Illustration - 12 *Find the electron affinity of chlorine from the following data (in kcal/mol).*

Enthalpy of formation of LiCl is –97.5; Lattice energy of LiCl = 197.7 ; *Dissociation energy of chlorine* = 57.6

Sublimation enthalpy of Lithium = 38.3 ; *Ionisation energy of Lithium* = 123.8 ;

SOLUTION :

For a ionic compound of type LiCl :

$$\Delta_{Lattice}H^{\ominus}_{LiCl} = \Delta_{EA}H^{\ominus}_{Cl} - \Delta_f H^{\ominus}_{LiCl} + \frac{1}{2}\Delta_{bond}H^{\ominus}_{Cl_2} + \Delta_{sub}H^{\ominus}_{Li} + \Delta_{IE}H^{\ominus}_{Li}$$

$$197.7 = \Delta_{EA}H^{\ominus}_{Cl} - (-97.5) + \frac{1}{2}\times 57.6 + 38.3 + 123.8 \quad \Rightarrow \quad \Delta_{EA}H^{\ominus}_{Cl} = -90.7\ \text{kcal/mol}$$

Relation between $\Delta_r H$ and $\Delta_r U$ Section - 6

Enthalpy (H) and Internal Energy (U) are related as :

$$H = U + PV$$

$$\Rightarrow \quad \Delta H = \Delta U + \Delta(PV)$$

$$\text{or} \quad dH = dU + d(PV)$$

Now, for a reaction, we can write : $\Delta_r H = \Delta_r U + P\Delta V$ [Chemical reactions occur at constant T and P]

or $\Delta_r H = \Delta_r U + \Delta n_g RT$ where $\Delta n_g = \sum (n_g)_{products} - \sum (n_g)_{reactants}$ = Change in the number of gaseous moles

Illustration - 13 *Find the sign of* $\Delta_r H - \Delta_r U$ *for the following reactions :*

(i) $H_2(g) + Cl_2(g) \longrightarrow HCl(g)$ **(ii)** $N_2(g) + O_2(g) \longrightarrow NO_2(g)$

(iii) $PH_3(g) \longrightarrow P_4(s) + H_2(g)$ **(iv)** $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow CO_2(g) + H_2O(\ell)$

SOLUTION :

First, balance each reaction :

(i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ **(ii)** $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$

(iii) $4PH_3(g) \longrightarrow P_4(s) + 6H_2(g)$ **(iv)** $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$

Now, Use : $\Delta_r H - \Delta_r U = \Delta n_g RT$ and $\Delta n_g = \sum (n_g)_{products} - \sum (n_g)_{reactants}$

$\Rightarrow$ If $\Delta n_g > 0,\ \Delta_r H - \Delta_r U > 0$;

If $\Delta n_g < 0,\ \Delta_r H - \Delta_r U < 0$;

If $\Delta n_g = 0,\ \Delta_r H - \Delta_r U = 0$

(i) $\Delta n_g = 2 - (1+1) = 0$ **(ii)** $\Delta n_g = 2 - (1+2) = -1$ **(iii)** $\Delta n_g = (6+0) - 4 = 2$

(iv) $\Delta n_g = (2+0) - \left(1 + \frac{7}{2}\right) = -\frac{5}{2}$ [***Note*** : For $H_2O\ (\ell),\ n_g = 0$]

Illustration - 14 *The enthalpies of combustion of carbon and carbon monoxide in excess of oxygen at 298 K and constant pressure are –393.5 kJ/mol and –283.0 kJ/mol respectively. Calculate the heat of formation of carbon monoxide at constant volume.*

SOLUTION :

Heat change at constant pressure means enthalpy change ($\Delta_r H = q_p$)

Heat of formation of CO is written as : $C\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow CO\,(g)\;;\qquad \Delta_f H^{\ominus} = ?$

Now we have :

I. $C\,(g)\; + O_2\,(g) \longrightarrow CO_2\,(g)\;;\qquad \Delta_c H_1^{\ominus} = -393.5\ \text{kJ/mol}$

II. $CO\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow CO_2\,(g)\;;\qquad \Delta_c H_2^{\ominus} = -283\ \text{kJ/mol}$

Adding appropriately (i.e., **I – II**), we get ; $C\,(s) + \frac{1}{2}O_2\,(g) \longrightarrow CO(g)\;;\quad \Delta_f H^{\ominus}$

From Hess's Law : $\Delta_f H^{\ominus} = \Delta_c H_1^{\ominus} - \Delta_c H_2^{\ominus}$

$$\Delta_f H^{\ominus} = -393.5 - (-283) = \mathbf{-110.5\ kJ/mol}$$

Now, calculation of the heat of formation at constant volume means that we have to calculate change in internal energy (i.e. $\Delta_r U$).

Using : $\Delta_r H = \Delta_r U + P\Delta V$ [For a chemical reaction]

$= \Delta_r U + \Delta n_g RT$ [Δn_g = gaseous moles of products – gaseous moles of reactant]

$\Rightarrow \quad \Delta_r U = \Delta_r H - \Delta n_g RT$

Now putting the values : $\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$ $\quad T = 298\ \text{K}$ $\quad R = 8.314\ \text{J/K/mol.}$ $\quad \Delta_f H^{\ominus} = -110.5\ \text{kJ/mol}$

$$\Rightarrow \quad \Delta_f U^{\ominus} = -110.5 - \frac{1}{2} \times 8.314 \times 298 \times 10^{-3} = \mathbf{-111.7\ kJ/mol}$$

Illustration - 15 *Standard enthalpy of formation of $C_3H_7NO_2(s)$, $CO_2(g)$ and $H_2O(\ell)$ are –133.6, –94.0 and –68.3 kcal/mol respectively. Standard enthalpy of combustion of $CH_4(g)$ at 25°C is –212.8 kcal/mol.*

Calculate $\Delta_r H^{\ominus}$ for the reaction: $2CH_4(g) + CO_2(g) + \frac{1}{2}N_2(g) \longrightarrow C_3H_7NO_2(s) + \frac{1}{2}H_2(g)$

Also calculate heat of reaction at constant volume for combustion of $C_3H_7NO_2(s)$.

SOLUTION :

$$2CH_4(g) + CO_2(g) + \frac{1}{2}N_2(g) \longrightarrow C_3H_7NO_2(s) + \frac{1}{2}H_2(g) : \quad \Delta_r H^{\ominus} = ?$$

To calculate $\Delta_r H^{\ominus}$ of the above reaction, we need to find out the $\Delta_f H^{\ominus}$ for CH_4 as :

Given : $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) : \qquad \Delta_c H^{\ominus} = -212.8\ \text{kcal/mol}$

Using the definition of $\Delta_r H$, we have :

$$\Delta_r H^{\ominus} = [\Delta_f H^{\ominus}{}_{(CO_2)} + 2\Delta_f H^{\ominus}{}_{(H_2O)}] - [\Delta_f H^{\ominus}{}_{(CH_4)} + 2\Delta_f H^{\ominus}{}_{O_2}] \qquad [\text{Note : } \Delta_f H^{\ominus}{}_{(O_2)} = 0\,]$$

$$\Rightarrow \quad -212.8 = [-94.0 + 2(-68.3)] - \Delta_f H^{\ominus}{}_{(CH_4)} \qquad \Rightarrow \quad \Delta_f H^{\ominus}{}_{(CH_4)} = -17.8\ \text{kcal/mol}$$

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

$$\Delta_r H^{\ominus} = [\Delta_f H^{\ominus}{}_{(C_3H_7NO_2)} + 0] - [2 \times \Delta_f H^{\ominus}{}_{(CH_4)} + \Delta_f H^{\ominus}{}_{(CO_2)}]$$

$$\Rightarrow \quad \Delta_r H^{\ominus} = (-133.6) - 2(-17.8) - (-94.0) = -4.0 \text{ kcal/mol}$$

Now calculate $\Delta_c H^{\ominus}{}_{(C_3H_7NO_2)}$: $\quad C_3H_7NO_2(s) + \frac{15}{4} O_2(g) \longrightarrow 3CO_2(g) + \frac{1}{2} N_2(g) + \frac{7}{2} H_2O(\ell)$

$$\Delta_c H^{\ominus}{}_{(C_3H_7NO_2)} = 3(-94.0) + \frac{7}{2}(-68.3) - (-133.6) = -387.45 \text{ kcal/mol}$$

Find $\Delta_r U^{\ominus} = \Delta_r H^{\ominus} - \Delta n_g RT = -387.45 - \left(-\frac{1}{4}\right) \times 2 \times 10^{-3}(298) = -387.6 \text{ kcal/mol}$ $\qquad \left[\Delta n_g = \left(3 + \frac{1}{2}\right) - \frac{15}{4}\right]$

Illustration - 16 *From $N_{avogardo}$ atoms of an element A, when half the atoms transfer one electron to another atom, 405 kJ/mol of energy was found to be consumed. An additional energy of 745 kJ was further required to convert all the A^- ions to A^+. Calculate the ionisation energy and the electron affinity of atom A in eV.*

SOLUTION :

Let I.E. be x eV/atom and E.A. be y eV/atom (magnitudes)

$A \longrightarrow A^+ + e^-$; $\quad \Delta_r H = \text{I.E.} = x \qquad A + e^- \longrightarrow A^-$; $\quad \Delta_r H = \text{E.A.} = -y$

I : $\quad$ Energy absorbed in eV $= \dfrac{405 \times 10^3}{1.6 \times 10^{-19}} \quad \Rightarrow \quad \dfrac{405 \times 10^3}{1.6 \times 10^{-19}} = x \times \dfrac{6.02 \times 10^{23}}{2} - y \times \dfrac{6.02 \times 10^{23}}{2}$ $\quad$ ....(i)

$A^- \longrightarrow A \longrightarrow A^+$

II : $\quad$ Energy absorbed in eV $= \dfrac{745 \times 10^3}{1.6 \times 10^{-19}} \quad \Rightarrow \quad \dfrac{745 \times 10^3}{1.6 \times 10^{-19}} = x \times \dfrac{6.02 \times 10^{23}}{2} + y \times \dfrac{6.02 \times 10^{23}}{2}$ $\quad$ ....(ii)

Solve for IE and EA using (i) and (ii), $\quad$ IE = 11.93 eV/atom $\quad$ and $\quad$ EA = 3.52 eV/atom (Magnitudes)

Illustration - 17 *In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Heats of combustion : CH_4 = 809 kJ/mol; C_4H_{10} = 2878 kJ /mol.*

SOLUTION :

First calculate the amount of energy required in the burner per hour using methane as follows :

$$\Delta_c H^{\ominus}{}_{CH_4} = 809 \text{ kJ mol}^{-1} \equiv \frac{809}{24.48} \text{ kJ/L (at } 25°\text{C)}$$

$\Rightarrow \quad$ 1 mol CH_4 ($\equiv$ 24.48 L at 25°C) on combustion produces 809 kJ

$\Rightarrow \quad$ x L/hr CH_4 on combustion produces energy $= \dfrac{x}{24.48} \times 809$ kJ/hr

Now, this much energy will be required by burning of butane and we can find its rate of consumptiom as :

$$\Delta_c H^{\ominus}{}_{C_4H_{10}} = 2878 \text{ kJ mol}^{-1} \equiv \frac{2878}{24.48} \text{ kJ/L (at } 25°\text{C)}$$

$\Rightarrow$ Required Rate of combustion of butane $= \dfrac{\dfrac{x}{24.48}\times 809}{\dfrac{2878}{24.48}}\dfrac{\text{L}}{\text{hr}} = 0.28x\ \text{L/hr}$

$$C_4H_{10}(g) + \frac{13}{2}O_2\,(g) \longrightarrow 4CO_2(g) + 5H_2O(\ell)$$

$\Rightarrow$ 1 mol $CH_4 \equiv \dfrac{13}{2}$ mol O_2 (theoretically)

$\Rightarrow$ $\left(3\times\dfrac{13}{2}\right)$ mol of O_2 is required/mol of CH_4 (practically) [Given]

$\Rightarrow$ rate of O_2 per hour $= (0.28x)\times\left(\dfrac{39}{2}\right) = (5.48x)\,\text{L}\ \ O_2$

Bomb Calorimeter

Calorimetry is the study of heat transfer during physical and chemical processes. A calorimeter is a device for measuring energy transferred as heat. The most common device for measuring ΔU, is the adibatic bomb calorimeter, shown in figure (figure 1 & 2). The inner vessel or the 'bomb' (figure 2) and its cover are made of strong steel coated inside with gold or platinum or some other non-oxidisable material. The cover can be fitted tightly to the vessel by means of a metallid screwed down on a lead washer. A weighed amount of the substance is taken in a platinum cup C which is supported on a rod R.

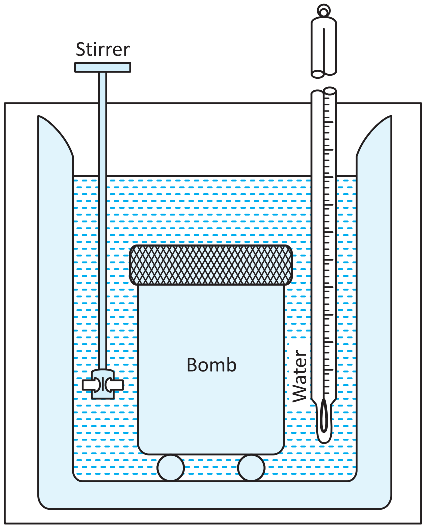

Figure 1 : The Bomb Calorimeter

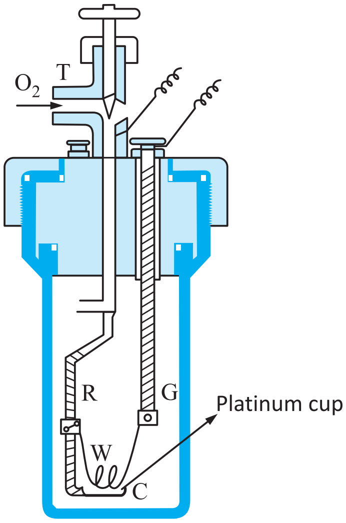

Figure 2 : The Bomb

A thin platinum wire W is connected between the rods R and G, as shown. This serves to initiate the combustion when heated electrically. The bomb is tightly closed and oxygen introduced through the inlet tube T until a pressure of about 20 – 25 atmospheres is attained. The bomb is then lowered in water placed in a double jacketed and polished metallic calorimeter so as to minimise error due to radiation. The arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the process is adiabatic. A mechanical stirrer is provided as shown. When the temperature of the water has become steady, the substance of inginited by calorimeter is noted after every minute by means of a Beckmann thermometer graduate to read up to a hundredth of a degree. The final temperature when corrected for the radiation error in the usual way, minus the initial temperature, gives the rise of temperature. The heat capacity of the calorimeter system, called the calorimeter constant, C, is obtained by burning a known mass of a substance of known enthalpy of combustion. For this purpose, usually benzoic acid of high grade purity is taken. Its q_v which has been very carefully measured is taken as –3226.7 kJ mol^{-1}. Suppose the thermal capacity of the calorimeter system including water is C and θ is the change in temperature produced by burning a quantity *m* of the given substance of molar mass M. Then, the constant volume heat of combustion, q_v of the substance is given by $C \times q \times M/m$. The enthalpy of combustion q_p is then obtained with the help of the equation $q_p = q_v + \Delta n_g RT$.

***Illustrating the concepts* :**

(i) 0.50 g of benzoic acid was subjected to combustion in a bomb calorimeter when the temperature of the calorimeter system (including water) was found to rise by 0.55°C. Calculate the enthalpy of combustion of benzoic acid. The ΔT calorimeter constant was found to be 23.85 kJ K^{-1}.

$q_v = C \times q \times M/m$

$= 23.85 \text{ kJ K}^{-1} \times 0.55 \text{ K} \times 122 \text{ g mol}^{-1}/0.50 \text{ g} = 3200.7 \text{ mol}^{-1} = -3200.7 \text{ kJ mol}^{-1}$

(Heat of combustion has always a negative sign)

$$C_6H_5COOH(s) + \frac{15}{2} O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(\ell)$$

We know that $q_p = q_v + \Delta n_g RT$; $\Delta n = 7 - 7.5 = -0.5$

$q_p = -3200.7 \text{ kJ mol}^{-1} + (-0.5)(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = -3201.9 \text{ kJ mol}^{-1}$

(ii) Explain why the following statement, made by a student doing an experiment on bomb calorimeter, is wrong :

"ΔH = ΔU + PΔV. Since in the experiment, ΔV = 0, hence, ΔH = ΔU."

The error is due to the fact that the student has applied the equation ΔH = ΔU + PΔV, which holds at constant pressure, to a process which occurs at constant volume.

We know that $H = U + PV$

$\therefore$ $\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P$

For a constant pressure process, ΔP = 0 so that ΔH = ΔU + PΔV

However, for a constant volume process, ΔV = 0 so that ΔH = ΔU + VΔP

We many mention here that a calorimeter for studying processes at constant pressure, called an isobaric calorimeter is also available commercially. A simple example is thermally insulated vessel, open to the atmosphere; the heat released in the reaction monitored by measuring the change in temperature of the contents. For a combustion reaction, an adiabatic flame calorimeter can be used to measure ΔT when a given amount of substance burns in oxygen.

Enthalpy of Polymerization :

The difference between the enthalpy of one mole of monomer and the enthalpy of the products of the polymerization reaction. Addition polymerizations are exothermic, values ranging from about 35 to 100 kJ/mol

Let us consider an example of polyethene.

$$n(H_2C = CH_2) \longrightarrow \ldots\ldots -CH_2-CH_2-CH_2-CH_2-\ldots\ldots$$

$$\Delta H_{(\text{Per mole})} = \text{B.E. of Reactants} - \text{B.E. of products}$$

$$(\text{B.E. of } C=C + 4 \times \text{B.E. of } C-H) - (2 \times \text{B.E. of } C-C + 4 \times \text{B.E. of } C-H)$$

Same logic can also be used in following reactions as well.

$$nN_{2(g)} + nH_{2(g)} \longrightarrow \left(NH-NH \right)_{n(g)}$$

$$n(H_3C-C \equiv C-CH_3)_{(g)} \longrightarrow \left(CH_2-CH=CH-CH_2 \right)_{n(g)}$$

CALCULATING RESONANCE ENERGY Section - 7

Resonance energy, as we know, is the difference in energy between resonance hybrid and the canonical form of the compound. It can be easily calculated using the following key points :

(i) If the resonance hybrid is more stable than the canonical forms, resonance energy is negative otherwise positive.

(ii) Simply figure out, which of the resonance hybrid and the canonical form is more stable based on the $\Delta_r H$ values as explained :

(a) **$\Delta_f H^{\ominus}$:** More negative is $\Delta_f H^{\ominus}$, more is the stability as this means when compound is formed, energy is getting lost to attain lower energy than the reactants.

(b) **$\Delta_c H^{\ominus}$ or $\Delta_{\text{Hydrogenation}} H^{\ominus}$:** More negative value in this case means less stability as more heat released means this compound is more reactive.

Note : In **(a)**, the compound under analysis is the product whereas in **(b)**, that compound is the reactant.

(iii) Now, calculate ΔH for the theoretical (canonical) and actual (resonance hybrid) compound and calculate the difference between the two to get resonance energy.

Illustration - 18 *The standard molar enthalpies of formation of cyclohexane(ℓ) and benzene(ℓ) at 25°C are −156 and +49 kJ/mole respectively. The standard enthalpy of hydrogenation of cyclohexene(ℓ) at 25°C is –119 kJ/mole. Use this data to estimate the magnitude of the resonance energy of benzene.*

SOLUTION :

Given : $C_6H_{10}(\ell) + H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_{\text{Hydrogenation}} H^{\ominus} = -119$ kJ/mole

Find the actual heat of hydrogenation of benzene from Hess's law as follows :

1. $6C(s) + 6H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_f H^{\ominus} = -156$ kJ/mole

2. $6C(s) + 3H_2(g) \longrightarrow C_6H_6(\ell)$; $\Delta_f H^{\ominus} = +49$ kJ/mole

$C_6H_6(\ell) + 3H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_{\text{Hydrogenation}} H^{\ominus}$

$\Rightarrow$ $(\Delta_{\text{Hydrogenation}} H^{\ominus})_{\text{Actual}} = -156 - 49 = -205$ kJ/mole [***Note :*** $\Delta_{\text{Hydrogenation}} H^{\ominus}$ is always negative]