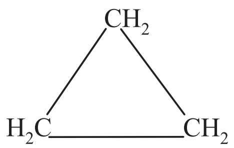
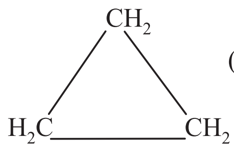
To the above reaction, if we add the reaction :



$(g) \longrightarrow CH_3CH = CH_2(g)$ $\qquad$ $\Delta_{isomerization}H^{\ominus} = -33.0 \text{ kJ mol}^{-1}$

Propene

we get :



$(g) + \frac{9}{2}O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(\ell)$

Hence, $\Delta_c H^{\ominus}_{(cyclopropane)} = (-2058.32 - 33.0) \text{ kJ mol}^{-1} = -2091.32 \text{ kJ mol}^{-1}$

Heat of Reaction and Bond Energy — Section - 4

Let us consider that the bond energy of AB molecule is x kcal/mol.

Bond Formation : $A + B \longrightarrow A - B$; $\Delta_r H = -x$ (*Bond formation is exothermic*)

Bond Dissociation : $A - B \longrightarrow A + B$; $\Delta_r H = +x$ (*Bond dissociation is endothermic*)

During a chemical reaction, atoms and molecules are rearranged to form new molecules. During the course of chemical reaction, old bonds are broken (of reactants) and new ones are formed (of products).

A given chemical reaction can be analysed energetically into two parts :

(i) *Bond Breaking* (endothermic, $\Delta_r H > 0$)

(ii) *Bond Formation* (exothermic, $\Delta_r H < 0$)

If $\Delta_r H_1$ is the enthalpy change during bond breaking (i) and $\Delta_r H_2$ is the enthalpy change during bond formation (ii), then overall enthalpy change of the reaction ($\Delta_r H$) is given by Hess's Law:

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2$$

As discussed, $\Delta_r H$ can be calculated using Hess's law of constant heat summation or using :

$$\Delta_r H = \sum H_{Poducts} - \sum H_{Reactants.}$$

$\Delta_r H$ can also be theoretically calculated using bond energies in the following manner :

(i) On the reactants side, calculate the energy required to break all the bonds. If there is an element in Solid / Liquid state, also consider the energy required to convert it into gaseous state.

(ii) On the products side, calculate the energy released when products are formed. If there is an elements/compound in Solid/Liquid state, also consider the energy released when it is converted from gaseous state to the required state.

(iii) Add total energy released and absorbed to get $\Delta_r H$.

Illustration - 6 *Find $\Delta_r H$ of the reaction : $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$;*

Average bond energies of O–F, O–H, O = O, H–F are 44, 111, 118 and 135 kcal/mol respectively.

SOLUTION : $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$; $\Delta_r H = ?$

(i) Bond Breaking: (endothermic) : $\Delta_r H_1$

$F - O - F(g) \longrightarrow O(g) + 2F(g)$; $\Delta_r H = +2 \times 44$ [bond energy of O–F = 44]

$H - O - H(g) \longrightarrow O(g) + 2H(g)$; $\Delta_r H = +2 \times 111$ [bond energy of O–H = 111]

$\Rightarrow \Delta_r H_1 = 2 \times 44 + 2 \times 111 = +310$ kcal.

(ii) Bond Formation: (exothermic) : $\Delta_r H_2$

$$O(g) + O(g) \longrightarrow O = O\ (g) \quad ; \quad \Delta_r H = -118 \quad [\text{bond energy of } O = O = 118]$$

$$2[H(g) + F(g) \longrightarrow H - F(g)] \quad ; \quad \Delta_r H = -2 \times 135 \quad [\text{bond energy of } H - F = 135]$$

$$\Rightarrow \quad \Delta_r H_2 = -118 + (-2 \times 135) = -388 \text{ kcal}$$

Now using Hess's Law ; $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 = 310 + (-388) = -78$ kcal

Illustration - 7 *Find $\Delta_f H$ of HCl (g) if bond energies of H_2, Cl_2 and HCl are 104, 58, 103 kcal/mol respectively.*

SOLUTION :

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g) \ ; \qquad \Delta_f H = ?$$

Now analyse the given thermochemical equation in two parts :

(i) Bond Breaking $[\Delta_r H_1]$: Endothermic Reaction

$$H_2(g) \longrightarrow 2H(g) \quad ; \quad \Delta_r H = 104 \text{ kcal/mol}$$

$$Cl_2(g) \longrightarrow 2Cl(g) \quad ; \quad \Delta_r H = 58 \text{ kcal/mol}$$

$$\frac{1}{2}[H_2(g) \longrightarrow 2H(g) \ ; \ 104] \qquad [\text{as we need mole of each reactant}]$$

$$\frac{1}{2}[Cl_2(g) \longrightarrow 2Cl(g) \ ; \ 58]$$

$$\Rightarrow \quad \Delta_r H_1 = \frac{1}{2} \times 104 + \frac{1}{2} \times 58 = 81 \text{ kcal}$$

(ii) Bond Formation : $(\Delta_r H_2)$: Exothermic reaction

$$H(g) + Cl(g) \longrightarrow HCl(g) \ ; \quad \Delta_r H = -103 \text{ kcal} \quad (\text{Bond energy of HCl} = 103 \text{ kJ/mol})$$

$$\Delta_r H_2 = -103 \text{ kcal}$$

Now $\Delta_r H = \Delta_f H = \Delta_r H_1 + \Delta_r H_2$ (using Hess's Law)

$$\Rightarrow \quad \Delta_f H = 81 + (-103) = -22 \text{ kcal/mol}$$

Illustration - 8 *Calculate $\Delta_r H$ for the following homogeneous gaseous reaction :*

$$CH_3COCH_3(g) + 2O_2(g) \longrightarrow CH_3COOH(g) + CO_2(g) + H_2O(g)$$

Use the data in kcal mol^{-1}. $\Delta_{bond\ C-H} = 99$; $\Delta_{bond\ C-C} = 83$; $\Delta_{bond\ C=O} = 173$;
$\Delta_{bond\ O=O} = 118$; $\Delta_{bond\ C-O} = 84$; $\Delta_{bond\ O-H} = 110$

SOLUTION :

First calculate the energy required to break all the bonds in reactants side and to convert them into gaseous atoms.

(i)
$$\begin{array}{ccccccc} & H & & O & & H & \\ & | & & \| & & | & \\ H- & C & - & C & - & C & -H(g) \longrightarrow 3C(g) + O(g) + 6H(g) \\ & | & & & & | & \\ & H & & & & H & \end{array}$$

Energy absorbed $= 6\Delta_{\text{Bond C-H}} + \Delta_{\text{Bond C=O}} + 2\Delta_{\text{Bond C-C}} = 6 \times 99 + 173 + 2 \times 83 = 933$ kcal

(ii) $2O=O(g) \longrightarrow 4O(g)$

Energy absorbed $= 2\Delta_{\text{Bond O=O}} = 2 \times 118 = 236$ kcal

$\Rightarrow$ Total energy absorbed $= 933 + 236 = 1169$ kcal

Now, calculate the energy released when these gaseous atoms form products.

(i) $4H(g) + 2C(g) + 2O(g) \longrightarrow \begin{array}{c} \text{H} \quad \text{O} \\ | \quad\;\; \| \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H}(g) \\ | \qquad\qquad \\ \text{H} \qquad\qquad \end{array}$

Energy released $= 3\Delta_{\text{Bond C-H}} + \Delta_{\text{Bond C-C}} + \Delta_{\text{Bond C=O}} + \Delta_{\text{Bond C-O}} + \Delta_{\text{Bond O-H}}$

$= 3 \times 99 + 83 + 173 + 84 + 110 = 747$ kcal

(ii) $C(g) + 2O(g) \longrightarrow O=C=O(g)$

Energy released $= 2\Delta_{\text{Bond C=O}} = 2 \times 173 = 346$ kcal

(iii) $2H(g) + O(g) \longrightarrow H-O-H(g)$

Energy released $= 2\Delta_{\text{Bond O-H}} = 2 \times 110 = 220$ kcal

$\Rightarrow$ Total energy released $= 1313$ kcal

$\Rightarrow$ $\Delta_r H = 1169 + (-1313) = -144$ kcal mol^{-1}

Note : **(i)** While calculating $\Delta_r H$ using the bond energy concept, it is important to know the structure of the molecules/compounds taking part in the reaction.

(ii) If the reaction would have been :

$$CH_3COCH_3(g) + 2O_2(g) \longrightarrow CH_3COOH(g) + CO_2(g) + H_2O(\ell)$$

then we also need to consider the energy released for the conversion of $H_2O(g) \longrightarrow H_2O(\ell)$

$\Delta_r H = -144 - 9.72 = -153.72$ kcal

Illustration - 9 *Compute the heat of formation of liquid methyl alcohol, using the following data (in kJ/mol) :*

Heat of vaporization of liquid methyl alcohol = 38.

Heat of formation of gaseous atoms from the elements in their standard states: $H = 218$; $C = 715$; $O = 249$.

Average bond energies : $C-H = 415$; $C-O = 356$; $O-H = 463$.

SOLUTION :

The given data is as follows :

(i) $CH_3OH(\ell) \longrightarrow CH_3OH(g) \quad \Delta_r H_1^\ominus = 38\text{ kJ mol}^{-1}$

(ii) $\frac{1}{2}H_2(g) \longrightarrow H(g) \quad \Delta_r H_2^\ominus = 218\text{ kJ mol}^{-1}$

(iii) $C(\text{graphite}) \longrightarrow C(g) \quad \Delta_r H_3^\ominus = 715\text{ kJ mol}^{-1}$

(iv) $\frac{1}{2}O_2(g) \longrightarrow O(g) \quad \Delta_r H_4^\ominus = 249\text{ kJ mol}^{-1}$

(v) $C-H(g) \longrightarrow C(g) + H(g) \quad \Delta_r H_5^\ominus = 415\text{ kJ mol}^{-1}$

(vi) $C-O(g) \longrightarrow C(g) + O(g) \quad \Delta_r H_6^\ominus = 356\text{ kJ mol}^{-1}$

(vii) $O-H(g) \longrightarrow O(g) + H(g) \quad \Delta_r H_7^\ominus = 463\text{ kJ mol}^{-1}$

We have to calculate the enthalpy of formation of liquid methyl alcohol, i.e.,

(viii) $C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(\ell) \qquad \Delta_r H_8^\ominus = ?$

First of all, we calculate the enthalpy of reaction :

(ix) $CH_3OH(g) \longrightarrow C(g) + 4H(g) + O(g)$; $\Delta_r H_9^\ominus = ?$

$$\Delta_r H_9^\ominus = 3\Delta_r H_5^\ominus + \Delta_r H_6^\ominus + \Delta_r H_7^\ominus$$

$$\left[\begin{array}{c} \because\ CH_3OH \equiv \begin{array}{c} \ \ \ \ \ \ H \\ \ \ \ \ \ \ | \\ H-C-O-H \\ \ \ \ \ \ \ | \\ \ \ \ \ \ \ H \end{array} \\ \text{contains one } C-O, \text{ one } O-H \\ \text{and three } C-H \text{ bonds} \end{array}\right]$$

$$\Delta_r H_9^\ominus = (3 \times 415 + 356 + 463)\ \text{kJ mol}^{-1} = 2064\ \text{kJ mol}^{-1}$$

The equation (viii) can be generated as follows : Eq. (iii) + 4 × Eq. (ii) + Eq. (iv) – Eq. (ix) – Eq. (i)

Hence, the enthalpy of reaction of equation (viii) is given as :

$$\Delta_r H_8^\ominus = \Delta_r H_3^\ominus + 4\Delta_r H_2^\ominus + \Delta_r H_4^\ominus - \Delta_r H_9^\ominus - \Delta_r H_1^\ominus = (715 + 4 \times 218 + 249 - 2064 - 38)\ \text{kJ mol}^{-1} = -266\ \text{kJ mol}^{-1}$$

Illustration - 10 *The heat of formation of ethane is -19.5 kcal. Bond energies of H – H, C – H and C – C bonds are 104.2, 99.0 and 80.0 kcal/mol respectively. Calculate the heat of atomisation of graphite.*

SOLUTION :

$\Delta_f H$ of ethane $(C_2H_6) = -19.5$ kcal/mol

$2\,C(s) + 3\,H_2(g) \longrightarrow C_2H_6(g)$; $\Delta_f H = -19.5$ kcal/mol

Let the heat of atomisation is x kcal/mol

Bond Breaking : $(\Delta_r H_1)$

$2[C(s) \longrightarrow C(g);\ +x]$

$3[H_2(g) \longrightarrow 2\,H(g);\ +104.2]$

$\Delta_r H_1 = 2x + 312.6$

Bond Formation : $(\Delta_r H_2)$

$1[C(g) + C(g) \longrightarrow C-C(g)\ ;\ -80]$

$6[C(g) + H(g) \longrightarrow C-H(g);\ -99]$

$\Delta_r H_2 = (-80) + (6 \times -99) = -674$

From Hess's Law : $\Delta_f H = \Delta_r H_1 + \Delta_r H_2$

$-19.5 = (2x + 312.6) - 674 \Rightarrow x = 171$ kcal.

Illustration - 11 *Using the data given below (all values are in kcal/mol at 25°C), calculate the bond energies of C–C and C–H bonds.*

$\Delta_c H^\ominus(ethane) = -372.0$; $\Delta_c H^\ominus(propane) = -530.0$; $\Delta_a H^\ominus_{C(Graphite)} = 172.0$; $\Delta_{bond} H^\ominus_{H-H} = 104.0$;

$\Delta_f H^\ominus(H_2O) = -68.0$; $\Delta_f H^\ominus(CO_2) = -94.0$

SOLUTION :

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 and C_3H_8) as follows :

(a) Writing the equation for combustion of ethane:

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(\ell) \quad ; \quad \Delta_c H^\ominus = -372.0$$

From definition of $\Delta_r H$ of a reaction : $\Delta_r H = \Sigma H_{Products} - \Sigma H_{Reactants}$

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

$$\Delta_c H^{\ominus} = \left[2\Delta_f H^{\ominus}_{(CO_2)} + 3\,\Delta_f H^{\ominus}_{(H_2O)}\right] - \left[\Delta_f H^{\ominus}_{(C_2H_6)} + \frac{7}{2}\,\Delta_f H^{\ominus}_{(O_2)}\right]$$

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

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

$\Rightarrow \quad \Delta_f H^{\ominus}_{(C_2H_6)} = -20$ kcal/mol

(b) Writing the equation for combustion of propane :

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(\ell) \quad ; \quad \Delta_c H^{\ominus} = -530.0$$

From definition of $\Delta_r H$ of a reaction :

$$\Delta_r H = \Sigma H_{\text{Products}} - \Sigma H_{\text{Reactants}}$$

$$\Delta_c H^{\ominus} = \left[3\,\Delta_f H^{\ominus}_{(CO_2)} + 4\Delta_f H^{\ominus}_{(H_2O)}\right] - \left[\Delta_f H^{\ominus}_{(C_3H_8)} + 5\Delta_f H^{\ominus}_{(O_2)}\right]$$

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

$\Rightarrow \quad \Delta_f H^{\ominus}_{(C_3H_8)} = -24$ kcal / mol

Calculations of bond energies :

Let the bond energy of C – C bond = x kcal mol^{-1} and the bond energy of C – H bond = y kcal mol^{-1}

(a) *For ethane*, heat of formation is given as :

$$2\,C(s) + 3\,H_2(g) \longrightarrow C_2H_6(g) \quad ; \quad \Delta_f H^{\ominus} = -20 \text{ kcal mol}^{-1}$$

Bond breaking ($\Delta_r H_1$) :

$2[\,C(s) \longrightarrow C(g) \quad ; \quad +172\,]$

$3[\,H_2(g) \longrightarrow 2H(g) \quad ; \quad +104\,]$

$\Rightarrow \quad \Delta_r H_1 = 2\times 172 + 3\times 104 = 656$

Bond formation ($\Delta_r H_2$) :

$1[\,C(g) + C(g) \longrightarrow C-C(g) \quad ; \quad -x\,]$

$6[\,C(g) + H(g) \longrightarrow C-H(g) \quad ; \quad -y\,]$

$\Rightarrow \quad \Delta_r H_2 = -(x + 6y)$

$\Rightarrow \quad \Delta_f H^{\ominus}$ = heat absorbed + heat released = $\Delta_r H_1 + \Delta_r H_2$

$\Rightarrow \quad -20 = 656 - (x + 6y) \quad \Rightarrow \quad x + 6y = 676 \quad$ .... (i)

(b) *For propane*, heat of formation is given as :

$$3\,C(s) + 4\,H_2(g) \longrightarrow C_3H_8(g) \quad ; \quad \Delta_r H^{\ominus} = -24 \text{ kcal mol}^{-1}$$

Bond breaking ($\Delta_r H_1$) :

$3[\,C(s) \longrightarrow C(g) \quad ; \quad +172\,]$

$4[\,H_2(g) \longrightarrow 2H(g) \quad ; \quad +104\,]$

$\Delta_r H_1 = 3\times 172 + 4\times 104 = 932$

Bond formation ($\Delta_r H_2$) :

$2[\,C(g) + C(g) \longrightarrow C-C(g)\,; \quad -x\,]$

$8[\,C(g) + H(g) \longrightarrow C-H(g)\,; \quad -y\,]$

$\Rightarrow \quad \Delta_r H_2 = -(2x + 8y)$

$\Rightarrow \quad \Delta_f H^{\ominus} = \Delta_r H_1 + \Delta_r H_2$

$\Rightarrow \quad -24 = 932 - (2x + 8y) \quad \Rightarrow \quad x + 4y = 478 \quad$ .... (ii)

Solving (i) and (ii), we get $x = 82$ and $y = 99$.

$\Rightarrow \quad$ Bond energy of C – C bond = 82 kcal mol^{-1} and C – H bond = 99 kcal mol^{-1}