

**General Chemistry C, Fall 2023**  
**Problem Set 3**

- Due date: 2023/10/27 10:00 AM.
- Write down how you calculate the answer step-by-step (don't forget about the units).
- Please upload a PDF file containing your answers to NTU COOL.

1. (4 pt) (a) Crystalline silicon has a density of  $2.33 \text{ g cm}^{-3}$  in a cubic structure. The unit cell edge length is 543 pm. Calculate the number of silicon atoms in one unit cell. (b) What is the Bravais lattice of silicon? How many atoms are in the basis of silicon?

(a)

The weight of silicon in a unit cell is equal to the density of silicon times the volume of it in a unit cell.

$$W_{Si} = D_{Si} \times V_{Si} = (5.43 \times 10^{-10})^3 (\text{m}^3) \times (2.33 \times 10^3) (\text{Kg/m}^3)$$

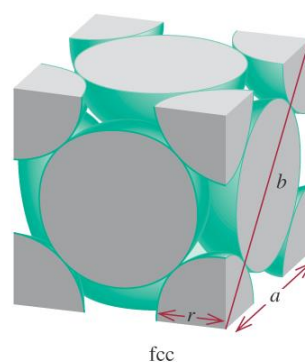
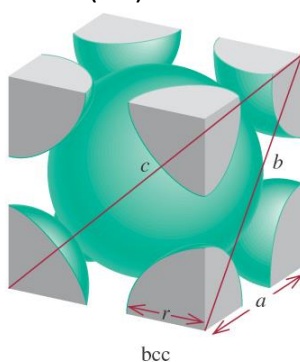
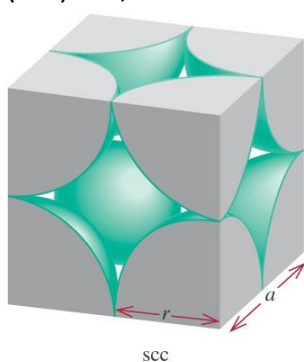
$$= 3.73 \times 10^{-25} (\text{Kg}) = 3.73 \times 10^{-22} (\text{g}) \text{ (1 pt)}$$

$$\# \text{ of silicon in a unit cell} = \frac{W_{Si}}{M_{Si}} = \frac{3.73 \times 10^{-22} (\text{g})}{28.0855 (\frac{\text{g}}{\text{mol}})} \times 6.02 \times 10^{23} (\frac{\#}{\text{mol}}) = 8 \text{ (1 pt)}$$

(b)

The Bravais lattice of silicon is a face-centered cubic (FCC) (1 pt). The FCC structure has 4 lattice point in a unit cell. Besides, there are 8 atoms inside the unit cell. So, the number of atoms in the basis of silicon is 2. (1 pt)

2. (6 pt) A quantitative measure of how efficiently spheres pack into unit cells is called *packing efficiency*, which is the percentage of the cell space occupied by the spheres. Calculate the packing efficiencies of a simple cubic (scc) cell, a body-centered cubic (bcc) cell, and a face-centered cubic (fcc) cell.



(a) SC:

$$r = \frac{a}{2}$$

$$V_{sphere} = \frac{4}{3}\pi \left(\frac{a}{2}\right)^3$$

$$V_{occupied} = V_{sphere} \times 1$$

$$efficiency = \frac{V_{occupied}}{V_{cubic}} \times 100\% = \frac{100\pi}{6}\% = 52.4\%$$

(b) BCC

$$r = \frac{\sqrt{3}a}{4}$$

$$V_{sphere} = \frac{4}{3}\pi \left(\frac{\sqrt{3}a}{4}\right)^3$$

$$V_{occupied} = V_{sphere} \times 2$$

$$efficiency = \frac{V_{occupied}}{V_{cubic}} \times 100\% = \frac{100\sqrt{3}\pi}{8}\% = 68\%$$

(c) FCC

$$r = \frac{\sqrt{2}a}{4}$$

$$V_{sphere} = \frac{4}{3}\pi \left(\frac{\sqrt{2}a}{4}\right)^3$$

$$V_{occupied} = V_{sphere} \times 4$$

$$efficiency = \frac{V_{occupied}}{V_{cubic}} \times 100\% = \frac{100\sqrt{2}\pi}{6}\% = 74\%$$

2 pt for each correct answer

3. (8 pt) A gas with a pressure of 6.0 bar and volume of 2.0 L undergoes isothermal expansion to  $V = 8.0$  L through a few pathways: (a) against a vacuum, (b) against a constant external pressure of 1.5 bar, (c) first against a constant external pressure of 3 bar until  $V = 4.0$  L, then against a new external pressure of 1.5 bar until  $V = 8.0$  L, (d) through a reversible pathway. Calculate the work, heat, and  $\Delta U$  (in joules) involved in each pathway.

$\Delta U = C_v \Delta T$ . For ideal gas system,  $C_v$  is constant.  $\Delta U = 3/2 n R \Delta T$

Therefore,  $\Delta U$  is zero under isothermal processes.

(a) No external pressure  $\rightarrow w = 0$

$\Delta U = 0 \rightarrow q = -w = 0$

(b) 1 bar =  $10^5$  pa; 1 L =  $10^{-3}$  m<sup>3</sup>

$w = -1.5 \times 10^5 \times (8.0 - 2.0) \times 10^{-3} = -9.0 \times 10^2$  (J)

$\Delta U = 0 \rightarrow q = -w = 9.0 \times 10^2$  (J)

(c)  $w = -3 \times 10^5 \times (4.0 - 2.0) \times 10^{-3} - 1.5 \times 10^5 \times (8.0 - 4.0) \times 10^{-3} = -1.2 \times 10^3$  (J)

$\Delta U = 0 \rightarrow q = -w = 1.2 \times 10^3$  (J)

(d) For reversible pathway,  $P_{\text{ext}} = P_{\text{int}} = nRT/V$

$w = - \int_{2.0}^{8.0} (nRT/V) dV = -nRT(\ln 8.0 - \ln 2.0) = -P_1 V_1 (\ln 8.0 - \ln 2.0) = -6.0 \times 10^5 \times 2.0 \times 10^{-3} \times \ln 4.0$   
 $= 1.7 \times 10^3$  (J)

$\Delta U = 0 \rightarrow q = -w = 1.7 \times 10^3$  (J)

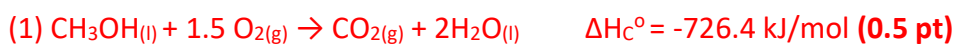
2pt for each question

-2 if any of ( $\Delta U$ ,  $w$ , or  $q$ ) is incorrect (-1.5 if the sign(+/-) is incorrect in each question)

-0.5 if the unit/s.f. is incorrect

4. (5 pt) (a) Write down respectively the combustion reactions for  $\text{CH}_3\text{OH}(\text{l})$ , graphite, and  $\text{H}_2(\text{g})$ , assuming the water product is in liquid state. (b) The enthalpies of combustion for  $\text{CH}_3\text{OH}(\text{l})$ , graphite, and  $\text{H}_2(\text{g})$  are  $-726.4$ ,  $-393.5$ , and  $-285.8$  kJ/mol, respectively. Calculate the standard enthalpy of formation ( $\Delta H_f^\circ$ ) for methanol ( $\text{CH}_3\text{OH}$ ).

(a)



(b) The enthalpy of combustion for methanol  $\Delta H_c^\circ(\text{methanol}) = -726.4$

$$= \Delta H_f^\circ(\text{H}_2\text{O}) * 2 + \Delta H_f^\circ(\text{CO}_2) - \Delta H_f^\circ(\text{O}_2) * 1.5 - \Delta H_f^\circ(\text{methanol}) \text{ (from reaction(1)) (2 pt)}$$

$$= (-285.8 * 2) + (-393.5) - (0) - \Delta H_f^\circ(\text{methanol})$$

(standard enthalpy of formation for pure element at its most stable form is 0 kJ/mol by definition)

Therefore, we can obtain  $\Delta H_f^\circ(\text{methanol}) = -238.7 \text{ kJ/mol}$

**(1.5 pt, -0.5 if unit/s.f. is incorrect)**

5. (5 pt) (a) Write down the balanced chemical reaction of naphthalene ( $\text{C}_{10}\text{H}_8$ ) burning in oxygen to produce  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ . (b) When 1.034 g of naphthalene is burned completely in a constant-volume calorimeter (heat capacity 4.67 kJ/°C), the temperature rises from 20.32°C to 29.22°C. Calculate the  $\Delta U$  and  $\Delta H$  for the reaction in (a) on a molar basis (in kJ/mol).

(a)



(b)

For a constant-volume calorimeter, the system is considered to be an isolated system, which means the heat of the system should be 0. With Naphthalene being burned completely in a constant volume  $\Delta V = 0$ .

$$q_{\text{sys}} = q_{\text{cal}} + q_{\text{rxn}} = 0$$

$$\Delta U = q_{\text{rxn}} + w = -q_{\text{cal}} + P\Delta V + V\Delta P = -q_{\text{cal}} \text{ (1 pt)}$$

$$q_{\text{cal}} = C_v \times \Delta T = \frac{4.67(\text{KJ}/^\circ\text{C}) \times (29.22 - 20.32)(^\circ\text{C})}{1.034/128.1705(\text{mol})} = 5.152 \times 10^3 \text{ KJ/mol}$$

$$\Delta U = -q_{\text{cal}} = -5.15 \times 10^3 \text{ KJ/mol (1 pt)}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P = \Delta U + R(n_{\text{co}_2}T_2 - n_{\text{o}_2}T_1) \text{ (1 pt)}$$

$$= -5152 \frac{\text{KJ}}{\text{mol}} + 8.314 \frac{\text{JK}}{\text{mol}} \times (10 \times 293 - 12 \times 302) = -5156 \frac{\text{KJ}}{\text{mol}} = -5.16 \times$$

$$10^3 \text{KJ/mol}$$

(1 pt)

(-0.5pt for s.f. & unit)

6. (6 pt) Using the equipartition theorem, calculate  $\overline{C}_V$  and  $\overline{C}_P$  (in J/mol·K) for O<sub>2</sub> and CH<sub>4</sub>, assuming both gases follow the ideal gas equation.

For the diatomic molecule **Oxygen**, we must consider the rotational (2 modes) (0.5 pt) and vibrational (1 mode) (0.5 pt) contribution, which contribute 0.5R and R respectively. Therefore, its constant volume heat capacity is:

$$\overline{C}_V = \frac{3}{2}R + 2 \times \frac{R}{2} + R = \frac{7}{2}R \text{ (1.5 pt)}$$

Hence, the constant pressure heat capacity considering PV work is  $\overline{C}_P = \overline{C}_V + R = \frac{9}{2}R$  (1.5 pt)

We must consider the rotational (3 modes) (0.5 pt) and vibrational (9 modes) (0.5 pt) contribution of the five-atom molecule methane, which contributes 0.5R and R respectively. Therefore, its constant volume heat capacity is:

$$\overline{C}_V = \frac{3}{2}R + 3 \times \frac{R}{2} + 9 \times R = 12R \text{ (1.5 pt)}$$

Hence, the constant pressure heat capacity considering PV work is  $\overline{C}_P = \overline{C}_V + R = 13R$  (1.5 pt)

7. (6 pt) The standard molar entropies  $S^0$  and constant-pressure molar heat capacities  $\overline{C}_P^0$  of N<sub>2</sub>O<sub>4</sub>(g) and NO<sub>2</sub>(g) are listed in the table to the right. (a) Calculate the molar entropy of N<sub>2</sub>O<sub>4</sub>(g) at 450 K. (b) Calculate the standard entropy change  $\Delta S_{\text{rxn}}^0$  for the reaction N<sub>2</sub>O<sub>4</sub>(g) → 2 NO<sub>2</sub>(g). (c) Calculate  $\Delta S_{\text{rxn}}$  for the same reaction at 450 K.

	$S^0$ (J/mol·K)	$\overline{C}_P^0$ (J/mol·K)
N <sub>2</sub> O <sub>4</sub> (g)	304.3	79.2
NO <sub>2</sub> (g)	240.5	27.2

Assuming that molar heat capacities are independent of temperature, so the entropy change at different temperatures can be derived from the equation below, where T<sub>2</sub> is the final temperature and T<sub>1</sub> is the temperature of the standard state.

$$S(T_2) = S^0(T_1) + C_P^0 \ln \frac{T_2}{T_1} \dots \dots (1)$$

(a)

$$S(450\text{K}) = S^0(298.15\text{K}) + C_P^0 \ln \frac{450}{298.15} \text{ (1 pt)}$$

$$S(450K) = 304.3 \left( \frac{J}{mol \cdot K} \right) + 79.2 \left( \frac{J}{mol \cdot K} \right) \times \ln \left( \frac{450}{298.15} \right) = 337 \left( \frac{J}{mol \cdot K} \right)$$

The molar entropy at 450K is **336.9 (J mol<sup>-1</sup>K<sup>-1</sup>)**. (1 pt)

(b)

The entropy change of the reaction can be derived by the summation of the standard entropy of the product minus that of the standard entropy of the reactant.

$$\Delta S_{rxn}^0 = 2S^0(NO_2) - S^0(N_2O_4) = 146.7 \left( \frac{J}{mol \cdot K} \right) \text{ (1 pt)}$$

The standard molar entropy change of the reaction is **176.7(J mol<sup>-1</sup>K<sup>-1</sup>)**. (1 pt)

(c)

Assuming the molar reaction heat capacities are independent of temperature. One can first construct the molar reaction heat capacity by the same rule of deriving the molar entropy of the reaction. The entropy change of reaction also obeys the same equation as (1). After computing the heat capacity of the reaction, one can use the equation, in which the entropy part is substituted by reaction entropy.

$$\Delta C_{p,rxn}^0 = 2C_p^0(NO_2) - C_p^0(N_2O_4) = -24.8 \left( \frac{J}{mol \cdot K} \right)$$

$$\Delta S_{rxn}(450K) = \Delta S_{rxn}^0(298.15K) + \Delta C_{p,rxn}^0 \ln \frac{450}{298.15} \text{ (1 pt)}$$

$$\Delta S_{rxn}(450K) = 176.7 \left( \frac{J}{mol \cdot K} \right) - 24.8 \left( \frac{J}{mol \cdot K} \right) \ln \frac{450}{298.15} = 167 \left( \frac{J}{mol \cdot K} \right)$$

The molar entropy of the reaction at 450K is **166.5 (J mol<sup>-1</sup>K<sup>-1</sup>)**. (1 pt)  
(-0.5pt for s.f. & units)