HINTS & SOLUTIONS WORKBOOK - 2

Thermochemistry

Daily Tutorial Sheet	Level-0

Very Short Answer Type (1 Mark)

1. The reaction is: $C_6H_6(\ell)+7\frac{1}{2}O_2(g) \longrightarrow 6CO_2(g)+3H_2O(\ell)$

In this reaction, O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$\therefore \quad \Delta n_g = n_p - n_r = 6-7\frac{1}{2} = -1\frac{1}{2} = -\frac{3}{2}$

Also, we are given ΔU (or q_v) $= 3263.9$ kJ mol^{-1}

$$T = 25°C = 298\,K$$

$$R = 8.314\,J\ K^{-1}\,mol^{-1} = \frac{8.314}{1000}\,kJ\ K^{-1}\,mol^{-1}$$

$$\Delta H\ (\text{or } q_p) = \Delta U + \Delta n_g RT = -3263.9\,kJ\ mol^{-1} + \left(-\frac{3}{2}mol\right)\left(\frac{8.314}{1000}kJ\ K^{-1}mol^{-1}\right)(298\ K)$$

$$= -3263.9 - 3.7\,kJ\ mol^{-1} = -3267.6\,kJ\,mol^{-1}.$$

2. $\Delta H = -122.56\,kJ\ mol^{-1}$, $\Delta U = -125.04\,kJ\ mol^{-1}$

3. Rise in temperature of the calorimeter $= 299 - 298\,K = 1\,K$

Heat capacity of the calorimeter $= 20.7\,kJ\ K^{-1}$

$\therefore \quad$ Heat absorbed by the calorimeter $= C_v \times \Delta T = (20.7\,kJ\ K^{-1})(1\,K) = 20.7\,kJ$

This is the heat evolved in the combustion of 1 g of graphite.

$\therefore \quad$ Heat evolved in the combustion of 1 mole of graphite, i.e., 12 g of graphite

$= 20.7 \times 12\,kJ = 248.4\,kJ$

As this is the heat evolved and the vessel is closed, therefore, enthalpy change of the reaction

$(\Delta U) = -248.4\,kJ\ mol^{-1}$

4. We are given :

(i) $CuSO_4(s) + aq \longrightarrow CuSO_4(aq)\ ;\ \Delta_{sol}H = -66.5\,kJ\ mol^{-1}$

(ii) $CuSO_4 \cdot 5H_2O(s) + aq \longrightarrow CuSO_4(aq);\ \Delta_{sol}H = +11.7\,kJ\ mol^{-1}$

We aim at $CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s);\ \Delta_{hyd}H = ?$

Equation (i) can be written in two steps as:

(iii) $CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4 \cdot 5H_2O(s); \Delta H = \Delta H_1 kJmol^{-1}$

(iv) $CuSO_4 \cdot 5H_2O(s) + aq \longrightarrow CuSO_4(aq);\ \Delta H = \Delta H_2\ kJ\ mol^{-1}$

According to Hess's law, $\Delta H_1 + \Delta H_2 = -66.5\,kJ\ mol^{-1}$

Further, equation (ii) and (iv) are same

$\therefore \quad \Delta H_2 = +11.7\,kJ\ mol^{-1}$

Putting this value above, we get : $\Delta H_1 + 11.7 = -66.5$ or $\Delta H_1 = -66.5 - 11.7\,kJ = -78.2\,kJ\ mol^{-1}$

Thus, equation (iii) may be written as $CuSO_4(s) + 5H_2O(\ell) \rightarrow CuSO_4 \cdot 5H_2O(s);\ \Delta_{hyd}H = 78.2\,kJ\ mol^{-1}$

This is what we aimed at. Hence, the required value of the enthalpy of hydration is

$$\Delta_{hyd}H = -78.2\,kJ\ mol^{-1}$$

5. $-445.9\,kJ\ mol^{-1}$ **6.** 110.6 kcal

Short Answer Type-I (2 Marks)

7. Heat transferred $= 60.1\,kJ,\ \Delta_C H = 5481.1\,kJ\ mol^{-1}$

8. $q_v = -885\,kJ\,mol^{-1},\ q_p = -890\,kJ\,mol^{-1}$

9. We aim at : $C(s) + 2H_2(g) \longrightarrow CH_4(g);\ \Delta_f H^\circ = ?$

Multiplying equation (ii) with 2, adding to equation (i) and then subtracting equation (iii) from the sum, i.e., operating equation (i) + 2 × equation (ii) – equation (iii), we get

$$C(s) + 2H_2(g) \longrightarrow CH_4(g);\ \Delta_r H^\circ = -393.5 + 2(-285.8) - (-890.3) = -74.8\,kJ\ mol^{-1}$$

or $$C(s) + 2H_2(g) \longrightarrow CH_4(g);\ \Delta_f H^\circ = -74.8\,kJ\ mol^{-1}$$

Hence, enthalpy of formation of methane is : $\Delta_f H^\circ = -74.8\,kJ\ mol^{-1}$

10. $+51.0\,kJ\,mol^{-1}$ **11.** $-2677.1\,kJ\,mol^{-1}$

12. ΔH for glucose $= 15.6\,kJ\ g^{-1}$, ΔH for the sucrose $= -16.5\,kJ\ g^{-1}$.

13. **(a)** No because after breaking of C–H bonds one by one, the electronic environments change. The reported value is the average value of the bond dissociation energies of the four C–H bonds.

(b) Heat evolved will be different. This is because they have different crystal structure.

Short Answer Type-II (3 Marks)

14. Here, we are given

$C(s) + 2H_2(g) \longrightarrow CH_4(g),\ \Delta_r H^\circ = -74.8\,kJ$ **... (i)**

$C(s) \longrightarrow C(g),\ \Delta_r H^\circ = +719.6\,kJ$ **... (ii)**

$H_2(g) \longrightarrow 2H(g),\ \Delta_r H^\circ = +435.4\,kJ$ **... (iii)**

We aim at: $CH_4(g) \longrightarrow C(g) + 4H(g);\ \Delta_r H = \Delta_f H$ **... (iv)**

Equation (ii) + 2 × equation (iii) – Equation (i) gives

$$C(s) + 2H_2(g) \longrightarrow C(g) + 4H(g)$$
$$-C(s) - 2H_2(g) = -CH_4(g)$$
$$0 = C(g) + 4H(g) - CH_4(g),\ \Delta_r H^\circ = 719.6 + 2(435.4) - (-74.8)$$

or $$CH_4(g) \longrightarrow C(g) + 4H(g);\ \Delta H = +1665.2\,kJ$$

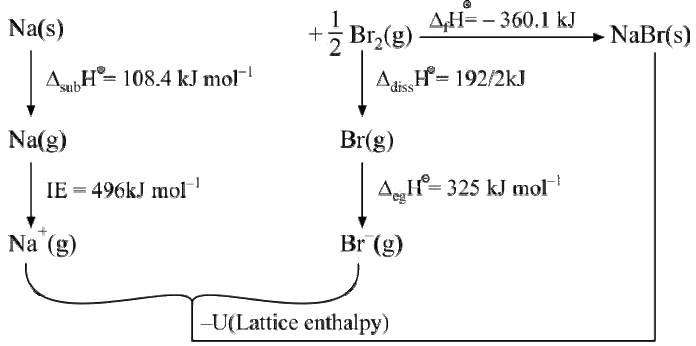
This gives the enthalpy of dissociation of four moles of C–H bonds (called enthalpy of atomization). Hence, bond energy for C–H bond (average value) i.e., $\Delta_{C-H}H^\circ = \dfrac{1665.2}{4} = 416.3\,kJ\ mol^{-1}$

15. Given that, $\Delta_{sub}H^\circ$ for Na metal $= 180.4\,kJ\ mol^{-1}$

IE of Na $= 496\,kJ\ mol^{-1}$, $\Delta_{eg}H^\circ$ of Br $= -325\,kJ\ mol^{-1}$, $\Delta_{diss}H^\circ$ of Br $= 192\,kJ\,mol^{-1}$, $\Delta_f H^\circ$

For NaBr NaBr $= 360.1\,kJ\ mol^{-1}$

Born-Haber cycle for the formation of NaBr is as



By applying Hess's law : $\Delta_f H^o = \Delta_{sub}H^o + IE + \Delta_{diss}H^o + \Delta_{eg}H^o + U$

$$-360.1 = 108.4 + 496 + 96 + (-325) - U$$

$$U = +735.5\,\text{kJ mol}^{-1}$$

16. ΔG° (for the reaction)

$$= G^\circ_{(f)}(\text{products}) - G^\circ_{(f)}(\text{reactants}) = G^\circ_{(f)}(CO_2) - \left[G^\circ_{(f)}(CO) + \frac{1}{2}G^\circ_{(f)}(O_2)\right]$$

$$= -394.4 - [-137.2 + 0]\left[\because G^\circ_{(f)}(O_2) = 0\right] = -257.2 \text{ kJ}$$

Since, ΔG° for reaction is negative, so the reaction is spontaneous.

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ or $-257.2 = \Delta H^\circ - (300 \times -0.094)$

$\therefore$ $\Delta H^\circ = -285.4$ kJ

ΔH° is negative and thus reaction is exothermic.

17. **(i)** $CHCl_2COOH + OH^- \longrightarrow CHCl_2COO^- + H_2O$; $\Delta H_1 = 12830$ cal

(ii) $H^+ + OH^- \longrightarrow H_2O$; $\Delta H_2 = 13680$ cal

(iii) $NH_4OH + H^+ \longrightarrow NH_4^+ + H_2O$; $\Delta H_3 = -12270$ cal

Consider

(iv) $CHCl_2COOH + NH_4OH \longrightarrow CHCl_2COO^- + NH_4^+ + H_2O$

(v) Will be obtained by applying [(i) + (iii) – (ii)]

ΔH (iv) = $\Delta H_1 + \Delta H_3 - \Delta H_2 = -12830 - 12270 + 13680 = -11420$ cal

Now,

(vi) $CHCl_2COOH \longrightarrow CHCl_2COO^- + H^+$

(vii) Will be obtained by applying (i) – (ii)

$\therefore$ ΔH (v) = $\Delta H_1 - \Delta H_2 = 13680 - 12830 = 850$ cal/mol

Similarly $\Delta H_{ionization}$ for $NH_4OH = 13680 - 12270 = 1410$ cal/mol

18. Let, V be the volume of CH_4 in 10 L mixture. We have

Amount of methane = $\frac{V}{22.4}$; Amount of ethane = $\frac{10-V}{22.4}$

The expression of heat evolved, we will get

$$\frac{V}{22.4} \times 894 + \frac{10-V}{22.4} \times 1560 = 474.6$$

V = 7.45 litre

% of CH_4 = 74.5%

% of C_2H_6 = 25.5%

19. $H_2O(l) \rightleftharpoons H_2O(g)$

Enthalpy change at 373 K is $\Delta H_1 = 40.67 \text{ kJ mol}^{-1} = 40670 \text{ J mol}^{1}$

$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$

$\Delta C_p = \Delta C_{p,\ H_2O(g)} - \Delta C_{p,\ H_2O(l)}$

$33.89 - 75.312 = -41.422$

Enthalpy of evaporation at 353 K,

$\Delta H = 40670 - 41.522 (353 - 373) = 40670 + 41.421 \times 20 = 41498.44 \text{ J}$

Similarly, enthalpy of evaporation at 393 K = $40670 - 41.422 (393 - 373) = 39841.56$ J

Long Answer Type (5 Marks)

20. A,C.D → exothermic B, E → endothermic

21. For the enthalpy of combustion of ethane and propane, we write

$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta H_{comb} = 3\Delta H_{f(H_2O,l)} + 2\Delta H_{f(CO_2,g)} - \Delta H_{f(C_2H_6,g)}$

$\Delta H_{f(C_2H_6,g)} = -\Delta H_{comb} + 3\Delta H_{f(H_2O,l)} + 2\Delta H_{f(CO_2,g)}$

$= (372 - 3 \times 68 - 2 \times 94) \text{ kcalmol}^{-1} = -20 \text{ kcal mol}^{-1}$

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$

$\Delta H_{comb} = 3\Delta H_{f(CO_2,g)} + 4\Delta H_{f(H_2O,l)} - \Delta H_{f(C_3H_8,g)}$

Thus, $\Delta H_{f(C_3H_8,g)} = -\Delta H_{comb} + 3\Delta H_{f(CO_2,g)} + 4\Delta H_{f(H_2O,l)}$

$= (530 - 3 \times 94 - 4 \times 68) \text{ kcalmol}^{-1} = -24 \text{ kcal mol}^{-1}$

To calculate ε_{C-H} and $\varepsilon_{C-C,}$ we carry out the following operations.

(i) $2C_{(graphite)} + 3H_2(g) \rightarrow C_2H_6(g)$; $\Delta H = -20 \text{ kcal mol}^{-1}$

$2C(g) + 6H(g) \rightarrow C_2H_6(g)$; $\Delta H = -2 \times 172 \text{ kcal mol}^{-1}$

On Adding, $2C(g) + 6H(g) \rightarrow C_2H_6(g)$; $\Delta H = -3 \times 104 \text{ kcal mol}^{-1}$

We get $2C(g) + 6H(g) \rightarrow C_2H_6(g)$

$\Delta H_{(i)} = (-20 - 2 \times 172 - 3 \times 104) \text{ kcal mol}^{-1} = \mathbf{-676} \text{ kcal mol}^{-1}$

(ii) $3C_{(graphite)} + 4H_2(g) \rightarrow C_3H_8(g)$; $\Delta H = -24 \text{kcal mol}^{-1}$

$3C(g) \rightarrow 3C_{(graphite)}$; $\Delta H = -3 \times 172 \text{kcal mol}^{-1}$

$8H(g) \rightarrow 4H_2(g)$; $\Delta H = -4 \times 104 \text{ kcal mol}^{-1}$

On Adding,
We get $3C(g) + 8H(g) \rightarrow C_3H_8(g)$

$\Delta H_{(ii)} = (-24 - 3 \times 172 - 4 \times 104) \text{ kcal mol}^{-1} = -956 \text{ kcal mol}^{-1}$

Now $\Delta H_{(i)} = -\varepsilon_{C-C} - 6\varepsilon_{C-H} = -676 \text{ kcal mol}^{-1}$

$\Delta H_{(ii)} = -2\varepsilon_{C-C} - 8\varepsilon_{C-H} = -956 \text{ kcal mol}^{-1}$

Solving for ε_{C-C} and $\varepsilon_{C-H,}$ we get :

$\varepsilon_{C-H} = 99 \text{ kcal mol}^{-1}$

$\varepsilon_{C-H} = 82 \text{ Kcal mol}^{-1}$

22. Bond energies are calculated from heat of formation of a compound. Now from the data given for heats of combustion for ethane and propane, we can calculate the heats of formation of two compounds $(C_2H_6 \text{ and } C_3H_8)$ as follows:

For ethane: The equation for combustion of ethane:

$$C_2H_6(g) + 7/2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)\ \Delta_{comb}H^{\Theta} = -372.0$$

From definition of ΔH^{Θ} of reaction: $\Delta H^{\Theta} = \Delta H^{\Theta}{}_{P} - \Delta H^{\Theta}{}_{R}$

The enthalpy of a compound is the enthalpy of formation of that compound at standard conditions (i.e. $\Delta_f H^{-}$).

$$\Delta_{comb}H^{\Theta} = [2\Delta_f H^{\Theta}(CO_2) + 3\Delta_f H^{\Theta}(H_2O)] - [\Delta_f H^{\Theta}(C_2H_6) - 7/2\Delta_f H^{\Theta}(O_2)]$$

$[\Delta_f H^{\Theta}(O_2) = 0$ (as enthalpy of formation of an element in standard state is taken as zero).

$\Rightarrow\ -372 = 2\times(-94) + 3\times(-68) - \Delta_f H^{\Theta}(C_2H_6) \quad \Rightarrow\ \Delta_f H^{\Theta}(C_2H_6) = -20$ kcal

For propane : The equation for combustion of propane.

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)\ \Delta_{comb}H^{\Theta} = -530.0$

From definition of ΔH of a reaction ; $\Delta H = H_P - H_R$

$$\Delta_{comb}H^{\Theta} = [3\Delta_f H^{o}(CO_2)] + 4\Delta_f H^{\Theta}(H_2O)\ -[\Delta_f H^{\Theta}(C_3H_8)) - \Delta_f H^{\Theta}(O_2)]$$

$\Rightarrow\ -530 = 3\times(-94) + 4\times(-68) - \Delta_f H^{\Theta}(C_3H_8) \quad \Rightarrow\ \Delta_f H^{\Theta}(C_3H_8) = -24$ kcal

23. $2CH_4 + CO_2 + 1/2N_2 \longrightarrow C_3H_7NO_2; \Delta H^{\Theta} = ?$

First find $\Delta_f H^{\Theta}$ of CH_4

Given $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O; \Delta H^{\Theta} = -212.8$

Using the definition of ΔH,

$$\Delta H^{\Theta} = [\Delta_f H^{\Theta}(CO_2) + 2\Delta_f H^{\Theta} 2(H_2O)] - \Delta_f H^{\Theta}(CH_4) \text{ (Note that } \Delta_f H^{\Theta} O_2 = 0\text{)}$$

$\Rightarrow\ -212.8 = [-94.05 + 2(-68.32) - \Delta_f H^{\Theta}(CH_4)]$

$\Rightarrow\ \Delta_f H^{\Theta}(CH_4) = -17.89$ kcal / mol

Now find the ΔH of the required equation using $\Delta_f H^{\Theta}(CH_4)$.

$$[\Delta_f H^{\Theta}(C_3H_7NO_2) - 0] - [2\times\Delta_f H^{\Theta}(CH_4) + \Delta_f H^{\Theta}(CO_2) + 0]$$

$\Rightarrow\ \Delta H = (-133.57) - 2(-17.89) - (-68.32) = -374$ kcal mol^{-1}

Now calculate ΔH (combustion) of $C_3H_7NO_2$

$$C_3H_7NO_2(s) + 15/4O_2 \longrightarrow 3CO_2(g) + 1/2N_2(g) + 7/2H_2O(g)$$

$$\Delta_{comb}H^{\Theta} = 3\Delta_f H^{\Theta}(CO_2) + 0 + 7/2\Delta_f H^{\Theta}(H_2O) - \Delta_f H^{\Theta}(C_3H_7NO_2) - 0$$

$$= 3(-94.05) + 7/2(-68.32) - (-133.57) = -387.70 \text{ kcal mol}^{-1}$$

Find ΔU^{Θ} using $\Delta U = \Delta H^{\Theta} - \Delta nRT$

$$\Delta U = -387.70 - (-1/4)\times 2\times 10^{-3}(298) = -387.72 \text{ kcal mol}^{-1}$$

24. According to the reaction $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l);\ \Delta H = -57.1$ kJ

When 1 mol of H^+ ions and 1 mol of OH^- ions are neutralized, 1 mol of water is formed and 57.1 kJ of energy is released.

(a) 0.50 mol HCl $\equiv$ 0.50 mol H^+ ions ; 0.50 mol NaOH $\equiv$ 0.50 mol OH^- ions

On mixing, 0.50 mol of water is formed.
Heat evolved for the formation of 0.50 mol of water $= 57.1 \times 0.5 = 28.55$ kJ

(b) 0.50 mol HNO_3 = 0.50 mol H^+ ions ; 0.30 mol KOH $\equiv$ 0.30 mol OH^- ions

i.e., 0.30 mol of H^+ ions reacts with 0.30 mol of OH^-
ions to form 0.30 mol of water molecules
Heat evolved in the formation of 0.3 mol of water $= 57.1 \times 0.3 = 17.13$ kJ

(c) 100 mL of 0.2 HCl will give $\left(\frac{0.2}{1000} \times 100\right) = 0.02$ mol of H^+ ions

and 100 mL of 0.3 M NaOH will give $\left(\frac{0.3}{1000} \times 100\right) = 0.03$ mol of OH^- ions, i.e., 0.02 mol

of H^+ ions reacts with 0.02 mole of OH^- ions to form 0.02 mol of water molecules.
Heat evolved in the formation of 0.02 mole of water $= 0.02 \times 57.1 = 1.142$ kJ

(d) 400 mL of 0.2 M H_2SO_4 will give $\left(\frac{2 \times 0.2}{1000} \times 400\right) = 0.16$ mol of H^+ ions

and 600 mL of 0.1 M KOH will give $\left(\frac{0.1}{1000} \times 600\right) = 0.06$ mol of OH^- ions

i.e., 0.06 mol of H^+ ions reacts with 0.06 mol of OH^- ions to form 0.06 mol of water molecules.
Heat evolved in the formation of 0.06 mol of water $= 0.06 \times 57.1 = 3.426$ kJ

25.(AB) $\Delta G = -394.4 - (-137.2) = -257.2$ kJ mol^{-1}
$\Delta G < 0$ so, reaction is spontaneous
$\Delta G = \Delta H - T\Delta S$
$-257.2 = \Delta H - 300 \times (-0.094)$
$\Delta H = -285.4$ kJ mole^{-1}
$\Delta H < 0$, so exothermic reaction

This reaction is exothermic (combustion) and entropy is decreasing so reaction is spontaneous at lower temperature and non-spontaneous at higher temperature.