have to write down the final answer. No explanation is necessary.

Answer)

(d) Z=29. So 29 electrons around a nucleus of +29e charge. The Hamiltonian contains 29 kinetic terms, 29 electron-nucleus attraction terms, and 406 (=29x28/2) electron-electron repulsion terms. The electron-nucleus attraction term for the first electron is $-29e^2/r_1$ and the electron-electron repulsion term for the first electron is $+e^2/r_{12}$.

[5] (10 pts)

a) (2.5 pts) A 10-kg watermelon is packed in a crate so that it can shift its position by only 1cm in any direction. Estimate the uncertainty in the watermelon's momentum in a given direction. 2.5 pts will be given to a correct answer. 1.5 pts will be given to a correct equation and the other 1 pt will be given to a correct final numerical value. [Plank's constant h = 6.6261 x 10^{-34} J s]

   Answer)

$$\Delta p_x = \frac{h}{4\pi\Delta x} = \frac{6.63 \times 10^{-34} kg\, m^2/s}{4\pi(0.01m)} = 5.3 \times 10^{-33} kg\, m/s$$

b) (2.5 pts) Estimate its zero point kinetic energy in the case of a). 1.5 pts will be given to a correct equation and the other 1 pt will be given to a correct final numerical value.

   Answer)

$$K \approx \frac{(\Delta p_x)^2}{2m} = \frac{(5.3 \times 10^{-33} kg\, m/s)^2}{2(10kg)} = 1.4 \times 10^{-66} j$$

c) (2.5 pts) Repeat the calculation for a beryllium atom (atomic mass = 9) packed in a beryllium metal crystal, where the constraint on motion is 0.05 Å. Estimate the uncertainty in the beryllium's momentum in a given direction. 1.5 pts will be given to a correct equation and the other 1 pt will be given to a correct final numerical value.

   Answer)

$$\Delta p_x = 1 \times 10^{-23} kg\, m/s$$

d) (2.5 pts) Estimate its zero point kinetic energy in the case of c). 1.5 pts will be given to a correct equation and the other 1 pt will be given to a correct final numerical value.
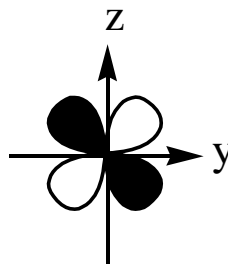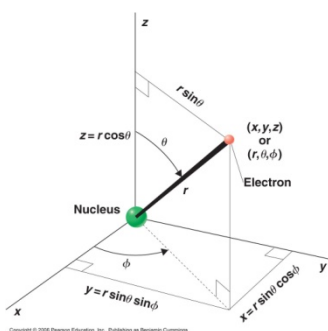
   Answer)

$$K \approx 4 \times 10^{-21} j$$

[6] (15 pts)

(a) (5 pts) Let's recall the shape of p_x orbital whose angular part is $\sin\theta\cos\varphi$. By taking this statement as a hint, please sketch the shape of the orbital $Y_{lm} \sim \sin\theta\cos\theta\sin\varphi$ in case of $\varphi = 90°$. In your sketch, please clearly specify the axes and the signs.

  Answer)

(a) From the spherical polar coordinates in relation to Cartesian coordinates shown below, the given orbital $Y_{lm} \sim \sin\theta\cos\theta\sin\varphi$ has y and z components. At $\varphi = 90°$, the function of $\sin\theta\cos\theta$ should be drawn to know that when θ varies from $0°$ to $360°$, the sign of $\sin\theta\cos\theta$ varies from $+$ to $-$ to $+$ to $-$ at every $90°$ intervals, giving rise to shape shown below right. Open and filled lobes denote $+$ and $-$, respectively.

(b) (5 pts) What is the total number of nodes contained within each orbital in the fifth shell (n = 5)? You have to consider all possible orbital with n = 5. How many are angular nodes, and how many are radial nodes?

  Answer)

(b) The total number of nodes is n-1, and the number of angular nodes is l.

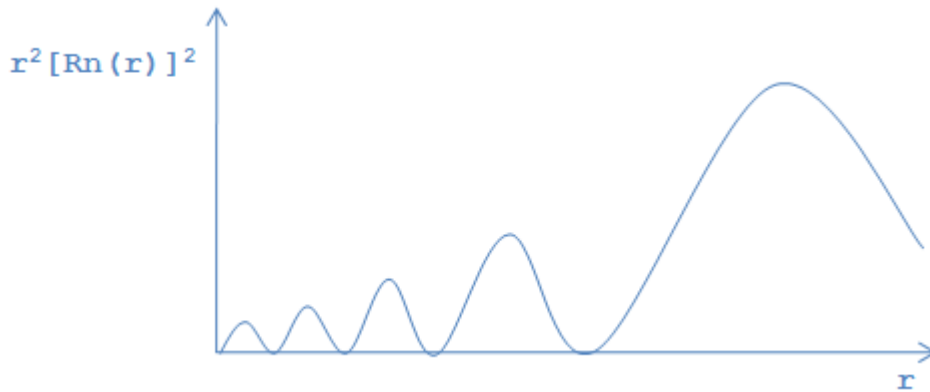| Orbital	n	l	Angular Nodes	Radial Nodes	Total
5s	5	0	0	4	4
5p	5	1	1	3	4
5d	5	2	2	2	4
5f	5	3	3	1	4
5g	5	4	4	0	4

Each orbital in the fifth shell contains four nodes, split between angular and radial.

(c) (5 pts) Draw the radial distribution function of 5s over the distance.

Answer)

[7] (10 pts) Modern lasers are such intense light sources that some of the "rules of the game" in the photoelectric effect now have been revised. For example, when light from a focused, high-power carbon dioxide laser, which emits infrared light of wavelength 21 μm, strikes a metal surface with a work function of a few electron-volts, electrons are in fact ejected. This phenomenon is a multiphoton absorption effect; so many photons impinge on the surface in such a short time that a single electron can collide with and absorb the energy of several photons. How many CO_2 laser photons must an electron absorb to be emitted from a surface of work function 5.7eV? 5 pts will be given to a correct equation and the other 5 pts will be given to a correct final numerical value. [Plank's constant h = 6.6261 x 10^{-34} J s, speed of light c = 2.9979 x 10^{8} m s^{-1}]

Answer)

$$n = W\frac{\lambda}{hc} = (5.7eV)\frac{21 \times 10^3 nm}{1240e\,Vnm} = 96.5$$

The number of photons : 97

[8] (8 pts) Let' assume we carried out a photoelectron experiment, in which a photoelectron spectrum for Ne(neon) excited by X-rays with wavelength of 9.890 x 10^{-11} m was obtained. The spectrum showed three peaks with kinetic energy of 383.4 eV, 1205.2 eV, and 1232.0 eV, respectively.

[Plank's constant h = 6.6261 x 10^{-34} J s, speed of light c = 2.9979 x 10^{8} m s^{-1}, converting factor for 1 eV = 1.6022 x 10^{-19} J]

(a) (2 pts) Calculate the energy of the incident photon in eV. 2 pts will be given to a correct final numerical answer. Only 0.5 pts for each will be given if the final numerical value is wrong.

   Answer)

   (a) ε_{photon} = hc/λ = [(6.6261 x 10^{-34} J s)(2.9979 x 10^{8} ms^{-1})] / (0.9890 x 10^{-10} m)(1.6022 x 10^{-19} J eV^{-1})]

= **12536.09 eV**

(b) (3 pts) Calculate each BE (binding energy) for the individual value of three peaks. 1 pts will be given to a correct final numerical answer for each. Only 0.5 pts for each will be given if the final numerical value is wrong.

   Answer)

(b) Becasue BE = $h\nu_{photon}$ - (1/2)$m_e v^2_{electron}$

Therefore,BE for 383.4 eV --> **12152.69 eV**

BE for 1205.2 eV --> **11330.89 eV**

BE for 1232.0 eV --> **11304.09 eV**

(c) (3 pts) Provide the name of each orbital which corresponds to the obtained values (from (b)) of the binding energy level. 1 pts will be given to a correct final numerical answer for each, and incorrect answers will get zero point.

   Answer)

   (c)

BE **12152.69** eV --> **1s orbital**

BE **11330.89** eV --> **2s orbital**

BE **11304.09** eV --> **2p orbital**

[9] (10 pts; 1 pt each) Classify each of the following statements as 'True' or 'False' and correct any 'False' statement to 'True' statement. Answers without proper explanation will get zero point even if you guessed True or False correctly.

(a) The wave number of the electromagnetic radiation <u>increases</u> in the order of γ-rays < X-rays < Ultraviolet < Visible light < Infrared < Radio < Microwave.

Answer)

False: $E = h\nu = hc/\lambda$ Thus, the wave number = $1/\lambda$ is proportional to energy and decreases as the energy of the electromagnetic radiation decreases. Thus, the sign of inequality should be changed along with the correction in the order of energy for Radio and Microwave. The corrected statement would be "The wave number of the electromagnetic radiation decreases in the order of γ-rays > X-rays > Ultraviolet > Visible light > Infrared > Microwave > Radio."

(b) Planck's interpretation of the blackbody radiation spectra includes the concept of energy quanta and particle nature of light.

Answer)

False: Planck's interpretation does not require the concept of particle nature of light. The corrected statement would be "Planck's interpretation of the blackbody radiation spectra includes the concept of energy quanta."

(c) The ionization energy of Li^{2+} in the ground state is 3 times greater than that of H in the ground state.

Answer)

False: Since the energy for the hydrogen-like species is $E_n \propto -Z^2/n^2$, $Z(Li^{2+}) = 3$, and $Z(H) = 1$. For the ground state, $n = 1$. The corrected statement would be "The ionization energy of Li^{2+} in the ground state is nine times greater than that of H in the ground state."

(d) The uncertainty in momentum of an electron in hydrogen <u>cannot be greater</u> than its momentum.

Answer)

False: Depending on the intended Δr and the total energy, Δp can be greater than p. The corrected statement would be "The uncertainty in momentum of an electron in hydrogen can be greater than its momentum."

(e) The energy and the shape of hydrogen orbital are governed by only the quantum numbers n and l, respectively.

Answer)

False: The magnetic quantum number also dictates the shape. The corrected statement would be "The

energy of hydrogen orbital is governed by the quantum numbers n while the shape of the orbital is dictated by l and m."

(f) The occurrence of a closely spaced doublet Na D-line is solely due to the electron spins.

Answer)

False: The screening effect that removes the energy degeneracy of $3s$ and $3p$, should be included. The corrected statement would be "The occurrence of a closely spaced doublet Na D-line is due to the screening effect and the electron spins

(g) The <u>increasing</u> order of the atomic number for the second period is Li-B-Be-C-N-O-F-Ar.

Answer)

False: The order of B and Be should be changed. And Ar belongs to the third period. The corrected statement would be "The increasing order of the atomic number for the second period is Li-Be-B-C-N-O-F.

(h) Helium that has the electron configuration of $1s^1 2s^1$ in its first excited state can have four possible wave functions.

Answer)

True: $1s^1 2s^1$ can have four $(n, l, m, m_s)(n, l, m, m_s)$ combinations: $(1,0,0,\frac{1}{2})(2,0,0,\frac{1}{2})$, $(1,0,0,\frac{1}{2})(2,0,0,-\frac{1}{2})$, $(1,0,0,-\frac{1}{2})(2,0,0,\frac{1}{2})$, and $(1,0,0,-\frac{1}{2})(2,0,0,-\frac{1}{2})$.

(i) For NaX (X = Cl, Br, I), the separation distance at which Na + X becomes $Na^+ + X^-$ <u>increases</u> in the order of Cl < Br < I and the bond energy <u>decreases</u> in the order of Cl > Br > I.

Answer)

False: The electron-transfer distance r_x is given by $e^2/r_x = [IE(Na) - EA(X)]$ and the bond energy by $D_e \sim e^2/r_e - [IE(Na) - EA(X)]$. Since EA decrease in the order of Cl > Br > I, both r_x and D_e decrease in the same order. The corrected statement would be "For NaX (X = Cl, Br, I), the separation distance at which Na + X becomes $Na^+ + X^-$ decreases in the order of Cl > Br > I and the bond energy also decreases in the order of Cl > Br > I."

(j) The reaction $Tl^{2+} + Tl^{2+} \rightarrow Tl^{1+} + Tl^{3+}$ is an example of disproportionation.

Answer)

True: Disproportionation is defined by a reaction where a substance reacts with itself. Thus, the statement is true. The given reaction is a redox reaction as well.

2008 SPRING Semester Final Examination
For General Chemistry I

Time Limit: 7:00 ~ 9:00 p.m.

Professor Name	Class	Student Number	Name

Problem No.	points	Problem No.	points	TOTAL pts
1	/15	**5**	/15	
2	/10	**6**	/10	
3	/15	**7**	/20	**/120**
4	/15	**8**	/20	

** This paper consists of 10 sheets with 8 problems. Please check all page numbers before taking the exam.

NOTICE: SCHEDULES on DISTRIBUTION and CORRECTION of the FINAL EXAM PAPER SCORED.
(채점답안지 분배 및 정정 일정)

  1. Period, Location, and Procedure

   1)   Distribution and Correction Period: *May 31 (Sat), time; 10:00 ~ 12:00*

   2) *Location : Creative Learning Bldg.(E11):   Class A&B-Room 101, Class C&D-Room 102*

   3) Procedure: During the period, you can take your final exam 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 to the paper scored (Please, write your name, professor, and class.). Submit them to the TA. The papers with the claims will be re-examined by TA.

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

2. Final Confirmation

   1) Period: June 3 (Tue), 9:00 – 24:00

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

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

[1] (15 pts) Consider triiodide ion I_3^-. The atomic number of I is 53.

(a) (2 pts) How many lone electron pairs does the central iodine atom have (2 pts for a correct answer and otherwise 0 pt)?

Answer)

3 lone pairs.

(b) (3 pts) What is the vibrational degree of freedom of this molecule (3 pts for a correct answer and otherwise zero pts)?

Answer)

The molecule is **linear**. Therefore the vibrational degree of freedom = 3N-5 = 3*3-5 = **4**.

(c) (3 pts) How many π bonds and σ bonds does this molecule have (3 pts if both answers are correct and otherwise zero pts)?

Answer)

zero π bonds and **two σ** bonds.

(d) (3 pts) Would this molecule show pure rotational spectrum or not (3 pt for a correct answer with a correct reason and otherwise 0 pt)?

Answer)

Due to the **zero dipole moment**, **no pure rotational spectrum**

(e) (4 pts) Write valence bond wave function for the I-I bond. Consider the hybridized orbital of the central atom (1 pts for a correct hybridization of the central atom, 1 pts for the correct orbital for the other atom, and 2 pts for a correct form of the wave function).

Answer)

$\Psi_{I-I} = (1/\sqrt{2})[dsp^3(\mathbf{r}_1)5p(\mathbf{r}_2) + dsp^3(\mathbf{r}_2)5p(\mathbf{r}_1)]$

[2] (10 pts) Consider HCl, HBr, and HI. Atomic numbers of H, Cl, Br, and I are 1, 17, 35, and 53, respectively.

(a) (2 pts) Among HCl, HBr, and HI, which one have the shortest rotational period (2 pts for a correct answer with a correct reason and otherwise 0 pt even if your answer is correct)?

Answer)

HCl has the **largest moment of inertia**. Therefore its rotational period is shortest.

(b) (2 pts) Among HCl, HBr, and HI, which one would show the smallest number of peaks in the wavenumber range from 0 to 200 cm^{-1} (2 pts for a correct answer with a correct reason and otherwise 0 pt even if your answer is correct).

Answer)

HCl has the **smallest moment of inertia** and therefore the **largest B**. Therefore the spacing would be larger and the number of peaks is the smallest.

(c) (3 pts) Among HCl, HBr, and HI, which one has the smallest constant a in the Van der Waals equation of state ($(P + \frac{n^2 a}{V^2})(V - nb) = nRT$) (2 pts for a correct answer with a correct reason and otherwise 0 pt even if your answer is correct)? (Hint: consider electronegativity). Express the unit of a in terms of L, atm, K, and mol (1 pt).

Answer)

The constant a increases with the increasing intermolecular attraction. Since **HCl** is the least polarizable and thus has the **weakest intermolecular attraction**. Therefore, HCl has the smallest a. a(n/V)2 has the unit of atm. Therefore the unit of a should be **atm L^2 / mol^2**.

(d) (3 pts) Among HCl, HBr, and HI, which one has the largest constant b in the Van der Waals equation of state (2 pts for a correct answer with a correct reason and otherwise 0 pt even if your answer is correct)? Express the unit of b in terms of L, atm, K, and mol (1 pt).

Answer)

The constant b is proportional to the **size of the molecule**. Therefore **HI** has the largest b. nb has the unit of volume. Therefore the unit of b should be **L/mol**.

[3] (15 pts)

(a) (2 pts) Arrange N_2, O_2, and F_2 in the order of increasing reduced mass (2 pts for a correct answer and otherwise 0 pt). Atomic numbers of N, O, and F are 7, 8, and 9, respectively.

   Answer)

   $\mu(N_2) < \mu(O_2) < \mu(F_2)$

(b) (4 pts) Name the geometries of SF_4, PCl_5, IF_5, and SF_6 by using VSEPR model (1 pt for each). Atomic numbers of S, F, P, Cl, and I are 16, 9, 15, 17, and 53, respectively.

   Answer)

   SF_4: sawhorse, PCl_5: trigonal bipyramidal, IF_5: square pyramidal, SF_6: octahedral

(c) (3 pts) Arrange SF_4, PCl_5, IF_5, and SF_6 in the order of increasing electric dipole moments (3 pts for a correct answer with a correct reason and otherwise 0 pt even if your answer is correct). Atomic numbers of S, F, P, Cl, and I are 16, 9, 15, 17, and 53, respectively.

   Answer)

   $0 = \mu(PCl_5) = \mu(SF_6) < \mu(SF_4) < \mu(IF_5)$

(d) (6 pts) Make a geometrically realistic sketch of the amino acid glycine H_2NCH_2COOH. Include in your structural sketch an indication of approximate bond angles and hybridizations. Atomic numbers of H, N, C, and O are 1, 7, 6, and 8, respectively.
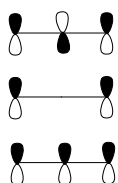
   Answer)
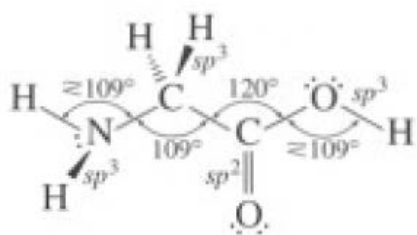
[4] (15 pts) Consider the allyl radical, CH_2CHCH_2 ·

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

(a) (6 pts) Construct the molecular orbitals from the $2p_z$ atomic orbitals perpendicular to the plane of the carbon atoms. Relative energy level for each molecular orbital has to be indicated.
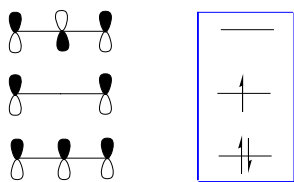
Answer)

(2 pts for each) or a more correct answer is with the consideration of the overlap of p orbitals with the same phase (for example for the lowest MO).

(b) (5 pts) Show the number of electrons occupying each molecular orbital in the ground state (place the possible number of electrons in each molecular orbital). Also indicate HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital).

Answer)

 3 pts for a correct answer. From the top, LUMO, HOMO, (these two have to be indicated, 1 pt each) and HOMO-1 (this does not have to be indicated).

(c) (4 pts) Indicate whether the molecule would be paramagnetic or diamagnetic and explain why (1 pt for a correct answer and 3 pts for a correct reason).
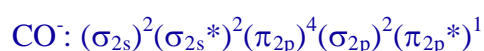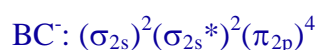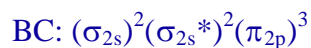
Answer)

paramagnetic due to unpaired electron.

[5] (15 pts) Consider BC (boron-carbon) and CO (carbon-oxygen) and the effect of adding an electron, $AB + e^- \rightarrow AB^-$.

(a) (4 pts) Write the molecular electronic configurations for BC, CO, BC⁻ and CO⁻ (1 pt for each).

  Answer)

  BC: $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^3$

  CO: $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^4(\sigma_{2p})^2$

  BC⁻: $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^4$

  CO⁻: $(\sigma_{2s})^2(\sigma_{2s}*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}*)^1$

(b) (4 pts) Assess the effect of adding an electron, $AB + e^- \rightarrow AB^-$, on the bond lengths and strengths of the molecules BC and CO and explain why (for each, 2 pts for a correct answer with a correct reason and otherwise 0 pt even if your answer is correct. You should provide correct answers for both the bond length and bond strength, and otherwise 0 pt).

  Answer)

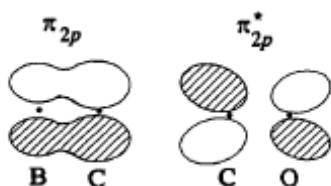 **Bond order**:

       BO: 1/2(5-2)=3/2, BO⁻: 1/2(6-2)=2

       ⇨ **Bond order increases and therefore bond length decreases and the bond is strengthened**.

       CO: 1/2(8-2)=3, CO⁻: 1/2(8-3)=5/3

       ⇨ **Bond order decreases and therefore bond length increases and the bond is weakened**.

(c) (4 pts) In each case, sketch a boundary surface for the newly occupied MO when an electron is added (2 pts for each).

  Answer)

(d) (3 pts) Between CO and CO⁻, which one would show higher vibrational frequency (3 pts for a correct answer with a correct reason and otherwise 0 pt even if your answer is correct)?

Answer)

(d) CO has stronger bond than CO⁻ and therefore CO is more stiff (larger k). The larger k means higher vibrational frequency. In conclusion, CO has higher vibrational frequency.

[6] (10 pts)

(a) (5 pts) Ultra-high-vacuum chambers suitable for studying the chemistry of surfaces must be evacuated to better than 10^{-10} Torr. At this pressure, how many molecules are present in a 100-L chamber at 25 °C (2 pts for a correct concept (formula) and 3 pts for a correct answer)?

Answer)

$$N = \frac{N_A PV}{RT}$$
$$= \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})(1 \times 10^{-10}\ \text{torr})(1\ \text{atm}/760\ \text{torr})(100\ \text{L})}{(0.08206\ \text{L atm}/\text{K mol})(298\ \text{K})} = 3.24 \times 10^{11}\ \text{molecules}$$

(b) (5 pts) If the vacuum chamber is sealed with a 25.0-cm-diameter plate (called a vacuum flange), what is the force of the atmosphere (1 atm = 101,325 Pa = 101,325 N/m²) in newtons (2 pts for a correct concept (formula) and 3 pts for a correct answer)?

Answer)

(b)

From Equation 9.1, $F = PA$. The vacuum flange's area is $A = \pi r^2 = \pi (d/2)^2$. Thus
$$F = (101{,}325\ \text{Pa})[\pi (0.125\ \text{m})^2] = 4970\ \text{N}$$

[7] (20 pts) Consider N_2 gas trapped inside the J-tube at 273.15 K in the following picture. Initially the volume (V) occupied by the gas was 20 mL and at that time the height (Δh) of the mercury liquid was 20 mm. Then more mercury was added to the tube so that the height increases from 20 mm to 800 mm. When this experiment was conducted, the barometer in the same room indicated a pressure of 1 atm. The gas constant R = 0.0820574 L atm K^{-1} mol^{-1}.

Maxwell - Boltzmann velocity distribution law is

$$f(u)du = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right) dv$$

and, m of N_2 is 4.65×10^{-26}kg, and Boltzman's constant is 1.38×10^{-23}J K^{-1}. Avogadro's number is 6.02214×10^{23}/mol. The density of liquid N_2 is 0.707 g/ml. Assume that the trapped gas can be treated as ideal gas.
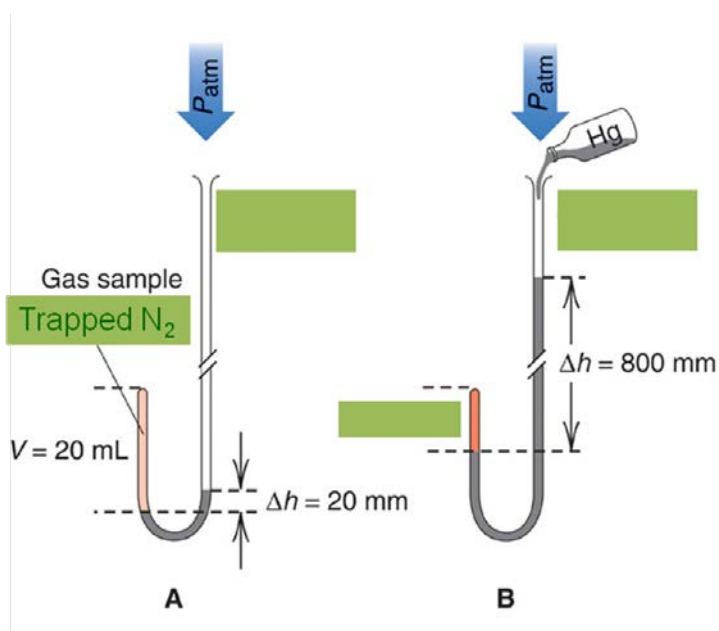
(a) (4 pts) What is the pressure of the trapped N_2 gas in the initial state (that is, before more mercury was added as shown in A) and the final state (after adding more mercury as shown in B) (2 pt for each correct answer and otherwise 0 pt)?

Answer)

The pressure of the nitrogen gas is counter-balanced by the pressure exerted by the liquid mercury and the air.

Therefore in the state A, P = 20 Torr + 760 Torr = **780 Torr = 1.026 atm**

In the state B, P = 800 Torr + 760 Torr = **1560 Torr = 2.053 atm**

(b) (4 pts) What is the volume of the trapped N_2 gas in the final state (4 pt for a correct answer and otherwise 0 pt)?

Answer)

The pressure has doubled. Therefore according to Boyle law, the volume should be reduced by a factor of 2. So the volume decreases to **10 mL**.

(c) (4 pts) What is the average kinetic energy of a single N_2 molecule trapped in the J-tube in the initial state (4 pt for a correct answer and otherwise 0 pt)?

Answer)

$<\varepsilon> = 3kT/2 = 3*1.38\times10^{-23}J\ K^{-1}*273K/2 = 5.65\times10^{-21}J$

(d) (4 pts) Suppose that 10,000 molecules travel at a speed of 500 ms^{-1}, then how many would travel at a speed of 1000 ms^{-1} (4 pt for a correct answer and otherwise 0 pt)?

Answer)

$$\frac{f(v_2)}{f(v_1)} = \frac{v_2^2}{v_1^2}\exp\left(\frac{-m(v_2^2 - v_1^2)}{2k_BT}\right)$$

$$= \frac{1000^2}{500^2}\exp\left(\frac{-4.65\times10^{-26}\times(1000^2 - 500^2)}{2\times1.38\times10^{-23}\times273}\right)$$

$$= 0.0391 = \frac{391}{10000}$$

Therefore about **391 molecules** travel at 1000 m/s when 10,000 molecules travel at 500 m/s.

(e) (4 pts) Estimate the volume occupied by one single molecule of N_2 in terms of Å^3. $1\ L = 10^{27}\ \text{Å}^3$. (4 pt for a correct answer and otherwise 0 pt)

Answer)

Molar volume for liquid N_2 = (28 g/mol) / (0.707 g/ml) = 0.00396 L/mol.

Volume of single molecule

= molar volume/N_A = (0.00396 L/mol)/(6.02*10^{23}/mol)=6.58$\times10^{-27}$ L = 65.8 Å^3.

[8] (20 pts) Classify each of the following statements as 'True' or 'False'. You don't have to write down proper explanation. Try to write down either 'True' or 'False' even if you don't know the answer (**10 correct answers will get 20 pts, 9 correct answers will get 18 pts, 8 correct answers will get 15 pts, 7 correct answers will get 11 pts, 6 correct answers will get 6 pts and otherwise 0 pt**).

(a) The valence bond model indicates that the CH_2 and CD_2 planes in $CH_2=C=CD_2$ are perpendicular.

Answer)   T

(b) Consider the replacement of one CH unit in benzene (C_6H_6) molecule by N. The resulting molecule is pyridine (C_5H_5N). According to the valence bond model, N has one lone pair electrons in an orbital that is coplanar with pyridine ring.

Answer)   T

(c) Molecular shapes of CO_3^{2-}, NO_3^- and SO_3^{2-} are all the same as trigonal planar.

Answer)   F

(d) Molecular orbital analysis indicates that linear H_3 is stable with respect to dissociation to three H atoms.

Answer)   T

(e) Linear H_3 is less stable than bent H_3.

Answer)   F

(f) Oxygen-oxygen stretching vibrational frequency ν_{O-O} in reciprocal centimeter (cm^{-1}) increases in the order of $O_2^- < O_2 < O_2^+$.

Answer)   T

(g) Vibrational frequency of D_2 is larger than that of H_2 by a factor of 2.

Answer)   F

(h) Rotational and vibrational motions of heteronuclear triatomic centrosymmetric molecules such as CO_2 and CS_2 cannot be detected by microwave and infra-red spectroscopy, respectively.

Answer)   F

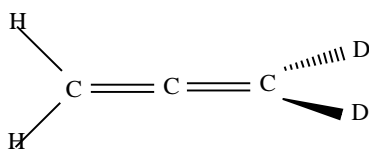(i) The gas constant per molecule is called Boltzmann's constant.

Answer)   T

(j) The fraction N_ε / N of molecules with energy ε is proportional to $exp(-\varepsilon/k_BT)$.

Answer)   T

Solution:

(a) True: C=C=C fragment is linear and thus the central C has *sp*-hybridization, leaving two p-orbitals for π-bondings that are orthogonal. The structure would be following and the statement is true.

(b) True: N adopts sp^2 hybridization and 4 out of 5 valence electrons of N occupy sp^2 orbitals. Among 4 electrons in sp^2 orbitals, 2 form two C-N bonds and the remaining electron pair resides in sp^2 orbital that is coplanar with pyridine ring.

(c) False: According to the Lewis structures of CO_3^{2-}, NO_3^- and SO_3^{2-}, the central atoms are considered to have 3, 3 and 4 electron pairs, respectively. Thus, the molecular shapes of CO_3^{2-}, NO_3^- and SO_3^{2-} are not the same as trigonal planar since SO_3^{2-} has trigonal pyramidal geometry.

(d) True: Linear combination of 3 hydrogen 1s orbitals will be following:
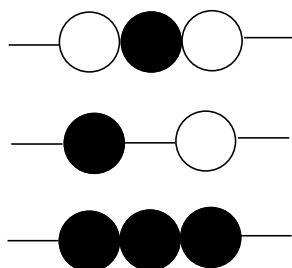
Thus, two electrons enter the lowest σ-bonding orbital and the third electron enters the next higher σ orbital, which is relatively weakly antibonding between the end atoms and nonbonding between end and center H atoms. The net effect is that H_3 has bond order of at least 1/2 and is stable with respect to dissociation to three H atoms.

(e) False: Since the last electron of H_3 is in an orbital that is antibonding between the end atoms, any bending of the molecule brings the two atoms together, and this is opposed by the antibonding electron. Thus, the most stable geometry of H_3 is linear.

(f) True: It is correct statement since molecular orbital energy diagram indicates that the bond order (BO) increases in the order of O_2^- (BO = 1½) < O_2 (BO = 2) < O_2^+ (BO = 2½) and thereby the frequency increases in the order of $O_2^- < O_2 < O_2^+$.

(g) False: The use of the following equation gives $v_{D-D}/v_{H-H} = (\mu_{H-H}/\mu_{D-D})^{\frac{1}{2}} = 2^{\frac{1}{2}}$.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

(h) False: Heteronuclear triatomic centrosymmetric molecules such as CO_2 and CS_2 do not have a permanent dipole moment. Thus, they cannot be detected by rotational spectroscopy. But, the asymmetric stretching vibration of these molecules accompanies the change in dipole moment and thus can be seen in the infra-red spectroscopy.

(i) True: Correct statement since $k_B = R/N_A$.

(j) True: Maxwell-Boltzmann velocity distribution indicates that the fraction N_υ / N of molecules with the velocity υ is proportional to $exp(-\frac{1}{2}m\upsilon^2/k_BT)$. Similarly, the fraction N_ε / N of molecules with energy ε is proportional to $exp(-\varepsilon/k_BT)$.