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Military Institute of Science and Technology

Fundamentals of Chemistry

CHEM 101

Thermochemistry

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Thermochemistry



Thermochemistry is concerned with the quantities of heat transections (evolved or absorbed) during chemical reactions and/or phase changes such as melting and boiling.



The energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and the formation of new bonds. Thus, thermochemistry provides useful information regarding the **bond energies**.

What is Heat?

A form of energy that is transferred between two objects (systems) as a result of a temperature difference.

So, What about temperature?

It is a property of a substance or system

while heat is a form of energy

Temperature is the degree Celsius (°C) or Kelvin (K), while the unit of measurement for heat energy is the joule (J).

Heat



Heat energy from the gas burner warms the water

Temperature



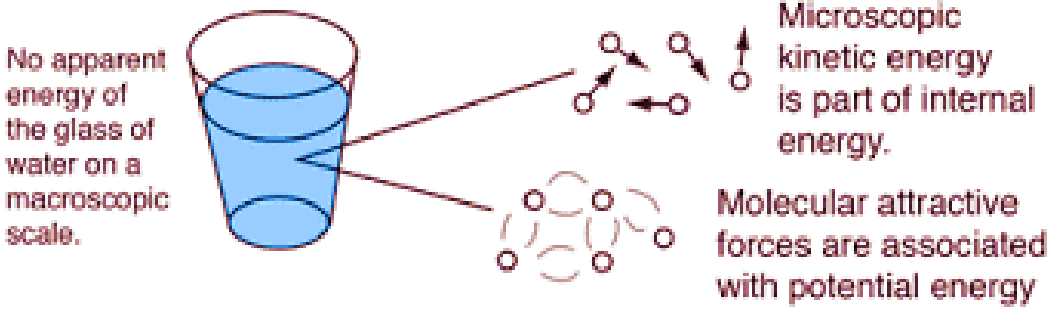
A thermometer is measuring the Temperature of the warmed water

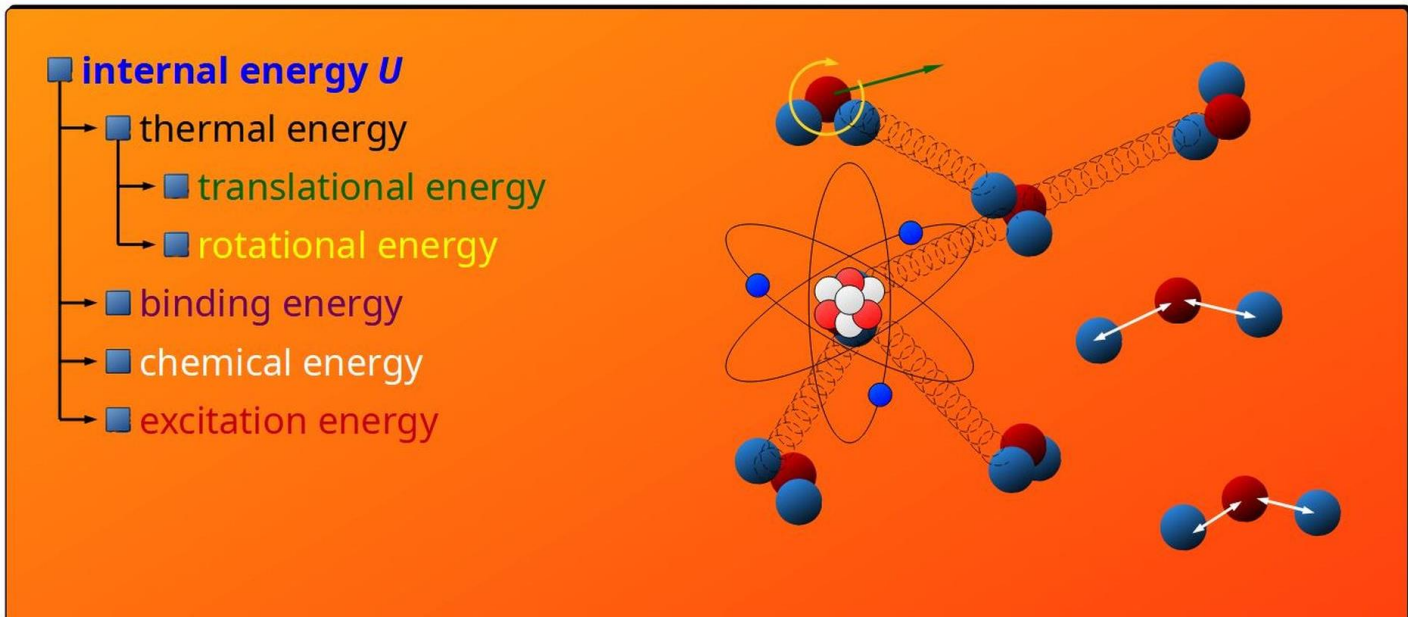
Internal Energy

Every substance has a definite amount of energy known as the **intrinsic energy or internal energy**, E. Its exact value cannot be determined but the change in internal energy, ΔE, can be accurately measured experimentally.

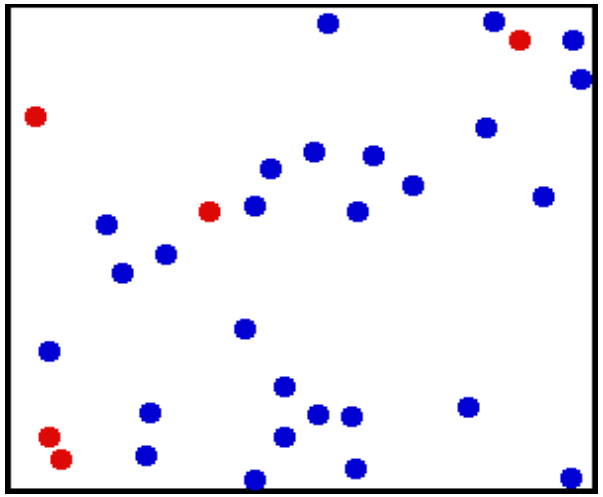
$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$
$$\Delta E = E_p - E_r$$

Does a glass of water sitting on a table have any energy?

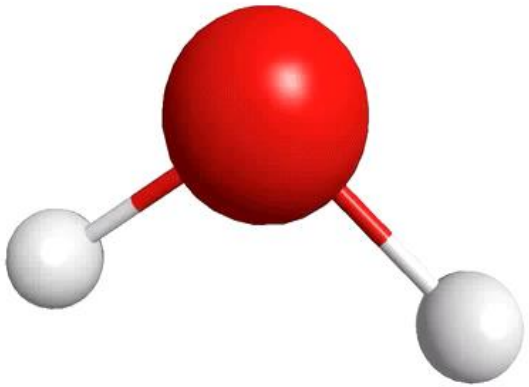




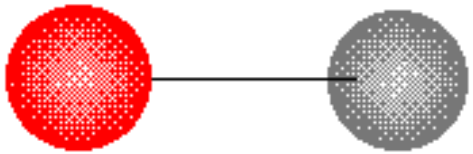
Internal Energy



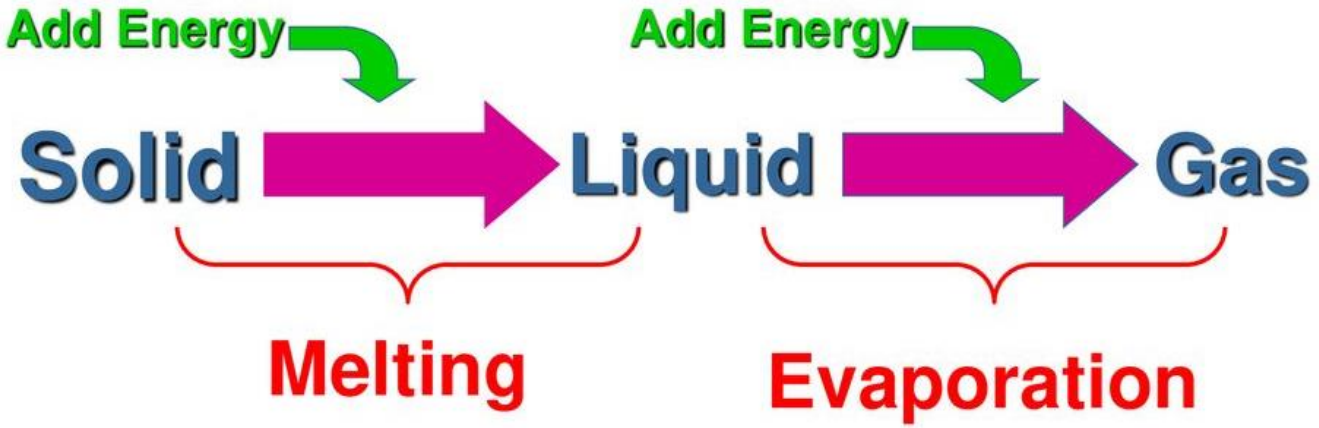
Transitional Motion



Vibrational Motion



Rotational Motion



Enthalpy

Thermochemical measurements are made either at (a) constant volume or (b) constant pressure.

At **constant volume**, The change in internal energy (ΔE) is the heat change accompanying a chemical reaction because no external work is performed.

At **constant pressure**, not only does the change in internal energy take place but **work is also involved** because of expansion or contraction.

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.**

Enthalpy

A change in enthalpy (ΔH) accompanying a process can be measured accurately and is given by the expression

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

Thus if ΔV be the change in volume in case of a reaction at constant temperature and pressure, the thermal effect observed will be the sum of the change in internal energy (ΔE) and the work done in expansion or contraction. That is,

$$\Delta H = \Delta E + P \times \Delta V$$

Therefore, while the heat change in a process is equal to its change in internal energy ΔE at constant volume, it gives at constant pressure the enthalpy change ΔH.

For reactions involving solids and liquids only the change in volume (ΔV) is very small and the term $P \times \Delta V$ is negligible. For such reactions ΔH is equal to ΔE. In case of gases, however, we must specify whether the reaction has taken place at constant volume or at constant pressure because the value of $P \times \Delta V$ is appreciable. Most of such reactions are, however, studied at constant pressure and change in enthalpy (ΔH) is involved.

Calculation of ΔH from ΔE

Let us consider a reaction

$$aA + bB \longrightarrow cC + dD$$

Change in number of moles

$$= \text{No. of moles of products} - \text{No. of moles of reactants}$$

$$= (c + d) - (a + b)$$

$$= \Delta n$$

Let the volume occupied by one mole of the gas be V. Then, change in volume, ΔV = change in No. of moles × volume occupied by one mole of the gas.

$$\Delta V = \Delta n \times V$$

or $$P \times \Delta V = P\,(\Delta n \times V)$$ [Multiplied by P on both sides]

$$P \times \Delta V = PV \times \Delta n \quad \ldots(ii)$$

But $$PV = RT$$ (for one mole of gas)

Putting RT in place of PV in equation (ii) we get

$$P\Delta V = RT\,\Delta n$$

Substituting the value of $P\Delta V$ in equation (i) we get

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

Numericals

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. ($R = 2$ cal degree^{-1} mol^{-1})

SOLUTION

The chemical equation for the combustion of ethylene is

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$$

1 mole 3 moles 2 moles negligible volume.

No. of moles of the products $= 2$

No. of moles of the reactants $= 4$

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

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

Given that $\Delta E = -332.19$ kcal

$T = 273 + 17 = 290$ K

$R = 2$ cals $= 2 \times 10^{-3}$ kcals

$\therefore \quad \Delta H = -332.19 + 2 \times 10^{-3} \times -2 \times 290$

$= \mathbf{-333.3\ kcal}$

Numericals

SOLVED PROBLEM 2. The heat of combustion of carbon monoxide at constant volume and at 17°C is – 283.3 kJ. Calculate its heat of combustion at constant pressure ($R = 8.314$ J degree^{-1} mol^{-1}).

SOLUTION

$$CO(g) + \tfrac{1}{2}\, O_2(g) \longrightarrow CO_2(g)$$

1 mole $\frac{1}{2}$ mole 1 mole

No. of moles of products = 1

No. of moles of reactants = $1\frac{1}{2}$

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

$$= 1 - 1\frac{1}{2} = -\frac{1}{2}$$

Given that $\Delta E = -283.3$ kJ

$T = (273 + 17) = 290$ K

and $R = 8.314$ J or 8.314×10^{-3} kJ

Substituting these values in the equation

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

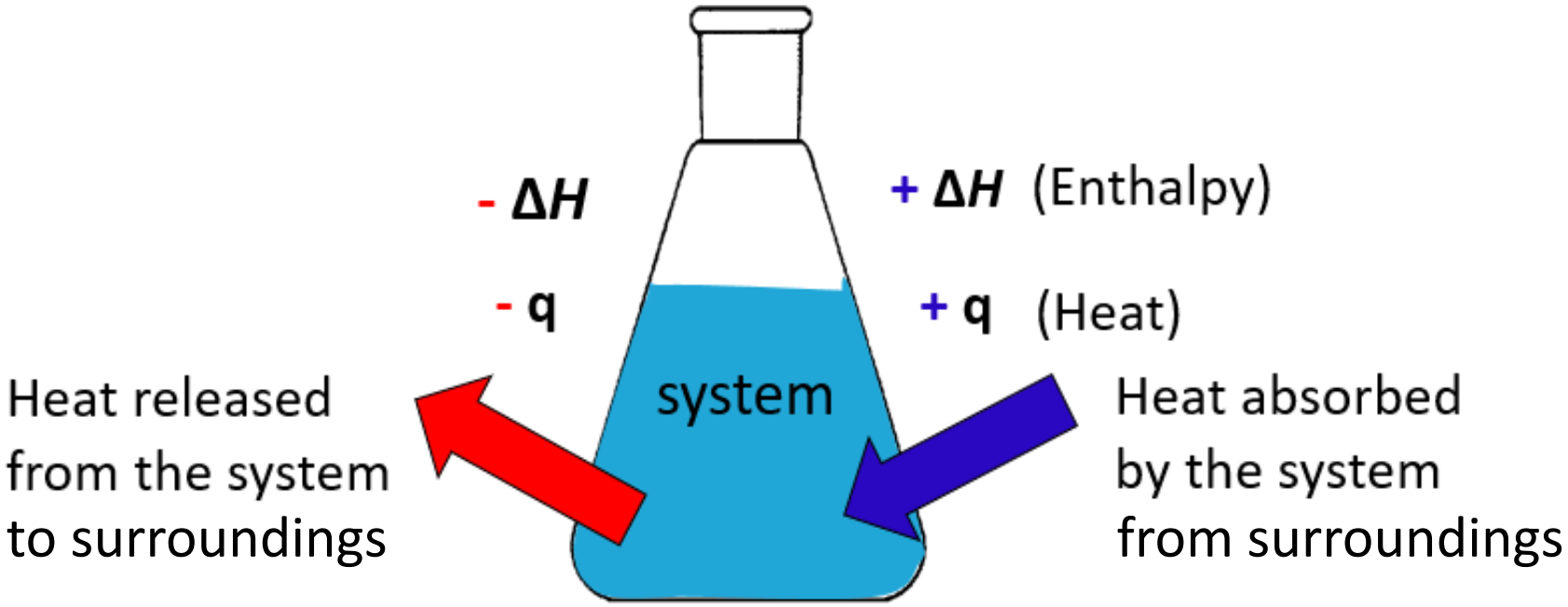
we get $$\Delta H = -283.3 + \left[-\frac{1}{2} \times (8.314 \times 10^{-3}) \times 290 \right]$$

$$= -283.3 - 1.20$$

$$= -284.5 \text{ kJ}$$

∴ Heat of combustion of CO at constant pressure is – **284.5 kJ.**

Exothermic and Endothermic Reaction

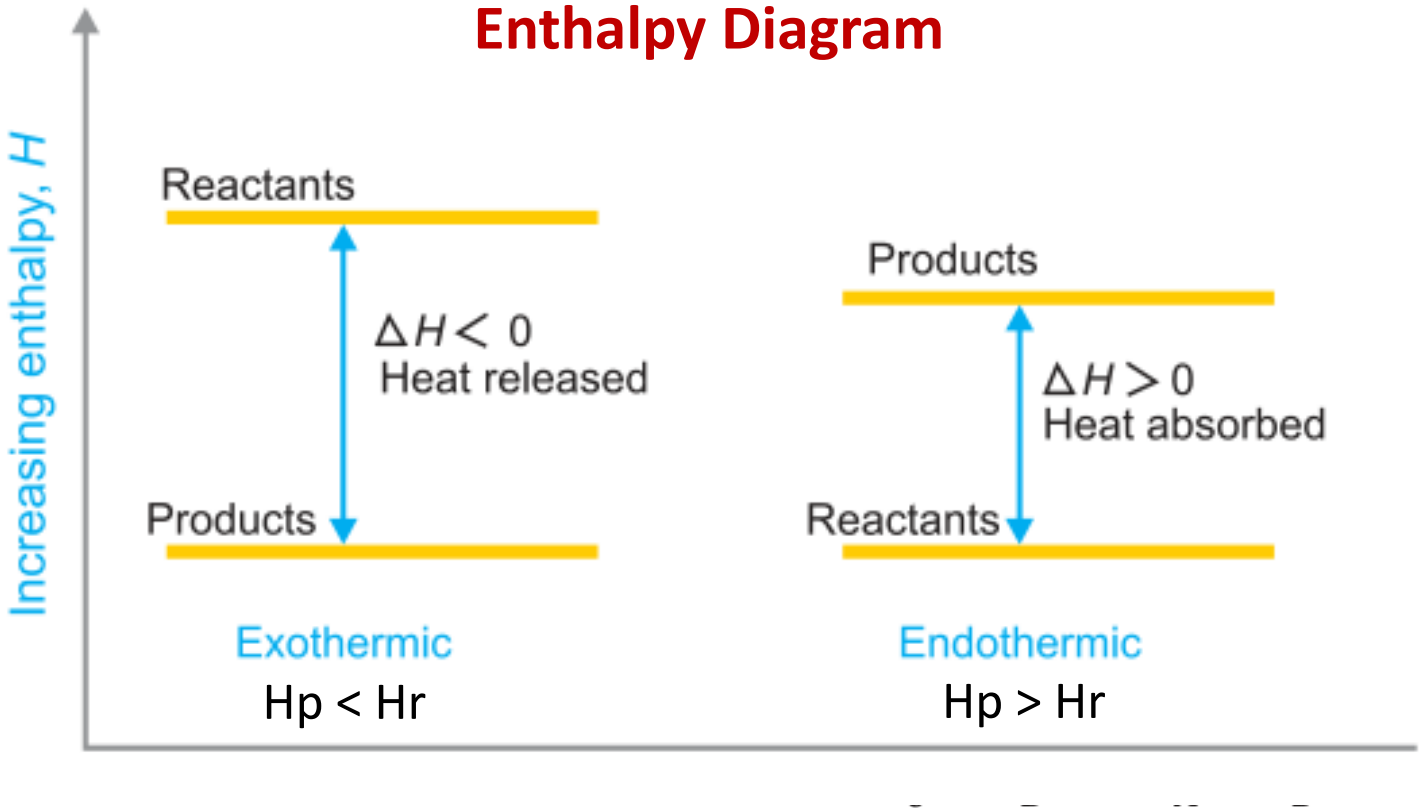


When a reaction results in evolution of heat, it is said to be *exothermic* (energy flows out of system).

When a reaction absorbs energy from the surroundings, it is called an *endothermic* reaction.

Exothermic and Endothermic Reaction

Enthalpy Diagram



When ΔH is positive, the enthalpy of the reactants and an equivalent of heat is absorbed by the system from the surroundings.

The value of ΔH may be either zero, negative or positive. Where ΔH is zero, the enthalpies of the products and reactants being the same, the heat is evolved or absorbed. In case ΔH is negative, the sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.

Heat of Reaction



The heat of a reaction is simply the amount of heat absorbed or evolved in a reaction

The amount of heat absorbed or evolved at constant temperature and pressure is called **enthalpy.**

The amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products.

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -284.5\,kJ$$

Thermochemical equation

An equation which indicates the amount of heat change (evolved or absorbed) in the reaction or process is called a Thermochemical equation.

It must essentially : (*a*) be balanced; (*b*) give the value of ΔE or ΔH corresponding to the quantities of substances given by the equation; (*c*) mention the physical states of the reactants and products. The physical states are represented by the symbols (*s*), (1), (*g*) and (aq) for solid, liquid, gas and gaseous states respectively.

Kirchoff's Equations

The equations representing the variation of heat change of reaction with temperature are known as Kirchoff's equations.

At constant volume, the heat of reaction, ΔE, is given by the relation

$$\Delta E = E_2 - E_1$$

where E_1 and E_2 are the internal energies of the reactants and products.

Differentiating this equation with respect to temperature at constant volume, we get

$$\left[\frac{d(\Delta E)}{dT}\right]_v = \left(\frac{dE_2}{dT}\right)_v - \left(\frac{dE_1}{dT}\right)_v \quad \ldots(1)$$

But we have already seen that

$$\left(\frac{dE}{dT}\right)_v = C_v$$

$$\therefore \quad \frac{d(\Delta E)}{dT} = (C_v)_2 - (C_v)_1 = \Delta C_v \quad \ldots(2)$$

Change in heat of reaction at constant volume per degree change in temperature is equal to the difference in heat capacities at constant volume of products and reactants.

Kirchoff's Equations

$$\frac{d(\Delta E)}{dT} = (C_v)_2 - (C_v)_1 = \Delta C_v \qquad \ldots(2)$$

Integrating the above equation between temperatures T_1 and T_2, we have

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \, dT$$

or
$$\Delta E_2 - \Delta E_1 = \Delta C_v [T_2 - T_1] \qquad \ldots(3)$$

where ΔE_2 and ΔE_1 are heats of reaction at temperatures T_2 and T_1 respectively.

Herein, Eq. (2) and (3) are Kirchoff's Equation

Kirchoff's Equations

Similarly, at **constant pressure** the heat of reaction ΔH is given by the reaction

$$\Delta H = H_2 - H_1$$

where H_2 is the heat content (enthalpy) of the products and H_1 being that of the reactants.

Differentiating with respect to temperature at constant pressure, we have

$$\left(\frac{d(\Delta H)}{dT}\right)_P = \left(\frac{dH_2}{dT}\right)_P - \left(\frac{dH_1}{dT}\right)_P \qquad \ldots(4)$$

According to the equation, we have

$$\left(\frac{dH}{dT}\right)_P = C_P$$

$$\therefore \quad \left(\frac{d(\Delta H)}{dT}\right)_P = (C_P)_2 - (C_P)_1 = \Delta C_P \qquad \ldots(5)$$

where $(C_P)_2$ and $(C_P)_1$ are the heat capacities of products and reactants respectively.

or $$d(\Delta H) = \Delta C_P \times dT$$

Kirchoff's Equations

Change in heat of reaction at constant pressure per degree change of temperature is equal to difference in heat capacities of products and reactants at constant pressure.

$$\left(\frac{d(\Delta H)}{dT}\right)_P = (C_P)_2 - (C_P)_1 = \Delta C_P \qquad \ldots(5)$$

Integrating the equation between temperature T_1 and T_2, we have

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$$

or

$$\Delta H_2 - \Delta H_1 = \Delta C_p \, [T_2 - T_1] \qquad \ldots(6)$$

Herein, Eq. (5) and (6) are Kirchoff's Equation

These equations may be used for calculating heat of reaction at a given temperature when it is known at some other temperature and when the heat capacities of products and reactants are known.

Kirchoff's Equations

SOLVED PROBLEM 1. The heat of reaction $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$ at 27°C is – 22.1 kcal. Calculate the heat of reaction at 77°C. The molar heat capacities at constant pressure at 27°C for hydrogen, chlorine and HCl are 6.82, 7.70 and 6.80 cal mol^{-1} respectively.

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl \qquad \Delta H = -22.1 \text{ kcal}$$

ΔC_P = Heat capacities of products – Heat capacities of reactants

$$= 6.80 - \left[\frac{1}{2}(6.82) + \frac{1}{2}(7.70)\right]$$

$$= 6.80 - 7.26 = -0.46 \text{ cal} = -0.46 \times 10^{-3} \text{ kcal}$$

$$T_2 = 273 + 77 = 350 \text{ K}; \; T_1 = 273 + 27 = 300 \text{ K}$$

$$T_2 - T_1 = (350 - 300) \text{ K} = 50 \text{ K}$$

Substituting these values in Kirchoff's equation, we have

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$= -22.1 + (-0.46 \times 10^{-3}) \times 50$$

$$= -22.1 + (-0.023)$$

$$= -22.123 \text{ kcal}$$

$\therefore$ Heat of reaction at 77°C is – **22.123 kcal**

Heat of Formation

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 ΔH_f. For example, the heat of formation of ferrous sulphide and acetylene may be expressed as :

$$Fe\,(s) + S(s) \longrightarrow FeS(s) \qquad \Delta H_f = -24.0\,\text{kcal}$$

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H_f = +53.14\,\text{kcal}$$

Similarly, the reaction between gaseous hydrogen and gaseous chlorine to form gaseous hydrogen chloride is represented by the equation

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -44.0\,\text{kcal}$$

It may be noted in this case that – 44.0 kcal is not the heat of formation of hydrogen chloride because this amount of heat is evolved when two moles of hydrogen chloride are formed. The heat of formation of hydrogen chloride, therefore, would be – 44.0/2 = – 22.0 kcal and the equation can be written as

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H_f = -22.0\,\text{kcal}$$

Heat of Formation

SOLVED PROBLEM 2. The heat of combustion of ethyl alcohol is – 330 kcal. If the heat of formation of $CO_2(g)$ and $H_2O(l)$ be – 94.3 kcal and – 68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.

SOLUTION

We are given

$$(a) \quad C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -330.0\,\text{kcal}$$

$$(b) \quad C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94.3\,\text{kcal}$$

$$(c) \quad H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -68.5\,\text{kcal}$$

We have to manipulate these equations so as to get the required equation :

$$2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \quad \Delta H = ?$$

where ΔH is the heat of formation of ethyl alcohol.

Multiplying equation (b) by 2 and equation (c) by 3 and adding up these, we get

$$2C(s) + 3H_2(g) + \tfrac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta H = -394.1\,\text{kcal}$$

Subtracting equation (c) from the above equation, we have

$$2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$$

$$\Delta H = -394.1 - (-330.0)$$

Thus the heat of formation of ethyl alcohol is **– 64.1 kcal.**

Heat of Formation

SOLVED PROBLEM 3. Determine ΔH of the reaction

$$C(s) + 2H_2(g) \longrightarrow CH_4(g)$$

from the following data :

$$(i) \quad C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.7\,kJ$$

$$(ii) \quad H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.7\,kJ$$

$$(iii) \quad CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.3\,kJ$$

SOLUTION

Multiplying equation (*ii*) by 2 and adding to equation (*i*), we get

$$(iv) \quad C(s) + O_2(g) + 2H_2(g) + O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H = (2 \times -285.7) + (-393.7)$$

$$= -965.1\,kJ$$

On subtracting equation (*iii*) from equation (*iv*), we get

$$C(s) + 2H_2(g) = CH_4(g) \qquad \Delta H = -965.1 - (-890.3)$$

$$\Delta H = -74.8\,kJ$$

Thus the heat of formation of methane is – **74.8 kJ.**

Standard Heat of Formation



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

Standard Heat of Reaction (ΔH°) from Standard Heat of Formation (ΔH_f^o)

We can calculate the heat of reaction under standard conditions from the values of standard heat of formation of various reactants and products. **The standard heat of reaction is equal to the standard heat of formation of products minus the standard heat of formation of reactants.**

$$\Delta H^\circ = \begin{bmatrix}\text{Total standard heat}\\ \text{of formation of products}\end{bmatrix} - \begin{bmatrix}\text{Total standard heat}\\ \text{of formation of reactants}\end{bmatrix}$$

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

Let us consider a general reaction

$$aA + bB \longrightarrow cC + dD$$

The standard heat of reaction is given by

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

$$= [c \times \Delta H_f^o\,(C) + d \times H_f^o\,(D)] - [a \times \Delta H_f^o\,(A) + b \times \Delta H_f^o\,(B)]$$

Standard Heat of Formation

SOLVED PROBLEM 2. The standard heats of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are – 277.0, –393.5 and –285.5 kJ mol^{-1} respectively. Calculate the standard heat change for the reaction

$$C_2H_5OH(l) + 3O_2(l) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

SOLUTION

We know that :

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

In the present case

$$\Delta H^\circ = [2 \times \Delta H_f^o [CO_2(g)] + 3 \times \Delta H_f^o [H_2O(l)]$$

$$- \Delta H_f^o [C_2H_5OH(l)] + 3 \times \Delta H_f^o [O_2(g)]$$

$$= [2 \times (-393.5) + 3 \times -285.5] - [-277.0 - 0]$$

$$= -1643.5 - (-277)$$

$$= \mathbf{-\ 1366.5\ kJ}$$

Heat of Combustion



The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.

It is denoted by ΔH_c. As for example, heat of combustion of methane is – 21.0 kcal (= 87.78 kJ) as shown by the equation

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -21.0\,\text{kcal}$$

Now consider the chemical equations

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.3\,\text{kcal}$$

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = -26.0\,\text{kcal}$$

Heat of combustion of a substance (ΔH_c) is always negative.

Applications of Heat of Combustion

- **Calculation of heat of formation**

  Since the heats of combustion of organic compounds can be determined with considerable ease, these are employed to calculate their heats of formation.

- **Calorific value of foods and fuels**

  The amount of heat produced in calories (or joules) when one gram of a substance is completely burnt.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -890.3\ \text{kJ}$$

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c = -1559.7\ \text{kJ}$$

In case of methane heat produced per gram is 890.3/16 = 55.64 kJ g^{-1} while for ethane it is –1559.7/30 = 51.90 kJ g^{-1}. Thus methane has better fuel efficiency than ethane as it produces more heat per gram.

- **Deciding constitution**

  Heat of combustion of organic compounds has thus proved very valuable in deciding their chemical constitution.

Numericals

SOLVED PROBLEM. Calculate the standard heat of formation of propane (C_3H_8) if its heat of combustion is – 2220.2 kJ mol^{-1}. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.5 and – 285.8 kJ mol^{-1} respectively.

SOLUTION

We are given

$$(i)\quad C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H_c = -2220.2\,kJ$$

$$(ii)\quad C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\,kJ$$

$$(iii)\quad H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8\,kJ$$

We should manipulate these equations in a way so as to get the required equation

$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H = ?$$

Multiplying equation (*ii*) by 3 and equation (*iii*) by 4 and adding up we get

$$3C(s) + 3O_2(g) \longrightarrow 3CO_2(g) \qquad \Delta H = -1180.5\,kJ$$

$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l) \qquad \Delta H = -1143.2\,kJ$$

$$(iv)\quad 3C(s) + 4H_2(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2323.7\,kJ$$

Subtracting equation (*i*) from equation (*iv*), we have

$$3C(s) + 4H_2(g) + 5O_2(g) - 5O_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H = -103.5\,kJ$$

$\therefore$ The heat of formation of propane is – **103.5 kJ mol^{-1}.**

Heat of Neutralization



The change in the 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.

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l) \qquad \Delta H = -13.69\ \text{kcal}$$

$$HNO_3(aq) + KOH(aq) \longrightarrow KNO_3(aq) + H_2O(l) \qquad \Delta H = -13.87\ \text{kcal}$$

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H = -13.68\ \text{kcal}$$

$$HCl(aq) + LiOH(aq) \longrightarrow LiCl(aq) + H_2O(l) \qquad \Delta H = -13.70\ \text{kcal}$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H = -13.7\ \text{kcal}$$

Thus the heat of neutralisation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxyl ions.

The heat of neutralisation of a strong acid and strong base is **–13.7 kcal (57.32 kJ)**

Heat of Neutralization

When weak acids or weak bases are neutralised by strong bases or strong acids respectively, the heat of neutralisation differs widely from – 13.7 kcal.

$$HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(l) \qquad \Delta H = -12.3\ \text{kcal}$$
$$HCN(aq) + NaOH(aq) \longrightarrow NaCN(aq) + H_2O(l) \qquad \Delta H = -12.3\ \text{kcal}$$
$$HNO_3(aq) + NH_4OH(aq) \longrightarrow NH_4NO_3(aq) + H_2O(l) \qquad \Delta H = -12.3\ \text{kcal}$$

In such cases, the neutralisation process involves not only the union of hydrogen and hydroxyl ions but also the dissociation/ionization of the weak acid or base.

$$NH_4OH(aq) \longrightarrow NH_4^+(aq) + OH^-(aq) \qquad \Delta H = Q\ \text{kcal}$$
$$\text{and} \quad H^+(aq) + OH^-(aq) + Cl^-(aq) \longrightarrow H_2O(l) + Cl^-(aq) \qquad \Delta H = -13.7\ \text{kcal}$$

$$NH_4OH(aq) + H^+(aq) + Cl^-(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq) + H_2O(l) \quad \Delta H = Q - 13.7\ \text{kcal}$$

But the measured heat of neutralisation is – 12.3 kcals. Therefore,

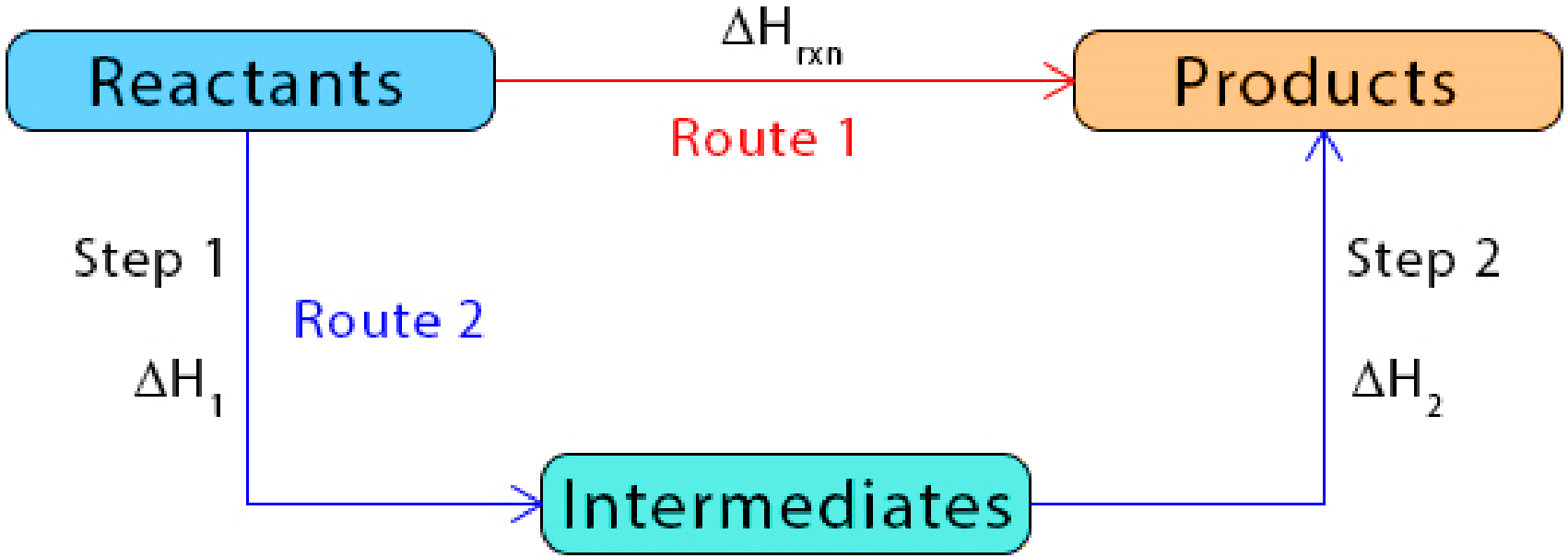
$$Q - 13.7 = -12.3$$
$$Q = 13.7 - 12.3 = 1.4\ \text{kcal}$$

The heat of dissociation of NH_4OH; 1.4 Kcal is absorbed when 1 mole of NH_4OH is dissociated into ions.

Laws of Thermochemistry

Hess's Law

Total enthalpy change (ΔH) of a reaction equals to the sum of all the enthalpy changes occurring in each step of the reaction



$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2$$

Examples of Hess's Law

This law is a manifestation that enthalpy is a state function.

A state function is a property of a system that depends only on the current state or condition of the system, and not on the path taken to reach that state.

