

# Thermochemistry

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## ■ Thermochemistry:

→ Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

→ When the **internal energy of reactants** ( $E_r$ ) is greater than the **internal energy of the products** ( $E_p$ ), the difference of internal energy,  $\Delta E$ , is released as heat energy. Such a reaction is called **exothermic reaction**.

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$
$$\Delta E = E_p - E_r$$

If the **internal energy of the products** ( $E_p$ ) is greater than that of the **reactants** ( $E_r$ ), heat is absorbed from the surroundings. Such a reaction is called **endothermic reaction**.

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## ■ Heat of reaction:

→ The amount of heat released or absorbed in a chemical reaction is termed the heat of reaction.

## ■ Enthalpy of reaction:

The enthalpy of a system is defined as the sum of the internal energy and the product of its pressure and volume. That is,

$$H = E + PV$$

where E is the internal energy, P is the pressure and V is the volume of the system. It is also called Heat content.

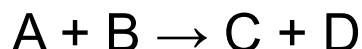
→ **Common types of enthalpies:**

**(a)** Enthalpy of Formation. **(b)** Enthalpy of Combustion. **(c)** Enthalpy of Solution. **(d)** Enthalpy of Neutralisation. **(e)** Enthalpy of Hydration. **(f)** Enthalpy of Vaporisation. **(g)** Enthalpy of Sublimation.

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## ■ Exothermic and Endothermic Reactions:

Let us consider a general reaction at constant pressure,



If  $H_A$ ,  $H_B$ ,  $H_C$  and  $H_D$  be the enthalpies of A, B, C and D respectively, the heat of reaction at constant pressure viz.,  $\Delta H$  is equal to the difference in enthalpies of the products and the reactants i.e.,

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

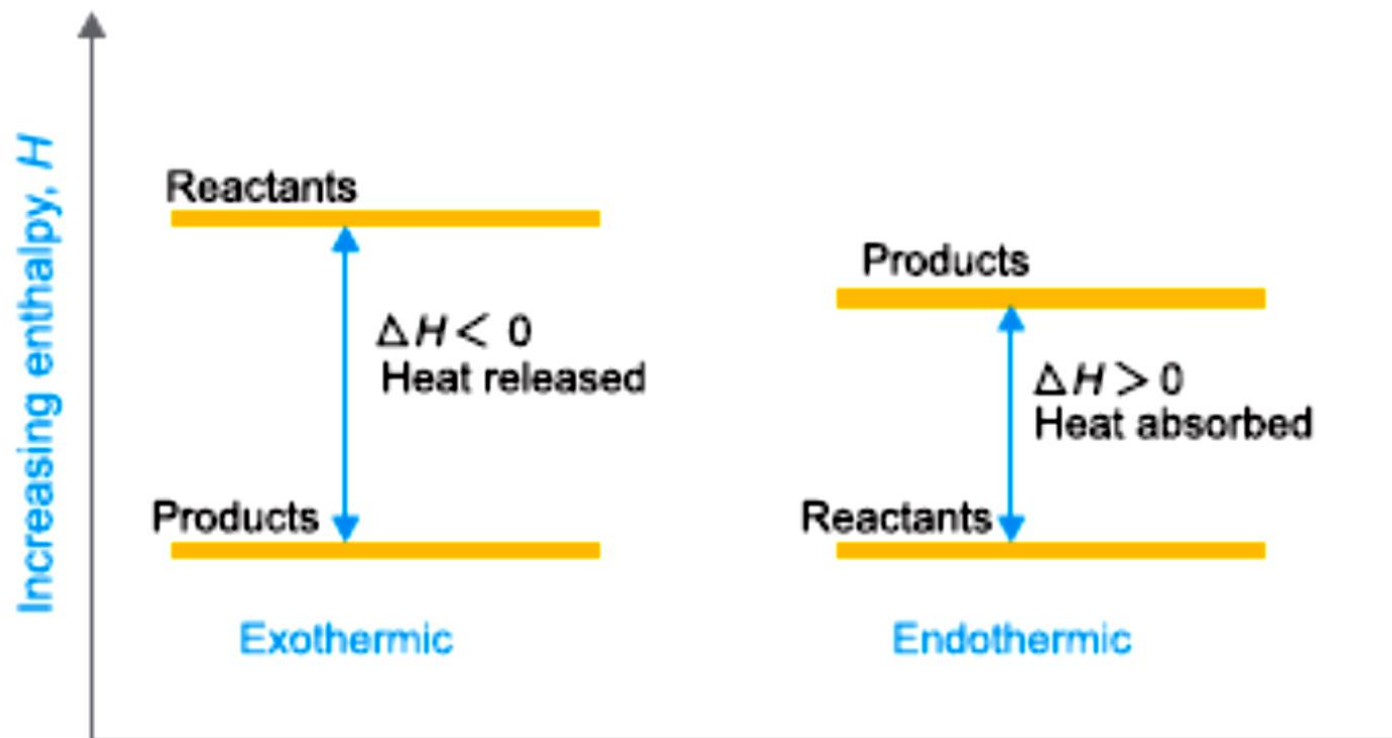
$$= (H_C + H_D) - (H_A + H_B)$$

The value of  $\Delta H$  may be either zero, negative or positive.

**TABLE 8.1. SIGN CONVENTIONS FOR ENERGY**

| Energy   | Terms used  | Sign |
|----------|-------------|------|
| Released | Exothermic  | –    |
| Absorbed | Endothermic | +    |

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Enthalpy diagram for an exothermic and endothermic reaction

## EXAMPLES OF EXOTHERMIC AND ENDOTHERMIC PROCESSES

When trying to classify a process as exothermic or endothermic, watch how the temperature of the surroundings changes. An exothermic process releases heat, and causes the temperature of the immediate surroundings to rise. An endothermic process absorbs heat and cools the surroundings.

### Exothermic processes

Making ice cubes

Formation of snow in clouds

Condensation of rain from water vapour

Mixing sodium sulfite and bleach

Rusting iron

Burning sugar

Forming ion pairs

Mixing water and strong acids

Mixing water with an anhydrous salt

Crystallizing liquid salts (as in sodium acetate in chemical handwarmers)

Nuclear fission

mixing water with calcium chloride

### Endothermic processes

Melting ice cubes

Conversion of frost to water vapour

Evaporation of water

Baking bread

Cooking an egg

Producing sugar by photosynthesis

Separating ion pairs

Mixing water and ammonium nitrate

Making an anhydrous salt from a hydrate

Melting solid salts

Reaction of barium hydroxide octahydrate crystals with dry ammonium chloride

Reaction of thionyl chloride ( $\text{SOCl}_2$ ) with cobalt(II) sulfate heptahydrate

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## ■ Calculation of $\Delta H$ from $\Delta E$ and *vice versa*:

→ The enthalpy change of a reaction at constant pressure ( $\Delta H$ ) and internal energy change ( $\Delta E$ ) at constant volume are related to each other as:

$$\Delta H = \Delta E + \Delta n RT$$

→ It may be pointed out that while determining the value of  $\Delta H$ , only the number of moles of gaseous reactants and products are taken into consideration. The value of gas constant  $R$  is taken either in calories or joules per degree per mol and is 1.987 cal (approximately 2 calories) or 8.314 joules.

→ Change in number of moles ( $\Delta n$ )

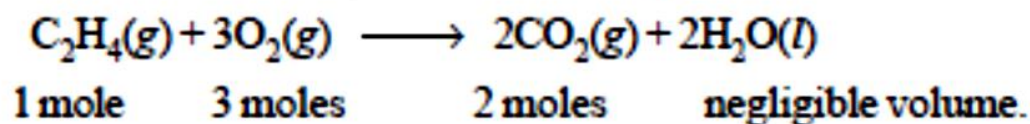
= No. of moles of products – No. of moles of reactants

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**SOLVED PROBLEM 1.** The heat of combustion of ethylene at 17°C and at constant volume is -332.19 kcals. Calculate the heat of combustion at constant pressure considering water to be in liquid state. ( $R = 2 \text{ cal degree}^{-1} \text{ mol}^{-1}$ )

## SOLUTION

The chemical equation for the combustion of ethylene is



No. of moles of the products = 2

No. of moles of the reactants = 4

$$\therefore \Delta n = (2 - 4) = -2$$

We know that  $\Delta H = \Delta E + \Delta n RT$

Given that  $\Delta E = -332.19 \text{ kcal}$

$$T = 273 + 17 = 290 \text{ K}$$

$$R = 2 \text{ cal} = 2 \times 10^{-3} \text{ kcal}$$

$$\begin{aligned} \therefore \Delta H &= -332.19 + 2 \times 10^{-3} \times -2 \times 290 \\ &= -333.3 \text{ kcal} \end{aligned}$$



# Thermochemistry

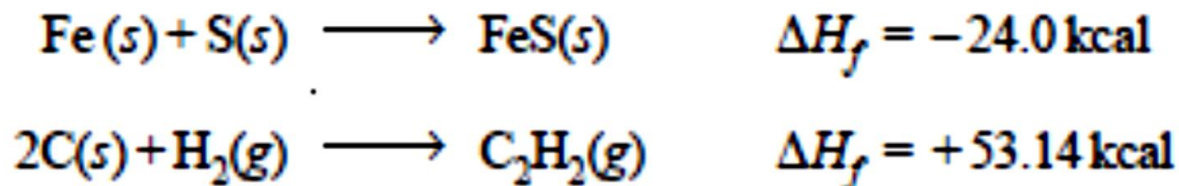
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## ■ Heat of Formation ( $\Delta H_f$ ):

→ The heat of formation of a compound is defined as:

**The change in enthalpy that takes place when one mole of the compound is formed from its elements.**

It is denoted by  $\Delta H_f$ . For example, the heat of formation of ferrous sulphide and acetylene may be expressed as:



## ■ Standard Heat of Formation ( $\Delta H_f^\circ$ ):

The standard heat of formation of a compound is defined as :

**The change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances being in their standard states (298 K and 1 atm pressure).**



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## ■ Standard Heat of Reaction ( $\Delta H^\circ$ ) from Standard Heat of Formation ( $\Delta H_f^\circ$ ):

→ The standard heat of reaction is equal to the standard heat of formation of products minus the standard heat of formation of reactants.

$$\Delta H^\circ = \left[ \begin{array}{c} \text{Total standard heat} \\ \text{of formation of products} \end{array} \right] - \left[ \begin{array}{c} \text{Total standard heat} \\ \text{of formation of reactants} \end{array} \right]$$

$$\Delta H^\circ = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants})$$

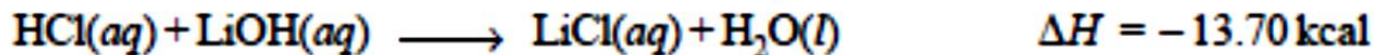
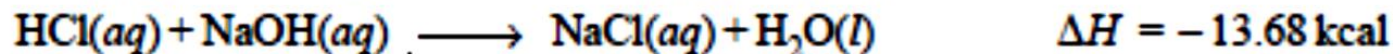
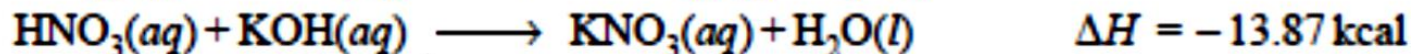
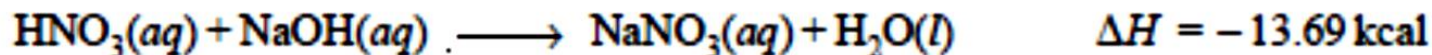
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## ■ Heat of Neutralisation:

→ The heat of neutralisation is defined as:

**The change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or vice versa in dilute solution.**

The following may be considered as typical examples of the heat of neutralisation.



→ It may be concluded from the above data that the heat of neutralisation of a strong acid and strong base is  $-13.7 \text{ kcal}$ , no matter which acid or base is employed.

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## ■ Hess's Law of Constant Heat Summation:

→ Hess's Law and may be stated as :

**If a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat change is same no matter by which method the change is brought about.**

Let us suppose that a substance A can be changed to Z directly.



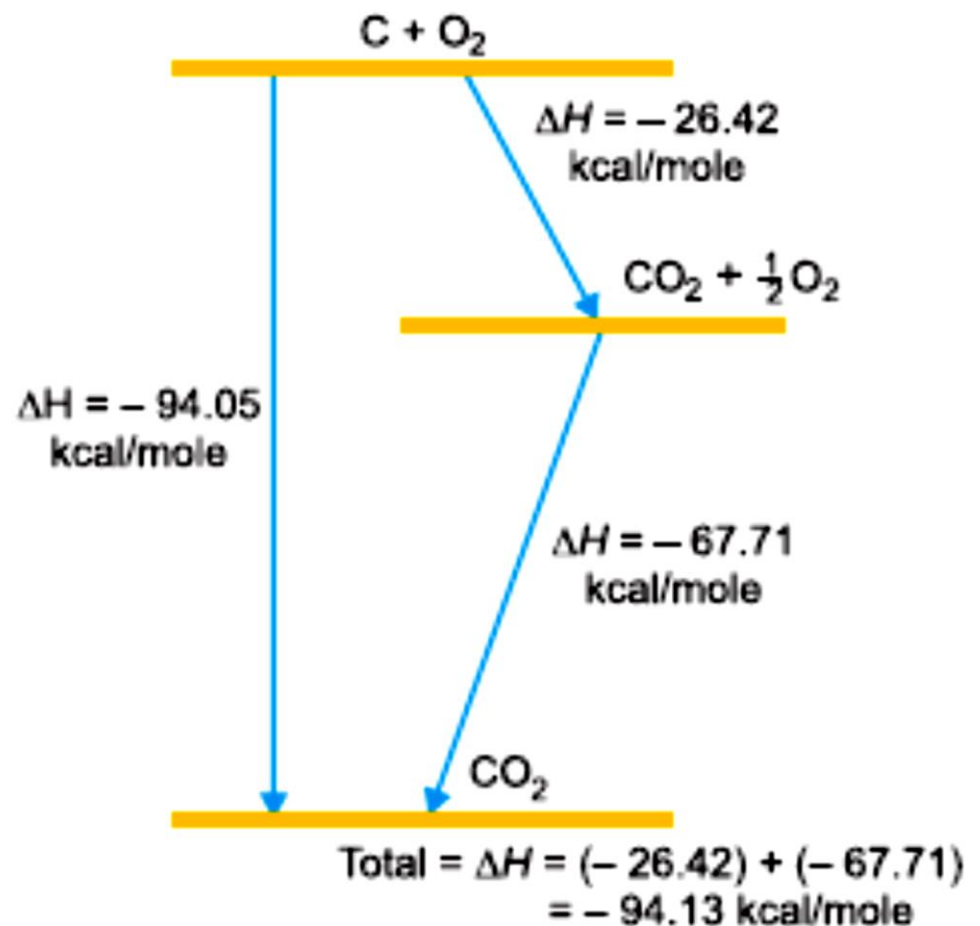
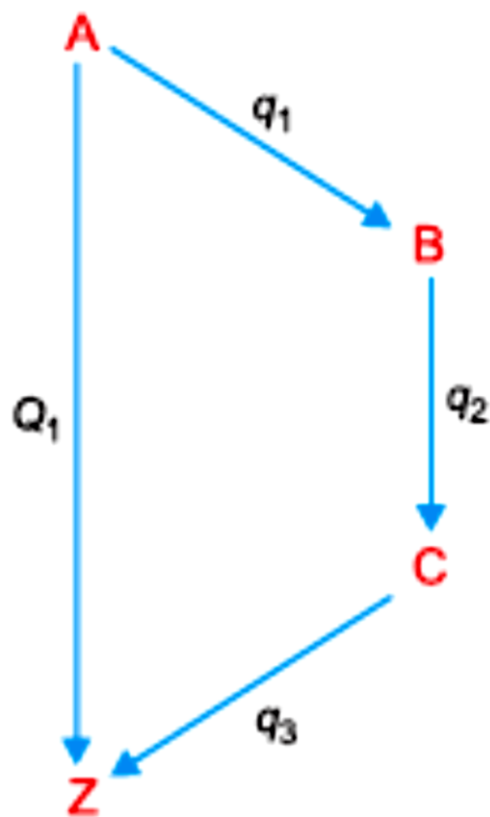
where  $Q_1$  is the heat evolved in the direct change. When the same change is brought about in stages :



The total evolution of heat =  $q_1 + q_2 + q_3 = Q_2$ .

**According to Hess's law  $Q_1 = Q_2$**

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Illustrations of Hess's Law

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## ■ Example of Hess's Law of Constant Heat Summation:

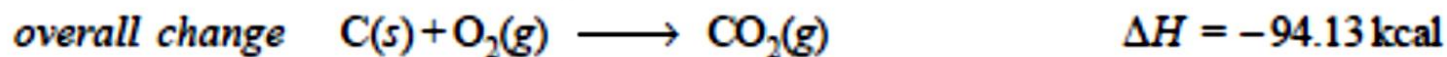
### → (1) Burning of carbon to CO<sub>2</sub>:

Carbon can be burnt to carbon dioxide directly or it may first be changed to carbon monoxide which may then be oxidised to carbon dioxide.

1st way :



2nd way :



→ It is evident from above that the total heat energy evolved is the same in the two cases

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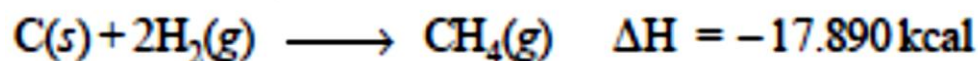
## ■ Application of Hess's Law of Constant Heat Summation:

- (1) Determination of heat of formation of substances which otherwise cannot be measured experimentally.
- (2) Determination of Heat of Transition.
- (3) Determination of heats of various reactions

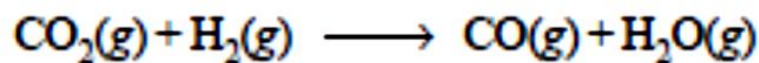
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**SOLVED PROBLEM 3.** The heat of formation of methane at 298 K at constant pressure is  $-17.890$  kcal. Calculate its heat of formation at constant volume. ( $R = 1.987$  cal degree $^{-1}$  mol $^{-1}$ )



**SOLVED PROBLEM 1.** Calculate  $\Delta H^\circ$  for the reaction



given that  $\Delta H_f^\circ$  for  $\text{CO}_2(g)$ ,  $\text{CO}(g)$  and  $\text{H}_2\text{O}(g)$  are  $-393.5$ ,  $-111.31$  and  $-241.80$  kJ mol $^{-1}$  respectively.



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**SOLVED PROBLEM 2.** The standard heats of formation of  $\text{C}_2\text{H}_5\text{OH}(l)$ ,  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  are  $-277.0$ ,  $-393.5$  and  $-285.5 \text{ kJ mol}^{-1}$  respectively. Calculate the standard heat change for the reaction



## ■ SOLVED PROBLEM 2.

The heat of combustion of carbon monoxide at constant volume and at  $17^\circ\text{C}$  is  $-283.3 \text{ kJ}$ . Calculate its heat of combustion at constant pressure ( $R = 8.314 \text{ J degree}^{-1} \text{ mol}^{-1}$ ).

