

**2013 Fall Semester Midterm Examination
CH101 General Chemistry I**

Date: October 23 (Wednesday), 2013

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.	Student Name

Problem	points	Problem	points	TOTAL pts
1	/8	6	/6	/100
2	/16	7	/10	
3	/10	8	/12	
4	/6	9	/12	
5	/10	10	/10	

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

Write down your work and answers in the Answer sheet.

Include 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

(i) Return and Claim Period: **October 28 (Mon), 6: 30 ~ 7:30 p.m.**

(ii) Location: Room for quiz session

(iii) 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. A solution file will be uploaded on 10/27(Sun).

2. Final Confirmation

(i) Period: October 31 (Thu)-November 1 (Fri)

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

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

1. (a) Calculate the maximum wavelength of light needed to eject electrons from the surface of cesium, if light of wavelength 400 nm strikes the surface of the metal giving photoelectrons whose maximum kinetic energy is 1.54×10^{-19} J. (4 points)

(b) During an experiment, the maximum kinetic energy of ejected photoelectrons from the surface of cesium was found to be 11.4 eV. Determine the de Broglie wavelength of an electron with this energy. (4 points)

[Planck's constant $h = 6.63 \times 10^{-34}$ J s; velocity of $c = 3.00 \times 10^8$ m/s; electron mass $m_e = 9.11 \times 10^{-31}$ kg; $1\text{eV} = 1.60 \times 10^{-19}$ J]

(a) Using the Einstein equation,

$$h\nu = \Phi + \frac{1}{2}mv_{\text{max}}^2$$

or $\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + KE_{\text{max}}$ where λ_0 is the maximum wavelength of light needed to eject electrons from the surface of cesium

$$\frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{(4.00 \times 10^{-7} \text{ m})} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{\lambda_0} + 1.54 \times 10^{-19} \text{ J}$$

$$3.43 \times 10^{-19} \text{ J} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{\lambda_0}$$

$$\lambda_0 = \underline{5.80 \times 10^{-7} \text{ m or } 580 \text{ nm}} \quad (4 \text{ points})$$

Allow partial points or alternative correct working

(b) Using the de Broglie matter wave equation,

$$\lambda = \frac{h}{m_e v} = \frac{h}{\sqrt{2m_e KE_{\text{max}}}} \quad KE_{\text{max}} \text{ is maximum kinetic energy}$$

$$= \frac{(6.63 \times 10^{-34} \text{ Js})}{\sqrt{2(9.11 \times 10^{-31} \text{ kg})(11.4 \text{ eV} \times 1.60 \times 10^{-19} \text{ J/eV})}}$$

$$= \underline{3.64 \times 10^{-10} \text{ m or } 3.64 \text{ \AA} \text{ or } 0.364 \text{ nm}}$$

Allow partial points

(4 points)

2. (a) The energy of a particle, such as an electron, confined to a one-dimensional box of length L , such that its potential energy is 0 for $x = 0-L$ and ∞ for all other values of x , is given by

$$E_n = \frac{h^2}{8m_e} \frac{n^2}{L^2}$$

Calculate the energy difference in kJ/mol between the ground state and first excited state for an electron,

(i) in a 1.0 \AA box, and

(ii) in a 1.0 m box (total 6 points for (i) and (ii)).

(iii) Comment on the result. (2 points)

[Electron mass $m_e = 9.110 \times 10^{-31} \text{ kg}$; Planck's constant $h = 6.626 \times 10^{-34} \text{ Js}$; Avogadro's number is $6.022 \times 10^{23} / \text{mol}$; $1 \text{ \AA} = 10^{-10} \text{ m}$]

(b) Write an equation for the energy of an electron confined to a 3-dimensional cubic box of length L , under the conditions described above. (2 points)

(c) Write an equation for the ground state energy level. (2 points)

(d) Write an equation for one of the first excited state energy levels. (2 points)

(e) State how many first excited energy levels exist and state whether or not they are degenerate (of equal energy). (2 points)

(a)

$$\begin{aligned} \text{(i) } E_2 - E_1 &= \frac{3h^2}{8m_e L^2} = \frac{3(6.626 \times 10^{-34} \text{ Js})^2}{8(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^{-10} \text{ m})^2} = 1.8 \times 10^{-17} \text{ J} \\ &= \frac{(1.8 \times 10^{-17} \text{ J}) \times (6.022 \times 10^{23} / \text{mol})}{10^3 \text{ (J/kJ)}} = \underline{11,000 \text{ kJ/mol}} \end{aligned}$$

$$\begin{aligned} \text{(ii) Same calculation as above, but } L^2 &= 1.0 \text{ m}^2, \text{ so } E_2 - E_1 = 1.8 \times 10^{-37} \text{ J} \\ &= \underline{1.1 \times 10^{-16} \text{ kJ/mol}} \quad \text{(6 points for (i) and (ii) combined)} \end{aligned}$$

(iii) In (i) the electron is confined in a box of atomic dimensions and therefore quantization of energy levels is clear, whereas in (ii), the electron is confined in a very much larger box, is almost classical in its behavior and the energy levels are almost continuous.

(2 points)

$$\text{(b) } E_{n_1 n_2 n_3} = \frac{h^2}{8m_e L^2} (n_1^2 + n_2^2 + n_3^2)$$

(2 points)

$$\text{(c) } E_{111} = \frac{3h^2}{8m_e L^2} \quad (n_1 = n_2 = n_3 = 1) \quad \text{(2 points)}$$

$$\text{(d) } E_{211} = \frac{3h^2}{4m_e L^2} \quad (n_1 = 2; n_2 = n_3 = 1) \quad \text{(for example; there is also } E_{121} \text{ and } E_{112}) \text{ (2 points)}$$

(e) There are 3 energy levels and they are degenerate. (2 points)

3. Give the value of quantum numbers (n , l , and m) and the number of radial nodes and angular nodes for each of the following hydrogen atomic orbitals in the table. (5 x 2 points)

Orbital	n	l	m	No. of radial nodes	No. of angular nodes
2s	2	0	0	1	0
2p _y	2	1	±1	0	1
4s	4	0	0	3	0
5p _x	5	1	±1	3	1
4d _{z²}	4	2	0	1	2

2 points for completely correct entries for each orbital, otherwise zero.

4. The cesium atom has one of the lowest ionization energies of all neutral atoms in the periodic table (375.5 kJ/mol). Calculate the longest wavelength of light that could ionize a cesium atom (in the gas phase) and state the region of the electromagnetic spectrum to which this light belongs. (6 points)

[Planck's constant $h = 6.626 \times 10^{-34}$ Js; Avogadro's number is 6.022×10^{23} /mol; velocity of light $c = 2.998 \times 10^8$ m/s]

$$IE = 375.7 \text{ kJ/mol} = \frac{375700 \text{ (J)}}{6.022 \times 10^{23} \text{ (/mol)}} \quad \text{J}$$

$$IE = h\nu = hc/\lambda$$

$$\text{Hence } \lambda = \frac{6.626 \times 10^{-34} \text{ (Js)} \times 2.998 \times 10^8 \text{ (m/s)} \times 6.022 \times 10^{23} \text{ (/mol)}}{375700 \text{ (J/mol)}}$$

$$= 3.184 \times 10^{-7} \text{ m or } 318.4 \text{ nm}$$

This is in the near ultraviolet region of the electromagnetic spectrum (close to the low wavelength-violet-visible region). (6 points)

5. (a) Using the standard notation, write ground state electronic configurations for the following species and describe each one as diamagnetic or paramagnetic.

(i) Li^- (ii) S^- (iii) Br^+ (iv) Te^{2-} (v) Xe^+ (2.5 points)

(b) For each of the following pairs of atoms or ions, state which you expect to have the larger radius. No explanation is needed.

(i) Ge or As (ii) Sm and Sm^{3+} (iii) Rb^+ or Kr (iv) Sr^+ or Rb (v) I^- or Xe (2.5 points)

(c) (i) Arrange the following in order of their first ionization energies: Li, Be, B.

No explanation is needed. (2 points)

(ii) Explain briefly which of the following atoms has the smallest radius: Si, S, Mg.

(3 points)

(a) (i) Li^- : $1s^2 2s^2$ diamagnetic (ii) S^- : $1s^2 2s^2 2p^6 3s^2 3p^5$ or $[\text{Ne}]3s^2 3p^5$ paramagnetic (iii) Br^+ : $[\text{Ar}]3d^{10} 4s^2 4p^4$ paramagnetic (iv) Te^{2-} : $[\text{Kr}]4d^{10} 5s^2 5p^6$ diamagnetic (v) Xe^+ : $[\text{Kr}]4d^{10} 5s^2 5p^5$ paramagnetic. (2.5 points)

(b) (i) Ge (ii) Sm (iii) Kr (iv) Rb (v) I^- (2.5 points)

(c) (i) $\text{Be} > \text{B} > \text{Li}$ (2 points)

(ii) S, because all three elements are in period (row) 3, but S has highest Z and radius decreases with increase in Z across a period. (3 points)

6. (a) Write the equation that defines the lattice energy of calcium oxide. (2 points)

(b) Predict which of the following pairs of ions would have the greater coulombic attraction in a solid compound: (i) K^+ , O^{2-} (ii) Ga^{3+} , O^{2-} (iii) Ca^{2+} , O^{2-} (2 points)

(c) Predict which of $\text{LiCl}(\text{s})$ or $\text{RbCl}(\text{s})$ would have the higher lattice energy, given that they have similar arrangements of ions in the crystal lattice. (2 points)

(a) $\text{CaO}(\text{s})$ (or $\text{Ca}^{2+} \text{O}^{2-}(\text{s})$) \rightarrow $\text{Ca}^{2+}(\text{g}) + \text{O}^{2-}(\text{g})$ (2 points)

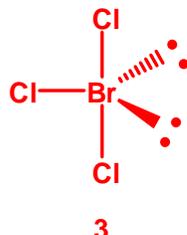
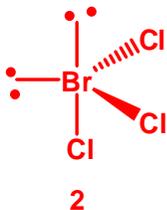
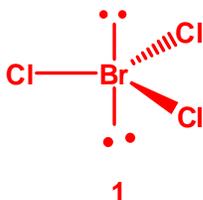
(b) (ii) Ga^{3+} , O^{2-} (2 points)

(c) $\text{LiCl}(\text{s})$ (2 points)

8. Consider the molecule bromine trichloride (BrCl_3) and answer the following questions.

- (a) Draw the three possible structures of BrCl_3 , according to the VSEPR model. (6 points)
(b) Select the most stable structure. (2 points)
(c) State whether the geometry of the most stable structure is regular or distorted. (2 points)
(d) State whether the most stable structure has a dipole moment. (2 points)

(ii) (The Lewis diagram requires 5 electron pairs around the central atom Br, meaning its geometry is based on a trigonal bipyramid. Hence there are three possible structures.)



(3 x 2 points)

(iii) The most stable structure is the T-shaped geometry (3, as written above) (2 points)

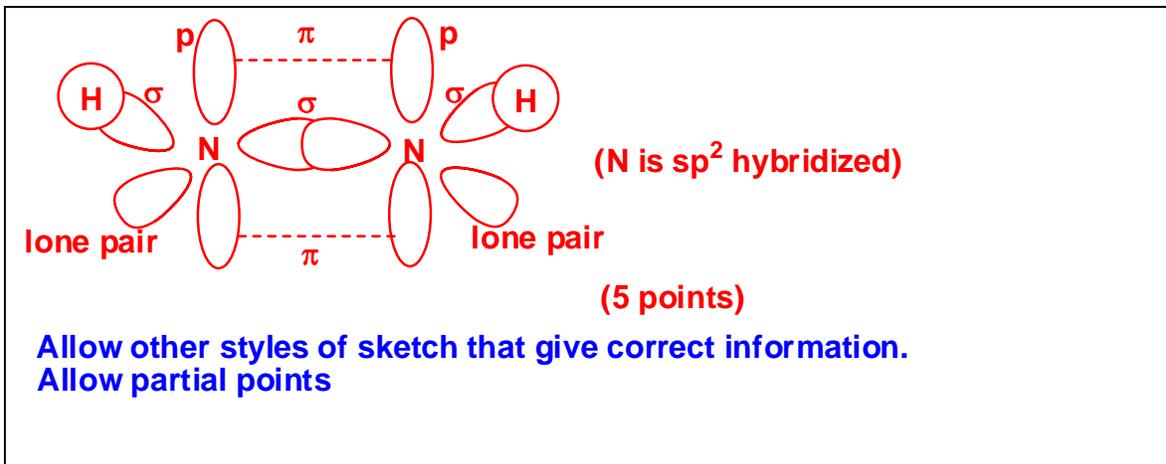
(iv) Distorted geometry (2 points)

(v) It has a dipole moment (2 points)

\therefore

9. (a) Sketch a valence bond (VB) model of the *cis* stereoisomer of diazene (HNNH), showing the hybridization on the N atoms, the σ skeletal structure, lone pair electrons and π -bonding. (5 points)

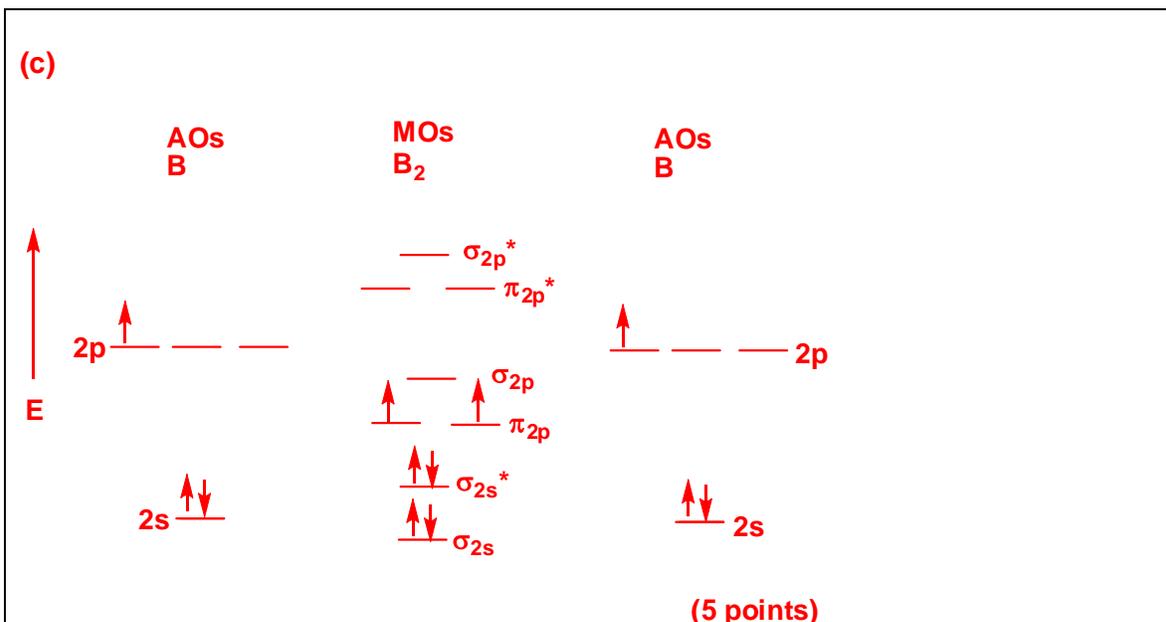
(b) State whether *cis*-diazene has a molecular dipole moment. (1 point)



(b) It has a dipole moment (1 point)

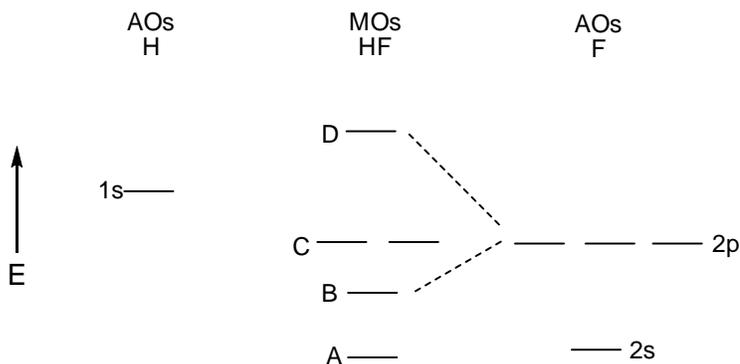
(c) Sketch a molecular orbital energy diagram (showing all relevant atomic and molecular orbitals) for the homonuclear diatomic molecule B_2 . (5 points)

(d) Determine, from its electronic structure, whether B_2 is paramagnetic or diamagnetic. (1 point)



(d) B_2 is paramagnetic (1 point)

10. Consider the LCAOMO diagram for HF below and answer the following questions.



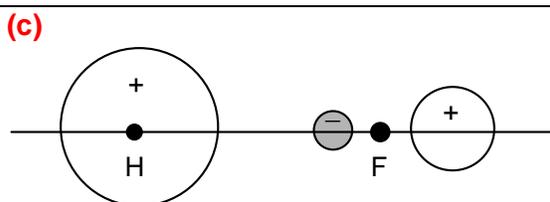
(a) Label the MOs of HF. (4 points)

(a) A = σ_{2s} , B = σ_{2p} , C = n_{2p} , D = σ^*_{2p} (4 points)

(b) Write the electron configuration of HF and determine the highest (energy) occupied MO (HOMO) and the lowest (energy) unoccupied MO (LUMO). (3 points)

(b) $(\sigma_{2s})^2(\sigma_{2p})^2(n_{2p})^4(\sigma^*_{2p})$ HOMO is n_{2p} LUMO is σ^*_{2p} (3 points)

(c) Sketch the LUMO of HF. (3 points)



or similar diagram, emphasizing higher concentration on H

(3 points)

**2013 Fall Semester Final Examination
CH101 General Chemistry I**

Date: December 18 (Wednesday), 2013

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.	Student Name

Problem	points	Problem	points	TOTAL pts
1	/12	6	/10	
2	/10	7	/6	
3	/10	8	/12	
4	/10	9	/8	
5	/10	10	/12	
				/100

** This paper consists of 10 sheets with 10 problems. There is also a page of constants (page 8), a periodic table (page 9), and a claim form (page 10). Please check all page numbers before taking the exam.

Write down your work and answers in the Answer sheet. Include 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.

1. Period, Location and Procedure

- 1) Return and Claim Period: **Dec 20 (Friday, 12:00-14:00)**
- 2) **Location: Creative Learning Bldg.(E11)**

<i>Class</i>	<i>Room</i>
CH101	412

- 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. The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 12/20 on the web.)

2. Final Confirmation

- 1) Period: **Dec 21(Sat) – 22(Sun)**
- 2) Procedure: During this period, you can check the final score of the examination *on the website* again.

To get more information, visit the website at www.gencheminkaist.pe.kr.

1. (a) Arrange the following gases in order of increasing density at STP.

HCl, CO, CO₂, H₂S, Cl₂ (5 points)

(b) Associate one van der Waals constant a (17.58, 1.378, 3.392, 2.253, 0.2107 L² atm mol⁻²) with each of the following gases: O₂, CH₃CN, Ne, CH₄, CO₂. (5 points)

(c) Give a brief explanation for the very high value in part (b) (2 points)

(Answer)

(a) CO < H₂S < HCl < CO₂ < Cl₂ (3 points)

(b) Ne = 0.2107; O₂ = 1.378; CH₄ = 2.253; CO₂ = 3.392; CH₃CN = 17.53 (L² atm mol⁻²)
(5 points)

(c) Constant a for CH₃CN (17.58 L² atm mol⁻²) is very high because of relatively strong dipole-dipole attractions between the molecules (the CH₃CN molecule has a high dipole moment) (2 points – can give partial points)

2. A sample of an oxide of osmium (1.509 g) is gaseous at 200.0 °C /0.980 atm pressure and occupies 235 mL under these conditions. Assuming ideal gas behavior, determine the molecular formula of the oxide. [Molar masses (g mol⁻¹): Os = 190.2; O = 16.00. R = 0.08206 L atm K⁻¹mol⁻¹. Take 0 °C to be 273 K]. Show working. (10 points)

(Answer)

Since the gas has ideal behavior,

$PV = nRT$, where $n = m/M_r$ (M_r is molar mass)

$$n = (0.980 \text{ atm})(0.235 \text{ L}) / (0.08206 \text{ L atm/K mol})(473 \text{ K})$$
$$= 0.00590 \text{ mol}$$

Hence $M_r = (1.509 \text{ g}) / 0.00590 \text{ mol}$

$$= 254 \text{ g mol}^{-1}$$

If the molecular formula of the oxide is OsO_x, then the molar mass is

$$192.0 \text{ g mol}^{-1} + x(16.00 \text{ g mol}^{-1}) = 254 \text{ g mol}^{-1}$$

$$x = 3.99 \sim 4$$

Molecular formula is OsO₄ (10 points) (Allow for correct alternative working. Can give partial points)

3. If the root mean square velocity of helium gas is 1477 m s^{-1} ,

(a) calculate the temperature of the gas and then

(b) calculate the root mean square velocity of nitrogen gas at this temperature.

[Molar masses (g mol^{-1}): He = 4.00; N = 14.01. $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]. Show working. (2 x 5 points)

(Answer)

$$\begin{aligned} \text{(a) } u_{\text{rms}} &= \sqrt{\frac{3RT}{M_r}} \\ T &= \frac{u_{\text{rms}}^2 M_r}{3R} = \frac{(1477 \text{ m/s})^2 (4.00 \times 10^{-3} \text{ kg/mol})}{3(8.314 \text{ J/K mol})} \\ &= \underline{349.9 \text{ K}} \quad (5 \text{ points}) \end{aligned}$$

$$\begin{aligned} \text{(b) } u_{\text{rms}} &= \sqrt{\frac{3RT}{M_r}} = \sqrt{\frac{3(8.314 \text{ J/K mol})(349.9 \text{ K})}{(28.02 \times 10^{-3} \text{ kg/mol})}} \\ &= \underline{558.1 \text{ m s}^{-1}} \quad (5 \text{ points}) \end{aligned}$$

Can give partial points

4. (a) Identify the substance that has the higher boiling point in the following pairs.

(i) BF_3 and BCl_3 (ii) pentane and 2,2-dimethylpropane (iii) *cis*- $\text{ClHC}=\text{CHCl}$ and *trans*- $\text{ClHC}=\text{CHCl}$ (iv) hexane (C_6H_{14}) and benzene (C_6H_6) (v) SO_2 and CO_2 (vi) CH_3COOH and HOOC-COOH (6 x 1 points)

(b) An oxide of manganese (Mn) has a unit crystal in which Mn ions are situated at the corners and oxide ions are found half way along the edges of the cube. Determine the formula unit of the oxide. Show working. (4 points)

(Answer)

(a) (i) BCl_3 (ii) pentane (iii) *cis*- $\text{ClHC}=\text{CHCl}$ (iv) benzene (v) SO_2 (vi) HOOC-COOH
(6 x 1 points)

(b) Each unit cell has $8 \times 1/8 = 1$ Mn ion and $12 \times 1/4 = 3$ oxide ions.

Hence the oxide has 6,2 coordination and its formula unit is MnO_3 (4 points)

5. (a) Calculate the atomic radius of aluminum (Al) atoms (in picometers) in a face-centered cubic (fcc) crystal lattice, whose density is 2.718 g cm^{-3} . [Avogadro number = $6.022 \times 10^{23} \text{ mol}^{-1}$; molar mass of Al = 26.98 g mol^{-1}]. Show working. (7 points)

(b) From your answer for part (a), calculate the fraction of the volume of aluminum occupied by its atoms. [The volume of a sphere is $\frac{4\pi r^3}{3}$]. Show working. (3 points)

(Answer)

(a) Since an fcc structure has 4 atoms/unit cell,

$$\text{density} = 2.718 \text{ g/cm}^3 = \frac{4 \times 26.98 \text{ g/mol}}{6.022 \times 10^{23} / \text{mol}} \frac{1}{a^3} \quad \text{where } a \text{ is the unit cube length}$$

$$a^3 = 6.594 \times 10^{-23} \text{ cm}^3, \text{ hence } a = 4.04 \times 10^{-8} \text{ cm}$$

$$= 404 \text{ pm}$$

$$\text{Since for a fcc structure } a = \frac{4r}{\sqrt{2}} \quad \text{where } r \text{ is the atomic radius}$$

$$r = \underline{142.8 \text{ pm}} \quad (7 \text{ points}) \quad \text{Can give partial points}$$

(b) The ratio of the volume occupied by 4 atoms to the unit cell volume is

$$\frac{4 \left(\frac{4}{3} \pi r^3 \right)}{a^3} = \underline{0.740} \quad (3 \text{ points})$$

6. Water (400.0 g) in an aluminum pan weighing 151.5 g was heated from $22.0 \text{ }^\circ\text{C}$ to boiling point ($100.0 \text{ }^\circ\text{C}$). Calculate the percentage (%) of the total heat supplied that is used to raise the temperature of the water to its boiling point. [Specific heat capacities ($\text{J }^\circ\text{C}^{-1} \text{ g}^{-1}$): Al = 0.900; Water = 4.18]. Show working. (10 points)

(Answer)

Since the supplied heat is transferred to both the water and the aluminum,

$$q = m(w) C_p(w) \Delta T(w) + m(\text{Al}) C_p(\text{Al}) \Delta t(\text{Al})$$

$$= (400.0 \text{ g})(4.18 \text{ J }^\circ\text{C}^{-1} \text{ g}^{-1})(78.0 \text{ }^\circ\text{C}) + (151.5 \text{ g})(0.900 \text{ J }^\circ\text{C}^{-1} \text{ g}^{-1})(78.0 \text{ }^\circ\text{C})$$

$$= 1.30 \times 10^5 \text{ J} + 0.106 \times 10^5 \text{ J} = 1.41 \times 10^5 \text{ J}$$

Hence % of heat attributable to raising the temperature of water is

$$(1.30 \times 10^5 \text{ J} / 1.41 \times 10^5 \text{ J}) \times 100$$

$$= \underline{92.2\%} \quad (10 \text{ points}) \quad \text{Can give partial points. Allow correct alternative working}$$

7. According to the equipartition theorem of Boltzmann, the heat capacity at constant pressure (C_p) of ideal gases can be expressed in terms of R (e.g. $5R/2$), depending on the nature of the gas particles (atoms, diatomic molecules, etc). Determine the values of C_p for the following, assuming ideal gas behavior.

(i) Hydrazoic acid, $\text{HN}=\text{N}=\text{N}$ (ii) Hydrogen cyanide, HCN (iii) Acetylene, $\text{HC}\equiv\text{CH}$ (iv) Argon, Ar (v) Hydrogen bromide, HBr (vi) Ozone, O_3 (6 x 1 points)

(Answer)

(i) $4R$ (ii) $7R/2$ (iii) $7R/2$ (iv) $5R/2$ (v) $7R/2$ (vi) $4R$ (6 x 1 points)

8. (a) Calculate the lattice energy of the sodium oxide lattice, given the following data (in kJ mol^{-1}). Show working.

ΔH° (sublimation or atomization) of $\text{Na(s)} = 107.32$; ΔH° (dissociation) of $\text{O}_2(\text{g}) = 498$;

ΔH° (ionization) (ionization energy, IE_1) of $\text{Na(g)} = 494$; Electron affinities of O(g) $\text{EA}_1 = -141$ and $\text{EA}_2 = +844$; ΔH° (formation) of $\text{Na}_2\text{O(s)} = -409$. (10 points)

(b) State whether (i) calcium oxide (CaO) and (ii) potassium oxide (K_2O) will have higher or lower lattice energies than sodium oxide. (2 points)

(Answer)

(a) $\text{Na}_2\text{O(s)} \rightarrow 2\text{Na}^+(\text{g}) + \text{O}^{2-}(\text{g}); \Delta H_L$

$\Delta H_L = 2\Delta H^\circ$ (sublimation or atomization) of $\text{Na(s)} + \frac{1}{2} \Delta H^\circ$ (dissociation) of $\text{O}_2(\text{g}) + 2\text{IE}_1$ of $\text{Na(g)} - \text{EA}_1$ of $\text{O(g)} - \text{EA}_2$ of $\text{O(g)} - \Delta H^\circ$ (formation) of $\text{Na}_2\text{O(s)}$

$= 2(107.32 \text{ kJ/mol}) + 249 \text{ kJ/mol} + 2(494 \text{ kJ/mol}) - 141 \text{ kJ/mol} + 844 \text{ kJ/mol} + 409 \text{ kJ/mol}$

$= 2564 \text{ kJ/mol}$ (10 points)

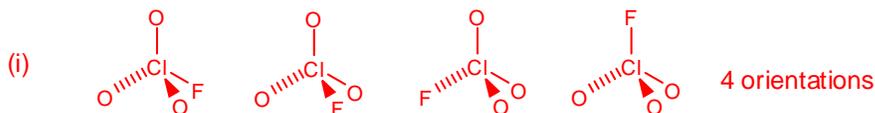
Allow for correct alternative method (e.g. using Hess's Law cycle). Can give partial points

(b) (i) Higher (ii) Lower (2 points)

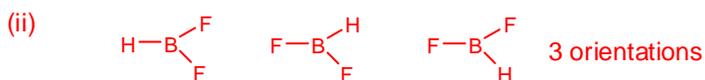
9. The Boltzmann equation $S = k_B \ln W$, allows us to calculate the residual entropy of a crystal at (or very close to) 0 K. W is the number of microstates, which for a molecular crystal is the number of possible degenerate (same energy) orientations of molecules. Write the possible orientations of the following molecules and calculate their molar residual entropies according to the Boltzmann expression. [Avogadro's number is 6.02×10^{23} and k_B is $1.38 \times 10^{-23} \text{ J K}^{-1}$]. Show working.

(i) FCIO_3 (ii) HBF_2 (iii) BF_3 (4 + 3 + 1 = 8 points)

(Answer)



$$\begin{aligned}
 S &= k_B \ln W = k_B \ln 4^{6.02 \times 10^{23}} \\
 &= (1.38 \times 10^{-23} \text{ J/K}) \times (6.02 \times 10^{23} / \text{mol}) \times \ln 4 \quad (4 \text{ points}) \\
 &= \underline{11.5 \text{ J/K mol}}
 \end{aligned}$$



$$\begin{aligned}
 S &= k_B \ln W = k_B \ln 3^{6.02 \times 10^{23}} \quad \text{Can allow partial points} \\
 &= (1.38 \times 10^{-23} \text{ J/K}) \times (6.02 \times 10^{23} / \text{mol}) \times \ln 3 \\
 &= \underline{9.13 \text{ J/K mol}} \quad (3 \text{ points})
 \end{aligned}$$



$$\begin{aligned}
 S &= k_B \ln W = k_B \ln 1^{6.02 \times 10^{23}} \\
 &= \underline{0} \quad (1 \text{ point})
 \end{aligned}$$

10. Thermodynamic data for the reaction between BF_3 and water,

$2\text{BF}_3(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{B}_2\text{O}_3(\text{s}) + 6\text{HF}(\text{g})$, is given below.

Standard enthalpies of formation (ΔH_f° in kJ mol^{-1}): $\text{BF}_3(\text{g}) = -1137.0$; $\text{H}_2\text{O}(\text{l}) = -285.83$; $\text{B}_2\text{O}_3(\text{s}) = -1272.8$; $\text{HF}(\text{g}) = -271.1$.

Standard entropies (S° in $\text{J K}^{-1} \text{mol}^{-1}$): $\text{BF}_3(\text{g}) = 254.12$; $\text{H}_2\text{O}(\text{l}) = 69.91$; $\text{B}_2\text{O}_3(\text{s}) = 53.97$; $\text{HF}(\text{g}) = 173.78$.

(a) Calculate the Gibbs free energy of reaction at 700 K and state whether the reaction is spontaneous at this temperature, assuming variation of ΔH° and ΔS° with temperature is negligible. Show working. (9 points)

(b) Determine the temperature at which the reaction is reversible. Show working. (3 points)

(Answer)

(a)

$$\begin{aligned}\Delta H_r^\circ &= 2\Delta H_f^\circ(\text{BF}_3, \text{g}) + 3\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) - [\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{s}) \\ &\quad + 6\Delta H_f^\circ(\text{HF}, \text{g})] \\ &= 2(-1137.0 \text{ kJ} \cdot \text{mol}^{-1}) + 3(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad - [(-1272.8 \text{ kJ} \cdot \text{mol}^{-1}) + 6(-271.1 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -232.1 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta S_r^\circ &= 2S_m^\circ(\text{BF}_3, \text{g}) + 3S_m^\circ(\text{H}_2\text{O}, \text{l}) \\ &\quad - [S_m^\circ(\text{B}_2\text{O}_3, \text{s}) + 6S_m^\circ(\text{HF}, \text{g})] \\ &= 2(254.12 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 3(69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad - [53.97 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 6(173.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -378.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = (+232.1 \text{ kJ mol}^{-1}) - (700 \text{ K})(-0.37868 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= \underline{-32.98 \text{ kJ mol}^{-1}}. \text{ The reaction is spontaneous at this temperature.}\end{aligned}$$

(9 points) Can give partial points.

(b) At equilibrium, $\Delta G^\circ = 0$, so that $\Delta H^\circ = T\Delta S^\circ$

$$\begin{aligned}T &= \Delta H^\circ / \Delta S^\circ = (+232.1 \text{ kJ mol}^{-1}) / (+0.37868 \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= \underline{612.9 \text{ K}} \quad (3 \text{ points})\end{aligned}$$

FUNDAMENTAL CONSTANTS

Name	Symbol	Value
Atomic mass constant	m_u	$1.660\ 54 \times 10^{-27}$ kg
Avogadro's constant	N_A	$6.022\ 14 \times 10^{23}$ mol ⁻¹
Boltzmann's constant	k	$1.380\ 65 \times 10^{-23}$ J·K ⁻¹
Fundamental charge	e	$1.602\ 18 \times 10^{-19}$ C
Faraday's constant	$F = N_A e$	$9.648\ 53 \times 10^4$ C·mol ⁻¹
Gas constant	$R = N_A k$	$8.314\ 47$ J·K ⁻¹ ·mol ⁻¹ $8.314\ 47$ L·kPa·K ⁻¹ ·mol ⁻¹ $8.205\ 74 \times 10^{-2}$ L·atm·K ⁻¹ ·mol ⁻¹ $62.36\ 37$ L·Torr·K ⁻¹ ·mol ⁻¹ $8.314\ 47 \times 10^{-2}$ L·bar·K ⁻¹ ·mol ⁻¹
Mass of electron	m_e	$9.109\ 38 \times 10^{-31}$ kg
Mass of neutron	m_n	$1.674\ 93 \times 10^{-27}$ kg
Mass of proton	m_p	$1.672\ 62 \times 10^{-27}$ kg
Planck's constant	h	$6.626\ 08 \times 10^{-34}$ J·s
	$\hbar = h/2\pi$	$1.054\ 57 \times 10^{-34}$ J·s
Rydberg constant	\mathcal{R}	$3.289\ 84 \times 10^{15}$ Hz
Speed of light	c	$2.997\ 92 \times 10^8$ m·s ⁻¹
Standard acceleration of free fall	g	$9.806\ 65$ m·s ⁻²
Vacuum permittivity	ϵ_0	$8.854\ 19 \times 10^{-12}$ J ⁻¹ ·C ² ·m ⁻¹

RELATIONS BETWEEN UNITS*

Property	Common unit	SI unit
Mass	2.205 lb (lb = pound)	1.000 kg
	1.000 lb	453.6 g
	1.000 oz (oz = ounce)	28.35 g
	1.000 ton (= 2000 lb)	907.2 kg
	1 t (t = tonne, metric ton)	10 ³ kg
Length	1.094 yd (yd = yard)	1.000 m
	0.3937 in. (in. = inch)	1.000 cm
	0.6214 mi (mi = mile)	1.000 km
	1 in.	2.54 cm
	1 ft (ft = foot)	30.48 cm
	1.000 yd	0.9144 m
	1 Å (Å = ångström)	10 ⁻¹⁰ m
Volume	1 L (L = liter)	10 ³ cm ³ , 1 dm ³
	1.000 gal (gal = gallon) [†]	3.785 dm ³ (3.785 L)
	1.00 ft ³ (ft ³ = cubic foot)	2.83×10^{-2} m ³ (28.3 L)
	1.00 qt (qt = quart) [†]	9.46×10^{-2} m ³ (0.946 L)
Time	1 min (min = minute)	60 s
	1 h (h = hour)	3600 s
	1 day	86 400 s
Pressure	1 atm (atm = atmosphere)	$1.013\ 25 \times 10^5$ Pa
	1.000 Torr or 1.000 mmHg	133.3 Pa
	1.000 psi (psi = pounds per square inch)	6.895 kPa
	1 bar	10 ⁵ Pa
Energy	1 cal	4.184 J
	1 eV	1.60218×10^{-19} J; 96.485 kJ·mol ⁻¹
	1 C·V	1 J
	1 kWh (kWh = kilowatt hour)	3.600×10^3 kJ
	1 L·atm	101.325 J

Temperature conversions (Fahrenheit temperature)/°F = $\frac{9}{5} \times$ (Celsius temperature)/°C + 32
 (Celsius temperature)/°C = $\frac{5}{9} + \{$ (Fahrenheit temperature)/°F - 32}
 (Kelvin temperature)/K = (Celsius temperature)/°C + 273.15

*Entries in boldface type are exact.

[†]The European and Canadian Imperial quart and gallon are 1.201 times as large.

Class: _____, Professor Name: _____, Student I.D.: _____, Name: _____

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