

**2016 Fall Semester Midterm  
For General Chemistry I (CH101)**

**Date: October 22 (Sat), Time Limit: 19:00 ~ 22:00**

Student I.D. Number	Name

90 Normal Points + 8 Bonus Points

If you get 90 points out of 98 points, you will get the full 40% assigned to the mid-term exam. We suggest that you skim through all the problems quickly. There are some straightforward problems whose solution you can easily write down without much calculation.

### Your scores

- 1) out of 11
- 2) out of 6
- 3) out of 8
- 4) out of 6
- 5) out of 10
- 6) out of 10
- 7) out of 7
- 8) out of 14
- 9) out of 16
- 10) out of 10

**Total: out of 98**



1. In ionic compounds, the potential energy ( $V(R_{12})$ ) is expressed as a function of the distance between the ions ( $R_{12}$ ), choosing as zero the potential energy of the neutral atoms when they are infinitely far apart. (Total 11 pts)

$$V(R_{12}) = A e^{-\alpha R_{12}} - B \left( \frac{e(-e)}{R_{12}} \right) + \Delta E_{\infty}$$

(1)                      (2)                      (3)

(a) What do the three terms of the equation ((1), (2), (3)) represent? (3 pts) (1 pt each, No partial pts)

Answer)

(1) : repulsion between the ions as they get very close together

(2) : attractive Coulomb potential

(3) : energy required to create the ions from their respective neutral atoms

1 pt each

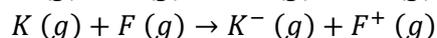
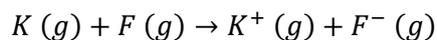
(b) Consider the ionic compound KF. Given that the first ionization energy of potassium is 419 kJ/mol and electron affinity of fluorine is 328 kJ/mol, calculate  $\Delta E_{\infty}$ . (1 pt) (No partial pts)

Answer)

$$\Delta E_{\infty} = IE_1(K) - EA(F) = +91 \text{ kJ mol}^{-1}$$

No partial points

(c) Calculate the energy changes ( $\Delta E$ ) for the following pairs of reactions:



Explain why  $K^+F^-$  forms in preference to  $K^-F^+$ .

The first ionization energy of fluorine is 1681 kJ/mol and the electron affinity of potassium is 48 kJ/mol. (2 pts) (0.5 pts for each reaction, 1 pt for correct explanation)

Answer)

1<sup>st</sup> reaction : 419-328=91 kJ/mol, 2<sup>nd</sup> reaction : 1681-48=1633 kJ/mol 0.5 pts each

1<sup>st</sup> reaction is energetically favored prior to form ionic compound. 1 pt

(d) Estimate the energy of dissociation ( $\Delta E_d$ ) to neutral atoms for KF, which has a bond length  $2.17 \times 10^{-10}$  m. (2 pts) (No partial pts)

Answer)

Example 3.6

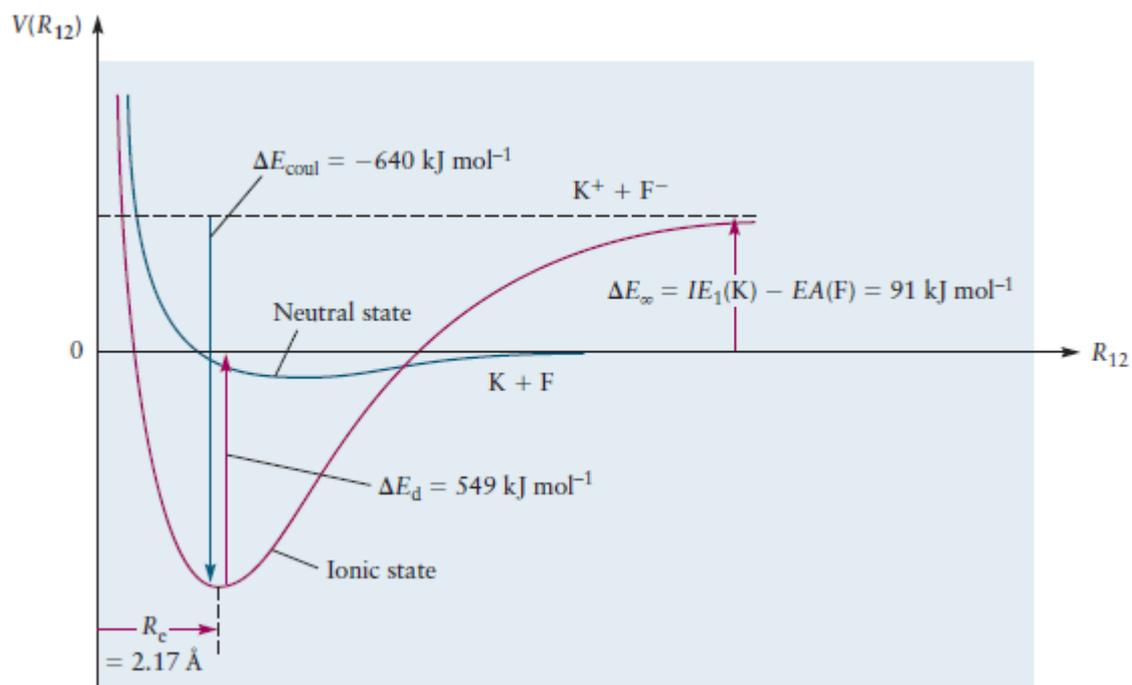
$$\begin{aligned} \Delta E_d &\approx -\frac{q_1 q_2}{4\pi\epsilon_0 R_c} \frac{N_A}{10^3} - \Delta E_\infty \\ &= -\frac{-(1.602 \times 10^{-19} \text{C})^2 (6.022 \times 10^{23} \text{mol}^{-1})}{(4)(3.1416)(8.854 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1})(2.17 \times 10^{-10} \text{m})(10^3 \text{J kJ}^{-1})} \\ &\quad -91 \text{ kJ mol}^{-1} \\ &= 640 \text{ kJ mol}^{-1} - 91 \text{ kJ mol}^{-1} \\ &= 549 \text{ kJ mol}^{-1} \end{aligned}$$

No partial points, pts are given if only the procedure and the answer are shown correctly.

(e) From the bond length and energy values calculated above, draw the potential energy curve of the ions  $K^+$  and  $F^-$  as a function of their internuclear separation  $R_{12}$ . (3 pts) (No partial pts)

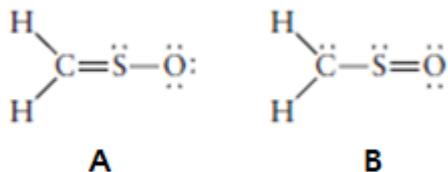
Answer)

Figure 3.13



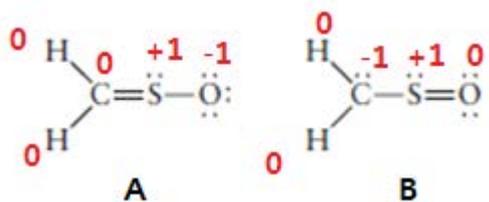
No partial points  $R_e$ ,  $\Delta E_d$ ,  $\Delta E_{\infty}$ , base line should be clearly shown.

2. Two possible Lewis structure are shown for sulfine ( $\text{H}_2\text{CSO}$ ). (Total 6 pts)



(a) Assign the formal charges on all atoms including 0 charge. (2 pts) (1 pt each, No partial pts)

Answer)



1 pt for each structure, pts are given if formal charges of all atom in structure are correctly shown.

(b) Of the two structures shown, which is “better”? Explain your selection. (2 pts) (No partial pts)

Answer)

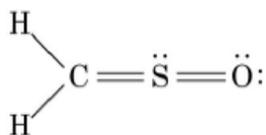
A : As negative formal charge is on the more electronegative element.

Keyword : negative formal charge/electronegative

Pts are given if the answer and explanation are correctly shown.

(c) Draw a best Lewis structure for sulfine, for which all atoms have a formal charge of zero. (2 pts)  
(No partial pts)

Answer)



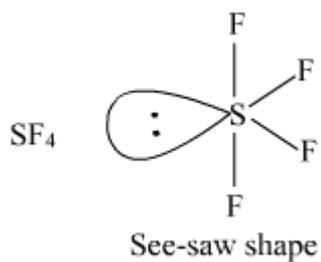
No partial points

3. Sketch the correct geometries of the following molecules, using the VSEPR method. The lone pairs must be shown and if the molecules have 3D structure, you must give exact 3D structure clearly.  
 (Total 8 pts, Each 2 pts) (-1 pt for lone pair missing)

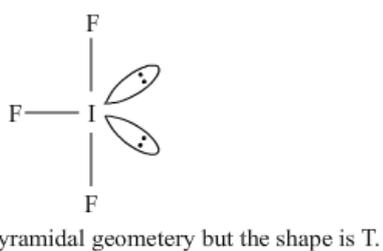
- (a) SF<sub>4</sub>
- (b) IF<sub>3</sub>
- (c) IF<sub>5</sub>
- (d) ICl<sub>3</sub> (Cl : chlorine)

Answer)

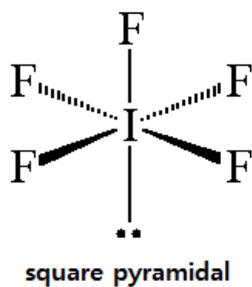
(a)



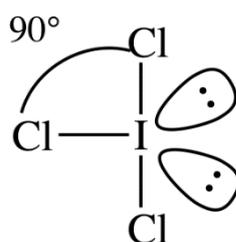
(b)



(c)



(d)



Minor mistakes(lone pair missing) -1 pts

4. Answer the following questions. (Total 6 pts)

(a) Explain the postulation used in the Bohr model. (2 pts) (No partial pts)

Answer)

The angular momentum of the electron is quantized in integral multiples of  $h/2\pi$ , where  $h$  is Planck's constant.

No partial points

(b) Calculate the energy required to remove the electrons from 1 mol of  $\text{Be}^{3+}$  in  $n = 4$  state. (2 pts) (-1 pt for calculation error)

Answer)

$$1.31 \times 10^6 \text{ J/mol}$$

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

The negative of the second answer is the input of energy needed to remove the electron from a single  $\text{Be}^{3+}$  ion in its  $n=4$  state. Multiply by Avogadro's number to put this on the basis of a mole of  $\text{Be}^{3+}$  ions

$$E = \frac{-(-2.18 \times 10^{-18} \text{ J})}{\text{atom}} \times \frac{6.022 \times 10^{23} \text{ atom}}{\text{mol}} = 1.31 \times 10^6 \text{ J/mol}$$

Calculation error -1 pt

(c) What frequency of light would be emitted in a transition from the  $n=4$  to the  $n=2$  state of this ion?  
(2 pts) (-1 pt for calculation error)

Answer)

$$9.87 \times 10^{17} \text{ s}^{-1}$$

The energy change in a  $\text{Be}^{3+}$  ion undergoing the  $4 \rightarrow 2$  transition equals the difference b/w the energies of the two states.

$$\Delta E = E_2 - E_4 = \left( -\frac{4^2}{2^2} \times 2.18 \times 10^{-18} \text{ J} \right) - \left( -\frac{4^2}{4^2} \times 2.18 \times 10^{-18} \text{ J} \right) = -6.54 \times 10^{-18} \text{ J}$$

The change in energy is negative because the  $\text{Be}^{3+}$  ion loses energy. It relaxes from the higher energy state to the lower. The energy gained by surrounding in the form of a photons in the  $4 \rightarrow 2$  transition is  $-6.54 \times 10^{-16} \text{ J}$ . Dividing by  $h$  gives the frequency of the photon,

$$\nu = -\frac{\Delta E}{h} = \frac{-(-6.54 \times 10^{-18} \text{ J})}{6.626 \times 10^{-34} \text{ Js}} = 9.87 \times 10^{15} \text{ s}^{-1}$$

Calculation error -1 pt

5. Answer the following questions. (Total 10 pts)

(a) A particle of mass  $m$  is placed in a 1D box with a length  $L$  ( $L > 0$ ). Inside the box the potential is zero, and outside it is infinite; therefore, the wavefunction goes smoothly to zero at both end of the box. Derive the normalized wave function ( $\psi_n$ ) and the energy ( $E_n$ ) for the one-dimensional particle-in-a-box. (6 pts) (Partial pts exist)

Answer)

Time independent Schrodinger Equation.

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x), \quad \hbar = \frac{h}{2\pi}$$

if  $0 < x < L, V(x) = 0$

$$\therefore -\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E\Psi(x) \quad \dots 1 \text{ pt}$$

$$\Psi(x) = A\sin(kx) + B\cos(kx) \quad \dots 1 \text{ pt}$$

By Boundary condition,  $\Psi(0) = 0, \Psi(L) = 0$

When  $x = 0, \sin(0) = 0$  and  $\cos(0) = 1$

Therefore  $B=0$  ( $\because \Psi(0) = B = 0$ )

$$\therefore \Psi(x) = A\sin(kx) \quad \dots 1 \text{ pt}$$

$$\Psi(L) = A \sin(kL) = 0$$

$$\therefore kL = n\pi \text{ where } n = 1, 2, 3 \dots$$

$$k = \frac{n\pi}{L} \dots 1 \text{ pt}$$

For normalization,

$$\int_0^L [\Psi(x)]^2 dx = A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = A^2 \int_0^L \frac{1 - \cos\left(\frac{2n\pi x}{L}\right)}{2} dx = \frac{AL^2}{2} = 1$$

$$\therefore A = \sqrt{\frac{2}{L}}, \Psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) \text{ where } n = 1, 2, 3 \dots \dots 1 \text{ pt}$$

$$\frac{d\Psi(x)}{dx} = kA \cos(kx)$$

$$\frac{d^2\Psi(x)}{dx^2} = -k^2 A \sin(kx) = -k^2 \Psi(x) = -\left(\frac{n\pi}{L}\right)^2 \Psi(x)$$

$$\text{Since } -\left(\frac{n\pi}{L}\right)^2 \Psi(x) = -\frac{2mE}{\hbar^2} \Psi(x), \quad -\left(\frac{n\pi}{L}\right)^2 = -\frac{2mE}{\hbar^2}$$

$$\therefore E = \frac{n^2 \hbar^2}{8mL^2} \text{ where } n = 1, 2, 3 \dots \dots 1 \text{ pt}$$

(b) A particle of mass  $m$  is placed in a 3D rectangular box with edge lengths  $2L$ ,  $L$ , and  $L$  ( $L > 0$ ). Inside the box the potential energy is zero, and outside it is infinite; therefore, the wavefunction goes smoothly to zero at the sides of the box. Calculate the lowest energy having degeneracy and give the quantum numbers of it for the particle in the box. (4 pts) (2 pts for energy calculation, 2 pts for quantum numbers)

Answer)

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

$$E_{112} = E_{121} = \frac{h^2}{8mL^2} \left( \frac{1}{4} + 4 + 1 \right) = \frac{21}{4} \frac{h^2}{8mL^2}$$

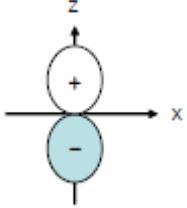
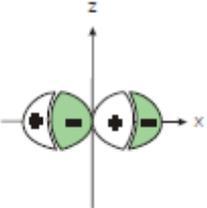
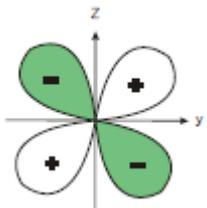
$$\text{energy: } E = \frac{21}{4} \frac{h^2}{8mL^2}$$

$$\text{quantum numbers: } (n_x, n_y, n_z) = (1, 1, 2), (1, 2, 1)$$

Energy : 2 pt

Quantum number : each 1 pt

6. There are several atomic orbitals below. Answer the following questions. (Total 10 pts)

(1)	(2)	(3)
		

(a) Write down the name of each of these orbitals. (3 pts) (1 pt each, No partial pts)

Answer)

(1)	(2)	(3)

(1) :  $2p_z$ , (2) :  $3p_x$ , (3) :  $3d_{yz}$

Each 1 pt

(b) For hydrogen atom (H), choose the two orbitals that have the same energy level. (2 pts) (No partial pts)

Answer)

(2), (3)

No partial points

(c) For boron atom (B), compare the energy level of (1), (2) and (3). (2 pts) (No partial pts)

Answer)

(1)<(2)<(3)

No partial points

(d) For one hydrogen atom (H), is light emitted or absorbed in an electron transition from the (3) to the (1) state? Calculate the frequency (in  $s^{-1}$ ) and wavelength (in nm) of light emitted or absorbed in this situation. (3 pts) (1 pt for emission/absorption, 1 pt for correct frequency, 1 pt for correct wavelength)

Answer)

The image shows a handwritten solution on lined paper. It starts with the word "Emission" written at the top. Below it, the energy change is calculated using the Bohr model formula:  $\Delta E = -2.18 \times 10^{-18} \times \left(\frac{1^2}{2^2}\right) - \left(-2.18 \times 10^{-18}\right) \times \left(\frac{1^2}{3^2}\right)$ . This simplifies to  $= -3.03 \times 10^{-19} \text{ J}$ . The next line shows the energy being equal to  $h\nu$ , so  $3.03 \times 10^{-19} \text{ J} = h\nu$ , which leads to  $\nu = \frac{3.03 \times 10^{-19}}{6.626 \times 10^{-34}} = 4.57 \times 10^{14} \text{ s}^{-1}$ . Finally, the wavelength is calculated as  $\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8}{4.57 \times 10^{14}} = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}$ .

Emission

$$\Delta E = -2.18 \times 10^{-18} \times \left(\frac{1^2}{2^2}\right) - \left(-2.18 \times 10^{-18}\right) \times \left(\frac{1^2}{3^2}\right)$$
$$= -3.03 \times 10^{-19} \text{ J}$$
$$3.03 \times 10^{-19} \text{ J} = h\nu \rightarrow \nu = \frac{3.03 \times 10^{-19}}{6.626 \times 10^{-34}} = 4.57 \times 10^{14} \text{ s}^{-1}$$
$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8}{4.57 \times 10^{14}} = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}$$

Emission 1 pt, Frequency 1 pt, Wavelength 1 pt

7. Answer the following questions. (Total 7 pts)

(a) Chromium (Cr) is predicted by the building-up principle to have four unpaired electrons in its ground-state electron configuration, but in fact has six. Write the predicted and actual full ground-state electron configurations that explain this fact. You may use short hand noble gas configurations for core electrons. (2 pts) (1 pt for predicted electronic configuration, 1 pt for actual electronic configuration)

Answer)

Predicted electronic configuration :  $[\text{Ar}]3d^44s^2$

Actual electronic configuration :  $[\text{Ar}]3d^54s^1$

Each 1 pt

(b) Write the ground-state electron configuration of Sc and  $\text{Sc}^+$  ion, and predict them paramagnetic or diamagnetic. You may use short hand noble gas configurations for core electrons. (3 pts) (1 pt each for electron configuration, 0.5 pts each for paramagnetic or diamagnetic)

Answer)

Sc :  $[\text{Ar}]3d^14s^2$  (paramagnetic) 1 pt, 0.5 pt

$\text{Sc}^+$  ion :  $[\text{Ar}]3d^14s^1$  (paramagnetic) 1 pt, 0.5 pt

(c) Identify the element of period 2 that possesses the ionization energies (IE in  $\text{kJ mol}^{-1}$ ) in the table below. (2 pts)

1 <sup>st</sup> IE	2 <sup>nd</sup> IE	3 <sup>rd</sup> IE	4 <sup>th</sup> IE	5 <sup>th</sup> IE	6 <sup>th</sup> IE	7 <sup>th</sup> IE
1402.3	2856	4578.1	7475.0	9444.9	53266.6	64360

Answer)

N, Nitrogen

No partial points

8. Answer the following questions. (Total 14 pts)

(a) Construct the correlation diagram for  $O_2^-$ . (3 pts) (No partial pts)

Answer)

(b) Give the valence electron configuration for each of the following species:  $O_2^+$ ,  $O_2$ ,  $O_2^-$ ,  $O_2^{2-}$

(4 pts) (1 pt each)

Answer)

(c) Give the bond order of each species. (2 pts) (0.5 pts each)

Answer)

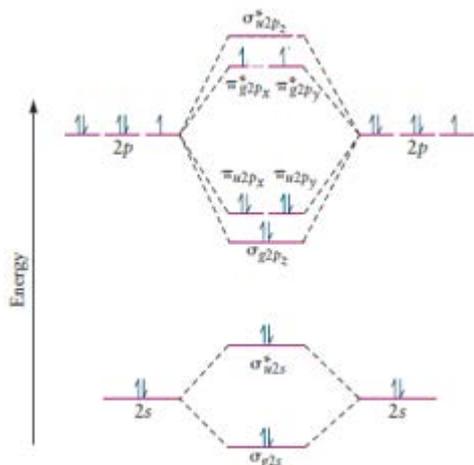
(d) Predict which species are paramagnetic. (3 pts) (No partial pts)

Answer)

(e) Predict the order of increasing bond dissociation energy among the species. (2 pts) (No partial pts)

Answer)

a)



From this diagram, there is one more electron in  $\pi_{g2px}^*$  or  $\pi_{g2py}^*$ .

a) The qualitative correlation diagram for  $O_2^-$  is identical to the diagram given for  $F_2$  in text Figure 6.17b except that an electron is removed from either the  $\pi_{2px}^*$  or the  $\pi_{2py}^*$  level.

b) The ground-state electron configuration of  $O_2$  is listed in Table 6.3. Derive the configurations of the ions in the problem by removal of electrons from the highest occupied or addition to the lowest unoccupied molecular orbitals:

$$O_2^+ : (\sigma_{g2s})^2 (\sigma_{u2s}^*)^2 (\sigma_{g2pz})^2 (\pi_{u2p})^4 (\pi_{g2p}^*)^1 \quad O_2 : (\sigma_{g2s})^2 (\sigma_{u2s}^*)^2 (\sigma_{g2pz})^2 (\pi_{u2p})^4 (\pi_{g2p}^*)^2$$

$$O_2^- : (\sigma_{g2s})^2 (\sigma_{u2s}^*)^2 (\sigma_{g2pz})^2 (\pi_{u2p})^4 (\pi_{g2p}^*)^3 \quad O_2^{2-} : (\sigma_{g2s})^2 (\sigma_{u2s}^*)^2 (\sigma_{g2pz})^2 (\pi_{u2p})^4 (\pi_{g2p}^*)^4$$

c) The bond orders of the species are  $\frac{5}{2}$  (for  $O_2^+$ ), 2 (for  $O_2$ ),  $\frac{3}{2}$  (for  $O_2^-$ ) and 1 (for  $O_2^{2-}$ ).

b) All of the species except  $O_2^{2-}$  should be paramagnetic. A species with an odd number of electrons is automatically paramagnetic. The reason for the paramagnetism of ordinary  $O_2$  is discussed in the text.

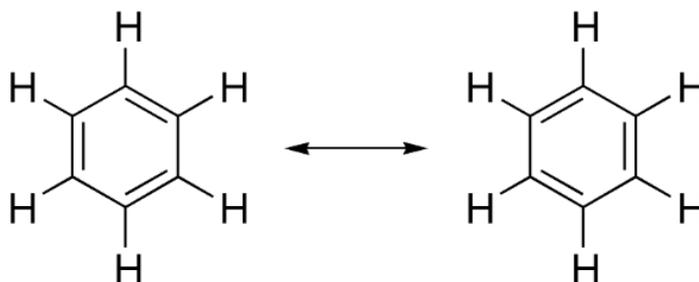
c) Members of the series  $O_2^+$  through  $O_2^{2-}$  are differentiated by successive addition of an electron. Each electron goes into a  $\pi^*$  antibonding orbital. The bond dissociation energy decreases along the series.

a, d, e) No partial points

9. Consider a benzene ( $C_6H_6$ ) molecule, having six-membered cyclic structure. (Total 16 pts)

(a) Based on the experimental observations that all C-C bonds are identical, draw the resonance hybrid Lewis diagrams for benzene. (2 pts) (No partial pts)

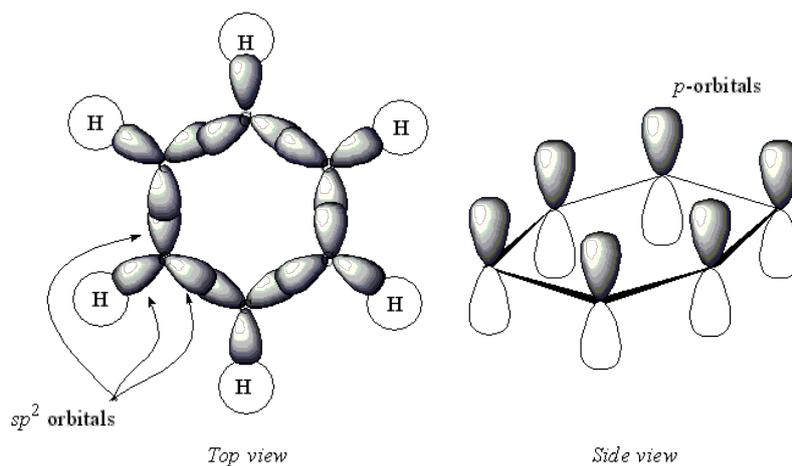
Answer)



No partial pts

(b) The structure of benzene can be explained using hybrid orbitals as well as Lewis diagrams. Draw 3D structure of benzene with hybrid orbitals, and mark for every bond if it is  $\sigma$  or  $\pi$  bond. (3 pts) (1 pt for correct 3D structure with hybrid orbitals, 1 pt for all  $\sigma$  bond marked, 1 pt for all  $\pi$  bond marked)

Answer)



Correct hybridization ( $sp^2$ ) 1 pt, sigma bond 1 pt, pi bond 1 pt

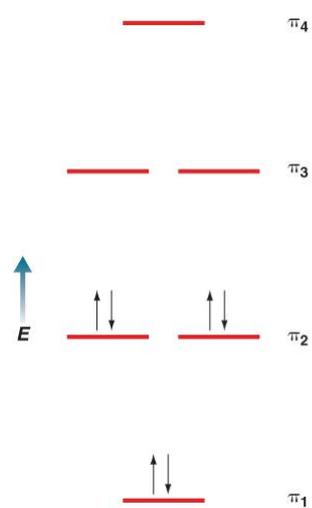
(c) As expected from (b), benzene molecule has delocalized  $\pi$  bonding. Draw molecular orbital energy level diagram for the  $\pi$  orbitals of benzene with its ground state electron configuration. (Hint : There are 6 p orbitals that can form delocalized  $\pi$  bonding) (3 pts) (2 pts for correct MO energy level diagram, 1 pt for correct electron configuration)

Answer)

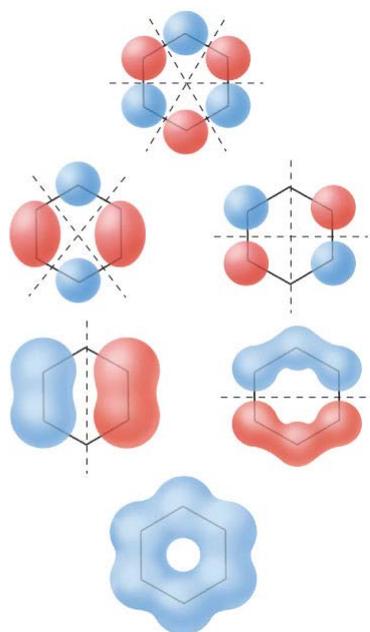
(d) The number of nodal planes increases with energy as in the particle-in-a-box problem. For each molecular orbital in the energy level diagram show the locations of nodes. If there is no node, write 'no node'. (3 pts) (0.5 pts each for correct node location, Maximum 3 pts)

Answer)

(c)



(d)

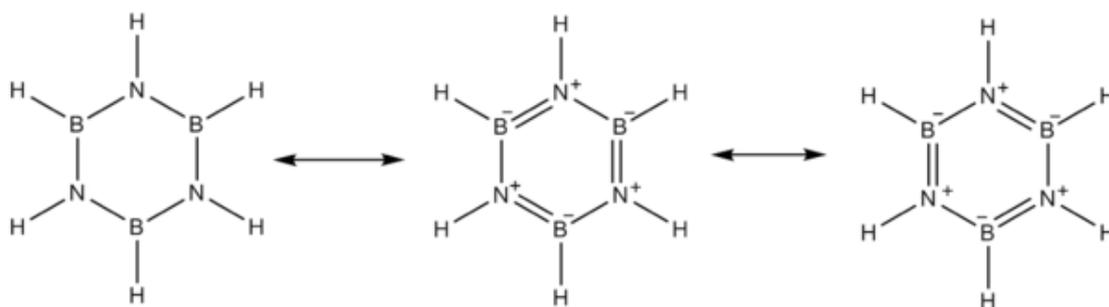


c) MO : 2 pts, electron configuration : 1 pt

d) Each 0.5 pts(The plane of benzene ring itself is a nodal plane, Dashed line above and interatomic plane of benzene ring must be shown.)

(e) Borazine, referred to as “inorganic benzene”, is an inorganic compound with the chemical formula  $(\text{BH})_3(\text{NH})_3$ , three BH units and three NH units alternating. The boron-nitrogen bond length is between that of the boron-nitrogen single bond (0.151 nm) and the boron-nitrogen double bond (0.131 nm). Draw the all possible resonance hybrid Lewis diagrams of borazine and explain this result (boron-nitrogen bond length) with the Lewis diagram of borazine. (Show lone pairs and formal charge too.) (5 pts) (3 pts for all correct Lewis diagrams, -0.5 pts for incorrect formal charge, 2 pts for correct explanation)

Answer)



The low electronegativity of boron (2.04) compared to that of nitrogen and the electron deficiency on the boron atom makes nitrogen lone-pair electrons partially delocalized throughout six B-N bonds.

Lewis diagram : 3 pts (each 1 pt), formal charge error in each diagram : -0.5 pts, explanation 2 pts

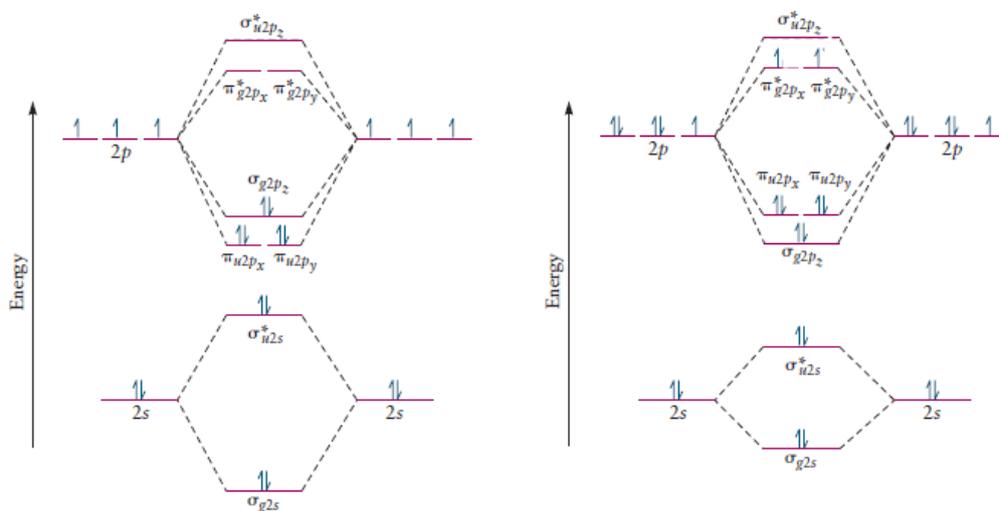
10. Answer the following questions (Total 10 pts)

(a) Determine the ground-state electron configuration and bond order of the  $N_2$  and  $O_2$  molecule from the correlation diagram for the molecules. (3 pts) (1 pt for each correlation diagram, 0.5 pts for each bond order)

Answer)

nitrogen molecule (left), oxygen molecule (right).

Bond order=3 for nitrogen molecule, 2 for oxygen molecule



Correlation diagram : 1 pt each, bond order : 0.5 pts each

(b) Explain about the difference in ordering energy of the molecules. (2 pts) (No partial pts)

Answer)

For homonuclear diatomic molecules of  $Z \leq 7$ , reversed ordering of energy occurs due to large electron-electron spatial repulsions between electrons in  $\sigma_{g2p_z}$  and  $\sigma_{u2s}^*$  MOs. For homonuclear diatomic molecules of  $Z > 7$ , it has normal ordering of energy because as  $Z$  increases, the repulsion decreases since electrons in  $\sigma_{g2s}$  and  $\sigma_{u2s}^*$  MO's are drawn more strongly toward the nucleus.

(c) Are molecular oxygen and molecular nitrogen paramagnetic or diamagnetic? (1 pt) (0.5 pts each)

Answer)

$N_2$  : Diamagnetic (No unpaired electrons)  $O_2$  : Paramagnetic (Unpaired electrons exist)

0.5 pts each

(d) Predict the order of the first ionization energy of molecular nitrogen, molecular oxygen, atomic nitrogen, and atomic oxygen. (4 pts) (1 pt for correct order, 3 pts for correct explanation)

Answer)

$O_2$  (1205 kJ/mol) < O (1313 kJ/mol) < N (1402 kJ/mol) <  $N_2$  (1503 kJ/mol)

In the correlation diagram of  $O_2$ , a 2p electron of a ground state of O atom lies lower in energy than the  $\pi_{g2p}^*$  electron, which is the highest energy electron in the ground state  $O_2$  molecule. Therefore, it requires more energy to ionize O than  $O_2$ . Similarly, for molecular nitrogen and atomic nitrogen, it requires less energy to ionize N than  $N_2$ . For nitrogen atom and oxygen atom, oxygen has small first ionization energy due to the repulsion between paired electrons in 2p orbitals.

Correct order : 1 pt, 1 pt for each correct explanation of order( $O_2 < O$ ,  $O < N$ ,  $N < N_2$ )

**2016 Fall Semester Final Exam  
For General Chemistry I (CH101)**

**Date: December 17 (Sat), Time Limit: 19:00 ~ 22:00**

Student I.D. Number	Name

100 Normal Points + 11 Bonus Points

If you get 100 points out of 111 points, you will get the full 60% assigned to the final exam. We suggest that you skim through all the problems quickly. There are some straightforward problems whose solution you can easily write down without much calculation.

*\*\*\*No partial points given for wrong or missing units\*\*\**

**Your scores**

- |               |                   |
|---------------|-------------------|
| 1)            | out of 9          |
| 2)            | out of 12         |
| 3)            | out of 10         |
| 4)            | out of 9          |
| 5)            | out of 12         |
| 6)            | out of 12         |
| 7)            | out of 10         |
| 8)            | out of 10         |
| 9)            | out of 12         |
| 10)           | out of 8          |
| 11)           | out of 7          |
| <b>Total:</b> | <b>out of 111</b> |

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.

(채점답안지분배및이의신청일정)

1. Period, Location, and Procedure

1) Return and Claim Period: **December 22 (Thu, 7:00 ~ 9:00 p.m.)**

2) **Location: Room 101 (Bldg. E11)**

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.

2. Final Confirmation

1) Period: December 24 (Sat) – December 25 (Sun)

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

***\*\* For further information, please visit General Chemistry website at [www.gencheminkaist.pe.kr](http://www.gencheminkaist.pe.kr).***

You may refer to the following information.

### Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ \AA} = 5.2917720859 \times 10^{-11} \text{ m}$
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	$1 \text{ \AA} = 10^{-10} \text{ m}$
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	$1 \text{ eV} = 1.602177 \times 10^{-19} \text{ J}$ $= 96.485335 \text{ kJ mol}^{-1}$
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	$1 \text{ lb} = 16 \text{ oz} = 0.45359237 \text{ kg}$ (exactly)
Rydberg	$1 \text{ Ry} = 2.17987197 \times 10^{-18} \text{ J}$ $= 1312.7136 \text{ kJ mol}^{-1}$ $= 13.60569193 \text{ eV}$
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	$1 \text{ torr} = 133.3224 \text{ Pa}$

Raoult's law: vapor pressure of the solvent  $P_1 = X_1 P_1^*$

Henry's law: vapor pressure of the solute  $P_2 = X_2 k_2$

Mole fraction:  $X_i = n_i/n_{\text{tot}}$  where  $n_i$  is the number of moles of component  $i$

Molarity:  $M = \text{moles of solute per liter of solution}$  <sup>1ts</sup>

Molality:  $m = \text{moles of solute per kg of solvent}$

For *dilute, aqueous* solutions  $m \approx M$

$\Delta U = q + w$ . The internal energy of a system is a state function.

$$\Delta H^\circ = \sum_{i=1}^{\text{prod}} n_i \Delta H_i^\circ - \sum_{i=1}^{\text{react}} n_i \Delta H_i^\circ$$

Gibbs free energy,  $G = H - TS$

Isothermal processes:  $dw = -PdV$

Heat capacities of ideal monatomic gases

$$c_V (\text{ideal gas}) = (3/2) R$$

$$c_P = c_V + R = (5/2)R$$

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

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} \quad (\text{for all processes})$$

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} \quad (\text{constant } T)$$

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T_{\text{trans}}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} \quad (\text{reversible phase transitions at constant } T \text{ and } P)$$

$$\Delta S = nR \ln \left( \frac{V_2}{V_1} \right) \quad (\text{ideal gas, change of } V \text{ at constant } T)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{n c_V}{T} dT = n c_V \ln \left( \frac{T_2}{T_1} \right) \quad (\text{constant } V \text{ and constant } c_V)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{n c_P}{T} dT = n c_P \ln \left( \frac{T_2}{T_1} \right) \quad (\text{constant } P \text{ and constant } c_P)$$

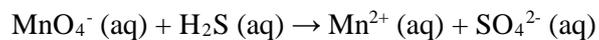
$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{surr}}} \quad (\text{surroundings are a large "heat bath" and pressure of the system is constant})$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (\text{spontaneous process})$$

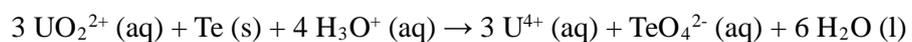


1. Answer the following questions. (Total 9 pts)

(a) Complete and balance the equation below for reaction taking place in acidic solution. (3 pts for correctly balanced equation, No partial pts)

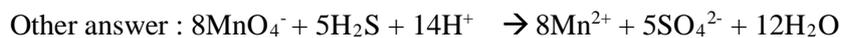
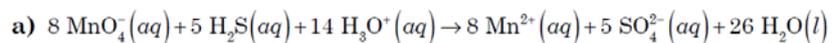


(b) Break the following balanced equation taking place in acidic solution into balanced oxidation and reduction half-equations. (6 pts, 3 pts for oxidation half equation, 3 pts for reduction half equation, No partial pts)



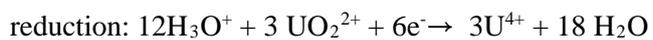
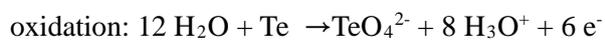
Answer)

In acidic solution,  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$  may be added either as reactants or as products to achieve balance.

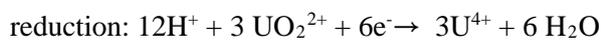
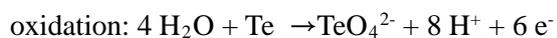


(3 pts, No partial pts)

b) 3 pts each, No partial pts



Other answer

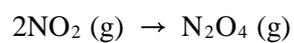


2. Answer the following questions. (Total 11 pts)

(a) Write down the underlying assumptions of the kinetic theory of gases. (4 pts) (1 pt for each correct assumption, maximum 4 pts, -1 pt for each incorrect assumption, No partial pts)

(b) For a nitrogen molecule, an argon atom, a krypton atom at a certain temperature, the root-mean-square speed of an argon atom was determined to be  $559 \text{ m s}^{-1}$ . Calculate the root-mean-square speed of a nitrogen molecule and a krypton atom at the same temperature. (4 pts) (2 pts for each correct answer, No partial pts)

(c) When  $\text{NO}_2$  is cooled to 298K, some of it reacts to form a dimer (dimeric molecule),  $\text{N}_2\text{O}_4$ , through the reaction



Initially, 15.2 g of  $\text{NO}_2$  is placed in a 10.0 L flask at 600K and the flask is cooled to 298K. The total pressure is measured to be 0.500 atm. Calculate the partial pressures (in atm) and mole fractions of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the flask after cooling to 298K. Assume that  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are ideal gases. (4 pts)  
(1 pt for each correct partial pressure and 1 pt for each correct mole fraction, No partial pts)

Answer)

(a) Each 1 pt (Max 4 pts)

- 1) A pure gas consists of a collection of identical molecules in continuous random motions.
- 2) Gas molecules are infinitesimally small (mass) points.
- 3) The molecules move in straight lines until they collide.
- 4) The molecules do not influence one another except during collisions.
- 5) All collisions of the molecules are perfectly elastic.
- 6) No phase transitions occur at any temperature and pressure.
- 7) The average kinetic energy of the gas particles depends only on the absolute temperature of the system. (Definition of temperature in kinetic theory)
- 8) The time during collision of molecule is negligible as compared to the time between successive collisions.

(b) Each 2 pt (No partial pts)

Handwritten calculations on lined paper showing the relationship between the root mean square speed ( $u_{rms}$ ) of different gases. The first line shows the formula  $u_{rms} = \sqrt{\frac{3RT}{M}} \propto \frac{1}{\sqrt{M}}$  and states  $u_{rms}(\text{Ar}) = 559 \text{ m/s}$ . The second line calculates  $u_{rms}(\text{Ne}) = u_{rms}(\text{Ar}) \times \sqrt{\frac{39.948 \text{ g/mol}}{28.014 \text{ g/mol}}} = 668 \text{ m/s} \dots 2 \text{ pts}$ . The third line calculates  $u_{rms}(\text{Kr}) = u_{rms}(\text{Ar}) \times \sqrt{\frac{39.948 \text{ g/mol}}{83.80 \text{ g/mol}}} = 386 \text{ m/s} \dots 2 \text{ pts}$ .

$$u_{rms} = \sqrt{\frac{3RT}{M}} \propto \frac{1}{\sqrt{M}}, \quad u_{rms}(\text{Ar}) = 559 \text{ m/s}$$
$$u_{rms}(\text{Ne}) = u_{rms}(\text{Ar}) \times \sqrt{\frac{39.948 \text{ g/mol}}{28.014 \text{ g/mol}}} = 668 \text{ m/s} \dots 2 \text{ pts}$$
$$u_{rms}(\text{Kr}) = u_{rms}(\text{Ar}) \times \sqrt{\frac{39.948 \text{ g/mol}}{83.80 \text{ g/mol}}} = 386 \text{ m/s} \dots 2 \text{ pts}$$

(c) 1 pt for each correct partial pressures and 1 pt for each correct mole fraction

1. c)

$$n_{\text{NO}_2, \text{initial}} = \frac{15.2 \text{ g}}{46.005 \text{ g} \cdot \text{mol}^{-1}} = 0.330 \text{ mol}$$
$$\Rightarrow n_{\text{NO}_2, \text{final}} + 2n_{\text{N}_2\text{O}_4, \text{final}} = 0.330$$
$$P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4} = \frac{RT}{V} n_{\text{NO}_2, \text{final}} + \frac{RT}{V} n_{\text{N}_2\text{O}_4, \text{final}} = 0.500 \text{ atm}$$
$$\Rightarrow n_{\text{NO}_2, \text{final}} + n_{\text{N}_2\text{O}_4, \text{final}} = 0.500 \text{ atm} \times \frac{10.0 \text{ L}}{(0.08206 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} = 0.204 \text{ mol}$$
$$\therefore n_{\text{NO}_2} = 0.078 \text{ mol}, \quad n_{\text{N}_2\text{O}_4} = 0.126 \text{ mol}$$
$$\Rightarrow X_{\text{NO}_2} = \frac{0.078}{0.078 + 0.126} = 0.382 \quad P_{\text{NO}_2} = \frac{RT}{V} n_{\text{NO}_2, \text{final}} = \frac{0.08206 \times 298}{10.0} \times 0.078 = 0.191 \text{ atm}$$
$$X_{\text{N}_2\text{O}_4} = \frac{0.126}{0.078 + 0.126} = 0.618 \quad P_{\text{N}_2\text{O}_4} = \frac{RT}{V} n_{\text{N}_2\text{O}_4, \text{final}} = \frac{0.08206 \times 298}{10.0} \times 0.126 = 0.308 \text{ atm}$$

3. Answer the following questions. (Total 10 pts)

(a) Write down the van der Waals equation of state and identify the unit of van der Waals constants ( $a$  and  $b$ ). (3 pts) (1 pt for correct equation, 1 pt for each correct unit, No partial pts)

(b) Explain the two modifications in the van der Waals equation of state against the ideal gas equation of state. (4 pts) (2 pts for each correct explanation on modification, No partial pts for incomplete explanation, You should explain them in detail!)

(c)The followings are the van der Waals constants for three gases: 1, 2 and 3. Identify the gases CO<sub>2</sub>, NO<sub>2</sub>, and SO<sub>2</sub> as 1, 2 or 3, giving brief reasons. (3 pts) (3 pts for correct matching and reasoning, No partial pts)

Gas	van der Waals constant a	Van der Waals constant b
1	3.592	0.04267
2	6.714	0.05636
3	5.284	0.04424

Answer)

(a)

$$\left( P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

(1 pt)

a : atm L<sup>2</sup> mol<sup>-2</sup>(1 pt)

b : L mol<sup>-1</sup>(1 pt)

(b)

- 1) Repulsion at short distance, excluded volume effect: Because of repulsive forces, molecules cannot occupy the same space at the same time. Therefore, the molecules exclude other molecules from the volumes they occupy, which leads to reduction in free volume. (2 pts)
- 2) Attraction at long distance: attractive forces between pairs of molecules (or tendency to cluster together) reduce the rate and frequency of collisions, which reduces the pressure below the ideal gas law prediction. (2 pts)

(c)(3 pts, No partial pts)

CO<sub>2</sub> : 1 – It has smallest value of constant a (nonpolar molecule).

NO<sub>2</sub> : 3 – It has high value of constant a (polar molecule), while similar value of constant b to CO<sub>2</sub> (because size of NO<sub>2</sub> is similar to that of CO<sub>2</sub>)

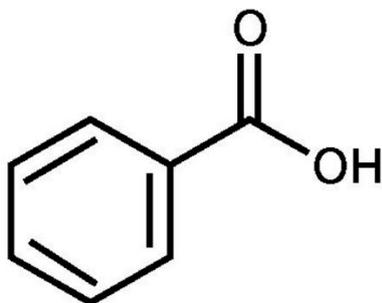
SO<sub>2</sub> : 2 – It has high value of constant a (polar molecule), while having highest value of constant b (because SO<sub>2</sub> is biggest molecule)

4. Answer the following questions. (Total 9 pts)

(a) State which attractive intermolecular forces are likely to predominate in associations amongst particles in the following substances: HF (liquid), SO<sub>2</sub> (liquid), NaCl (solid), and SO<sub>3</sub> (solid). (2 pts)  
(0.5 pts for each correct intermolecular force, No partial pts)

(b) List the following substances in order of increasing normalboiling points,  $T_b$ , and explain your reasoning: SO<sub>2</sub>, He, HF, CaF<sub>2</sub>, Ar. (2 pts)(No partial pts)

(c) Benzoic acid ( $C_6H_5COOH$ , refer to the structural formula below) is able to form dimers (dimeric molecules) in the gas phase and in nonpolar solvents. Sketch one unit of benzoic acid dimer clearly and name the major intermolecular force responsible for dimerization. Explain whether such dimers could be preferentially present in water with brief reason. (5 pts) (2 pts for correct dimer sketching, 1 pt for correct intermolecular force, 1 pt for dimer existence in water, 1 pt for correct reason)



Answer)

(a) Each 0.5 pts

HF : hydrogen bonding

SO<sub>2</sub> : dipole – dipole forces

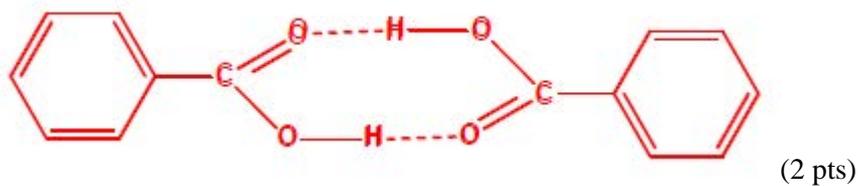
NaCl : ion – ion forces

SO<sub>3</sub> : London dispersion forces (van der Waals forces)

(b) 2 pts, No partial pts

He < Ar < SO<sub>2</sub> < HF < CaF<sub>2</sub>. Ar is heavier than He, while SO<sub>2</sub> has a dipole moment. Particularly strong dipole-dipole forces (hydrogen bonds) are present in HF, while CaF<sub>2</sub> is bound by ionic forces.

(c)



Major intermolecular force is hydrogen bonding. (1 pt)

This dimer would not form much in water because of the strong competition from water for hydrogen bonding. (1 pt)

5. Answer the following questions. (Total 10 pts)

(a) A 9.386 M aqueous solution of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) has a density of  $1.5091 \text{ g cm}^{-3}$ . Calculate the molality, the percentage by mass, and the mole fraction of sulfuric acid in this solution. (6 pts) (2 pts each for correct molality, mass percentage, mole fraction)

(b) A solution is prepared by dissolving 72.57 g of sucrose ( $C_{12}H_{22}O_{11}$ ) in 0.200 L of water. Taking the density of resulting solution to be  $1.14 \text{ g cm}^{-3}$ , calculate the mole fraction, molarity, and molality of sucrose in this solution. (6 pts) (2 pts each for correct mole fraction, molarity, molality)

Answer)

(a)

4. a) 1L of solution

$$M_{\text{solution}} = 1000 \text{ cm}^3 \times 1.5091 \text{ g} \cdot \text{cm}^{-3} = 1509.1 \text{ g}$$
$$M_{\text{H}_2\text{SO}_4} = 9.386 \text{ ml} \times 98.08 \text{ g} \cdot \text{mol}^{-1} = 920.6 \text{ g}$$
$$M_{\text{solvent}} = 588.5 \text{ g} = 0.5885 \text{ kg}$$
$$\Rightarrow \text{molality} = \frac{9.386}{0.5885} = 15.95 \text{ mol} \cdot \text{kg}^{-1} \quad \boxed{2 \text{ pts}}$$
  
$$\Rightarrow \text{mass percentage} = \frac{0.9206 \text{ kg}}{1.5091 \text{ kg}} \times 100 \% = 61.00 \% \quad \boxed{2 \text{ pts}}$$
$$n_{\text{H}_2\text{O}} = \frac{588.5 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} = 32.66 \text{ mol}$$
$$\Rightarrow \text{mole fraction} = \frac{9.386}{9.386 + 32.66} = 0.2232 \quad \boxed{2 \text{ pts}}$$

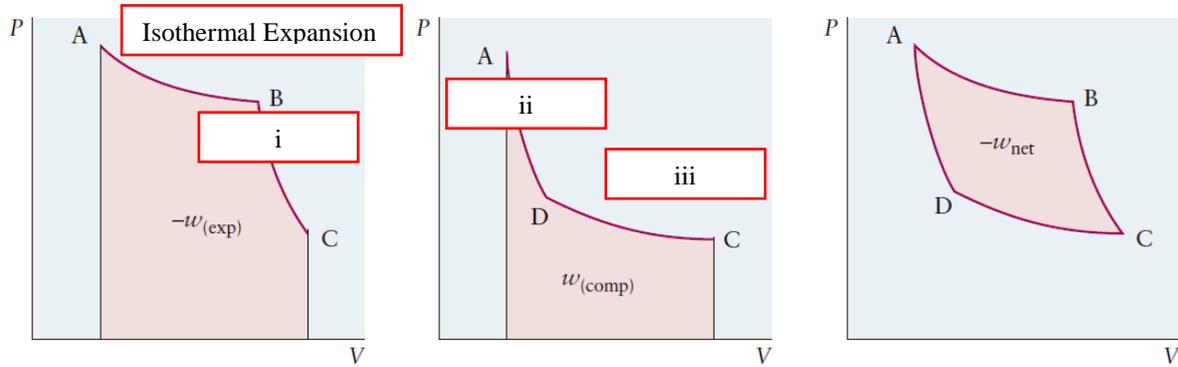
(b)

4. b)  $M_{\text{sucrose}} = 12.51 \text{ g}$

$$n_{\text{sucrose}} = \frac{12.51 \text{ g}}{342.2948 \text{ g/mol}} = 0.2120 \text{ mol}$$
$$\Rightarrow \text{molarity} = \frac{0.2120 \text{ mol}}{0.200 \text{ L}} = 1.06 \text{ mol} \cdot \text{L}^{-1} \quad \boxed{2 \text{ pts}}$$
$$M_{\text{solution}} = 1.14 \text{ g} \cdot \text{cm}^{-3} \times 200 \text{ cm}^3 = 228 \text{ g}$$
$$M_{\text{solvent}} = 155.43 \text{ g}$$
$$\Rightarrow \text{molality} = \frac{0.2120 \text{ mol}}{0.15543 \text{ kg}} = 1.364 \text{ mol} \cdot \text{kg}^{-1} \quad \boxed{2 \text{ pts}}$$
$$n_{\text{H}_2\text{O}} = \frac{155.43 \text{ g}}{18.02 \text{ g} \cdot \text{mol}^{-1}} = 8.625 \text{ mol}$$
$$\Rightarrow \text{mole fraction} = \frac{0.2120}{0.2120 + 8.625} = 0.02399 \quad \boxed{2 \text{ pts}}$$

6. Figure shows the stages of Carnot cycle. Answer the following questions. (Total 12 pts)

(a) Fill in the blanks on figure. (e.g., Part AB: isothermal expansion)(3 pts) (1 pt each, No



partial pts)

i (Part BC) : ii (Part DA) :

iii (Part CD) :

(b) Formulate (or calculate) the net work done in one passage around the Carnot cycle. (Use parameters: volume of each point  $V_A$ ,  $V_B$ ,  $V_C$ , and  $V_D$ ; high-temperature:  $T_h$ ; low-temperature:  $T_l$ ) (6 pts) (Partial pts exist)

(c) A thermodynamic engine (Carnot cycle) operates cyclically and reversibly between two temperature reservoirs, absorbing heat from the high-temperature bath at 450 K and discharging heat to the low-temperature at 300K. What is the thermodynamic efficiency of the engine? (3 pts) (No partial pts)

Answer) (a) i: Adiabatic Expansion    ii: Adiabatic Compression    iii: Isothermal Compression (1 pt each)

Path AB: Isothermal Expansion (temperature  $T_h$ )

$$w_{AB} = -q_{AB} = -nRT_h \ln\left(\frac{V_B}{V_A}\right) \quad \boxed{1 \text{ pt}}$$

Path BC: Adiabatic Expansion

$$q_{BC} = 0$$

$$w_{BC} = nc_V(T_i - T_h) = -nc_V(T_h - T_i) \quad \boxed{1 \text{ pt}}$$

Path CD: Isothermal Compression (temperature  $T_i$ )

$$w_{CD} = -q_{CD} = -nRT_i \ln\left(\frac{V_D}{V_C}\right)$$

$$= nRT_i \ln\left(\frac{V_C}{V_D}\right) \quad \boxed{1 \text{ pt}}$$

Path DA: Adiabatic Compression

$$q_{DA} = 0$$

$$w_{DA} = nc_V(T_h - T_i) \quad \boxed{1 \text{ pt}}$$

The net work done on the system is

$$w_{\text{net}} = w_{AB} + w_{BC} + w_{CD} + w_{DA}$$

$$= -nRT_h \ln\left(\frac{V_B}{V_A}\right) - nc_V(T_h - T_i)$$

$$+ nRT_i \ln\left(\frac{V_C}{V_D}\right) + nc_V(T_h - T_i)$$

$$= -nRT_h \ln\left(\frac{V_B}{V_A}\right) + nRT_i \ln\left(\frac{V_C}{V_D}\right)$$

This can be simplified by noting that  $V_B$  and  $V_C$  lie on one adiabatic path, and  $V_A$  and  $V_D$  lie on another. In Section 12.7, the relation for a reversible adiabatic process was found:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Hence,

$$\frac{T_h}{T_i} = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \quad \text{for path BC}$$

and

$$\frac{T_h}{T_i} = \left(\frac{V_D}{V_A}\right)^{\gamma-1} \quad \text{for path DA}$$

Equating these expressions gives

$$\left(\frac{V_C}{V_B}\right)^{\gamma-1} = \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

or

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \quad \text{and} \quad \frac{V_B}{V_A} = \frac{V_C}{V_D} \quad \boxed{1 \text{ pt}}$$

Hence, the net work done in one passage around the Carnot cycle is

$$w_{\text{net}} = -nR(T_h - T_i) \ln\frac{V_B}{V_A} \quad [13.19]$$

$\boxed{1 \text{ pt}}$

(b)

(c) 0.333 (3 pts, No partial pts)

7. Suppose 1.000 mol of argon (assumed to be an ideal gas) is confined in a container whose pressure is kept constant. Initially the volume and temperature of the gas were 22.41 L and 273.15K, respectively. When system is heated until 3.000kJ of heat has been added, the volume of the gas was doubled. The molar heat capacity of the gas does not change during the heating and equals  $20.79 \text{ J K}^{-1} \text{ mol}^{-1}$ . (Total 10 pts)

(a) Calculate the original pressure (in atm) inside the container. (1 pt) (No partial pts)

(b) Determine the heat ( $q$ ) (in J) and work ( $w$ ) (in J) for the system during the heating process. (4 pts)  
(2 pts for correct  $q$ , 2 pts for correct  $w$ )

(c) Compute the temperature (in K) of the gas after heating. Assume the container has zero heat capacity. (1 pt) (No partial pts)

(d) Compute the change in internal energy ( $\Delta U$ ) (in J) and the change in enthalpy ( $\Delta H$ ) (in J) of the gas during the heating process. (4 pts) (2 pts for correct  $\Delta U$ , 2 pts for correct  $\Delta H$ )

Answer)

(a)  $P = 0.9995 \text{ atm}$  (using ideal gas law) (1 pt)

(b)  $Q = +3000 \text{ J}$  (2 pts)

$W = -P_{\text{ext}} \Delta V = -0.9995 \text{ atm} \times 22.41 \text{ L} \times 101.325 \text{ J L}^{-1} \text{ atm}^{-1} = -2270 \text{ J}$  (2 pts)

(c)  $\Delta T = Q / n c_p = 3000 / 20.79 = 144.3 \text{ K}$

$T = 144.3 + 273.15 = 417.5 \text{ K}$  (1 pt)

(d)  $\Delta U = Q + W = 730 \text{ J}$  (2 pts)

$\Delta H = Q = 3000 \text{ J}$  (2 pts)

8. Boltzmann's statistical definition of entropy states that entropy is the measurement of the number of microstates available. (Total 10 pts)

(a) Express entropy ( $S$ ) in terms of the number of available microstates  $\Omega(E, V, N)$  at given energy ( $E$ ), volume ( $V$ ), and number of molecules ( $N$ ) with appropriate constants. Then, determine whether entropy is an extensive or intensive property. (3 pts) (2 pts for correct expression, 1 pt for correct property classification)

(b) The  $\text{CH}_3\text{D}$  ( $\text{D}=\text{}^2\text{H}$ ) molecule has a tetrahedral structure. In a random crystal (formed on rapid freezing), each molecule has four equally likely orientations. In an ordered crystal of  $\text{CH}_3\text{D}$ , the molecules are lined up in a regular fashion, with the orientation of each determined by its position in the crystal. Calculate the entropy change when 1.00 mol (consisted of  $N_A$  molecules) of an ordered crystal is converted to a random crystal at 0 K. (4 pts) (1 pt for entropy of random crystal, 1 pt for entropy of ordered crystal, 2 pt for the entropy change)

(c) Consider the entropy change when 1.00 mol of an ordered crystal of  $\text{N}_2\text{O}$  molecule (with the structure of N-N-O) is converted to a random crystal with the entropy change obtained at (b). Predict which one is larger and explain why. (3 pts) (1 pt for correct prediction, 2 pts for correct explanation)

Answer)

(a)  $S = k_B \ln \Omega(E, V, N)$  (2 pts)

Entropy is an extensive property. (1 pt)

(b)

$$S_{\text{random}} = k_B \ln 4^{N_A} \text{ (1 pt)}$$

$$S_{\text{ordered}} = k_B \ln 1 \text{ (1 pt)}$$

$$\Delta S = k_B \ln 4^{N_A} - k_B \ln 1 = N_A k_B \ln 4 = 11.53 \text{ J/K (2 pts)}$$

(c) The entropy change is larger for the CH<sub>3</sub>D molecule. (1 pt)

The N<sub>2</sub>O molecule has a linear structure (N-N-O backbone). For a random crystal, the N<sub>2</sub>O molecule has less possible orientations (2 possible, N-N-O or O-N-N), giving smaller entropy change. (2 pts)

9. Consider the reaction where carbon reduces iron (III) oxide to iron and carbon dioxide under atmospheric pressure (1 atm). Answer the following questions. (For calculation, refer to Appendix D attached.) (Total 12 pts)

(a) Write the balanced reaction equation corresponding to the reaction stated above. (2 pts) (No partial pts)

(b) Calculate  $\Delta G$  at  $T = 300 \text{ K}$ . (5 pts) (Partial pts exist)

(c) Is this reaction spontaneous at  $T = 300 \text{ K}$ ? If not, at which temperature (in K) would the reaction start to occur spontaneously? (3 pts) (1 pt for correct spontaneity prediction, 2 pt for correct temperature)

(d) At  $T = 1000 \text{ K}$ , calculate the equilibrium constant  $K$ . (2 pts) (No partial pts)

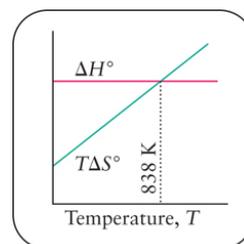
Answer)

(a) 2 pts, No partial pts



$$\begin{aligned}\Delta H^\circ &= (3 \text{ mol}) \times \Delta H_f^\circ(\text{CO}_2, \text{g}) - (2 \text{ mol}) \times \Delta H_f^\circ(\text{Fe}_2\text{O}_3, \text{s}) \\ &= 3(-393.5) - 2(-824.2) \text{ kJ} \\ &= +467.9 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \{(4 \text{ mol}) \times S_m^\circ(\text{Fe}, \text{s}) + (3 \text{ mol}) \times S_m^\circ(\text{CO}_2, \text{g})\} \\ &\quad - \{(2 \text{ mol}) \times S_m^\circ(\text{Fe}_2\text{O}_3, \text{s}) + (3 \text{ mol}) \times S_m^\circ(\text{C}, \text{s})\} \\ &= \{4(27.3) + 3(213.7)\} - \{2(87.4) + 3(5.7)\} \text{ J}\cdot\text{K}^{-1} \\ &= +558.4 \text{ J}\cdot\text{K}^{-1}\end{aligned}$$



(b) enthalpy 2 pt, entropy 2 pt, gibbs free energy 1 pt

$$\Delta G = 467.9 - 300 \times 558.4 \times 10^{-3} = 300.4 \text{ kJ}$$

No points for wrong or missing units.

(c)

Nonspontaneous at  $T = 300 \text{ K}$  (1 pt)

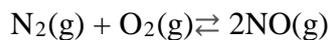
$$T = \frac{\overbrace{467.9 \text{ kJ}}^{4.679 \times 10^5 \text{ J}}}{558.4 \text{ J}\cdot\text{K}^{-1}} = 838 \text{ K} \quad , \text{ above } 838 \text{ K}$$

(2 pts)

$$(d) \text{ At } 1000\text{K}, \Delta G^\circ = 467.9 \times 10^3 - 1000 \times 558.4 = -90500 \text{ J} = -RT \ln K = -8.3145 \times 1000 \times \ln K$$

$$K = 5.335 \times 10^4 \text{ at } 1000 \text{ K} \text{ (2 pts)}$$

10. At 25 °C, the equilibrium constant for the reaction



is  $4.2 \times 10^{-31}$ . Suppose a container is filled with nitrogen (at an initial partial pressure of 0.41 atm), oxygen (at an initial partial pressure of 0.59 atm), and nitrogen oxide (at initial partial pressure of 0.22 atm). (Total 8 pts)

(a) Calculate the reaction quotient (Q) and predict direction of the reaction. (2 pts) (1 pt for reaction quotient, 1 pt for direction prediction, No partial pts)

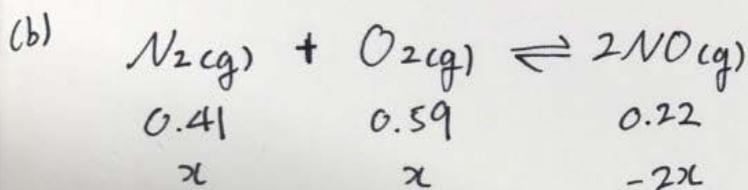
(b) Calculate the partial pressures (in atm) of all three gases after equilibrium is reached at this temperature. (6 pts) (2 pts for each partial pressure)

Answer)

$$(a) \quad Q = \frac{P_{NO}^2}{P_{N_2} P_{O_2}} = \frac{(0.22)^2}{0.41 \times 0.59} = 2.00 \times 10^{-1} = 0.20 \quad \boxed{1 \text{ pt}}$$

$$0.20 = Q > K = 4.2 \times 10^{-31}$$

reaction moves to the left. 1 pt



$$\hline \begin{array}{ccc} 0.41+x & 0.59+x & 0.22-2x \end{array}$$

$$K = 4.2 \times 10^{-31} = \frac{P_{NO}^2}{P_{N_2} P_{O_2}} = \frac{(0.22-2x)^2}{(0.41+x)(0.59+x)}$$

Equilibrium constant ( $K$ ) is very small. Suppose that all of the  $NO(g)$  reacts. Then,  $2x = 0.22 \rightarrow x = 0.11$

$$P_{N_2} = 0.41 + 0.11 = 0.52 \text{ atm} \quad \boxed{2 \text{ pt}}$$

$$P_{O_2} = 0.59 + 0.11 = 0.70 \text{ atm} \quad \boxed{2 \text{ pt}}$$

$$P_{NO} = 3.9 \times 10^{-16} \text{ atm} \quad \boxed{2 \text{ pt}}$$

11. Answer the following questions. (Total 7 pts)

(a) Formulate the equilibrium expression for the endothermic reaction (1 pt) (No partial pts)



(b) What is the effect on  $P_{\text{NH}_3}$ , at equilibrium if additional  $\text{AgCl}(\text{s})$  is added? (2 pts) (No partial pts)

(c) What is the effect on  $P_{\text{NH}_3}$ , at equilibrium if additional  $\text{NH}_3(\text{g})$  is pumped into the system, provided that neither of the two solid phases shown in the chemical equation is completely used up? (2 pts) (No partial pts)

(d) What is the effect on  $P_{\text{NH}_3}$  of lowering the temperature? (2 pts) (No partial pts)

Answer)

(a)  $K = P_{NH_3}$

(b) Addition of AgCl(s) has no effect on the equilibrium partial pressure of NH<sub>3</sub>.

(c) Pumping in NH<sub>3</sub> has no effect on the equilibrium partial pressure of NH<sub>3</sub> as long as some AgCl(s) remains. The added NH<sub>3</sub> simply reacts with AgCl(s) until  $P_{NH_3}$  again equals  $K$ .

(d) Lowering the temperature of an endothermic reaction decrease its equilibrium constant. The  $P_{NH_3}$  therefore decreases in order to stay equal to  $K$ .