

Thermochemistry

The branch of chemistry dealing with the measurement and computation of energy changes (ΔU) and enthalpy changes (ΔH) of various types of physical transformations and chemical reactions is called **thermochemistry**. Now ΔU and ΔH are related to the heat exchanged between the system and the surroundings, Therefore, these properties are also called as **heat of reactions**.

Types of heat of a reaction

Depending on the experimental condition the heat of a reaction is classified as follows.

- ❖ When the reaction is performed at constant volume the accompanying energy change (ΔU) is called **heat of reaction at constant volume** (q_v)

$$\Delta U = q_v = \text{Heat of reaction at constant volume}$$

- ❖ When the reaction takes place at constant pressure the accompanying enthalpy change (ΔH) is called the **heat of reaction at constant pressure**

$$\Delta H = q_p = \text{Heat of reaction at constant pressure}$$

Since most of the experiments are performed at constant pressure, the enthalpy change (ΔH) is used to describe the thermal changes in various types of chemical reactions and physical transformations.

Type of enthalpy changes. The enthalpy changes are classified as follows

(1) Enthalpy changes in reactions ($\Delta_r H$)

- (a) Enthalpy of formation ($\Delta_f H$)
- (b) Enthalpy of combustion ($\Delta_c H$)
- (c) Bond enthalpy $\Delta H(A-B)$
- (d) Enthalpy of neutralization ($\Delta_n H$)

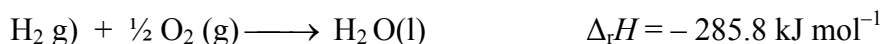
(2) Enthalpy changes in chemical physical transformation ($\Delta_{trss} H$)

- (i) Enthalpy of vaporization ($\Delta_{vap} H$)
- (ii) Enthalpy of fusion ($\Delta_{fus} H$)
- (iii) Enthalpy of sublimation ($\Delta_{sub} H$)
- (iv) Enthalpy of solution ($\Delta_{sol} H$)

Enthalpy of reaction ($\Delta_r H$)

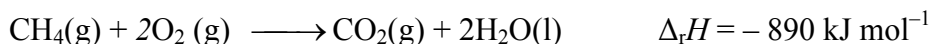
The enthalpy of a reaction is defined as **the heat absorbed or liberated when the reactants are completely converted into products as represented by the balanced chemical equation at a given temperature and pressure**. It is also called as the **heat of reaction** at constant pressure. Enthalpy of reaction is denoted by $\Delta_r H$ and expressed in the units of kJ mol^{-1} . For example,

- (i) When hydrogen gas is burnt in oxygen, a chemical reaction takes place. As a result of the reaction water is formed and 285.8 kJ heat is liberated. The reaction is represented by the equation



Interpretation of the above equation : The above equation tells that 286 kJ heat is liberated when 1 mole (2 g) of hydrogen gas completely reacts with half mole (16 g) of oxygen gas so that 1 mole (18 g) of water is formed. Thus heat of the reaction as represented by the above balanced chemical equation is $-285.8 \text{ kJ mol}^{-1}$

(ii) When methane gas is burnt in oxygen, a chemical reaction takes place. As a result of the reaction carbon dioxide and water are formed and 890 kJ heat is liberated. The reaction is represented by the equation

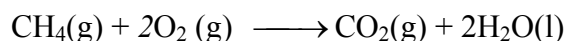


Interpretation of the above equation : The above equation tells that 890 kJ heat is liberated when 1 mole (16 g) of methane gas completely reacts with 2 moles (64 g) of oxygen gas so that 1 mole CO_2 (44 g) and 2 moles (36 g) of water are formed. Thus heat of the reaction as represented by the above balanced chemical equation is -890 kJ mol^{-1}

Role of mole to report the value of the enthalpy of reaction

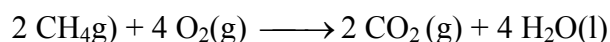
❖ Enthalpy of reaction is always reported as kJ mol^{-1} . Here per mole (mol^{-1}) corresponds to per mole of the extent (progress) of reaction. Thus $\Delta_r H$ is the change of enthalpy with the extent of reaction. For example,

(i) The enthalpy of reaction



is -890 kJ mol^{-1} . This value tells that when one mole of methane gas reacts completely with 2 moles of oxygen gas to produce one mole of $\text{CO}_2(\text{g})$ and 2 moles of $\text{H}_2\text{O}(\text{l})$ then progress of reaction is said to be hundred percent. In this case we state that one mole of reaction has occurred

(ii) The enthalpy of reaction



is $-1780 \text{ kJ mol}^{-1}$. This value tells that when two moles of methane react completely with 4 moles of oxygen to produce two moles of CO_2 and 4 moles H_2O then progress of this reaction is hundred percent. In this case we state that one mole of reaction as represented by the balanced chemical equation has occurred.

Notes:

- (i) While reporting the enthalpy of combustion of a fuel, the value is given as kJ per mole of the substance burnt. In the given example the enthalpy of combustion is 890 kJ mol^{-1} of methane
- (ii) Enthalpies of formation, vaporisation, fusion etc. are reported as kilojoules per mole (kJ mol^{-1}) of the substance concerned.

Standard state

The enthalpy change depends on temperature, pressure and the physical states of the reactants and products. Therefore, it is the recommendation of the IUPAC to mention the standard experimental condition while reporting the values of the enthalpy changes.

Standard states of different forms of matter

<i>Physical state</i>	<i>Notation</i>	<i>Conditions of standard states</i>
(1) Gas	(g)	Ideal gas at 1 bar at the specified temperature*
(2) Liquid	(l)	Pure liquid at 1 bar at the specified temperature*
(3) Solid	(s)	Pure crystalline and reactive form# at 1 bar and temperature T
(4) Solution in water	(aq)	Unit molarity (1 mol /dm ³) at 1 bar and temperature T

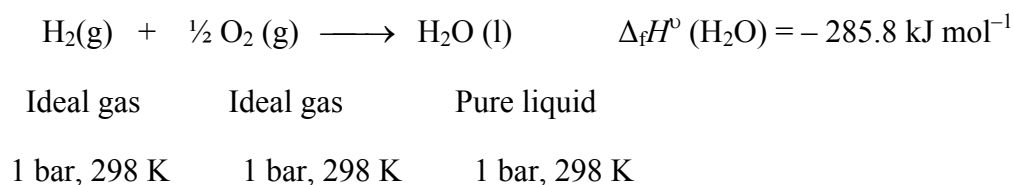
*The conventional temperature for thermodynamic tables is specified as 298.15 K

#graphite is taken as the standard state of carbon

#rhombic form is taken as the standard state of sulphur

Standard enthalpy of formation ($\Delta_f H^\ominus$)

Standard enthalpy of formation is defined as *the heat absorbed or liberated when one mole of a substance is formed from its constituent elements in their respective standard states*. Standard enthalpy of formation is denoted by $\Delta_f H^\ominus$ and it is called standard *heat of formation* also. It is expressed in the units of kJ mol^{-1} . For example, the standard enthalpy of formation of water is $-285.8 \text{ kJ mol}^{-1}$. It is written as $\Delta_f H^\ominus (\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$. This enthalpy change is described as follows:



Notes:

- (i) It is not always necessary to mention the standard conditions with the reactants and products in the balanced chemical equation, because $\Delta_f H^\ominus$ itself tells that the value refers to standard state

The values of standard enthalpy of formation of some substances are given in table 1

Table 1- a. Standard enthalpy of formation ($\Delta_f H^\ominus$) of some inorganic compounds

<i>Substance</i>	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	<i>Substance</i>	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$
H ₂ O (l)	- 285.8	NO (g)	90.4
H ₂ O (g)	- 241.8	N ₂ O (g)	81.5
H ₂ O ₂ (l)	- 188.0	N ₂ O ₄ (g)	9.6
HF (g)	- 268.6	NO ₂ (g)	33.8
HCl (g)	-92.3	NH ₃ (g)	-46.2
HBr (g)	-36.2	HNO ₃ (l)	- 173.2
HI (g)	25.9	NH ₄ Cl (s)	-315.4
HIO ₃ (s)	- 238.6	LiCl(s)	- 408.8
H ₂ S (g)	- 20.1	NaCl(s)	- 411.0
H ₂ SO ₄ (l)	- 814.0	KCl (s)	- 435.8
SO ₂ (g)	- 296.9	AgCl (s)	- 127.0
SO ₃ (g)	- 395.2	Br ₂ (g)	30.7
CO (g)	- 110.5	O ₃ (g)	+ 142.3
CO ₂ (g)	- 393.5	Na ₂ CO ₃	-1131.0

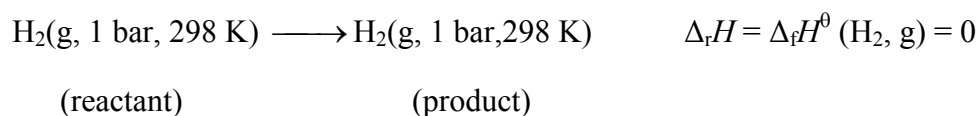
Table 1-b. Standard enthalpy of formation ($\Delta_f H^\ominus$) of some organic compounds

Compound	Formula	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$
Methane	CH ₄ (g)	- 74.85
Ethane	C ₂ H ₆ (g)	- 84.67
Propane	C ₃ H ₈ (g)	- 103.50
<i>n</i> -Butane	C ₄ H ₁₀ (g)	- 124.30
Ethene	C ₂ H ₄ (g)	+ 52.30
Ethyne	C ₂ H ₂ (g)	+ 226.70
Benzene	C ₆ H ₆ (l)	+ 49.03
Benzene	C ₆ H ₆ (g)	+ 82.93
Methanol	CH ₃ OH (l)	- 238.6
Ethanol	C ₂ H ₅ OH (l)	- 227.6
Ethanal	CH ₃ CHO (l)	- 166.3
Tetrachloromethane	CCl ₄ (l)	- 139.8
Trichloromethane	CHCl ₃ (l)	- 131.8
Urea	(NH ₂) ₂ CO (s)	- 333.2
Glucose	C ₆ H ₁₂ O ₆ (s)	- 1270.0
Cyclohexane	C ₆ H ₁₂ (l)	- 123.1

(A) Standard enthalpy of formation of an element

The standard enthalpy of formation of an element is taken as zero.. That is, $\Delta_f H^\ominus$ (element) = 0

Reason: An element can not be synthesized or decomposed by chemical or physical methods. For example, let us suppose that we want to represent the standard enthalpy of formation of element H₂(g) by a balanced chemical equation. Now, according to the definition of $\Delta_f H^\ominus$ it will be represented by



It is quite clear that there will not be any change of enthalpy for the formation of H₂(g) from H₂(g). It is to be kept in mind that $\Delta_f H^\ominus (\text{H}_2, \text{g}) = 0$, but $\Delta_f H^\ominus (\text{H}, \text{g}) \neq 0$. That is, the standard enthalpy of formation of hydrogen atom is not zero because atomic hydrogen is not the standard state of H₂. Similarly, we can write that:

(1) $\Delta_f H^\circ(\text{O}_2, \text{g}) = 0$ (2) $\Delta_f H^\circ(\text{N}_2, \text{g}) = 0$ (3) $\Delta_f H^\circ(\text{I}_2, \text{s}) = 0$ but $\Delta_f H^\circ(\text{I}_2, \text{g}) \neq 0$ because gaseous iodine is not its standard state.

(B) Standard enthalpy of formation of a gaseous atom

The heat absorbed when 1 mole of a gaseous atom is formed from its element in its standard state is called the *standard enthalpy of formation* of that atom. For example:

❖ The standard enthalpy of formation of gaseous hydrogen atom is equal to the enthalpy change for the following reaction.



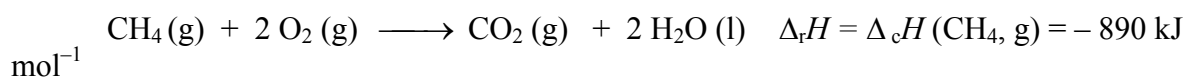
❖ The standard enthalpy of formation of gaseous carbon atom is equal to the enthalpy change for the following reaction.



Enthalpy of combustion ($\Delta_c H$)

The enthalpy of combustion is the *heat liberated at a constant pressure when one mole of a fuel is completely burnt in oxygen*. It is denoted by notation $\Delta_c H$ and expressed in the units of kJ mol^{-1} . Enthalpy of combustion is called heat of combustion also.

A combustion reaction is always **exothermic**. For example, when one mole of methane burns completely in the presence of oxygen, one mole of CO_2 and two moles of H_2O are formed and 890 kJ heat is liberated.



Relation between standard enthalpy of reaction and standard enthalpy of formation

Standard enthalpy of reaction ($\Delta_r H^\circ$) and standard enthalpy of formation ($\Delta_f H^\circ$) are related by

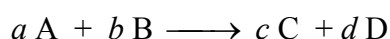
$$(\Delta_r H^\circ) = \sum V_p \Delta_f H^\circ(\text{products}) - \sum V_r \Delta_f H^\circ(\text{reactant})$$

where,

V_p = Stoichiometric coefficient of product

V_r = Stoichiometric coefficient of reactant

For a general chemical reaction



$$\sum V_p \Delta_f H^\circ(\text{products}) = c \Delta_f H^\circ(\text{C}) + d \Delta_f H^\circ(\text{D})$$

$$\sum V_r \Delta_f H^\circ(\text{reactants}) = a \Delta_f H^\circ(\text{A}) + b \Delta_f H^\circ(\text{B})$$

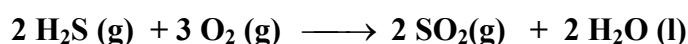
Thus

$$(\Delta_r H^\theta) = [c \Delta_f H^\theta (\text{C}) + d \Delta_f H^\theta (\text{D})] - [a \Delta_f H^\theta (\text{A}) + b \Delta_f H^\theta (\text{B})]$$

Comments:

- ❖ The above equation can be used to calculate any one of the quantities if others are known
- ❖ In the calculation it is assumed that $\Delta_f H^\theta (\text{element}) = 0$
- ❖ The values of $\Delta_f H^\theta$ for other substances are taken from the table of thermodynamic data.

Example: Use the given values of $\Delta_f H^\theta$ to calculate the enthalpy of the following reaction



Substance	H ₂ S (g)	SO ₂ (g)	H ₂ O (l)
$\Delta_f H^\theta / \text{kJ mol}^{-1}$	-20.1	-296.9	-285.8

Solution: Enthalpy of a reaction is related to the standard enthalpy of formation as

$$(\Delta_r H^\theta) = \sum_i \nu_p \Delta_f H^\theta (\text{products}) - \sum_r \nu_r \Delta_f H^\theta (\text{reactant})$$

For the given reaction

$$(\Delta_r H^\theta) = [2 \Delta_f H^\theta (\text{SO}_2, \text{g}) + 2 \Delta_f H^\theta (\text{H}_2\text{O}, \text{l})] - [2 \Delta_f H^\theta (\text{H}_2\text{S}, \text{g}) + 3 \Delta_f H^\theta (\text{O}_2, \text{g})]$$

On substituting the given $\Delta_f H^\theta$ values and assuming $\Delta_f H^\theta (\text{O}_2, \text{g}) = 0$, we get

$$\begin{aligned}(\Delta_r H^\theta) &= 2 \times (-296.9 \text{ kJ mol}^{-1}) + 2 \times (-285.8 \text{ kJ mol}^{-1}) - [2 \times (-20.1 \text{ kJ mol}^{-1}) - 3 \times 0 \text{ kJ mol}^{-1}] \\ &= -1125.2 \text{ kJ mol}^{-1}\end{aligned}$$

Example: Use the standard enthalpies of formation of various species to calculate the enthalpy change ($\Delta_r H^\theta$) for the reaction $\text{CH}_2\text{Cl}_2 \longrightarrow \text{C}(\text{g}) + 2 \text{H}(\text{g}) + 2 \text{Cl}(\text{g})$

Species	CH ₂ Cl ₂ (g)	C(g)	H(g)	Cl(g)
$\Delta_f H^\theta / \text{kJ mol}^{-1}$	-1162.4715.0	218.0	121.3	

Solution. For the reaction $\text{CH}_2\text{Cl}_2 \longrightarrow \text{C}(\text{g}) + 2 \text{H}(\text{g}) + 2 \text{Cl}(\text{g})$

$$\begin{aligned}\Delta_r H^\theta &= [\Delta_f H^\theta (\text{C}, \text{g}) + 2\Delta_f H^\theta (\text{H}, \text{g}) + 2 \Delta_f H^\theta (\text{Cl}, \text{g})] - \Delta_f H^\theta (\text{CH}_2\text{Cl}_2, \text{g}) \\ &= [715.0 + 2 \times 218.0 + 2 \times 121.3] \text{ kJ mol}^{-1} - (-1162.4 \text{ kJ mol}^{-1}) \\ &= 1556.0 \text{ kJ mol}^{-1}\end{aligned}$$

Difference between the enthalpy of formation and enthalpy of reaction

- ❖ The enthalpy change accompanying the formation of one mole of a compound from its constituent elements in their respective standard stable states is called *standard enthalpy of formation*. It is denoted by $\Delta_f H^\ominus$.
- ❖ The enthalpy change in any type of chemical reaction namely combination, combustion, hydrogenation, bond dissociation or neutralization is called the *enthalpy of reaction*. It is denoted by $\Delta_r H^\ominus$.

Important statements: *Enthalpy of formation is always equal to the enthalpy of reaction representing the formation of that compound. But the enthalpy of every reaction need not be the enthalpy of formation* For example,

- Reaction $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$ describes the formation of one mole of liquid water from its constituent elements. It also describes the combustion of hydrogen gas in the presence of oxygen to produce one mole of liquid water. Therefore, the enthalpy change of this reaction is equal to the enthalpy of combustion of hydrogen and also the standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$. Thus

$$\Delta_r H^\ominus = \Delta_c H^\ominus (\text{H}_2, \text{g}) = \Delta_f H^\ominus (\text{H}_2\text{O}, \text{l})$$

- The enthalpy of the reaction



does not represent the standard enthalpy of formation of $\text{NH}_4\text{Cl}(\text{s})$. That is,

$$\Delta_r H^\ominus \neq \Delta_f H^\ominus (\text{NH}_4\text{Cl}, \text{s})$$

Reason. The reactants $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$ are not elements.

- The enthalpy change for the reaction



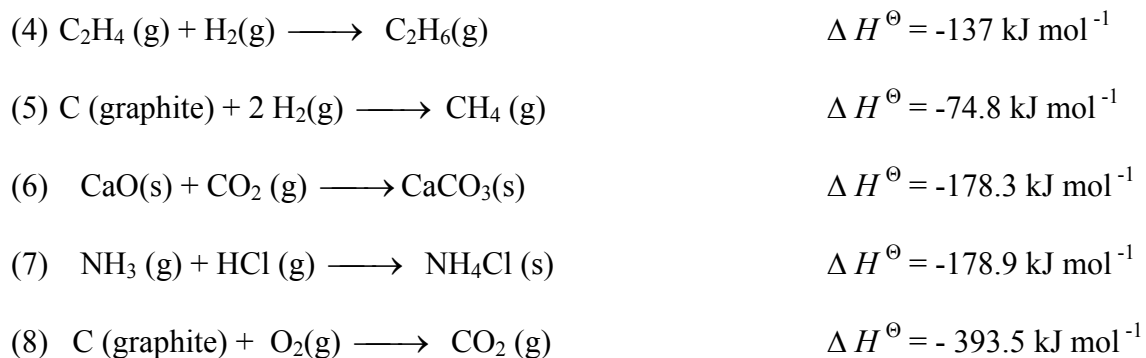
does not represent the standard enthalpy of formation of one mole of methane. That is,

$$\Delta_r H^\ominus \neq \Delta_f H^\ominus (\text{CH}_4, \text{g})$$

Reason. The reactants $\text{C}(\text{g})$ and $\text{H}(\text{g})$ are not the elements in their standard states.

Exercise. *Identify and justify the thermochemical equations representing standard enthalpy of formation and standard enthalpy of reaction in the following list.*

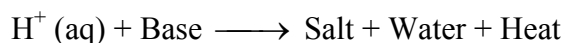




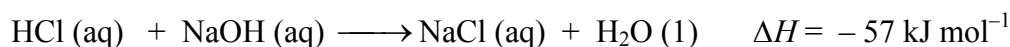
Hint: (i) Enthalpy of formation : (1), (5), (8) **(ii) Enthalpy of reaction:** Each one including 1, 5 and 8

Enthalpy of neutralization

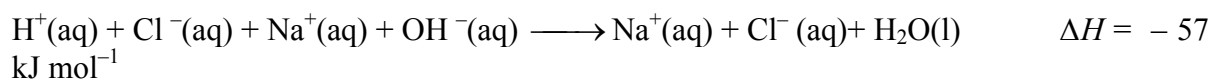
The heat liberated when one mole of hydrogen ions (H^+) is completely neutralized by a base in dilute aqueous solution at constant temperature and constant pressure is called **enthalpy of neutralization**. It is called the heat of neutralization also.



For example, at 25 °C and 1 atm when one mole HCl (aq) and one mole NaOH (aq) react, 57 kJ heat is liberated as represented by



In aqueous solution each one of HCl (aq), NaOH (aq) and NaCl (aq) is completely ionized. Therefore, the neutralization reaction may be represented as



Since equal number of $Na^+(aq)$ and $Cl^-(aq)$ ions appear on both the sides of the neutralization reaction they may be dropped while writing the balanced chemical equation so that we have



That is, the neutralization reaction between HCl (aq) and NaOH (aq) is essentially the reaction between $H^+(aq)$ and $OH^-(aq)$ to form unionized H_2O . This is exclusively valid for strong acid and strong base pair.

Comments:

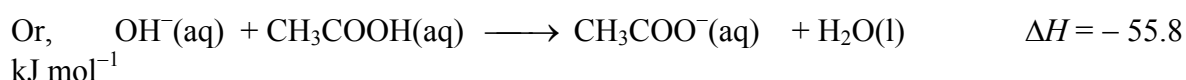
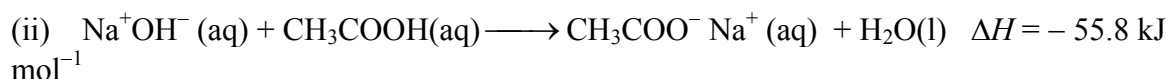
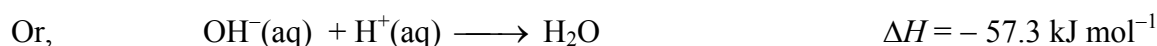
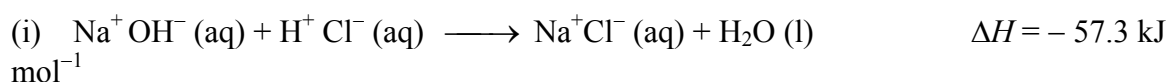
- (i) It is true that the neutralization reaction between a strong acid-base pair is the combination of $H^+(aq)$ and $OH^-(aq)$ ions to form $H_2O(l)$. But the value of heat of neutralization is different for various acid-base pairs at different concentrations. For example, the heat of neutralization of sulphuric acid and NaOH is 62 kJ at 25 °C and 1 atm.

(ii) In very dilute solutions the heat of neutralization of strong acid and strong base pair is constant and equal to about 57 kJ mol^{-1} at 298 K and 1 atm. If the acid and base are of appreciable concentrations (more than 1.0 M), then ΔH value is different.

(iii) For weak acid and strong base pair ($\text{CH}_3\text{COOH} + \text{NaOH}$), or strong acid and weak base pair ($\text{HCl} + \text{NH}_4\text{OH}$), the heat of neutralization is less than 57 kJ . *Why?* Because part of the heat liberated is utilized to cause the ionization of the weak acid or weak base.

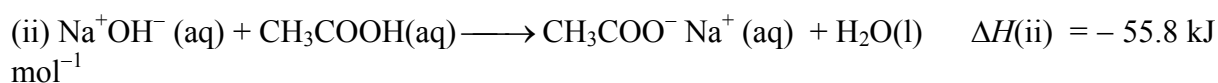
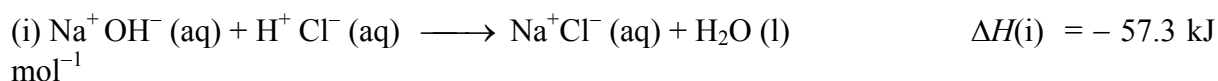
Example: The enthalpy of neutralization of ethanoic acid and NaOH is $-55.8 \text{ kJ mol}^{-1}$ and that of hydrochloric acid and NaOH is $-57.3 \text{ kJ mol}^{-1}$. Give a suitable reason for the difference in the two values.

Solution. The enthalpy changes may be represented by the following equations.

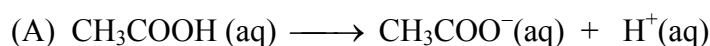


Ethanoic acid is a weak acid and is only partially ionized. Therefore, a part of the enthalpy change on neutralization is used in the ionization of CH_3COOH . Thus the magnitude of ΔH for the reaction (ii) is lower than that for the reaction (i)

Calculation of enthalpy of ionization of CH_3COOH



On subtracting equation (i) from equation (ii) we get



$$\Delta H(\text{A}) = \Delta H(\text{ii}) - \Delta H(\text{i}) = -55.8 \text{ kJ mol}^{-1} - (-57.3 \text{ kJ mol}^{-1}) = +1.8 \text{ kJ mol}^{-1}$$

Enthalpy on ionization of $\text{CH}_3\text{COOH} = 1.8 \text{ kJ mol}^{-1}$

Hess's law of constant heats summation

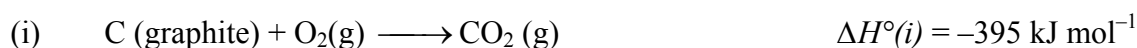
This law was formulated in 1840 by the Swiss-Russian chemist Germain Henri Hess and is stated as follows

The heat of a reaction (reaction enthalpy) is the same whether the reaction takes place in one step or in several steps under the same conditions.

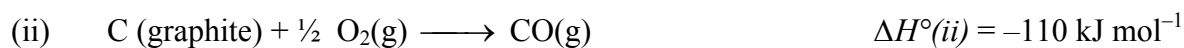
Illustration of the statement of the Hess's law

Let us consider the calculation of the standard enthalpy of formation of carbon dioxide. The formation of CO₂ may be described in the following two ways:

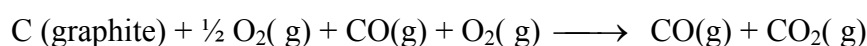
Method 1. A calculated quantity of carbon (graphite) is burnt directly in the presence of oxygen to form carbon dioxide



Method 2. A calculated quantity of carbon (graphite) is burnt in limited supply of oxygen to form carbon monoxide: then allowing CO to combine with oxygen and form carbon dioxide

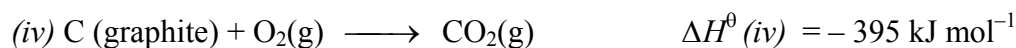


On adding equations (ii) and (iii) alongwith the ΔH° values we get



$$\text{and} \quad \Delta H^\circ(ii) + \Delta H^\circ(iii) = -110 \text{ kJ mol}^{-1} + (-285 \text{ kJ mol}^{-1}) = -395 \text{ kJ mol}^{-1}$$

On cancelling the common species on both the sides of the above equation we have



Since the chemical equations (i) and (iv) are the same, their enthalpy changes are also the same. Thus

$$\Delta H^\circ(i) = \Delta H^\circ(ii) + \Delta H^\circ(iii) = \Delta H^\circ(iv) = -395 \text{ kJ mol}^{-1}$$

Conclusion: From this illustration it is concluded that the standard enthalpy of formation of carbon dioxide is the same whether it is produced by burning graphite in sufficient quantity of oxygen or first burning graphite in limited supply of oxygen to form carbon monoxide then burning carbon monoxide to produce carbon dioxide

Discussion

(1) **Hess's law is a direct consequence of the law of conservation of energy.** Suppose in the above reaction the enthalpy changes in the two steps of the second method were greater than that of the first method *i.e.*, $\Delta H^\circ(ii) + \Delta H^\circ(iii) > \Delta H^\circ(i)$. This would mean that energy is not conserved though the amounts of the reactants and the product are the same in both the methods of performing the experiments. This would be contrary to the conservation law. Thus the enthalpy changes estimated by the two should be the same.

(2) Hess's law is also in line with the fact that enthalpy is a state function. Therefore, the

change of enthalpy will depend only on the initial and final states, and not on the path followed by the change. It implies that we cannot alter the enthalpy of a reaction by choosing different paths.

Applications of Hess's law of constant heat summation

- (i) This law provides a practical method for computing the enthalpy change of a reaction from the enthalpy changes of other reactions.
- (ii) Hess's law is used to calculate the reaction enthalpies even for those reactions which are otherwise difficult to carry out in the laboratory
- (iii) According to Hess's law the thermochemical equations may be treated as algebraic equations.

Working rules of applications of Hess's law

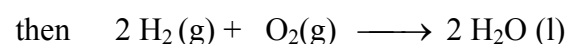
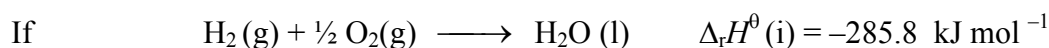
❖ **When a chemical equation is reversed, the sign of the enthalpy change is also reversed but magnitude remains the same.** For example, the standard enthalpy of formation of H₂O is given by the reaction



Now, according to the Hess's law, the enthalpy of decomposition of H₂O is represented by

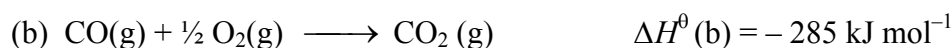


❖ **When an equation is multiplied by a number, the enthalpy change is also multiplied by the same number.** For example

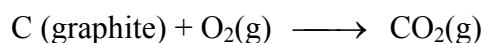


$$\Delta H^\circ(\text{ii}) = 2 \times \Delta_f H^\circ(\text{i}) = 2 \times (-285.8 \text{ kJ mol}^{-1}) = -571.6 \text{ kJ mol}^{-1}$$

❖ **When equations are added, the enthalpy changes are also added accordingly with proper signs.** For example



On adding equations (a) and (b) we get



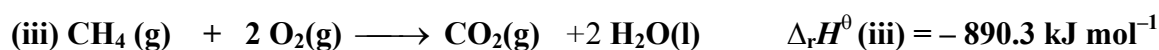
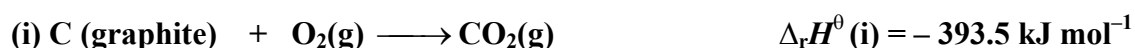
According to the Hess's law the enthalpy of reaction (c) is given by

$$\begin{aligned}\Delta H^{\circ}(c) &= \Delta H^{\circ}(a) + \Delta H^{\circ}(b) \\ &= -110 \text{ kJ mol}^{-1} + (-285 \text{ kJ mol}^{-1}) \\ &= -395 \text{ kJ mol}^{-1}\end{aligned}$$

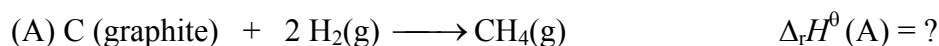
Example: Apply Hess's law to calculate the enthalpy change ($\Delta_r H^{\circ}$) of the following reaction



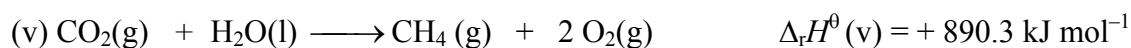
Data given:



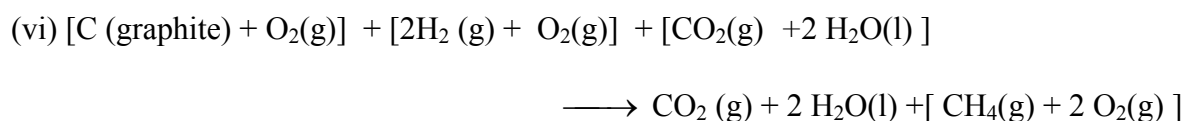
Solution. Our aim



Operations: On multiplying equation (ii) by 2 and reversing equation (iii) we get

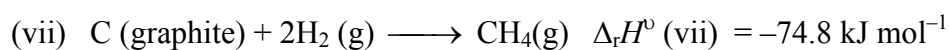


On adding equations (i), (iv) and (v) along with corresponding $\Delta_r H^{\circ}$ values, we get equation (vi)



$$\begin{aligned}\Delta_r H^{\circ} \text{ (vi)} &= \Delta_r H^{\circ} \text{ (iv)} + \Delta_r H^{\circ} \text{ (v)} + \Delta_r H^{\circ} \text{ (i)} \\ &= (-393.5 + (-2 \times 285.8 + 890.3) \text{ kJ mol}^{-1}) \\ &= -74.8 \text{ kJ mol}^{-1}\end{aligned}$$

On canceling the common terms on the two sides of equation (vi), we get equation (vii)

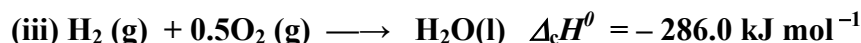
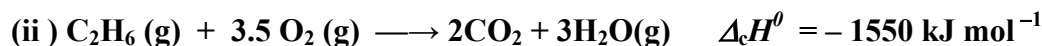
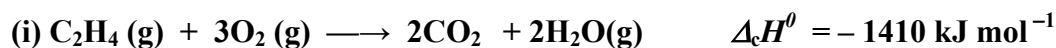


It is observed that equations (A) and (vii) are the same. Therefore, according to Hess's law their enthalpies should also be the same. Thus

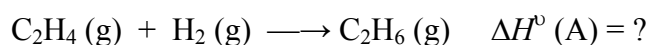
$$\Delta_r H^\circ (\text{A}) = \Delta_r H^\circ (\text{vii}) = -74.8 \text{ kJ mol}^{-1}$$

Example. Use the following combustion data to calculate the enthalpy change for the hydrogenation of ethene as represented by the reaction $\text{C}_2\text{H}_4 (\text{g}) + \text{H}_2 (\text{g}) \longrightarrow \text{C}_2\text{H}_6 (\text{g})$

Combustion data:

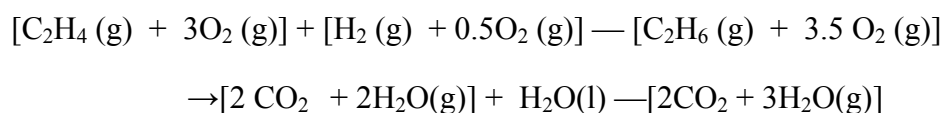


Solution. Our aim is to calculate ΔH° for the reaction

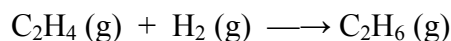


Operations: Subtract equation (ii) from the sum of equations (i) and (iii) to get

eq (i) + eq (iii) – eq (ii)



On canceling the common terms on the two sides of the above equation we get



and $\Delta_r H^\circ (\text{A}) = \Delta_r H^\circ (\text{i}) + \Delta_r H^\circ (\text{iii}) - \Delta_r H^\circ (\text{ii})$

$$= -1410 \text{ kJ mol}^{-1} + (-286 \text{ kJ mol}^{-1}) - (-1550 \text{ kJ mol}^{-1})$$

$$= -137 \text{ kJ mol}^{-1}$$

Relation between $\Delta_r H$ AND $\Delta_r U$

$$H = U + PV \quad \text{Definition of enthalpy}$$

$$\Delta H = \Delta U + P \Delta V + V \Delta P \quad \text{For changes in the states of the system}$$

$$= \Delta U + P \Delta V \quad \text{At constant pressure}$$

And for a chemical reaction the above relation can be written as $\Delta_r H = \Delta_r U + P \Delta_r V$

(i) For solids and liquids, the volume change in the reaction ($\Delta_r V$) is generally very small. Therefore, under atmospheric pressure $P \Delta_r V$ is negligible as compared to $\Delta_r H$ and $\Delta_r U$. Hence,

$$\Delta_r H = \Delta_r U \quad \text{For reactions involving solids and liquids only}$$

(ii) For gases $\Delta_r V$ is large and hence $P \Delta_r V$ has appreciable value. Thus

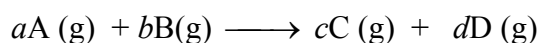
$$\Delta_r H = \Delta_r U + P \Delta_r V$$

For gases at constant pressure

(iii) In a chemical reaction involving gases

$$\begin{aligned}\Delta_r V &= \Sigma \text{volume of products} - \Sigma \text{volume of reactants} \\ &= \Sigma V(\text{products}) - \Sigma V(\text{reactants})\end{aligned}$$

For a general reaction involving gases



Reactants \longrightarrow Products

$$\Sigma V(\text{reactants}) = aV_m(A) + bV_m(B)$$

$$\Sigma V(\text{products}) = cV_m(C) + dV_m(D)$$

Where, $V_m =$ Molar volume of gas

For an ideal gas $PV = nRT$ and $V/n = RT/P$. Therefore, $V_m = RT/P$.

If temperature (T) and pressure (P) are kept constant, we shall have

$$\Sigma V(\text{reactants}) = a \times \frac{RT}{P} + b \times \frac{RT}{P} = \frac{RT}{P} (a + b)$$

$$\Sigma V(\text{products}) = c \times \frac{RT}{P} + d \times \frac{RT}{P} = \frac{RT}{P} (c + d)$$

$$\Delta_r V = \Sigma V(\text{products}) - \Sigma V(\text{reactants})$$

$$= \frac{RT}{P} [(c + d) - (a + b)]$$

Therefore,
$$P \Delta_r V = P \times \frac{RT}{P} [(c + d) - (a + b)]$$

$$= RT[(c + d) - (a + b)]$$

$$= \Delta n_g RT$$

Where, $\Delta n_g = (c + d) - (a + b)$

$= \Sigma$ coefficients of gaseous products $- \Sigma$ coefficients of gaseous reactants

Thus
$$\Delta_r H = \Delta_r U + P \Delta_r V = \Delta_r U + \Delta n_g RT$$

Or,
$$\Delta_r U = \Delta_r H - \Delta n_g RT$$

For the reaction $N_2(g) + 3 H_2(g) \longrightarrow 2 NH_3(g)$

$$\Delta n_g = 2 - (1 + 3) = -2$$

and
$$\Delta_r H = \Delta_r U - 2 RT$$

Or,
$$\Delta_r U = \Delta_r H + 2 RT$$

Remarks:

- (i) It must be noted that Δn_g is a number and it is not mole because it is the change in the moles of the substances per mole of the reaction occurred. Thus mole divided by mole is a number.
- (ii) For a reaction $\Delta_r H = q_p$ and $\Delta_r U = q_v$, thus, the relation $\Delta_r H = \Delta_r U + \Delta n_g RT$ may be written as

$$q_p = q_v + \Delta n_g RT$$

- (iii) For a reaction such as $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2 \text{HI}(\text{g})$, $\Delta n_g = 0$. Therefore, $\Delta_r H = \Delta_r U$ and $q_p = q_v$

Example: For a reaction $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$, $\Delta_r H^\ominus = -890.3 \text{ kJ mol}^{-1}$ at 298 K and 1 bar. Find the value of $\Delta_r U$ for the same reaction at the same temperature and pressure.

Solution: For the reaction $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$

$$\Delta n_g = 1 - (1 + 2) = -2$$

Therefore,
$$\Delta_r H^\ominus = \Delta_r U^\ominus - 2 RT$$

Or,
$$\Delta_r U^\ominus = \Delta_r H^\ominus + 2 RT$$

$$= -890.35 \text{ kJ mol}^{-1} + 2 \times 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}$$

$$= -890.35 \text{ kJ mol}^{-1} + 4.95 \text{ kJ mol}^{-1}$$

$$= -885.4 \text{ kJ mol}^{-1}$$

Example. The enthalpy change ($\Delta_r H$) for the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ is $-92.38 \text{ kJ mol}^{-1}$ at 298 K. Calculate the value of $\Delta_r U$ at 298 K.

Solution. For the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$

$$\Delta \nu = 2 - (1 + 3) = -2$$

$$\Delta_r H = -92.38 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K}$$

Therefore,
$$\Delta_r U = \Delta_r H - \Delta \nu RT$$

$$= -92.38 \text{ kJ mol}^{-1} - (-2) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$$= -92.38 \text{ kJ mol}^{-1} + 4.95 \text{ kJ mol}^{-1}$$

$$= -87.43 \text{ kJ mol}^{-1}$$

Example. Calculate the value of $\Delta_r H$ at 298 K for the reaction $\text{OF}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{HF}(\text{g}) + \text{O}_2(\text{g})$. It is given that the value of $\Delta_r U$ is $-320.9 \text{ kJ mol}^{-1}$ at 298 K.

Solution. For the reaction $\text{OF}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2 \text{HF}(\text{g}) + \text{O}_2(\text{g})$

$$\Delta \nu = (2 + 1) - (1 + 1) = 1$$

$$\Delta_r U = -320.9 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K}$$

Therefore,

$$\Delta_r H = \Delta_r U + \Delta \nu RT$$

$$= -320.9 \text{ kJ mol}^{-1} + 1 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$

$$= -92.38 \text{ kJ mol}^{-1} + 2.477 \text{ kJ mol}^{-1}$$

$$= -318.423 \text{ kJ mol}^{-1}$$

Example. When a sample of 1.25 g of gaseous chlorofluorocarbon ($\text{C}_2\text{Cl}_2\text{F}_2$) at a constant atmospheric pressure of 1 atm was cooled from 320 K to 293 K there was a decrease in its volume from 274 cm^3 to 248 cm^3 . Calculate the values of $\Delta_r H$ and $\Delta_r U$ for the process. The molar heat capacity of $\text{C}_2\text{Cl}_2\text{F}_2$ is $80.7 \text{ JK}^{-1} \text{ mol}^{-1}$.

Solution. Data given :

$$\text{Heat capacity of } \text{C}_2\text{Cl}_2\text{F}_2 \text{ at constant pressure} = C_p = 80.7 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\text{Initial temperature} = T_1 = 320 \text{ K}, \text{ Final temperature} = T_2 = 293 \text{ K}$$

$$\text{Therefore, } \Delta T = T_2 - T_1 = 293 \text{ K} - 320 \text{ K} = -27 \text{ K}$$

(i) Calculation of ΔH

$$\Delta H_m = C_p \times \Delta T$$

$$= 80.7 \text{ JK}^{-1} \text{ mol}^{-1} \times (-27 \text{ K})$$

$$= -2178.9 \text{ J mol}^{-1}$$

ΔH (to cool 1.25 g of $\text{C}_2\text{Cl}_2\text{F}_2$)

$$= \Delta H \text{ per mole of } \text{C}_2\text{Cl}_2\text{F}_2 \times \text{mole of } \text{C}_2\text{Cl}_2\text{F}_2 \text{ in } 1.25 \text{ g}$$

$$\text{Mole of } \text{C}_2\text{Cl}_2\text{F}_2 = \frac{\text{Mass of } \text{C}_2\text{Cl}_2\text{F}_2}{\text{Molar mass of } \text{C}_2\text{Cl}_2\text{F}_2} = \frac{1.25 \text{ g}}{133 \text{ g/mol}}$$

$$\text{Therefore, } \Delta H = -2178.9 \text{ kJ mol}^{-1} \times \frac{1.25 \text{ g}}{133 \text{ g/mol}} = -20.478 \text{ J}$$

(ii) Calculation of ΔU

$$\Delta H = \Delta U + P\Delta V \text{ gives}$$

$$\Delta U = \Delta H - P\Delta V$$

Data given

$$P = 1 \text{ atm} = 101325 \text{ N / m}^2$$

$$V_1 = 274 \text{ cm}^3 = 274 \times 10^{-6} \text{ m}^3$$

$$V_2 = 248 \text{ cm}^3 = 248 \times 10^{-6} \text{ m}^3$$

$$\text{Therefore, } \Delta V = V_2 - V_1 = 248 \times 10^{-6} \text{ m}^3 - 274 \times 10^{-6} \text{ m}^3 = -26 \times 10^{-6} \text{ m}^3$$

$$\text{and } P \times \Delta V = 101325 \text{ N m}^{-2} \times (-26 \times 10^{-6} \text{ m}^3) = -2.634 \text{ N m}^{-2} = 2.364 \text{ J}$$

Thus

$$\Delta U = \Delta H - P\Delta V$$

$$= -20.478 \text{ J} - (-2.364 \text{ J})$$

$$= -20.478 \text{ J} + 2.364 \text{ J} = -18.114 \text{ J}$$

Example. When the sample of 0.562 g of graphite was burnt in a bomb calorimeter in the presence of excess of oxygen at 298 K and 1 bar pressure the following reaction took place $\text{C (s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$. During the reaction an increase of temperature from 298 K to 298.8 K was observed. Calculate the molar enthalpy change for the above reaction. It is given that the heat capacity of the calorimeter and its content is 20.7 kJ K⁻¹.

Solution. $q(\text{calorimeter}) = C(\text{calorimeter}) \times \Delta T$

$$= 20.7 \text{ kJ K}^{-1} \times (298.8 \text{ K} - 298.0 \text{ K})$$

$$= 18.423 \text{ kJ}$$

$$q(\text{reaction}) = -q(\text{calorimeter})$$

$$= -18.423 \text{ kJ}$$

$$= \text{Heat liberated on burning 0.562 g of graphite}$$

$$\text{Heat liberated per mole of graphite} = \frac{q(\text{reaction})}{\text{mole of graphite}}$$

$$= \frac{-18.423 \text{ kJ}}{0.562 \text{ g} / 12 \text{ g mol}^{-1}}$$

$$= -393.378 \text{ kJ mol}^{-1}$$

(i) Calculation of ΔU : The experiment is carried in a bomb calorimeter

Therefore, q (reaction) /mol = ΔU (reaction) /mol = $-393.378 \text{ kJ mol}^{-1}$

(ii) Calculation of $\Delta H = \Delta U + \Delta n_g RT$

For the reaction $\text{C (s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2 (\text{g})$

$$\Delta n_g = 1 - 1 = 0$$

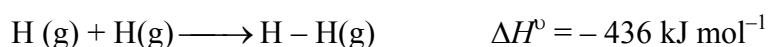
Therefore, $\Delta n_g RT = 0 \times RT = 0$

and $\Delta H = \Delta U = -393.378 \text{ kJ mol}^{-1}$

Bond enthalpy

When a chemical bond is formed heat is liberated. This heat liberated at constant pressure is referred to as **enthalpy of bond formation**. On the other hand, the heat needed to cause the breaking of a chemical bond at a constant pressure is called the **bond dissociation enthalpy**. Thus, the bond formation is an exothermic process whereas bond dissociation is an endothermic process. For example:

When two hydrogen atoms unite to form a covalent bond in hydrogen molecule as H–H, the heat liberated is 436 kilo joule per mole of bond formed. That is, the enthalpy of formation of one mole of H–H bond is -436 kJ . It is written as follows



On the other hand, when one mole of H – H covalent bonds are broken, 436 kJ heat is absorbed and is given as



The enthalpy of dissociation of one mole of H–H bonds is 436 kJ mol^{-1}

Preference of bond dissociation enthalpy over bond formation enthalpy

Bond formation enthalpy is a conceptual term. It is not possible to estimate directly its experimental value. *Why?* Because we cannot isolate the free gaseous atoms and force them to combine. On the other hand, bond dissociation enthalpy is an operational term. It is convenient to collect a sample of the substance and fragment (atomize) its molecules to produce the constituent atoms and then to estimate the heat needed to break the bonds.

Bond enthalpy of a diatomic molecule

. The bond dissociation enthalpy of a diatomic molecule is equal to the heat needed to break the bonds in one mole of molecules so that free gaseous atoms are produced. For example:

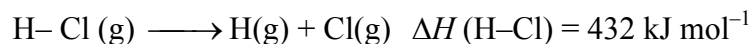
(i) The bond enthalpy of H –H bond is equal to the enthalpy change for breaking one mole of H–H bonds in H_2 molecules and to produce free gaseous H atoms



(ii) The bond enthalpy of O = O bond is equal to the enthalpy change for breaking one mole O = O bonds in O₂ molecules and to produce free gaseous O atoms.

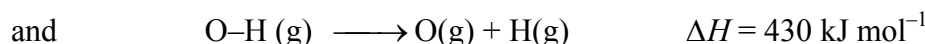


(iii) The bond enthalpy of H–Cl bond is equal to the enthalpy change in breaking one mole H–Cl bonds in HCl molecules so that 1 mole H atoms and 1 mole Cl atoms are produced.



Enthalpy of bond dissociation in polyatomic molecules

In a polyatomic molecule the energy needed to break the same type of bond is different in different chemical situations. For example, in H₂O there are two O–H bonds written as H–O–H (simplified). Both the O–H bonds are equivalent in length and strength. But, the experiment shows that the enthalpy change to break one mole O – H bonds in H – O –H is 498 kJ mol⁻¹. On the other hand, the enthalpy change to break one mole O – H bond in hydroxyl group (OH) is 430 kJ mol⁻¹

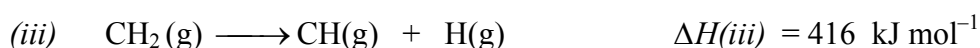
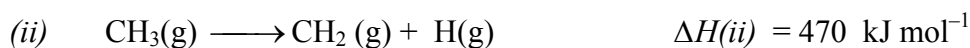
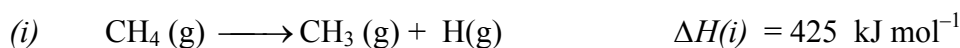


Thus the enthalpy of bond dissociation is defined as *the enthalpy change to breaking a given bond in specified chemical environment*.

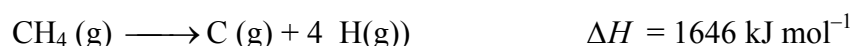
Bond enthalpy. Average of bond dissociation enthalpies of a given bond in different dissociating species is called its bond enthalpy. For example, in water molecule (H–O–H) the average of the two O–H bond dissociation enthalpies is called O–H bond enthalpy.

$$\Delta H (\text{O} - \text{H}) = \frac{498 \text{ kJ mol}^{-1} + 430 \text{ kJ mol}^{-1}}{2} = 464 \text{ kJ mol}^{-1}$$

Illustrative examples: Use the following bond dissociation enthalpies to compute the C–H bond enthalpy in methane (CH₄)



On adding equations (i), (ii), (iii) and (iv) and canceling the common terms on the two sides, we get



This is the sum of the individual C–H bond dissociation enthalpies. But bond enthalpy is equal to the average of the bond dissociation enthalpies. Therefore, the C–H bond enthalpy is given by

$$\Delta H(\text{C-H}) = \frac{(425 + 470 + 416 + 335) \text{ kJ mol}^{-1}}{4} = 411.5 \text{ kJ mol}^{-1}$$

A discussion of bond enthalpy and bond energy

Bond enthalpy and bond energy of a chemical bond A&B are related by

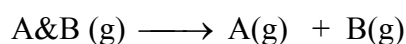
$$\Delta H^\theta(\text{A\&B}) = \Delta U^\theta(\text{A\&B}) + P \Delta V$$

If the bonded species A—B and its fragments A and B are assumed to obey ideal gas equation, then $P \Delta V = \Delta n_g RT$. Therefore,

$$\Delta H^\theta(\text{A\&B}) = \Delta U^\theta(\text{A\&B}) + \Delta n_g RT$$

or,
$$\Delta U^\theta(\text{A\&B}) = \Delta H^\theta(\text{A\&B}) - \Delta n_g RT$$

The dissociation of bond A&B is represented by



Therefore, $\Delta n_g = 1 + 1 - 1 = 1$. Thus,

$$\Delta U^\theta(\text{A\&B}) = \Delta H^\theta(\text{A\&B}) - RT$$

- At 0 K, $RT = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \times 0 \text{ K} = 0$. Therefore,

$$\Delta U^\theta(\text{A\&B}) = \Delta H^\theta(\text{A\&B})$$

- At 298 K,

$$RT = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \times 298 \text{ K} = 2.4775 \text{ kJ mol}^{-1} = 2.5 \text{ kJ mol}^{-1}$$

Therefore, $\Delta U^\theta(\text{A\&B}) = \Delta H^\theta(\text{A\&B}) - 2.5 \text{ kJ mol}^{-1}$.

For example, for H & H bond in H_2 , $\Delta H^\theta(\text{H\&H}) = 436 \text{ kJ mol}^{-1}$. Therefore,

$$\Delta U^\theta(\text{H\&H}) = 436 \text{ kJ mol}^{-1} - 2.5 \text{ kJ mol}^{-1} = 433.5 \text{ kJ mol}^{-1}$$

From the above example it is clear that in general the values of $\Delta H^\theta(\text{A\&B})$ and $\Delta U^\theta(\text{A\&B})$ differ only slightly. Therefore, for all practical purposes the two terms are used interchangeably.

Enthalpy of atomization

The enthalpy change in converting one mole of a substance into its constituent atoms in gaseous states is called the *enthalpy of atomization* or heat of atomization of that substance.

(1) Enthalpy of atomization of a diatomic molecule. The enthalpy of atomization of a diatomic molecule is equal to its enthalpy of dissociation $\Delta_d H$ Thus:



(2) Enthalpy of atomization of a polyatomic molecule

The enthalpy of atomization of a polyatomic molecule of a compound is equal to the enthalpy change to breaking all the covalent bonds so that gaseous constituent atoms are produced. The enthalpy of atomization of CH_4 is 1664 kJ mol^{-1} . which is equal to the enthalpy change associated with the breaking of the four C–H bonds per mole of CH_4 molecules.

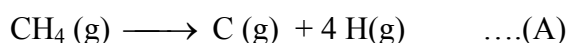


(3) The **enthalpy of atomization** of a solid element is equal to its heat of sublimation.



(A) Calculation of C–H bond energy from thermochemical data

The simplest molecule involving only C–H bonds is methane (CH_4) Therefore, the bond energy of C–H bond is calculated from the thermochemical data (enthalpy of atomization) of methane.



$$\Delta H(\text{C–H}) = \frac{\Delta_a H(\text{CH}_4)}{4}$$

But the enthalpy of atomization of methane is equal to the enthalpy of reaction (A)

$$\Delta_a H(\text{CH}_4) = \Delta_r H(\text{A})$$

$$\begin{aligned} \text{Now, } \Delta_r H(\text{A}) &= \Delta_f H(\text{C, g}) + 4 \Delta_f H(\text{H}) - \Delta_f H(\text{CH}_4) \\ &= 716.7 \text{ kJ mol}^{-1} + 4 \times 218 \text{ kJ mol}^{-1} - (-74.8 \text{ kJ mol}^{-1}) \\ &= 1663.5 \text{ kJ mol}^{-1} = \Delta_a H(\text{CH}_4) \end{aligned}$$

$$\text{Therefore, } \Delta H(\text{C–H}) = \frac{\Delta_a H(\text{CH}_4)}{4}$$

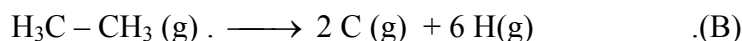
$$= \frac{1663.5 \text{ kJ mol}^{-1}}{4}$$

$$= 415.87 \text{ kJ ml}^{-1}$$

The actual value of $\Delta H(\text{C-H})$ is 414 kJ mol^{-1}

(B) Calculation of C–C bond energy from thermochemical data

The simplest molecule involving C – C bond (along with 6 C–H bonds) is ethane (C_2H_6) Therefore, the value of enthalpy of C– C bond is calculated from the thermochemical data (enthalpy of atomization) of ethane and C–H bond enthalpy ($= 414 \text{ kJ mol}^{-1}$).



But $\Delta_a H (\text{C}_2\text{H}_6) = \Delta_r H (\text{B})$

Now enthalpy of reaction (B) is the enthalpy of atomization of ethane which is the energy needed to break one mole C–C bonds and six moles C–H bonds in one mole of ethane. Thus

$$\Delta_a H (\text{C}_2\text{H}_6) = \Delta_r H (\text{B}) = \Delta H(\text{C-C}) + 6 \Delta H(\text{C-H})$$

Therefore, $\Delta H(\text{C-C}) = \Delta_r H (\text{B}) - 6 \Delta H(\text{C-H})$

Now $\Delta_r H (\text{B}) = 2 \Delta_f H (\text{C}, \text{g}) + 6 \Delta_f H (\text{H}) - \Delta_f H (\text{C}_2\text{H}_6, \text{g})$

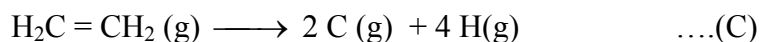
$$= 2 \times 716.7 \text{ kJ mol}^{-1} + 6 \times 218 \text{ kJ mol}^{-1} - (-85.6 \text{ kJ mol}^{-1})$$
$$= 2827 \text{ kJ mol}^{-1}$$

Therefore, $\Delta H(\text{C-C}) = \Delta_r H (\text{B}) - 6 \Delta H(\text{C-H})$

$$= 2827 \text{ kJ mol}^{-1} - 6 \times 214 \text{ kJ mol}^{-1}$$
$$= 2827 \text{ kJ mol}^{-1} - 2484 \text{ kJ mol}^{-1} = 343 \text{ kJ mol}^{-1}$$

(C) Calculation of C=C bond energy from thermochemical data

The simplest molecule involving C = C bond along with 4 C–H bonds is ethene (C_2H_4) Therefore, enthalpy of C = C bond is calculated from the thermochemical data (enthalpy of atomization) of ethene and C–H bond enthalpy.



The enthalpy of reaction (C) is the enthalpy of atomization of ethene which is the energy needed to break one mole C = C bonds and four moles C–H bonds in one mole of ethene. Thus

$$\Delta_a H (\text{C}_2\text{H}_4) = \Delta_r H (\text{C}) = \Delta H (\text{C} = \text{C}) + 4 \Delta H (\text{C-H})$$

Therefore, $\Delta H(\text{C} = \text{C}) = \Delta_r H (\text{C}) - 4 \Delta H(\text{C-H})$

Now, $\Delta_r H (\text{C}) = 2 \Delta_f H (\text{C}, \text{g}) + 4 \Delta_f H (\text{H}) - \Delta_f H (\text{C}_2\text{H}_4, \text{g})$

$$= 2 \times 716.7 \text{ kJ mol}^{-1} + 4 \times 218 \text{ kJ mol}^{-1} - (+52.3 \text{ kJ mol}^{-1})$$
$$= 2253 \text{ kJ mol}^{-1}$$

Therefore, $\Delta H(\text{C}=\text{C}) = \Delta_f H(\text{C}) - 4 \Delta H(\text{C}-\text{H})$

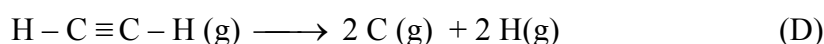
$$= 2827 \text{ kJ mol}^{-1} - 4 \times 414 \text{ kJ mol}^{-1}$$

$$= 597 \text{ kJ mol}^{-1}$$

The actual value of $\Delta H(\text{C}=\text{C})$ is 611 kJ mol^{-1}

(D) Calculation of $\text{C} \equiv \text{C}$ bond energy from thermo chemical data

The simplest molecule involving $\text{C} \equiv \text{C}$ bond (along with 2 $\text{C}-\text{H}$ bonds) is ethyne (C_2H_2)
Therefore, enthalpy of $\text{C} \equiv \text{C}$ bond is calculated from the thermochemical data (enthalpy of atomization) of ethyne and $\text{C}-\text{H}$ bond enthalpy



The enthalpy of reaction (D) is the enthalpy of atomization of ethyne which is the energy needed to break one mole $\text{C} \equiv \text{C}$ bonds and two moles $\text{C}-\text{H}$ bonds in one mole of ethyne.
Thus

$$\Delta_a H(\text{C}_2\text{H}_2) = \Delta_r H(\text{D}) = \Delta H(\text{C} \equiv \text{C}) + 2 \Delta H(\text{C}-\text{H})$$

Therefore, $\Delta H(\text{C} \equiv \text{C}) = \Delta_r H(\text{D}) - 2 \Delta H(\text{C}-\text{H})$

Now, $\Delta_r H(\text{D}) = 2 \Delta_f H(\text{C}, \text{g}) + 2 \Delta_f H(\text{H}) - \Delta_f H(\text{C}_2\text{H}_2, \text{g})$

$$= 2 \times 716.67 \text{ kJ mol}^{-1} + 2 \times 218 \text{ kJ mol}^{-1} - (+226.7 \text{ kJ mol}^{-1})$$

$$= 1642.7 \text{ kJ mol}^{-1}$$

Therefore, $\Delta H(\text{C} \equiv \text{C}) = \Delta_r H(\text{D}) - 2 \Delta H(\text{C}-\text{H})$

$$= 1642.7 \text{ kJ mol}^{-1} - 2 \times 414 \text{ kJ mol}^{-1}$$

$$= 814.7 \text{ kJ mol}^{-1}$$

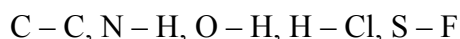
The actual value of $\Delta H(\text{C} \equiv \text{C})$ is 837 kJ mol^{-1}

Table 2. Single bond enthalpy data (ΔH^\ominus) expressed in kJ mol^{-1}

A – B	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436				569			339	431	368	297
C	414	347	293	351	439	289	264	259	330	276	238
N	389			201	272		209		201	243	
O	464			138	184				205		
F					159						
Si	293	289		368	540	176	213	226	360	289	213
P	318	264		351	490		213	230	331	272	213
S		259			327			213	251	213	
Cl				205	255				243		
Br					197				218	192	
I				201					209	180	151

Method to find the enthalpy of a bond from the table

- In the table the values of bond enthalpy are given for the bonds which are written as A – B, for example as



- Select the first atom (A) of the desired bond from the vertical column and the second atom (B) of the bond from the horizontal row.
- The value on the right side of the first atom and below the second atom is the bond enthalpy of the desired bond.

Illustration of the method: To find the bond enthalpy of the S – F bond, select S from the vertical column and F from the horizontal row. The value on the right of S and below F is the bond enthalpy of S – F bond. Thus,

$$\Delta H^\ominus (\text{S} - \text{F}) = 327 \text{ kJ mol}^{-1}$$

Table 3. Bond enthalpy data (ΔH^\ominus) expressed in kJ mol^{-1} for double and triple bonds

Bond	C=C	C=O	C=N	N=N	O=O	C≡C	C≡O	N≡N	C≡N
ΔH^\ominus	611	741	615	418	498	837	1070	946	891

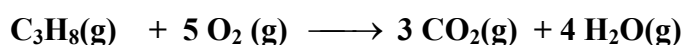
Note: The bond energy of a bond is assumed to be the same irrespective of the type of the molecule in which this bond is present. For example, the bond energy of a C – H bond is assumed to be the same whether it is present in a hydrocarbon or carboxylic acid or alcohol or aldehyde etc.

CALCULATION OF ENTHALPY OF REACTIONS FROM BOND ENTHALPY DATA

. The enthalpy of a reaction is given by the relation

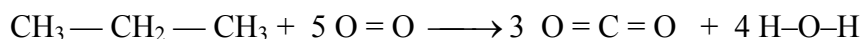
$$\Delta_r H^\ominus = \Sigma \text{Bond enthalpy of reactants} - \Sigma \text{Bond enthalpy of products}$$

Example: Use the bond enthalpy data to calculate the enthalpy change for the combustion of *n*-propane (C₃H₈) represented by the reaction



Bond	C – C	C – H	O – H	C = O
O = O				
ΔH^\ominus (bond)/ kJ mol ⁻¹	347	414	464	741
498				

Solution. The given reaction $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \longrightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$ may be represented in terms of breaking of bonds in reactants and formation of bonds in products as follows:



The enthalpy of reaction ($\Delta_r H^\ominus$) and bond enthalpies of reactant and product are related by

$$\Delta_r H^\ominus = \Sigma \text{Bond enthalpy of reactants} - \Sigma \text{Bond enthalpy of products}$$

The given reaction involves breaking of three C–C bonds, eight C–H bond in C₃H₈ and five O = O bond in O₂. Therefore,

$$\begin{aligned} \Sigma \text{Bond enthalpy of reactants} &= 3 \Delta H^\ominus (\text{C} - \text{C}) + 8 \Delta H^\ominus (\text{C} - \text{H}) + 5 \Delta H^\ominus (\text{O} = \text{O}) \\ &= 3 \times 347 \text{ kJ mol}^{-1} + 8 \times 414 \text{ kJ mol}^{-1} + 5 \times 498 \text{ kJ mol}^{-1} \\ &= 6843 \text{ kJ mol}^{-1} \end{aligned}$$

The given reaction involves formation of six C=O bonds in CO₂, four O–H bonds in H₂O. Therefore,

$$\begin{aligned} \Sigma \text{Bond enthalpy of products} &= 6 \Delta H^\ominus (\text{C} = \text{O}) + 8 \Delta H^\ominus (\text{O} - \text{H}) \\ &= 6 \times 741 \text{ kJ mol}^{-1} + 8 \times 464 \text{ kJ mol}^{-1} \\ &= 8158 \text{ kJ mol}^{-1} \end{aligned}$$

Therefore, $\Delta_r H^\ominus = \Sigma \text{ Bond enthalpy of reactants} - \Sigma \text{ Bond enthalpy of products}$

$$\begin{aligned} &= 6843 \text{ kJ mol}^{-1} - 8158 \text{ kJ mol}^{-1} \\ &= -1315 \text{ kJ mol}^{-1} \end{aligned}$$

Enthalpy of physical transformation

The process by which a substance is changed from one physical state into its another physical state is called **physical transformation** or phase transformation. Here we shall discuss the processes of vaporization, fusion and sublimation and the related enthalpy changes.

(A) Enthalpy of vaporization

The quantity of heat absorbed for complete conversion of one mole of a liquid into vapour at its boiling point is called its **enthalpy of vaporization**. It is denoted by $\Delta_{\text{vap}}H$. The enthalpy of vaporization is called the **heat of vaporization** also.

The enthalpy of vaporization per mole of water at 373 K is 40.70 kJ



Latent heat of vaporization: The heat absorbed to convert one gram liquid into vapour is called **latent heat** of vaporization. The latent heat of vaporization of water is 2.26 kJ per gram at 100 °C. This means that 1 g of liquid water at 100 °C will absorb 2.26 kilojoules of heat to be converted into 1 g of water vapour at 100 °C. Since no change of temperature is involved the absorbed heat is stored in water molecules in vapour state. That is why this is called latent heat.

(B) Enthalpy of fusion

The quantity of heat absorbed for complete conversion of one mole of solid into liquid at its melting point is called its **enthalpy of fusion**. The enthalpy of fusion is denoted by $\Delta_{\text{fus}}H$. It is called heat of fusion also. The enthalpy of fusion of water is 6.01 kJ mol⁻¹ at 273 K and 1 atm.



Latent of fusion of ice is 334 J g⁻¹

(C) Enthalpy of sublimation

The quantity of heat absorbed for complete conversion of one mole of solid directly into vapour is called **enthalpy of sublimation** or heat of sublimation. The enthalpy of sublimation of a substance is denoted by $\Delta_{\text{sub}}H$

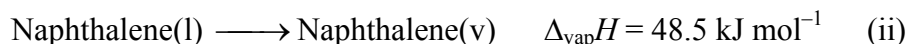
According to Hess's law of constant heat summation, the enthalpy of sublimation is equal to the sum of the enthalpy of fusion and the enthalpy of vaporization of the same substance (all the quantities refer to same temperature)

$$\Delta_{\text{sub}}H = \Delta_{\text{fus}}H + \Delta_{\text{vap}}H$$

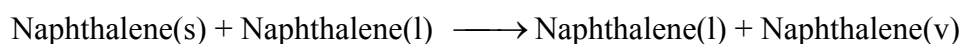
For example, the enthalpy of sublimation of naphthalene is computed as follows.

Aim : Naphthalene(s) \longrightarrow Naphthalene (v) $\Delta_{\text{sub}}H = ?$ (to be calculated)

Data given



On adding equations (i) and (ii) we get



On canceling the common terms on the two sides of the above equation, we have



and $\Delta H(\text{iii}) = \Delta H(\text{i}) + \Delta H(\text{ii})$

$$\begin{aligned} \text{or,} \quad \Delta_{\text{sub}}H &= \Delta_{\text{fus}}H + \Delta_{\text{vap}}H \\ &= 22.4 \text{ kJ mol}^{-1} + 48.5 \text{ kJ mol}^{-1} \\ &= 70.9 \text{ kJ mol}^{-1} \end{aligned}$$

Temperature dependence of reaction enthalpy (Kirchhoff's equation)

Statement Variation of reaction enthalpy ($\Delta_r H$, heat of reaction) with temperature is called **Kirchhoff's equation**. It is stated as follows

$$\left(\frac{\partial \Delta_r H}{\partial T} \right)_P = \Delta_r C_P$$

$$d\Delta_r H = \Delta_r C_P dT \quad \text{at constant pressure}$$

Where

$\Delta_r H$ = reaction enthalpy (heat of reaction at constant pressure)

and $\Delta_r C_P$ = reaction heat capacity at constant pressure

$$= \sum C_p(\text{products}) - \sum C_p(\text{reactants})$$

Similarly, for the heat of reaction at constant volume the Kirchhoff's equation is given by

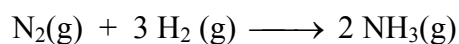
$$d \Delta_r U = \Delta_r C_V dT \quad \text{at constant volume}$$

Relevance of Kirchhoff's equation Standard enthalpy of reaction (heat of reaction at 298 K and at 1 bar) is calculated using the standard enthalpy of formation data of reactants and products given in the International tables. But when it is required to find the enthalpy of

reaction at other temperatures then we use Kirchhoff's equation.

Derivation of Kirchhoff's equation

Let us consider a familiar reaction of synthesis of ammonia from nitrogen and hydrogen as represented by chemical equation



The standard enthalpy of this reaction is given by

$$\Delta_r H^\ominus = 2 \times H_m^\ominus(\text{NH}_3) - [H_m^\ominus(\text{N}_2) + 3 \times H_m^\ominus(\text{H}_2)]$$

On differentiating the above equation with respect to T at constant P , we get

$$\left(\frac{\partial \Delta_r H^\ominus}{\partial T} \right)_P = 2 \left(\frac{\partial H_m^\ominus(\text{NH}_3)}{\partial T} \right)_P - \left[\left(\frac{\partial H_m^\ominus(\text{N}_2)}{\partial T} \right)_P + 3 \left(\frac{\partial H_m^\ominus(\text{H}_2)}{\partial T} \right)_P \right]$$

By definition

$$\left(\frac{\partial H_m^\ominus}{\partial T} \right)_P = C_{p,m}^\ominus = \text{Standard molar heat capacity at constant pressure}$$

$$\text{Therefore, } \left(\frac{\partial \Delta_r H^\ominus}{\partial T} \right)_P = 2 C_{p,m}^\ominus(\text{NH}_3) - [C_{p,m}^\ominus(\text{N}_2) + 3 C_{p,m}^\ominus(\text{H}_2)]$$

$$= \Sigma C_p^\ominus(\text{products}) - \Sigma C_p^\ominus(\text{reactants})$$

$$= \Delta_r C_p^\ominus$$

$$\text{Or, } d \Delta_r H^\ominus = \Delta_r C_p^\ominus dT$$

It is differential form of Kirchhoff's equation

Integrated form of Kirchhoff's equation

Case I. When heat capacity is independent of temperature, $\Delta_r C_p^\ominus$ is constant and integration of Kirchhoff's equation gives

$$\int_1^2 d \Delta_r H^\ominus = \Delta_r C_p^\ominus \int_1^2 dT$$

$$\text{Or, } \Delta_r H^\ominus(\text{at } T_2) - \Delta_r H^\ominus(\text{at } T_1) = \Delta_r C_p^\ominus (T_2 - T_1)$$

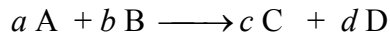
$$\text{Or, } \Delta_r H^\ominus(\text{at } T_2) = \Delta_r H^\ominus(\text{at } T_1) + \Delta_r C_p^\ominus (T_2 - T_1)$$

It is integrated form of Kirchoff's equation. From this equation the value of enthalpy of reaction at any temperature T_2 can be calculated provided its value at a temperature T_1 is known and the molar heat capacities of reactants and products are also known

Similarly, the Kirchoff's equation for heat of reaction at constant volume is given by

$$\Delta_r U^0 \text{ (at } T_2) = \Delta_r U^0 \text{ (at } T_1) + \Delta_r C_v^0 (T_2 - T_1)..$$

Kirchoff's equation for any general reaction



is given by

$$\Delta_r H^0 \text{ (at } T_2) = \Delta_r H^0 \text{ (at } T_1) + \Delta_r C_p^0 (T_2 - T_1)$$

where,

$$\begin{aligned} \Delta_r C_p^0 &= \Sigma C_p^0 \text{ (products)} - \Sigma C_p^0 \text{ (reactants)} \\ &= [c C_{p,m}^0 \text{ (C)} + d C_{p,m}^0 \text{ (D)}] - [a C_{p,m}^0 \text{ (A)} + b C_{p,m}^0 \text{ (B)}] \end{aligned}$$

Case II. When molar heat capacity depends on temperature as

$$C_{p,m}^0 = \alpha + \beta T + \gamma T^2$$

the heat capacity of reaction is given by

$$\Delta_r C_{p,m}^0 = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2$$

where

$$\Delta\alpha = [c\alpha + d\alpha] - [a\alpha + b\alpha]$$

$$\Delta\beta = [c\beta + d\beta] - [a\beta + b\beta]$$

$$\Delta\gamma = [c\gamma + d\gamma] - [a\gamma + b\gamma]$$

On ignoring integrating Kirchoff's equation we shall get

$$\begin{aligned} \int_1^2 d\Delta_r H^0 &= \int_1^2 \Delta_r C_p^0 dT \\ &= \int_1^2 \Delta\alpha dT + \int_1^2 \Delta\beta T dT + \int_1^2 \Delta\gamma T^2 dT \end{aligned}$$

$$\Delta_r H^\circ (\text{at } T_2) - \Delta_r H^\circ (\text{at } T_1) = \Delta \alpha (T_2 - T_1) + \frac{1}{2} \Delta \beta (T_2^2 - T_1^2) + \frac{1}{3} \Delta \gamma (T_2^3 - T_1^3)$$

$$\text{Or, } \Delta_r H^\circ (\text{at } T_2) = \Delta_r H^\circ (\text{at } T_1) + \Delta \alpha (T_2 - T_1) + \frac{1}{2} \Delta \beta (T_2^2 - T_1^2) + \frac{1}{3} \Delta \gamma (T_2^3 - T_1^3)$$

This equation is used to calculate accurate value of reaction enthalpy at any temperature T_2 when the value at a temperature T_1 and the values of heat capacities of reactants are known

Example: The enthalpy of decomposition of gaseous water at 298 K and 1 bar is 241.75 kJ mol⁻¹. Calculate its value at 348 K. The molar heat capacity values in JK⁻¹ mol⁻¹ are: $C_{p,m}^\ominus (\text{H}_2\text{O}) = 33.56$, $C_{p,m}^\ominus (\text{O}_2) = 29.12$, $C_{p,m}^\ominus (\text{H}_2) = 28.82$.

Solution. Kirchoff's equation $\Delta_r H^\circ (\text{at } T_2) = \Delta_r H^\circ (\text{at } T_1) + \Delta_r C_p^\ominus (T_2 - T_1)$ is used to perform the calculation

For the decomposition of water $\text{H}_2\text{O} (\text{g}) \longrightarrow \text{H}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g})$

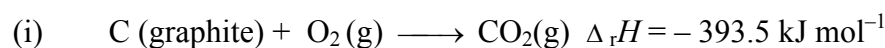
$$\Delta_r H^\circ (298 \text{ K}) = 241.75 \text{ kJ mol}^{-1}$$

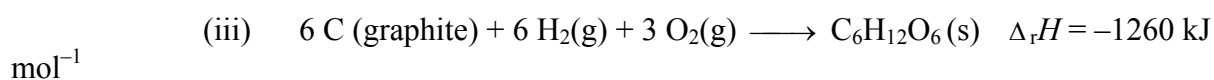
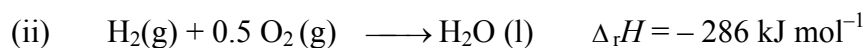
$$\begin{aligned} \Delta_r C_p^\ominus &= C_{p,m}^\ominus (\text{H}_2) + \frac{1}{2} C_{p,m}^\ominus (\text{O}_2) - C_{p,m}^\ominus (\text{H}_2\text{O}) \\ &= 28.82 \text{ JK}^{-1} \text{ mol}^{-1} + \frac{1}{2} (29.12 \text{ JK}^{-1} \text{ mol}^{-1}) - 33.56 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 9.83 \text{ JK}^{-1} \text{ mol}^{-1} = 9.83 \times 10^{-3} \text{ k JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Therefore, } \Delta_r H^\circ (348 \text{ K}) &= \Delta_r H^\circ (298 \text{ K}) + \Delta_r C_p^\ominus (T_2 - T_1) \\ &= 241.75 \text{ kJ mol}^{-1} + 9.83 \times 10^{-3} \text{ k JK}^{-1} \text{ mol}^{-1} (348 \text{ K} - 298 \text{ K}) \\ &= 242.24 \text{ kJ mol}^{-1} \end{aligned}$$

PROBLEMS:

1. Calculate the enthalpy of combustion of glucose from the following data :





[Ans. Application of Hess's law gives $\Delta_c H = -2817 \text{ kJ mol}^{-1}$]

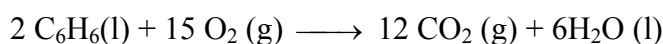
2. Calculate the enthalpy change of the reaction $\text{C}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_4(\text{g})$ at 298 K when the enthalpy of combustion data are $\Delta_c H(\text{H}_2, \text{g}) = -286 \text{ kJ mol}^{-1}$, $\Delta_c H(\text{C}_2\text{H}_2, \text{g}) = -1300 \text{ kJ mol}^{-1}$, $\Delta_c H(\text{C}_2\text{H}_4, \text{g}) = -1411 \text{ kJ mol}^{-1}$ **[Ans: -175 kJ mol^{-1}]**

3. The standard enthalpy of formation of $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -74.8 , -393.5 and $-241.6 \text{ kJ mol}^{-1}$ respectively. Calculate the enthalpy change on burning 1 m^3 of methane measured under standard conditions. **[Ans. $\Delta_r H = -35799.1 \text{ kJ mol}^{-1}$]**

4. Calculate the enthalpy of formation of ethane when its enthalpy of combustion is $-1560 \text{ kJ mol}^{-1}$ and $\Delta_f H(\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$ and $\Delta_f H(\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$

[Ans: $\Delta_f H(\text{C}_2\text{H}_6) = -84.4 \text{ kJ mol}^{-1}$]

5. What is the difference between $\Delta_r H$ and $\Delta_r U$ at 298 K for the reaction



[Ans. $-7.43 \text{ kJ mol}^{-1}$]

6. Using the given data calculate the C–H bond energy in CH_4 :

Species	:	$\text{CH}_4(\text{g})$	$\text{C}(\text{g})$	$\text{H}(\text{g})$
$\Delta_f H / \text{kJ mol}^{-1}$:	-74.8	716.7	218

[Ans. $415.87 \text{ kJ mol}^{-1}$]

7. If the enthalpy of the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2 \text{HCl}(\text{g})$ at 293 K is $-91.2 \text{ kJ mol}^{-1}$ what will be its value at 313 K. The molar heat capacities at constant pressure of $\text{H}_2(\text{g})$, $\text{Cl}_2(\text{g})$ and $\text{HCl}(\text{g})$ are 29.3, 34.7 and $28.9 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. **[Application of Kirchhoff's equation gives $\Delta_r H(313 \text{ K}) = -91.324 \text{ kJ mol}^{-1}$]**

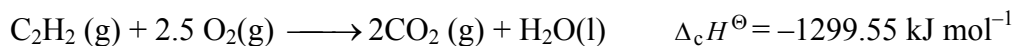
8. The enthalpy of reaction $\text{N}_2 + 3 \text{H}_2 \longrightarrow 2 \text{NH}_3$ at 27°C was found to be $-91.94 \text{ kJ mol}^{-1}$. What will be its value at 50°C . The molar heat capacities at constant pressure and at 27°C for N_2 , H_2 and NH_3 are 28.45, 28.32 and $37.07 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively.

[Ans: Application of Kirchhoff's equation gives $\Delta_r H(313 \text{ K}) = -92.843 \text{ kJ mol}^{-1}$]

9. The enthalpy of neutralization of CH_3COOH with NaOH is $-51.63 \text{ kJ mol}^{-1}$. Calculate the enthalpy of ionization of CH_3COOH . Assume that the enthalpy of neutralization of HCl with NaOH is $-57.35 \text{ kJ mol}^{-1}$.

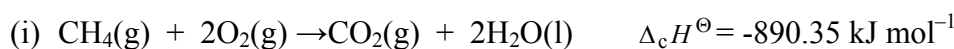
[Ans: For $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$, $\Delta_r H = 5.72 \text{ kJ mol}^{-1}$]

10. Calculate the enthalpy change for the polymerization of ethyne to benzene at 298 K as represented by the reaction. $3 \text{ C}_2\text{H}_2(\text{g}) \longrightarrow \text{C}_6\text{H}_6(\text{l})$ when



[Ans: Application of Hess's law gives $\Delta_r H^\ominus = -630.95 \text{ kJ mol}^{-1}$]

11. Calculate the standard enthalpy of formation of methane using the following data:



[Ans: Application of Hess's law gives $\Delta_f H^\ominus(\text{CH}_4) = 74.83 \text{ kJ mol}^{-1}$]

12. Find an expression for the variation of heat capacity of a reaction with temperature if the variation of its enthalpy change with temperature is expressed by $\Delta_r H^\ominus = A - BT - CT^2 - \frac{D}{T}$, where A, B, C, D are constants.

$$\text{[Ans: } \Delta_r C_p^\ominus = \left(\frac{\partial \Delta_r H^\ominus}{\partial T} \right)_p = -B - 2CT + \frac{D}{T^2} \text{]}$$

13. The standard enthalpy of combustion of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241 , -3800 and $-3920 \text{ kJ mol}^{-1}$ respectively at 298 K. Calculate the enthalpy of hydrogenation of cyclohexene in to cyclohexane. **[Ans. -121 kJ mol^{-1}]**