

**2012 FALL Semester Midterm Examination  
For General Chemistry I (CH101)**

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

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

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
<b>1</b>	/15	<b>6</b>	/14	<b>/150</b>
<b>2</b>	/10	<b>7</b>	/18	
<b>3</b>	/15	<b>8</b>	/20	
<b>4</b>	/16	<b>9</b>	/14	
<b>5</b>	/8	<b>10</b>	/20	

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

Please write down the unit (e.g. kJ/mol) of your answer when applicable. You will get 30% deduction for a missing unit.

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

(채점답안지 분배 및 이의신청 일정)

**1. Period, Location, and Procedure**

- 1) Return and Claim Period: **October 29 (Mon, 7:00 ~ 8:00 p.m.)**
- 2) **Location: Room for quiz session**
- 3) Procedure:

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

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

If you have any claims on it, you can submit the claim paper with your opinion. After writing your opinions on the claim form, attach it to your mid-term paper with a stapler. Give them to TA.

(The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 10/29 on the web.)

**2. Final Confirmation**

- 1) Period: November 1 (Thu) – 2 (Fri)
- 2) Procedure: During this period, you can check final score of the examination *on the website* again.

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

## The Answers

Problem	points	Problem	points	TOTAL pts
<b>1</b>	5+5+5 /15	<b>6</b>	3+3+3+3+2/14	<b>/150</b>
<b>2</b>	5x2 /10	<b>7</b>	5+5+5+3 /18	
<b>3</b>	5+5+5 /15	<b>8</b>	10+10 /20	
<b>4</b>	3+3+3+5+2/16	<b>9</b>	6+8 /14	
<b>5</b>	4+4/8	<b>10</b>	5+5+5+3+2/20	

1. For H (Z = 1)

$$E_n = -\text{constant} \left( \frac{1}{n^2} \right)$$

The constant is  $hR$  ( $R = \text{Rydberg constant}$ ),  $2.18 \times 10^{-18} \text{ J}$  or  $13.6 \text{ eV}$

For the transition,  $n_7 \rightarrow n_6$  (emission)

$$\Delta E = 13.6 \left( \frac{1}{36} - \frac{1}{49} \right) \text{ eV} = \text{energy of photon}$$

$$= \underline{0.100 \text{ eV}} \quad (5 \text{ points})$$

$$= 0.100 \text{ eV} \times \frac{96.5 \text{ kJ/mol}}{1 \text{ eV}} = \underline{9.65 \text{ kJ/mol}} \quad (5 \text{ points})$$

$$\Delta E = h\nu = hc/\lambda$$

$$\text{Hence } \lambda = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{9650 \text{ J/mol}} \times 6.022 \times 10^{23} / \text{mol}$$

$$\cong \underline{1.24 \times 10^{-5} \text{ m}} \quad (\text{or } 12.4 \mu\text{m}) \quad (5 \text{ points})$$

Allow partial points and give full points for correct alternative working, e.g. initial use of the Rydberg equation

$$\nu = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

rather than the Bohr equation

2. Orbital	3s	2p	6d	5f	5p
n	3	2	6	5	5
l	0	1	2	3	1
radial nodes	2	0	3	1	3
angular nodes	0	1	2	3	1

5 x 2 points  
(Allow partial points)

3. (a) Predicted electronic configuration of Pd (Z = 46) is  $[\text{Kr}]4d^85s^2$  (paramagnetic). Actual electronic configuration is  $[\text{Kr}]4d^{10}$  (diamagnetic) (5 points)

(b) Sc (Z = 21) is  $[\text{Ar}]3d^14s^2$  (paramagnetic)

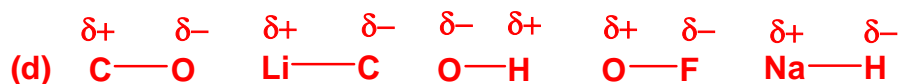
$\text{Sc}^+$  is  $[\text{Ar}]3d^14s^1$  (paramagnetic) (5 points)

(c) Phosphorus (P) (5 points)

4. (a) (i)  $\text{Li}^+\text{Cl}^-(\text{g})$  (3 points)

(b) (i)  $\text{Li}^+\text{Cl}^-(\text{s})$  (3 points)

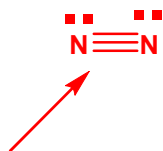
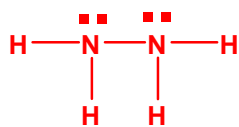
(c)  $\text{Br}^-$  is the most polarizable anion, as it is the largest. (3 points)



(5 x 1 = 5 points)

Li-C and Na-H have greatest ionic character (2 points)

5. (a)



The strongest NN bond is  $\text{N}\equiv\text{N}$  (a triple bond)

(3 + 1 = 4 points)

(b)  $\text{CO} > \text{CO}_2 > \text{CO}_3^{2-}$

Triple bond

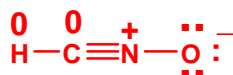
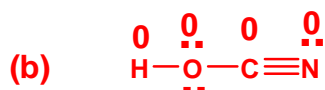
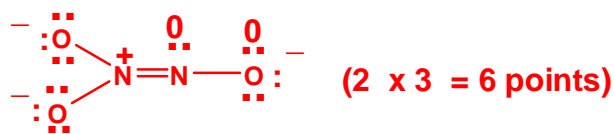
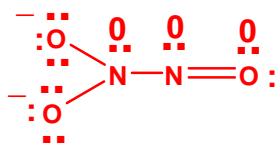
Double bonds

1 Double, 2 single bonds

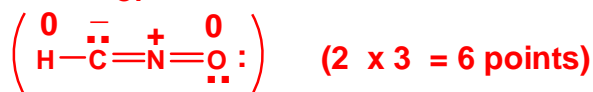
in Lewis structures

(4 points)

6. (a)

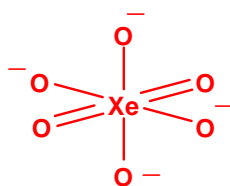
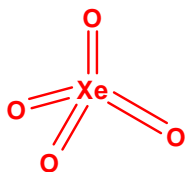
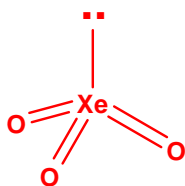


or



$\text{HOCN}$  (cyanic acid) is likely to be more stable (2 points)

7.



Trigonal pyramidal

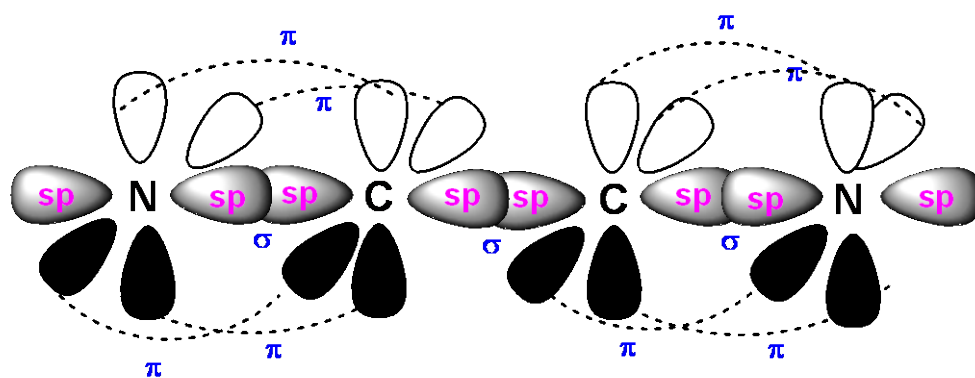
Tetrahedral

Octahedral

(3 x 5 = 15 points)

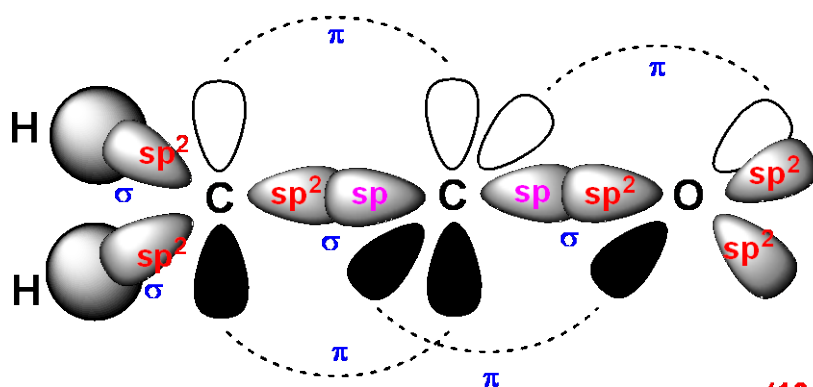
The longest Xe-O bond is in  $\text{XeO}_6^{4-}$  (it has more partial single bond character) (3 points)

8. (a)



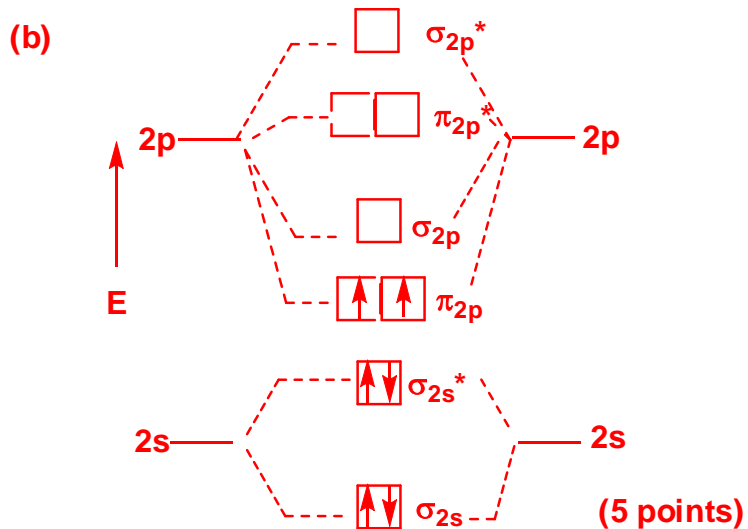
(10 points)

(b)



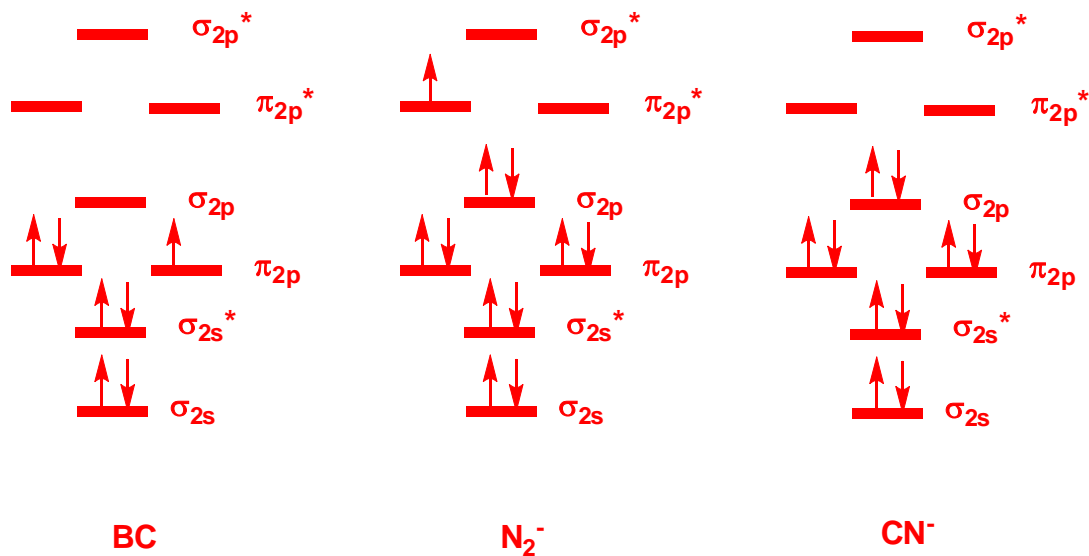
(10 points)

- 9.(a)  $B \equiv B$  (4 points)  
 Bond order is 3 (triple bond) (1 point)  
 $B_2$  is diamagnetic (1 point)



- Valence electron configuration  $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$  (1 point)  
 Bond order =  $\frac{1}{2}(4 - 2) = 1$  (1 point)  
 $B_2$  is paramagnetic (two unpaired electrons) (1 point)

10. (a)

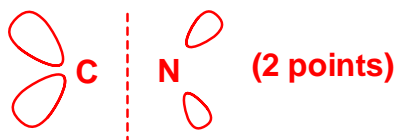


(3 x 5 = 15 points)

(b) Bond orders: BC = 1.5;  $N_2^-$  = 2.5;  $CN^-$  = 3 (3 points)

(c) LUMO in  $CN^-$  is  $\pi_{2p}^*$

(Greater presence on C)



(2 points)

1. The Humphreys series of lines in the emission spectrum of atomic hydrogen are based on the electronic transitions at the  $n = 6$  level.

(a) What is the energy, in eV and  $\text{kJ mol}^{-1}$ , of a photon that results from the longest wavelength transition in this series?

**(Answer)**

(b) What is the wavelength of this line?

**(Answer)**

*The Rydberg unit of energy =  $2.18 \times 10^{-18} \text{ J}$  or  $13.6 \text{ eV}$ ; the Rydberg constant =  $3.29 \times 10^{15} \text{ s}^{-1}$ ; Planck's constant  $h = 6.626 \times 10^{-34} \text{ J s}$ ; speed of light  $c = 2.998 \times 10^8 \text{ m s}^{-1}$ ;  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$  or  $96.5 \text{ kJ mol}^{-1}$ ; Avogadro number =  $6.022 \times 10^{23} \text{ mol}^{-1}$*



2. Give the value of the quantum numbers  $n$  and  $l$ , the number of radial nodes and the number of angular nodes for the orbitals  $3s$ ,  $2p$ ,  $6d$ ,  $5f$  and  $5p$ .

**(Answer)**

3. (a) Palladium (Pd) is predicted by the Aufbau Principle to be paramagnetic, but is in fact diamagnetic. Write the predicted and actual electron configurations that explain these facts. You may use short hand noble gas configurations for core electrons.

**(Answer)**

(b) Write the electron configuration of Sc and Sc<sup>+</sup>, given that they are both paramagnetic. You may use short hand noble gas configurations for core electrons.

**(Answer)**

(c) Identify the period 3 element that possesses the ionization energies (I in kJ mol<sup>-1</sup>) in the table below.

$I_1$	$I_2$	$I_3$	$I_4$	$I_5$	$I_6$
1012	1903	2910	4956	6278	22,230

**(Answer)**

4. (a) With which would you associate the bigger sum of first ionization energy and electron affinity for the production of ions from atoms in the gas phase? (i)  $\text{Li}^+\text{Cl}^-(\text{g})$  or (ii)  $\text{Rb}^+\text{Cl}^-(\text{g})$ ?

**(Answer)**

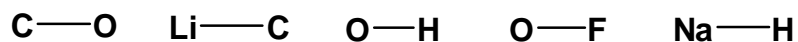
(b) With which would you associate the bigger lattice energy? (i)  $\text{Li}^+\text{Cl}^-(\text{s})$  or (ii)  $\text{Rb}^+\text{Cl}^-(\text{s})$ ?

**(Answer)**

(c) Determine which is the most polarizable anion amongst  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{N}^{3-}$ , and  $\text{O}^{2-}$ . Give a brief reason for your answer.

**(Answer)**

(d) Determine the polarity of the following covalent bonds, according to electronegativity difference, by writing  $\delta^+$  or  $\delta^-$  over the appropriate symbols.



Which two of the above bonds have the greatest ionic character?

**(Answer)**

5. (a) Draw a Lewis structure for each of the following and explain briefly which has the strongest NN bond.

$\text{NH}_2\text{NH}_2$        $\text{HNNH}$        $\text{N}_2$

**(Answer)**

(b) Place the molecules or ions in order of decreasing CO bond strength, giving a brief reason.

$\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CO}_3^{2-}$

**(Answer)**

6. (a) "Angeli's salt" is  $\text{Na}_2\text{N}_2\text{O}_3$ . The anion of this salt ( $\text{N}_2\text{O}_3^{2-}$ ) has the skeletal structure (ON-NO<sub>2</sub>). Write down two suitable Lewis structures for  $\text{N}_2\text{O}_3^{2-}$ , showing all formal charges.

**(Answer)**

(b) Write down suitable Lewis structures, with formal charges on all atoms, for the molecules cyanic acid (HOCN) and fulminic acid (HCNO). On the basis of formal charges, state which molecule is likely to be the more stable.

**(Answer)**

7. Using the best Lewis structures (those with the maximum number of zero formal atomic charges), sketch and name the VSEPR molecular geometries of  $\text{XeO}_3$ ,  $\text{XeO}_4$  and  $\text{XeO}_6^{4-}$ . Which one of these has the (overall) longest Xe-O bonds?

**(Answer)**

8. Use valence (VB) theory to predict the hybridization in cyanogen and ketene. Sketch the atomic orbitals depicting their overlap and  $\sigma$  and  $\pi$ -bonding and include lone pair orbitals.

(a) Cyanogen:  $\text{N}=\text{C}-\text{C}\equiv\text{N}$

**(Answer)**

(b) Ketene  $\text{H}_2\text{C}=\text{C}=\text{O}$

**(Answer)**

9. The MO model often gives a more accurate picture of bonding than the VB model. The molecule  $B_2$  has weak covalent bonding and is known to be paramagnetic.

(a) Draw the most likely Lewis structure for  $B_2$  (the one that comes closest to giving a full octet of electrons for each B atom) and from this predict its bond order and magnetic properties.

**(Answer)**

(b) Sketch a full molecular orbital (MO) energy diagram (showing atomic orbitals, molecular orbitals and electrons) for the  $B_2$  molecule and from this write the electron configuration of the molecule. Predict the bond order and magnetic properties of  $B_2$ .

10. (a) Sketch an MO energy diagram showing only the *molecular orbitals* and electron distribution in each of BC, N<sub>2</sub><sup>-</sup>, and CN<sup>-</sup>. Label the energy levels according to the type of orbitals from which they are made, whether they are σ- or π-orbitals, and whether they are bonding or antibonding (\*).

**(Answer)**

(b) Using your diagrams in (a), predict the bond orders for BC, N<sub>2</sub><sup>-</sup>, and CN<sup>-</sup>.

**(Answer)**

(c) Identify and sketch the MO boundary surface of the CN<sup>-</sup> lowest energy unoccupied MO (LUMO).

**(Answer)**



**2012 Fall Semester Final Examination**  
**2012 FALL Semester Final Examination**  
**For General Chemistry I (CH101)**

*Date: December 14 (Fri), Time Limit: 7:00 ~ 9:00 p.m.*

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

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/14	6	/10	<b>/150</b>
2	/10	7	/20	
3	/20	8	/10	
4	/10	9	/18	
5	/20	10	/18	

\*\* This paper consists of 13 sheets with 10 problems (page 11: claim form, page 12: periodic table, page 13: fundamental constants). Please check all page numbers before taking the exam. Write down your work and answers in the sheet. Please write down the unit (e.g. kJ/mol) of your answer when applicable. You will get 30% deduction for a missing unit.

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

(채점답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

- 1) Return and Claim Period: *December 18 (12:00 ~ 14:00 p.m., 2 hours)*
- 2) *Location: Creative Learning Bldg.(E11)*

Class	Room
	<b>408</b>

- 3) Claim Procedure:

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

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

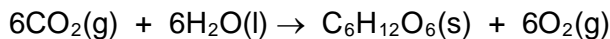
(During the period, you can check the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it.)

*To get more information, visit the website at [www.gencheminkaist.pe.kr](http://www.gencheminkaist.pe.kr).*

2. Final Confirmation

- 1) Period: *December 20 (Thu)*
- 2) Procedure: During this period, you can check the final score of the examination *on the website* again

1 (a) Calculate the mass of glucose ( $C_6H_{12}O_6$ ) produced, when 1630 mL of  $CO_2$ , adjusted to  $25\text{ }^\circ C$  and 1.0 atm, undergoes photosynthesis according to the equation:



The molar volume of  $CO_2$  at  $25\text{ }^\circ C$  and 1 atm is 24.47 L. (7 points)

From the equation, the stoichiometry of  $CO_2$ :glucose is 6:1.  
The molar mass of glucose is 180 g/mol.

$$\begin{aligned} \text{Mass of glucose} &= 1.63\text{ L} \times \frac{1\text{ mol } CO_2}{24.47\text{ L}} \times \frac{1\text{ mol glucose}}{6\text{ mol } CO_2} \times \frac{180\text{ g glucose}}{1\text{ mol glucose}} \\ &= \underline{2.00\text{ g glucose}} \quad (7\text{ points}) \end{aligned}$$

Give partial points and give full points for alternative correct working

(b) It takes a certain volume of pure argon 54.9 s to effuse through a porous barrier at a fixed temperature. The same volume of an unknown vapor at the same temperature takes 130 s to effuse through the same barrier. Calculate the molar mass of the unknown vapor. (7 points)

From Graham's law of effusion,

$$\frac{\text{Effusion time for Ar}}{\text{Effusion time for unknown}} = \sqrt{\frac{\text{Molar mass of Ar}}{\text{Molar mass of unknown}}}$$
$$\frac{54.9\text{ s}}{130\text{ s}} = \sqrt{\frac{39.95\text{ g/mol}}{M_r(\text{unknown})}}$$

$$M_r = 224\text{ g mol}^{-1}$$

Hence molar mass of unknown is  $224\text{ g mol}^{-1}$  (7 points)

Allow partial points

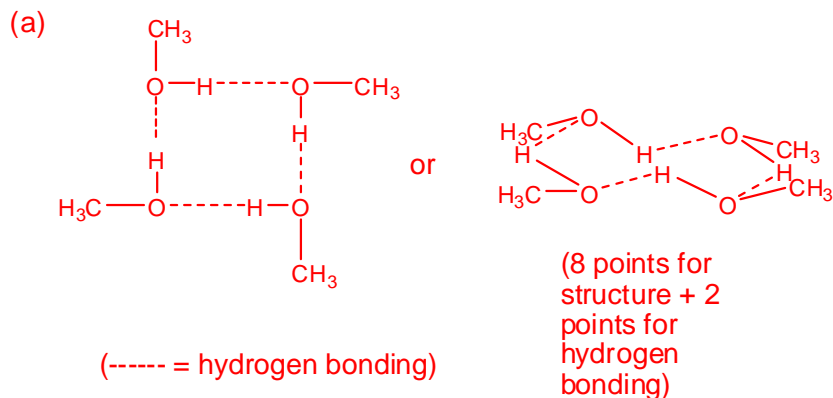
2 Explain briefly the difference in the van der Waals constants a and b for the following gases (2 x 5 points).

Gas	a / atm L <sup>2</sup> mol <sup>-2</sup>	b / L mol <sup>-1</sup>
Methane	2.253	0.04278
Ammonia	4.170	0.03707
Water	5.464	0.03049

Constants b increase with increase in molecular size:  $H_2O < NH_3 < CH_4$ . (5 points)

Constants a increase with increase in strength of intermolecular bonding:  $CH_4$  (London forces) <  $NH_3$  (dipole-dipole forces/hydrogen bonding) <  $H_2O$  (stronger dipole-dipole forces/hydrogen bonding) (5 points)

**3 (a)** Methanol is known to exist in the gas phase as tetrameric units,  $(\text{CH}_3\text{OH})_4$ . Draw a suitable structure for this tetramer and name the major kind of intermolecular attraction that holds the tetramer together. (10 points)

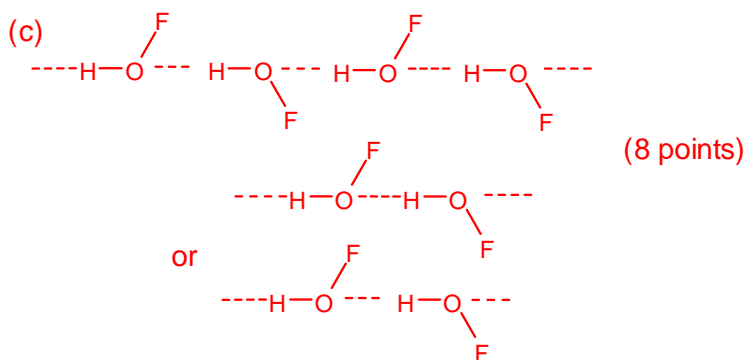


Allow Partial points for part (a), according to feasibility of suggested structure

**(b)** Is this structure in (a) likely to exist in an aqueous solution of methanol? (2 points)

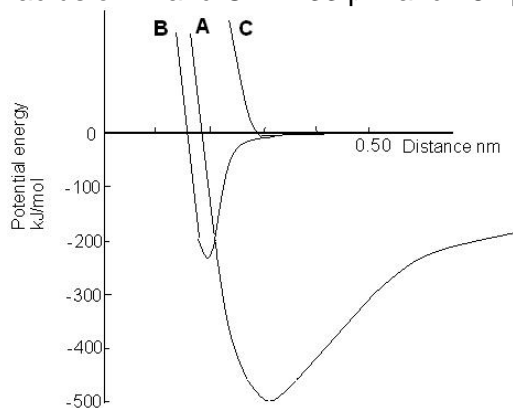
(b) No, hydrogen-bonding competition between methanol and water would be too high. (Methanol and water are very soluble in each other). (2 points)

**(c)** Liquid hypofluorous acid (HOF) is known to contain O...H hydrogen bonding only. Draw a diagram to show how four molecules are linked by hydrogen bonding. Bond angle HOF is  $101^\circ$ . (8 points)



Full points only for either of above diagrams, but can give partial points

**4 (a)** Below are potential energy *versus* distance diagrams, A, B, and C, for hydrogen chloride (HCl), potassium chloride (KCl), and Chlorine (Cl<sub>2</sub>). Identify curves A, B, or C belonging to HCl, KCl or Cl<sub>2</sub>. Ionic radius of K<sup>+</sup> and Cl<sup>-</sup> = 133 pm and 181 pm, respectively (6 points)



A: KCl  
 B: Cl<sub>2</sub>  
 C: HCl (6 points)

**(b)** List the following substances in order of increasing melting point (m.pt.):  
 HF, Cl<sub>2</sub>, Ar, KCl, C (diamond), SO<sub>2</sub> (4 points)

LOWEST m.pt. Ar < Cl<sub>2</sub> < SO<sub>2</sub> < HF < KCl < C (diamond) HIGHEST m.pt.

(4 points)

**5 (a)** If the ionic radius of  $\text{Tl}^+$  is 140 pm and ionic radius of  $\text{Cl}^-$  is 181 pm, determine the type (fcc, etc) of ionic crystal lattice that exists for thallium (I) chloride ( $\text{TlCl}$ ). (5 points)

$$\begin{aligned} \text{(a)} \quad \text{Radius ratio, } r &= \frac{\text{radius of smaller ion}}{\text{radius of larger ion}} = \frac{0.140 \text{ pm}}{0.181 \text{ pm}} \\ &= 0.77 \end{aligned}$$

This value is greater than 0.7 and is indicative of a body-centered cubic (cesium chloride) ionic crystal lattice (5 points)

(b) Using your result for (a) and the ionic radii, determine the density of the thallium (I) chloride crystal. (15 points)

(b)  $\text{TlCl}$  has a cesium chloride (bcc) type structure.

$$r(\text{Tl}^+) = 140 \text{ pm}; r(\text{Cl}^-) = 181 \text{ pm}$$

$$\text{Length of diagonal, } b = 2(140) + 2(181) = 642 \text{ pm}$$

$$\text{Length of side } a = 642/3^{1/2} = 371 \text{ pm}$$

$$\text{Hence unit cell volume is } = 5.11 \times 10^7 \text{ pm}^3 \text{ or } 5.11 \times 10^{-23} \text{ cm}^3$$

(1 pm<sup>3</sup> = 10<sup>-30</sup> cm<sup>3</sup>)

Each bcc unit cell has one  $\text{Tl}^+$  ion and one  $\text{Cl}^-$  ion,

Density = mass/volume =

$$\frac{(204.37 + 35.453) \text{ g mol}^{-1}}{(6.022 \times 10^{23} \text{ mol}^{-1})} \times 5.11 \times 10^{-23} \text{ cm}^3 = \underline{7.79 \text{ g cm}^{-3}}$$

(15 points)

Allow partial points and give full points for correct alternative working

**6** Adding a certain amount of heat to 100 g of water at constant pressure raises its temperature by 3.79 °C. Adding the same amount of heat to 100 g of benzene at constant pressure raises its temperature by 15.2 °C. Find the specific heat ( $C_p$ ) of benzene. (10 points)[ $C_p$  for water is 4.18 J °C<sup>-1</sup> g<sup>-1</sup>]

If  $q(\text{water}) = q(\text{benzene})$ ,

$$\text{then } m(\text{water})C_p(\text{water})\Delta T(\text{water}) = m(\text{benzene})C_p(\text{benzene}) \Delta T(\text{benzene})$$

Since the masses are equal,

$$\begin{aligned} C_p(\text{benzene}) &= C_p(\text{water}) \Delta T(\text{water}) / \Delta T(\text{benzene}) \\ &= (4.18 \text{ J g}^{-1} \text{ °C}^{-1}) \times (3.79 \text{ °C}) / 15.2 \text{ °C} \\ &= \underline{1.04 \text{ J g}^{-1} \text{ °C}^{-1}} \quad (10 \text{ points}) \end{aligned}$$

Can give partial points: give reduced points for longer method of calculation

**7 (a)** Suppose 1.00 mol of hydrogen gas is expanded reversibly from an initial volume of 10.0 L at 400 K to a final volume of 50.0 L, without changing the temperature. Assuming ideal behavior, determine the free energy change ( $\Delta U$ ), the enthalpy change ( $\Delta H$ ), the heat transferred ( $q$ ), and the work done ( $w$ ) for this process. (10 points)

(a) Since this is an isothermal expansion ( $\Delta T = 0$ ),  $\Delta U = \Delta H = 0$  (2 points)

For a reversible isothermal process,

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$= -(1.00 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(400 \text{ K}) \ln\left(\frac{50.0 \text{ L}}{10.0 \text{ L}}\right)$$

$$= \underline{-5353 \text{ J}} \quad (5 \text{ points})$$

From the first law of thermodynamics,  $q = -w$

Hence,  $q \equiv \underline{5353 \text{ J}}$  (3 points)

Can give partial points: give full points for correct alternative working

**(b)** When 1.000 g of potassium chlorate ( $\text{KClO}_3$ ) is dissolved in 50.00 g of water held in a Styrofoam calorimeter of negligible heat capacity, the temperature drops from 24.50 to 22.86 °C. Calculate  $q$  for water and molar  $\Delta H^\circ$  for the process  $\text{KClO}_3(\text{s}) \rightarrow \text{K}^+(\text{aq}) + \text{ClO}_3^-(\text{aq})$ . Specific heat of water is  $75.40 \text{ J K}^{-1} \text{ mol}^{-1}$ . (10 points)

(b) The system is  $\text{KClO}_3$  and the surroundings is  $\text{H}_2\text{O}$

Molar mass of water is  $18.02 \text{ g mol}^{-1}$  and molar mass of  $\text{KClO}_3$  is  $122.6 \text{ g mol}^{-1}$

$q(\text{water}) = \text{mass} \times \text{specific heat} \times \Delta T$

$$= (50.00 \text{ g}) \left( \frac{75.40 \text{ J K}^{-1} \text{ mol}^{-1}}{18.02 \text{ g mol}^{-1}} \right) (-1.64 \text{ K})$$

$$= \underline{-343.1 \text{ J}} \quad (6 \text{ points})$$

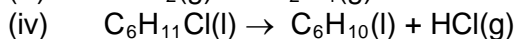
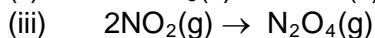
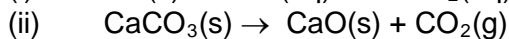
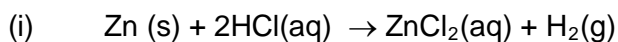
$\Delta H(\text{reaction}) = -q$ , scaled up to 1.00 mol: for 122.6 g of  $\text{KClO}_3$

$$= (+343.1 \text{ J}) \left( \frac{122.6 \text{ g mol}^{-1}}{1.00 \text{ g}} \right)$$

$$= \underline{+42.06 \text{ J mol}^{-1} \text{ or } +42.06 \text{ kJ mol}^{-1}} \quad (4 \text{ points})$$

Can give partial points: give full points for correct alternative working

**8** Deduce the sign of  $\Delta S$  for the following processes.



(v) Sample of air  $\rightarrow$  separate samples of pure  $\text{O}_2$ ,  $\text{N}_2$  and Ar at same pressure and temperature  
(5 x 2 points)

(i) +ve (ii) +ve (iii) -ve (iv) +ve (v) -ve

(5 x 2 points)

9 A well-insulated ice-water bath at 0.00°C contains 25.0 g of ice. When a piece of copper at 150.0°C is dropped into the bath, 15.6 g of the ice melts. Calculate the total entropy change for the thermodynamic universe of this process. Throughout the experiment, the bath is maintained at a constant pressure of 1 atm. (18 points)

[Specific heat at constant pressure ( $C_p$ ) of copper is  $0.385 \text{ J K}^{-1} \text{ g}^{-1}$ . Enthalpy of fusion of ice  $\Delta H_{\text{fus}} = +334 \text{ J g}^{-1}$ . Take  $0^\circ\text{C}$  to be  $273.15 \text{ K}$ ]

Copper is the system and ice the surroundings. All the heat that flows from the hot copper to ice is used to melt a certain amount of ice.

Heat lost by copper = heat gained by ice (heat needed to melt 15.6 g of ice)

$$-m(\text{Cu}) \times C_p(\text{Cu}) \times \Delta T = m\Delta H_{\text{fus}}$$

$$-m \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times (-150 \text{ K}) = (15.6 \text{ g}) \times (334 \text{ J g}^{-1})$$

$$m = 90.2 \text{ g}$$

For the system,  $\Delta S(\text{copper}) = mC_p \ln(T_2/T_1)$

$$= (90.2 \text{ g}) \times (0.385 \text{ J K}^{-1} \text{ g}^{-1}) \times \ln(273.15 \text{ K}/423.15 \text{ K})$$

$$= -15.2 \text{ J K}^{-1}$$

For the surroundings,  $\Delta S(\text{ice}) = m\Delta H_{\text{fus}}/T_{\text{fus}}$  (where  $T_{\text{fus}}$  is the fusion temperature of ice at 1 atm)

$$\Delta S = (15.6 \text{ g}) \times (334 \text{ J g}^{-1})/273.15 \text{ K}$$

$$= +19.1 \text{ J K}^{-1}$$

$$\Delta S(\text{total}) = \Delta S(\text{copper}) + \Delta S(\text{ice})$$

$$= +3.9 \text{ J K}^{-1} \quad (18 \text{ points})$$

Can give partial points: give full points for correct alternative solution.

10 Solid tin exists in two (allotropic) forms: white and gray.

For the transformation  $\text{Sn}(\text{s, white}) \rightarrow \text{Sn}(\text{s, gray})$ , the enthalpy change is  $-2.1 \text{ kJ}$ , and the entropy change is  $-7.4 \text{ J K}^{-1}$ .

(a) Calculate  $\Delta G$  for the reaction at  $-30.0^\circ\text{C}$  and  $100^\circ\text{C}$  and state whether the transformation is spontaneous at these two temperatures (2x4 points).

Determine the temperature at which the two forms of tin are in equilibrium (assume 1 atm pressure)(10 points). Take  $0^\circ\text{C}$  to be  $273 \text{ K}$ .

$$\Delta G = \Delta H - T\Delta S$$

At  $-30^\circ\text{C}$  ( $243 \text{ K}$ ),  $\Delta G = -2100 \text{ J} - (243 \text{ K})(-7.4 \text{ J/K})$

$$= -302 \text{ J} \text{ (or } -0.302 \text{ kJ)} \quad (4 \text{ points})$$

The reaction as written is spontaneous

At  $100^\circ\text{C}$  ( $373 \text{ K}$ ),  $\Delta G = -2100 \text{ J} - (373 \text{ K})(-7.4 \text{ J/K})$

$$= +660 \text{ J} \text{ (or } +0.660 \text{ kJ)} \quad (4 \text{ points})$$

The reaction as written is not spontaneous (the reverse reaction is spontaneous)

When the two allotropes are in equilibrium,  $\Delta G = 0$

Hence

$$T_{\text{eq}} = \frac{\Delta H_{\text{eq}}}{\Delta S_{\text{eq}}} = \frac{-2100 \text{ J}}{-7.4 \text{ J/K}}$$

$$= 284 \text{ K} \text{ (} 11.0^\circ\text{C)} \quad (10 \text{ points})$$

Can give partial points: give full points for correct alternative working