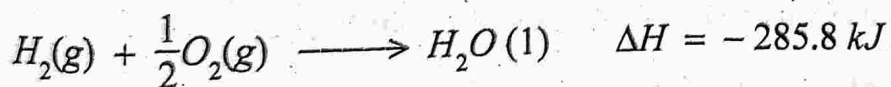
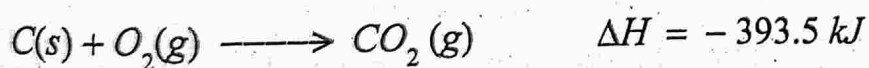
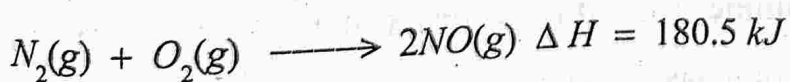


## Exothermic and endothermic reactions

The chemical reactions which proceed with the evolution of heat energy are called exothermic reactions. A few examples of exothermic reactions are



The chemical reactions which proceed with absorption of heat energy are called endothermic reactions. A few examples are



In an exothermic reaction, system loses heat to surroundings. Therefore,  $q$  will be negative and  $\Delta H$  will also be negative. Similarly in an endothermic reaction, system gains heat and hence  $\Delta H$  will be positive.

Since heat is given out in exothermic reactions, enthalpy of the products will be less than that of the reactants.

i.e.,  $H_{\text{products}} < H_{\text{reactants}}$  for exothermic reactions.

Because of the absorption of heat, the enthalpy of the products will be more than that of the reactants in endothermic reactions.

i.e.,  $H_{\text{products}} > H_{\text{reactants}}$  for endothermic reactions.

### Heat capacity

*Heat capacity of a substance or system is defined as the amount of heat required to raise its temperature through  $1^\circ\text{C}$ . It is denoted by  $C$ .*

Heat capacity is an extensive property because its value depends on the quantity of the material present. If the quantity of material is 1 gram, the heat required is called specific heat capacity or specific heat.

*Thus, the specific heat capacity or specific heat of a substance is defined as the amount of heat required to raise the temperature of 1 gram of the substance through  $1^\circ\text{C}$ . It is usually denoted by  $c$ .*

The heat  $q$  required to raise the temperature of a sample of mass  $m$  having specific heat ' $c$ ' from  $T_1$  to  $T_2$  is given by

$$q = mc(T_2 - T_1) = mc \Delta T$$

In terms of heat capacity  $C$ , expression is  $q = C \Delta T$

In chemistry, we generally take the amount of a substance as 1 mole. Then the heat involved is called molar heat capacity. For gases, there are two types of molar heat capacities.

- (i) **Molar heat capacity at constant pressure ( $C_p$ ):** It is defined as the amount of heat required to raise the temperature of one mole of a gas through  $1^\circ\text{C}$  when the pressure is kept constant.
- (ii) **Molar heat capacity at constant volume ( $C_v$ ):** It is defined as the amount of heat required to raise the temperature of one mole of a gas through  $1^\circ\text{C}$  when the volume of the system is kept constant.

## Relation between $C_p$ and $C_v$ for an ideal gas

If  $C_v$  is the molar heat capacity of a gas at constant volume, then the heat  $q_v$  involved in the temperature change  $\Delta T$  is given by  $q_v = C_v \Delta T$ .

$$\text{But } q_v = \Delta U \quad \therefore \Delta U = C_v \Delta T$$

If  $C_p$  is the molar heat capacity at constant pressure, then  $q_p = C_p \Delta T$

$$\text{But } q_p = \Delta H \quad \therefore \Delta H = C_p \Delta T$$

$$H = U + PV$$

For 1 mole of an ideal gas  $PV = RT$

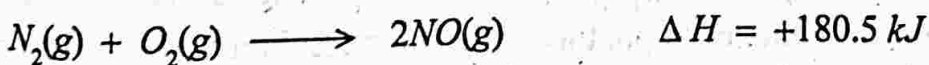
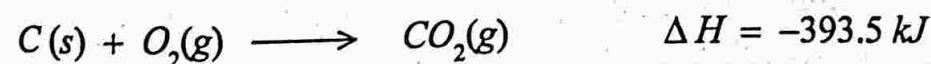
$$\therefore \Delta H = \Delta U + R \Delta T$$

Putting the values of  $\Delta H$  and  $\Delta U$ , we get  $C_p \Delta T = C_v \Delta T + R \Delta T$

$$\text{i.e., } C_p = C_v + R \quad \text{or} \quad C_p - C_v = R$$

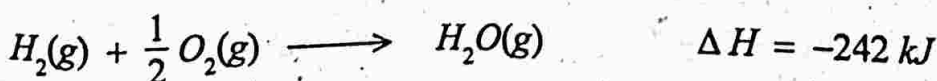
## Thermochemical equations

A chemical equation which indicates the enthalpy change occurring during the reaction is called the thermochemical equation. i.e., writing  $\Delta H = -ve$  for exothermic reactions and  $\Delta H = +ve$  for endothermic reactions. For example,

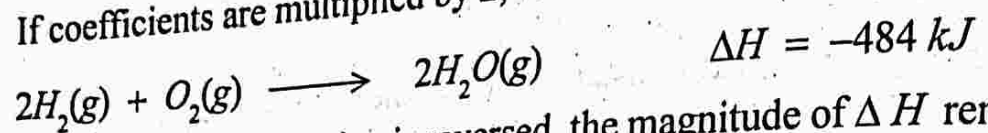


## Some important conventions about thermochemical equations

- (i) For exothermic reactions,  $\Delta H$  is negative and for endothermic reactions,  $\Delta H$  is positive.
- (ii) In thermochemical equations, physical states of the reactants and products should be specified.
- (iii) When the coefficients in the chemical equation are multiplied or divided by some number, the  $\Delta H$  value must also be multiplied or divided by the same number. For example, in the equation



If coefficients are multiplied by 2, we would write the equation



(iv) When a chemical equation is reversed, the magnitude of  $\Delta H$  remains the same, but its sign is reversed. If  $\Delta H$  is positive for the forward reaction, it would be negative for the reverse reaction.

### Enthalpy of a reaction or reaction enthalpy

The enthalpy of a reaction is the enthalpy change accompanying the reaction when the number of moles of reactants react completely to give the products. It is represented by  $\Delta_r H$  or  $\Delta_r H$ .

It is the difference between the enthalpies of products and reactants

$$\Delta_r H = \text{Sum of enthalpies of products} - \text{Sum of enthalpies of reactants.}$$

### Standard enthalpy of reactions

Reaction enthalpies depend on the conditions under which a reaction is carried out. It is, therefore, necessary to specify some standard condition for the comparison of enthalpies of reactions. According to thermodynamic convention, a substance is said to be in standard state when it is present in the pure form at a pressure of 1 bar. The enthalpy change for a reaction when all the participating substances are in their standard states is called standard enthalpy of the reaction. It is denoted as  $\Delta H^\theta$  or  $\Delta_r H^\theta$ .

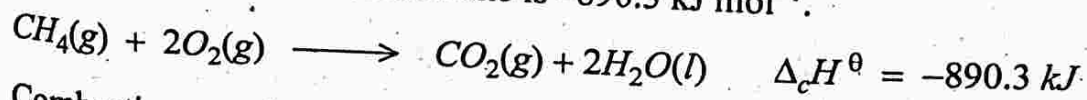
### Different types of enthalpy of reactions

The term 'enthalpy of reaction' is a general term used for the heat change accompanying any reaction. Depending upon the nature of the reaction, there can be different types of enthalpies of reactions.

#### 1. Enthalpy of combustion or heat of combustion

Standard enthalpy of combustion is defined as the enthalpy change accompanying the complete combustion of one mole of the substance in excess of air or oxygen when all the reactants and products are in their standard states at the specified temperature. It is denoted as  $\Delta_c H^\theta$ .

For example, the complete combustion of one mole of methane evolves 890.3 kJ of heat. Thus, the enthalpy of combustion of methane is  $-890.3 \text{ kJ mol}^{-1}$ .



Combustion reactions are always accompanied by the evolution of heat. Hence enthalpy of combustion is always negative.

**Example 6.5.** A cylinder of cooking gas contains 14.0 kg of butane. If a family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last? The enthalpy of combustion of butane is  $-2658 \text{ kJ mol}^{-1}$ .

**Solution:** Molecular mass of butane ( $\text{C}_4\text{H}_{10}$ ) = 58

$\therefore$  1 mole of butane = 58 g

58 g of butane on combustion gives 2658 kJ of heat

$\therefore$  Heat evolved by the combustion of 14.0 kg of butane =  $\frac{2658 \times 14 \times 1000}{58} \text{ kJ}$

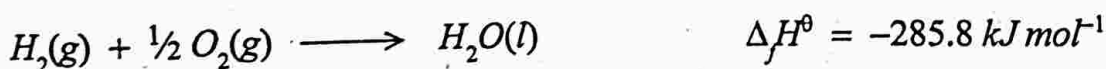
Energy requirement per day = 20000 kJ

$\therefore$  Number of days for which the cylinder would last

$$= \frac{2658 \times 14.0 \times 1000}{58 \times 20,000} = 32 \text{ days}$$

## 2. Enthalpy of formation

The standard enthalpy of formation of a compound is defined as the enthalpy change accompanying the formation of one mole of the compound from its constituent elements, in their most stable state (known as standard reference state). It is denoted by  $\Delta_f H^\circ$ . For example, the enthalpy of formation of  $\text{H}_2\text{O}(\text{l})$  and  $\text{CH}_4(\text{g})$  are  $-285.8 \text{ kJ mol}^{-1}$  and  $-74.8 \text{ kJ mol}^{-1}$  respectively. They may be represented as



It may be noted that the reference state of carbon is graphite

The standard enthalpy of formation of  $\text{HBr}(\text{g})$  is half of  $\Delta_r H^\circ$  of the following reaction because two moles of  $\text{HBr}$  are formed in the equation.



$$\therefore \Delta_f H^\circ \text{ of } \text{HBr}(\text{g}) = \frac{\Delta_r H^\circ}{2} = \frac{-72.8}{2} = -36.4 \text{ kJ mol}^{-1}$$

By convention, the standard enthalpy of formation of all elements in their standard states are assumed to be zero.

Standard state or reference state of an element is its most stable state at 25°C and 1 bar pressure. For example, the reference state of carbon and sulphur are  $C_{\text{graphite}}$  and  $S_{\text{rhombic}}$  respectively.

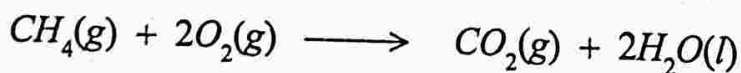
### Importance of standard enthalpies of formation

The knowledge of standard enthalpies of various substances is useful for calculating the standard enthalpies of a reaction. It is given by the relation

$$\begin{array}{rcl} \text{Standard enthalpy} & & \text{Standard enthalpies} \\ \text{change of a} & = & \text{of formation of} \\ \text{reaction} & & \text{products} \end{array} - \begin{array}{r} \text{Standard} \\ \text{enthalpies} \\ \text{of formation of} \\ \text{reactants.} \end{array}$$

$$\text{i.e., } \Delta_r H^\theta = \Delta_f H^\theta (\text{products}) - \Delta_f H^\theta (\text{reactant})$$

**Example 6.6.** Calculate the standard enthalpy change for the reaction



Given that the standard enthalpies of formation of  $CH_4(g)$ ,  $CO_2(g)$ , and  $H_2O(l)$  are  $-74.8 \text{ kJ mol}^{-1}$ ,  $-393.5 \text{ kJ mol}^{-1}$  and  $-285.8 \text{ kJ mol}^{-1}$  respectively.

**Solution:**  $\Delta_r H^\theta$  for the reaction is given as  $\Delta_r H^\theta = \Delta_f H^\theta (\text{products}) - \Delta_f H^\theta (\text{reactants})$

$$\text{i.e., } \Delta_r H^\theta = [\Delta_f H^\theta (CO_2) + 2\Delta_f H^\theta (H_2O(l))] - [\Delta_f H^\theta (CH_4) + 2\Delta_f H^\theta (O_2)]$$

$$\Delta_f H^\theta (O_2) = 0 \quad (\text{By convention})$$

Substituting all the given values of heat of formation, we get

$$\Delta_r H^\theta = [-393.5 + 2(-285.8)] - [-74.8 + 2 \times 0] = -965.1 + 74.8 = -890.3 \text{ kJ mol}^{-1}$$

### 3. Enthalpy of Solution

The enthalpy of solution of a substance in a particular solvent is defined as the enthalpy change when 1 mole of the substance is dissolved in a specified amount of the solvent. It has been found that the dissolution of certain solutes in water is endothermic while that of some others is exothermic. For example, dissolution of ammonium nitrate, ammonium chloride etc. in water involve absorption of heat (endothermic)

