

## SMNS, CHEMISTRY DEPARTMENT

### GENERAL CHEMISTRY (CH 110/CH 120/FO 130)

#### TUTORIAL 5 – Thermochemistry

13 December 2016

Useful data  $\Delta_f H(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$  and  $\Delta_f H(\text{H}_2\text{O}, \text{l}) = -286 \text{ kJ/mol}$

1. Define the following terms: potential energy, kinetic energy, path-dependent function, state function, system, surroundings.

**SOLUTION:** Ref: Zumdahl and Zumdahl 9<sup>th</sup> Edition, pp 246-248.

**Potential energy** is energy due to position or composition.

**Kinetic energy** of an object is energy due to the motion of the object and depends on the mass of the object  $m$  and its velocity  $v$ :  $E = \frac{1}{2} mv^2$ .

A **state function** refers to a property of the system that depends only on its present state.

**Path-dependent function** like heat or work, depend on the path taken.

The **system** is the part of the universe on which we wish to focus attention

**Surroundings** include everything else in the universe other than the system.

2. When a gas expands, what is the sign of  $w$ ? Why? When a gas contracts, what is the sign of  $w$ ? Why? What are the signs of  $q$  and  $w$  for the process of boiling water?

**SOLUTION:** Ref: Zumdahl and Zumdahl 9<sup>th</sup> Edition, pp 250

When a **gas expands**, the system does work on the surroundings  $w$  is negative. Sign is negative because energy flows out of the system.

When a **gas contracts**, the surroundings do work on the system  $w$  is positive. Sign is positive because energy flows into the system.

**Signs of  $q$  and  $w$  for boiling water:**

$q$  is positive since the system is heated by surrounding.

since  $w = -P\Delta V$  and water is lost during boiling, that is  $\Delta V$  is negative,  $w$  is also positive.

3. Calculate the internal energy change for each of the following processes.
- (a) One hundred (100) joules of work is required to compress a gas. At the same time, the gas releases 23 J of heat.

**SOLUTION:**

Since  $\Delta E = q + w$  or  $\Delta E = q - P\Delta V$

With  $q = -23 \text{ J}$  and  $\Delta V$  is negative,  $w = +100 \text{ J}$ ,

$\Delta E = -23 \text{ J} + 100 \text{ J} = 77 \text{ J}$

- (b) A piston is compressed from a volume of 8.30 L to 2.80 L against a constant pressure of 1.90 atm. In the process, there is a heat gain by the system of 350. J.

**SOLUTION:**

Since  $\Delta V = 2.80 \text{ L} - 8.30 \text{ L} = -5.5 \text{ L}$  or  $-5.5 \times 10^{-3} \text{ m}^3$

$P = 1.90 \text{ atm}$  or  $P = 1.90 \times 101325 \text{ Pa} = 192517.5 \text{ Pa}$

Thus  $w = -P\Delta V = -192517.5 \times -5.5 \times 10^{-3} \text{ J} = 1059 \text{ J}$

We are given that  $q = 350 \text{ J}$  therefore

$\Delta E = q + w = 350 \text{ J} + 1059 \text{ J} = 1409 \text{ J} = 1.41 \text{ kJ}$

**Given Ans 3(b)  $\Delta E = 1.41 \text{ kJ}$**

- (c) A piston expands against 1.00 atm of pressure from 11.2 L to 29.1 L. In the process, 1037 J of heat is absorbed.

**SOLUTION:**

Since  $\Delta V = 29.1 \text{ L} - 11.2 \text{ L} = 17.9 \text{ L}$  or  $1.79 \times 10^{-2} \text{ m}^3$

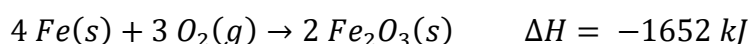
$P = 1.0 \text{ atm}$  or  $P = 101325 \text{ Pa}$

Thus  $w = -P\Delta V = -101325 \times 1.79 \times 10^{-2} \text{ J} = -1814 \text{ J}$

We are given that  $q = 1037 \text{ J}$  therefore

$\Delta E = 1037 - 1814 = -777 \text{ J}$

4. The overall reaction in a commercial heat pack can be represented



- (a) How much heat is released when 4.00 mol of iron is reacted with excess  $\text{O}_2$ ?

**SOLUTION:**

The stoichiometric equation states that 4 moles of Fe gives  $-1652 \text{ kJ}$

- (b) How much heat is released when 1.00 mol of  $\text{Fe}_2\text{O}_3$  is produced?

**SOLUTION:**

The stoichiometric equation, 1 mole of Fe gives  $\frac{-1652 \text{ kJ}}{2} = -826 \text{ kJ}$ . This heat value is twice the molar specific heat for Fe consumption of this reaction which is  $\frac{-1652 \text{ kJ}}{4} = -413 \text{ kJ}$

- (c) How much heat is released when 1.00 g of iron is reacted with excess  $\text{O}_2$ ?

**SOLUTION:**

$1.0 \text{ g} = \frac{1}{55.85} = 1.79 \times 10^{-2} \text{ mole of Fe}$

Using the molar enthalpy for Fe gives  $\frac{-413 \text{ kJ}}{55.85} = -7.39 \text{ kJ}$ .

- (d) How much heat is released when 10.0 g Fe and 2.00 g O<sub>2</sub> are reacted?

**SOLUTION:**

*We first have to determine the excess reagent*

$$10.0 \text{ g of Fe} = \frac{10.0}{55.85} = 1.79 \times 10^{-1} \text{ mole of Fe}$$

$$2.0 \text{ g of O}_2 = \frac{2.0}{32.0} = 6.25 \times 10^{-2} \text{ mole of O}_2$$

*A mole of Fe reacts with 0.75 mol of O<sub>2</sub>. Therefore,  $1.79 \times 10^{-1}$  mol of Fe uses  $1.79 \times 10^{-1} \times 0.75 = 0.134 \text{ mol of O}_2$ .*

*Clearly we only have half this number of moles of O<sub>2</sub>. Therefore the moles of Fe used up is  $\frac{6.25 \times 10^{-2}}{0.75} = 8.33 \times 10^{-2}$ .*

*Using the molar enthalpy for Fe gives  $-413 \text{ kJ} \times 8.33 \times 10^{-2} = -34.4 \text{ kJ}$ .*

5. The specific heat capacity of silver is  $0.24 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$ .

- (a) Calculate the energy required to raise the temperature of 150.0 g Ag from 273 K to 298 K.

**SOLUTION:**

*Energy required is  $\Delta E = C_p \times m_s \times \Delta T$*

*Since  $C_p = 0.24 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$ ,  $m_s = 150.0 \text{ g}$  and  $\Delta T = 298 \text{ K} - 273 \text{ K} = 25 \text{ K}$  or  $25 ^\circ\text{C}$ , substituting these values in the equation above gives*

$$\Delta E = 0.24 \times 150.0 \times 25 \text{ J} = \mathbf{900 \text{ J}}$$

- (b) Calculate the energy required to raise the temperature of 1.0 mol Ag by  $1.0 ^\circ\text{C}$  (called the *molar heat capacity* of silver).

**SOLUTION:**

*1 mol of silver is 107.9 g using the equation in a with  $\Delta T = 1.0 ^\circ\text{C}$  we have*

$$\Delta E = 0.24 \times 107.9 \times 1.0 \text{ J} = \mathbf{25.896 \text{ J}}$$

*Thus the molar specific heat capacity to two significant figures is  $26 \text{ J/mol}$*

**Given is Ans:  $26 \text{ J/mol}$**

- (c) It takes 1.25 kJ of energy to heat a sample of pure silver from  $12.0 ^\circ\text{C}$  to  $15.2 ^\circ\text{C}$ . Calculate the mass of the sample of silver.

**SOLUTION:**

*From the formula in (a) above the mass of the sample is give by the equation*

$$m_s = \frac{\Delta E}{C_p \times \Delta T}$$

*Where  $\Delta E = 1250 \text{ J}$  and  $\Delta T = 15.2 - 12.0 = 3.2 ^\circ\text{C}$*

*Using the above formula give*

$$m_s = \frac{1250}{0.24 \times 3.2} = \mathbf{1628 \text{ g or } 1.63 \text{ kg}}$$

6. In a coffee-cup calorimeter, 100.0 mL of 1.0 M NaOH and 100.0 mL of 1.0 M HCl are mixed. Both solutions were originally at 24.6 °C. After the reaction, the final temperature is 31.3 °C. Assuming that all the solutions have a density of 1.0 g/cm<sup>3</sup> and a specific heat capacity of 4.18 J/°C.g, calculate the enthalpy change for the neutralization of HCl by NaOH in kJ/mol. Assume that no heat is lost to the surroundings or to the calorimeter.

**SOLUTION:**

*Chemical reaction is:  $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$*

*Stoichiometry thus specifies that a mol of HCl consumes a mol of NaOH.*

*From the equation  $n = C_M \times V$  that specifies that the number of moles of a solution whose molarity is  $C_M$  and volume in L is  $V$ , we see that*

$$n_{\text{NaOH}} = 1.0 \times 0.1000 = 0.10 \text{ mol and } n_{\text{HCl}} = 1.0 \times 0.1000 = 0.10 \text{ mol}$$

*The above information gives the total volume of the solution as 200 ml which translates to a mass of 200 g since the density of each solution is 1.0 g/cm<sup>3</sup>.*

*Considering that  $\Delta T = 31.3 - 24.6 = 6.7^\circ\text{C}$ ,  $m_s = 200 \text{ g}$  and  $C_p = 4.18 \text{ J/}^\circ\text{C.g}$*

*We can use the equation  $\Delta H = C_p \times m_s \times \Delta T$  to get the energy as*

$$\Delta H = 4.18 \times 200 \times 6.7 = 5601 \text{ J}$$

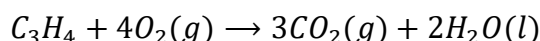
*Since the moles of HCl neutralised was 0.1 mole is  $\frac{5601}{0.1} = 56010 \text{ J/mol}$ . This value to two significant figures translates to **56 kJ/mol**.*

Given (Ans: **-56 kJ/mol**)

7. The standard enthalpies of formation of gaseous propyne (C<sub>3</sub>H<sub>4</sub>), propene (C<sub>3</sub>H<sub>6</sub>), and propane (C<sub>3</sub>H<sub>8</sub>) are +185.4, +20.4, and -103.8 kJ/mol, respectively.
- (a) Calculate the heat evolved per mole on combustion of each substance to yield CO<sub>2</sub>(g) and H<sub>2</sub>O(l).

**SOLUTION:**

(i) Combustion of propyne is



*Using the equation for the heats of formation, we have*

$$\Delta H_{\text{reaction}} = (\text{sum of } \Delta H_f \text{ of products}) - (\text{sum of } \Delta H_f \text{ of reactants})$$

*This becomes*

$$\Delta H_{\text{combustion}} = (3\Delta H_{f,\text{CO}_2} + 2\Delta H_{f,\text{H}_2\text{O}}) - \Delta H_{f,\text{C}_3\text{H}_4}$$

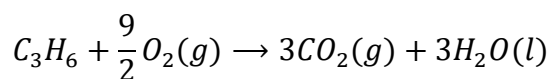
*Since  $\Delta H_{f,\text{CO}_2} = -393.5 \text{ kJ}$ ,  $\Delta H_{f,\text{H}_2\text{O}} = -286 \text{ kJ}$  and*

$$\Delta H_{f,\text{C}_3\text{H}_4} = +185.4 \text{ kJ}$$

*The above formula gives*

$$\Delta H_{\text{combustion}} = (-3 \times 393.5 + 2 \times (-286)) - 185.4 = -1937.9 \text{ kJ/mol}$$

(ii) Combustion of propene is



Using the equation for the heats of formation, we have

$$\Delta H_{\text{reaction}} = (\text{sum of } \Delta H_f \text{ of products}) - (\text{sum of } \Delta H_f \text{ of reactants})$$

This becomes

$$\Delta H_{\text{combustion}} = (3\Delta H_{f,CO_2} + 3\Delta H_{f,H_2O}) - \Delta H_{f,C_3H_6}$$

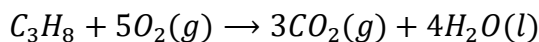
Since  $\Delta H_{f,CO_2} = -393.5 \text{ kJ}$ ,  $\Delta H_{f,H_2O} = -286 \text{ kJ}$  and

$$\Delta H_{f,C_3H_6} = +20.4 \text{ kJ}$$

The above formula gives

$$\Delta H_{\text{combustion}} = (-3 \times 393.5 + 3 \times (-286)) - 20.4 = -2058.9 \text{ kJ/mol}$$

(iii) Combustion of propane is



Using the equation for the heats of formation, we have

$$\Delta H_{\text{reaction}} = (\text{sum of } \Delta H_f \text{ of products}) - (\text{sum of } \Delta H_f \text{ of reactants})$$

This becomes

$$\Delta H_{\text{combustion}} = (3\Delta H_{f,CO_2} + 4\Delta H_{f,H_2O}) - \Delta H_{f,C_3H_8}$$

Since  $\Delta H_{f,CO_2} = -393.5 \text{ kJ}$ ,  $\Delta H_{f,H_2O} = -286 \text{ kJ}$  and

$$\Delta H_{f,C_3H_8} = -103.8 \text{ kJ}$$

The above formula gives

$$\Delta H_{\text{combustion}} = (-3 \times 393.5 + 4 \times (-286)) + 103.8 = -2220.7 \text{ kJ/mol}$$

(b) Calculate the heat evolved on combustion of 1 kg of each substance.

**SOLUTION:**

Molar mass of substance is ( $M_r$ )

moles/kg of substance is ( $n_{kg}$ )

$$C_3H_4 = 36.03 + 4.032 \text{ g} = 40.062 \text{ g/mol}$$

$$1000/40.062 = 24.96131 \text{ mol/kg}$$

$$C_3H_6 = 36.03 + 6.048 \text{ g} = 42.078 \text{ g/mol}$$

$$1000/42.078 = 23.76539 \text{ mol/kg}$$

$$C_3H_8 = 36.03 + 8.064 \text{ g} = 44.094 \text{ g/mol}$$

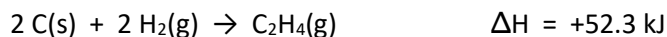
$$1000/44.094 = 22.67882 \text{ mol/kg}$$

Heat evolved per kg of substance is Molar  $\Delta H_{\text{combustion}} \times \text{moles/kg}$  ( $n_{kg}$ )

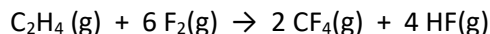
Substance	$\Delta H_{\text{combustion}}$	$n_{kg} \text{ (mol/kg)}$	$\Delta H_{\text{combustion}} \times n_{kg} \text{ (kJ/kg)}$
$C_3H_4$	$-1937.9 \text{ kJ/mol}$	24.96131	$-48373 = 4.84 \times 10^4$
$C_3H_6$	$-2058.9 \text{ kJ/mol}$	23.76539	$-48931 = 4.89 \times 10^4$
$C_3H_8$	$-2220.7 \text{ kJ/mol}$	22.67882	$-50363 = 5.04 \times 10^4$

Given (Ans  $q(C_3H_6) = -4.89 \times 10^4 \text{ kJ/kg}$ )

8. From the enthalpies of reaction

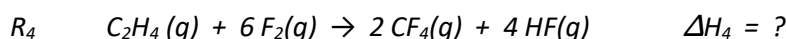
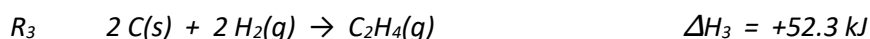


Calculate  $\Delta H$  for the reaction of ethene with  $F_2$ :



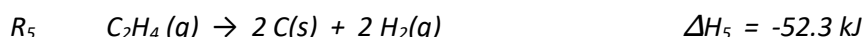
**SOLUTION:**

We renumber the above reactions as follows:

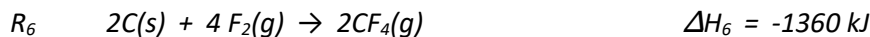


Our goal is to combine reactions  $R_1$  to  $R_3$  into  $R_4$

Getting the first reactant of  $R_4$  requires us to reverse  $R_3$  to give a new reaction  $R_5$  such that  $R_5 = -R_3$  and  $\Delta H_5 = -\Delta H_3 = -52.3 \text{ kJ}$ . This means



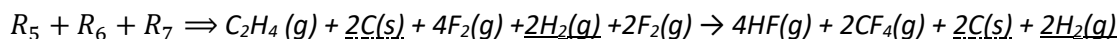
Getting the first product of  $R_4$  requires to double  $R_2$  to give us a new reaction  $R_6$  such that  $R_6 = 2R_2$  and  $\Delta H_6 = 2\Delta H_2 = 2 \times (-680 \text{ kJ}) = -1360 \text{ kJ}$ . This means



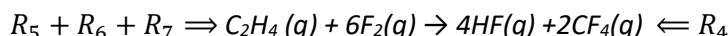
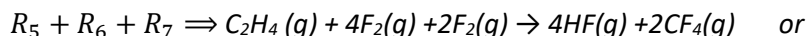
Getting the second product of  $R_4$  requires to double  $R_1$  to give us a new reaction  $R_7$  such that  $R_7 = 2R_1$  and  $\Delta H_7 = 2\Delta H_1 = 2 \times (-537 \text{ kJ}) = -1074 \text{ kJ}$ . This means



Combining these reactions gives the required reaction, that is,  $R_4 = R_5 + R_6 + R_7$  so that the enthalpy is given by the equation  $\Delta H_4 = \Delta H_5 + \Delta H_6 + \Delta H_7$  as shown below.



Cancelling out the common terms on each side of the equation gives



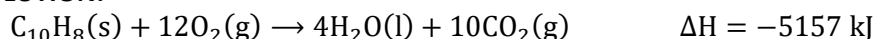
**Clearly,  $\Delta H_4 = \Delta H_5 + \Delta H_6 + \Delta H_7 = -52.3 + (-1360) + (-1074) \text{ kJ} = -2486.3 \text{ kJ}$**

**(Ans:  $\Delta H = -2486 \text{ kJ}$ )**

9. Naphthalene,  $C_{10}H_8$ , is a solid aromatic compound often sold as mothballs. The complete combustion of this substance to  $H_2O(l)$  and  $CO_2(g)$  at  $25^\circ C$  yields  $5157 \text{ kJ/mol}$ .

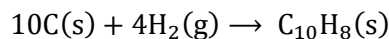
(a) Write a thermochemical equation for the combustion of  $C_{10}H_8$ .

**SOLUTION:**



(b) Write a balanced chemical equation for the formation of  $C_{10}H_8$  from the elements.

**SOLUTION:**



(c) Calculate the standard enthalpy of formation of  $C_{10}H_8$ .

**SOLUTION:**

*If we use Hess' Law for the combustion reaction, we have*

$$\Delta H_{rxn} = \sum_{i=1}^m n_{i^{th} \text{ product}} \Delta H_{i^{th} \text{ product}} - \sum_{j=1}^p n_{j^{th} \text{ reactant}} \Delta H_{j^{th} \text{ reactant}}$$

$$\Delta H_{rxn} = (n_{H_2O(l)} \times \Delta H_{f,H_2O(l)} + n_{CO_2(g)} \times \Delta H_{f,CO_2(g)}) - (n_{C_{10}H_8(s)} \times \Delta H_{f,C_{10}H_8(s)} + n_{O_2(g)} \times \Delta H_{f,O_2(g)})$$

*Since  $\Delta H_{rxn} = -5157 \text{ kJ}$ ,  $n_{H_2O(l)} = 4 \text{ mol}$ ,  $\Delta H_{f,H_2O(l)} = -286 \text{ kJ/mol}$ ,  $n_{CO_2(g)} = 10 \text{ mol}$ ,  $\Delta H_{f,CO_2(g)} = -393.5 \text{ kJ}$ ,  $n_{C_{10}H_8(s)} = 1 \text{ mol}$ ,  $n_{O_2(g)} = 12 \text{ mol}$ ,  $\Delta H_{f,O_2(g)} = 0 \text{ kJ}$ , substituting these values leaves  $\Delta H_{f,C_{10}H_8(s)}$  as the only unknown which can be solved for the equation as*

$$-5157 \text{ kJ} = (4 \times (-286 \text{ kJ}) + 10 \times (-393.5 \text{ kJ}) - (1 \times \Delta H_{f,C_{10}H_8(s)} + 12 \times 0))$$

*or*

$$-5157 \text{ kJ} = ((-1144 \text{ kJ}) + (-3935 \text{ kJ})) - \Delta H_{f,C_{10}H_8(s)}$$

*or*

$$-5157 \text{ kJ} = (-5079 \text{ kJ}) - \Delta H_{f,C_{10}H_8(s)}$$

*or*

$$\Delta H_{f,C_{10}H_8(s)} = (-5079 \text{ kJ}) - (-5157 \text{ kJ}) = 5157 - 5079 \text{ kJ} = 78 \text{ kJ}$$

**(Ans:  $\Delta_f H = +78 \text{ kJ/mol}$ )**

10. It has been determined that the body can generate  $5500 \text{ kJ}$  of energy during one hour of strenuous exercise. Perspiration is the body's mechanism for eliminating this heat. What mass of water would have to be evaporated through perspiration to rid the body of the heat generated during two hours of exercise? (The heat of vaporization of water is  $40.6 \text{ kJ/mol}$ .)

**SOLUTION:**

*Heat generated in 2 hours is  $11000 \text{ kJ}$  and each mole requires  $40.6 \text{ kJ}$  to evaporate.*

*Moles evaporated by  $11000 \text{ kJ}$  is  $\frac{11000}{40.6}$  and each mole has a mass of  $18.0 \text{ g}$ .*

*Therefore the mass of water evaporated is*

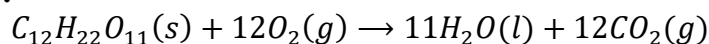
$$\frac{11000}{40.6} \times \frac{18}{1000} \text{ kg} = \frac{11 \times 18}{40.6} \text{ kg} = \frac{198}{40.6} \text{ kg} = 4.8768 \text{ kg} \approx 4.88 \text{ kg}$$

**(Ans:  $4.88 \text{ kg}$ )**

11. Combustion of table sugar produces  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$ . When 1.46 g table sugar is combusted in a constant-volume (bomb) calorimeter, 24.00 kJ of heat is liberated.

(a) Assuming that table sugar is pure sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$ , write the balanced equation for the combustion reaction.

**SOLUTION:**



(b) Calculate  $\Delta E$  in kJ/mol  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  for the combustion reaction of sucrose.

**SOLUTION:**

*Molar mass of sucrose is*

$$M_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} = 12.01 \times 12 + 22 \times 1.008 + 11 \times 16.00 = 342.3 \text{ g/mol}$$

$$1.46 \text{ g sucrose} = \frac{1.46}{342.3} \text{ mol} = 0.004265 \text{ mol}$$

$$\Delta E = \frac{24.00}{0.004265} \text{ kJ/mol} = 5627 \text{ kJ}$$

(c) Calculate  $\Delta H$  in kJ/mol  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  for the combustion reaction of sucrose at  $25^\circ\text{C}$ .

**SOLUTION:**

*Since  $\Delta V=0$  for a constant-volume calorimeter,  $w=0$  and  $\Delta H= \Delta E=5627 \text{ kJ}$*

**(Ans:  $\Delta H= \Delta E=5627 \text{ kJ/mol}$ )**