CHEMICAL THERMODYNAMICS

Heat capacity

To increase the temperature of a body, we have to supply heat to it. But the rise in temperature is not the same for all bodies for the same amount of heat supplied.

If we supply the same amount of heat ot 400 g and 700 g of water we find the rise in temperature is more in the former than in the latter case.

If equal masses of water and milk are supplied with the same amount of heat the rise in temperature of milk is more than that of water.

This rise in temperature and heat supplied to a body are related by a term called heat capacity or thermal capacity of body. It is denoted by ‘C’.

It is defined as an amount of heat needed to raise the temperature of a given mass of a body by 1 K or 1℃.

It is equal to the ratio of total heat supplied to the total rise in temperature of a body.

Let Q joule of heat be supplied to a body so that its temperature rise by $\Delta\theta$ K. Then heat capacity (C) of the body = $\frac{Q}{\Delta T}$

$$\therefore\ C = \frac{Q}{\Delta T}$$

Thus units of heat capacity = $\frac{\text{Unit of heat}}{\text{Unit of Temperature}}$

Hence S.I. unit of heat capacity is $\frac{\text{Joule}}{\text{Kelvin}}$ $(J\ K^{-1})$

Specific heat

You may have noticed that some food items remain hotter much longer than others do. If you remove a piece of toast from a toaster and pour hot soup into a bowl at the same time, a few minutes later the soup is still warm, while the toast has almost cooled off. If we heat a cup of water on a stove, it may require 5-10 minutes to raise it from room temperature to its boiling temperature (100 ℃). But, if we put a piece of copper of same mass on the same flame, it may rise through the same temperature range in only about 2 minutes. For silver, the time may be less than a minute. This means ‘different materials require different quantities of heat to raise the temperature of a given mass of the material for the same change in temperature’.

The amount of heat required for a unit increase in the temperature of unit mass of a substance is called it’s **specific heat**.

Heat absorbed or released by a substance, $\mathbf{Q = m\ c\ \Delta t}$

Where, m = mass of the substance ; c = specific heat of the substance ;

Δt = change in temperature of the substance.

SI Unit of specific heat : J/kg/K or J $kg^{-1}\ K^{-1}$.

Some other commonly used units are J/kg/℃ , J/g/℃, Cal/g/℃.

Specific heat depends on the state of substance i.e., solid, liquid or gas. For example, specific heats of water, ice and steam are different.

Specific heat	Cal g^{-1} ℃$^{-1}$	J kg^{-1} ℃$^{-1}$
Ice	0.5	2100
Water	1.0	4200
Steam	0.47	1970

BUILDING CONCEPTS

Why sand heats up (or cools down) faster than water ?

Explanation

Less heat is needed to change the temperature of a material with a low specific heat than one with a high specific heat. The sand on a beach has a lower specific heat than water. When you are at the beach during the day, the sand feels much warmer than the water does. Sun rays warms the sand and the water. Because of its lower specific heat, the sand heats up faster than the water. At night, however, the sand feels cool and the water feels warmer. This is because at night, both sand and water loose heat energy but the temperature of the water changes more slowly than the temperature of the sand. Specific heat signifies the resistance (opposition) of a substance to a change in its temperature.

Water has a much higher capacity for storing energy than most of the common materials. A small amount of water absorbs a large quantity of heat for a small temperature rise. Because of this, water is a very useful cooling agent and is used in the cooling systems of automobiles and other engines. If a liquid of lower specific heat capacity were used in cooling systems, its temperature would rise higher for the same absorption of heat. Water also takes a long time to cool, thus, hot-water bottles were employed in early times on cold winter nights. This tendency on the part of water to resist changes in temperature improves the climate in many locations.

CHECK YOUR CONCEPTS

1. Why does a piece of water melon stay cool for a longer time than sandwiches when both of them a taken out from the refrigerator on a hot day ?

2. Why is water used in hot water bags ?

3. Why the coastal area have a cooler summer and a milder winter than inland areas ?

NUMERICAL ABILITY

1. How many joules of heat must be given to heat 5 kg of water from 10 °C to 75 °C ?

Take, specific heat of water = 4200 J/kg/°C.

Solution

Given, mass of water, m = 5 kg ; specific heat of water, c = 4200 J/kg/°C ; change in temperature, $\Delta t = 75 - 10 = 65$ °C

Now, $Q = m\,c\,\Delta t = 5 \times 4200 \times 65 = 1365000$ J = $\mathbf{1.365 \times 10^6}$ **J**

2. How many joules of heat must be removed from 15 kg of copper to lower its temperature from 225 °C to 25 °C ?

Take, specific heat of copper = 385 J/kg/°C

Solution

Given, mass of copper, m = 15 kg ; specific heat of copper,

c = 385 J/kg/°C ;

change in temperature, $\Delta t = 225 - 25 = 200$ °C

Now, $Q = m\,c\,\Delta t = 15 \times 385 \times 200 = 1155000$ J = $\mathbf{1.115 \times 10^6}$ **J**

3. If we take 15 g of water and add 60 cal of heat to it, what is the rise in temperature ? Take specific of water = 1 cal/g/°C

Solution

Given, mass of water, m = 15 g ; specific heat of water, c = 1 cal/g/°C ;

Heat added, Q = 60 cal ; rise in temperature, Δt = ?

Now, $Q = m\,c\,\Delta t$ or $\Delta t = \dfrac{Q}{mc} = \dfrac{60}{15 \times 1} = \mathbf{4}$ **°C**

Differences between the heat capacity and specific heat capacity

	Heat capacity		Specific heat capacity
1	It is the amount of heat energy required to raise the temperature of entire body by 1℃	1	It is the amount of heat energy required to raise the temperature of unit mass of the body by 1 ℃.
2	It depends on the material and mass of the body. More the mass of the body, more is its heat capacity.	2	It does not depent on the mass of the body. It is the characteristic of the material of the body.
3	Its unit is J K^{-1}.	3	Its unit is J kg^{-1} K^{-1}.
4	Heat capacity C' = mass m × specific heat capacity C.	4	Specific heat capacity C $\boxed{= \frac{\text{heat capacity } C'}{\text{mass } m}}$

Calorimeter

Heat is a form of energy. Like other forms of energy, it can be measured. The branch of physics which deals with the measurement of heat is called calorimetry.

The device which is used to measure quantity of heat is called **calorimeter**. It uses the principle of mixture to find the specific heat capacity of different bodies. Hence the method is also called the method of mixtures.

Calorimeter consists of a thin cylindrical vessel. Its outer and inner surfaces are highly polished to prevent heat loss by radiation. The copper vessel is kept in rectangular wooden box and space between them is filled with materials like asbestos or cotton wool which are good insulators of heat. This prevents heat loss by conduction. At its top, the box has a wooden lid with two holes, one four inserting a thermometer and the other for a stirrer which is also made of copper. The lid is coated with tin or aluminum foil.

Principle of calorimetry

The branch of physics that deals with determination of specific heats, heat absorbed or released during a process, calorific values of combustible substances is called **calorimetry**.

When one body is kept in contact with another body, the body at higher temperature loses heat and the body at lower temperature gains heat such that finally both of them has same temperature. Such a temperature is called **equilibrium temperature**.

According to principle of calorimetry, when two bodies at different temperature are mixed together or kept in direct contact, heat will be transferred from body at higher temperature to the body at lower temperature till they acquire same temperature ; heat lost by hot body is equal to the heat gained by the cold body. Let two substances of specific heats c_1, c_2 ; temperature t_1, t_2 and masses m_1, m_2 respectively are kept in contact with each other. Let $t_1 > t_2$, after some time both the attain a final temperature t_e, then $t_1 > t_e > t_2$. According to principle of calorimetry,

heat gained by cold body = heat lost by hot body

$m_2c_2(t_e - t_2) = m_1c_1(t_1 - t_e)$

On solving, we get,

$$\boxed{t_e = \frac{m_1c_1t_1 + m_2c_2t_2}{m_1c_1 + m_2c_2}}$$

NUMERICAL ABILITY

1. 400 g of water at 100 ℃ is mixed with 200 g of water at 40 ℃. Find final temperature of the mixture.

Solution

Let the final temperature of the mixture be t ℃.

heat lost by water at 100 ℃,

Q_1 = mass × specific heat capacity × fall in temperature

= [400 × 4.2 × (100 – t)]J

heat gained by water at 40 °C,

Q_2 = mass × specific heat capacity × rise in temperature

$= [200 \times 4.2 \times (t - 40)]J$

By the principle of calorimetry, $Q_1 = Q_2$

so $400 \times 4.2 \times (100 - t) = 200 \times 4.2 \times (t - 40)$

or $600\,t = 48000$

or $t =$ **80 °C**

2. 2 litres of water at 80 °C is poured into a plastic bucket containing 10 litres of water at 20 °C. What is the final temperature of water ?

Solution

We know that 1 litre of water = 1 kg of water, thus, $m_1 = 2$ kg and $m_2 = 10$ kg. Also, $t_1 = 80$ °C ; $t_2 = 20$ °C

Since water is added to water i.e. same liquids are mixed together thus, $c_1 = c_2 = c$ (let).

Final temperature of solution,

$$t_e = \frac{m_1c_1t_1 + m_2c_2t_2}{m_1c_1 + m_2c_2} = \frac{m_1ct_1 + m_2ct_2}{m_1c + m_2c} = \frac{c(m_1t_1 + m_2t_2)}{c(m_1 + m_2)} = \frac{m_1t_1 + m_2t_2}{m_1 + m_2}$$

or $t_e = \frac{(2)(80) + (10)(20)}{2 + 10} = \frac{160 + 200}{12} = \frac{360}{12} =$ **30 °C**

3. If we take 15 g of water and add 60 cal of heat to it, what is the rise in temperature ? Take specific of water = 1 cal/g/°C

Solution

Given, mass of water, m = 15 g ; specific heat of water, c = 1 cal/g/°C ;

Heat added, Q = 60 cal ; rise in temperature, Δt = ?

Now, $Q = m\,c\,\Delta t$

or $\Delta t = \frac{Q}{mc} = \frac{60}{15 \times 1} =$ **4 °C**

Change of state (change of phase)

When heat energy is added to a material, the heat energy of the material increases. Then the temperature of the material increases. After achieving a certain temperature, the material changes from one state of matter to another. Heat energy must be added to a material or taken away to change it from one state of matter to another.

Changes between the solid and liquid states

The particles that make up the liquid and the solid are exactly the same. The difference between the liquid and the solid depends on the movement of the particles and the heat energy they contain. Particles in the liquid move faster and have more heat energy. Particles in the solid move more slowly and have less heat energy.

Melting

Melting occurs when a solid changes into a liquid. When you heat a solid, heat energy flows into the solid. Then the temperature of the solid increases until the temperature reaches the melting point.

The melting point of a material is the temperature at which the material changes from a solid to a liquid.

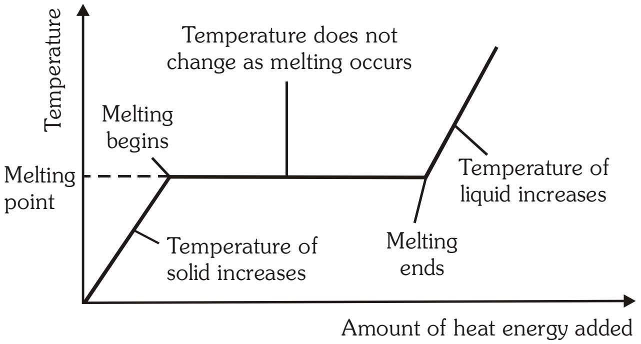


Fig.6 Changing solid to liquid by addition of heat energy

Fig.6 shows how the temperature of a solid material changes as it is heated. At first, the temperature of the solid increases. But when the temperature reaches the melting point, the temperature of the material stops increasing. As the material changes from a solid to a liquid, the temperature stays constant at the melting point.

Changes during melting

Heat energy still is being added to the material as it melts. Because the temperature is not changing, the average speed of the particles doesn't change. The added heat energy causes the attractive forces between particles to become weaker and thus, particles move farther apart. When melting occurs, these forces have become so weak that the particles can move freely from one place to another. After the solid has changed completely into a liquid, adding heat energy causes the temperature of the liquid to increase.

Freezing

Freezing occurs when a liquid changes into a solid. When a material cools, heat energy flows out of the material. The temperature of the material decreases until the freezing point is reached.

The freezing point is the temperature at which the liquid changes to a solid.

As heat energy continues to flow out of the material (see fig.7), the temperature remains constant at the freezing point. After all the liquid has changed to a solid, the temperature decreases once again as heat energy is removed.

Freezing is opposite of melting

While freezing is occurring, heat energy is being removed from the material. The temperature remains constant, so the average speed of the particles doesn't change. Removal of heat energy causes the particles move closer together. Then the attractive forces between the particles become so strong that particles are held in fixed positions. The liquid becomes a solid.

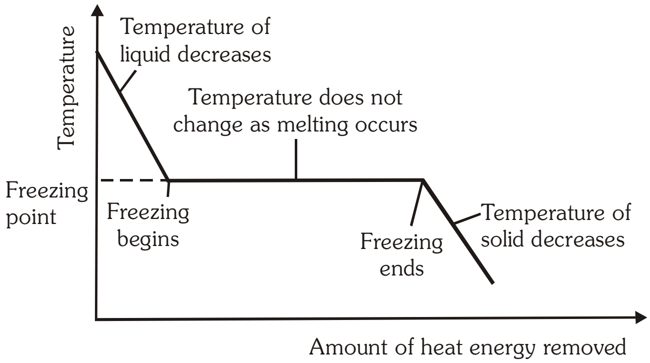


Fig.7 Changing liquid to solid by removal of heat energy

Changes between liquid and Gaseous state

If you heat a pot of water on the stove, you will notice bubbles forming in the water. Tiny water droplets in the form of steam rise into the air. Water in its invisible gas form, called water vapour, rises from the pot. The liquid is changing to a gas.

Vaporisation and boiling

When liquid water is heated, its temperature rises until it reaches 100°C. At this temperature, liquid water changes into water vapour. The change from a liquid to a gas is called 'vaporization'. When vaporization occurs, the attractive forces between particles are too weak to keep particles close to each other. Particles spread out and move independently.

Vaporization can occur within a liquid and at the surface of a liquid (see fig.8).

Vaporization that occurs within a liquid is called 'boiling'. When a liquid boils, bubbles form within the liquid. These bubbles contain particles of the material in the gaseous state.

The boiling point is the temperature at which boiling occurs in a liquid.

Fig.9 shows that the temperature doesn't change while a liquid is boiling. Boiling ends after the liquid has changed to a gas. If thermal energy continues to be added, then the temperature of the gas will continue to rise.

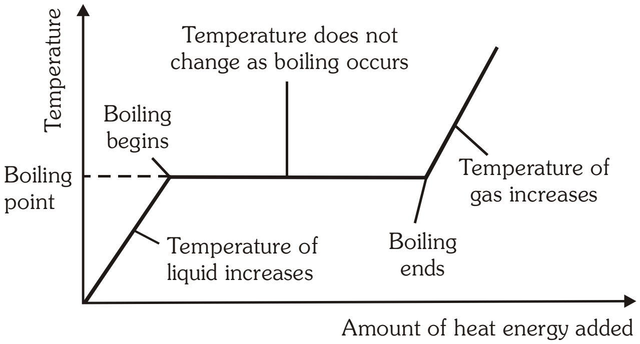


Fig.9 Changing liquid to gas by addition of heat energy

Changes during vaporisation (boiling)

Heat energy still is being added to the material as it vaporises (boils). Because the temperature is not changing, the average speed of the particles doesn't change. The added heat energy causes the attractive forces between particles to become weaker and thus, particles move farther apart. When boiling occurs, these forces have become so weak that the particles can move more freely from one place to another. After the liquid has changed completely into a gas, adding heat energy causes the temperature of the gas to increase (see fig.9).

Condensation

On a hot day, you might have see drops of water on the outside of a glass of ice-cold water. These drops of water come from the air surrounding the glass. The air contains water vapour - a gas. The cold glass cools the air next to it. When the water vapour in the air next to the glass becomes cool enough, it changes from a gas to a liquid.

The change from a gas to a liquid is called '**condensation**'. The temperature of the gas decreases until the condensation point is reached [see fig. 10 on next page].

The condensation point is the temperature at which the liquid changes to a solid. As heat energy continues to flow out of the gas, the temperature remains constant at the condensation point. After all the liquid has changed to a solid, the temperature decreases once again as heat energy is removed.

Condensation is reverse of vaporisation

For condensation to occur, heat energy must be removed from a gas. This causes the gas particles to move more slowly and the temperature of the gas to decrease. The gas continues to cool as heat energy continues to be removed. Finally its temperature becomes low enough for condensation to occur. Then particles move slowly enough so that the attractive forces are able to keep the particles close together. As a result, a liquid forms.

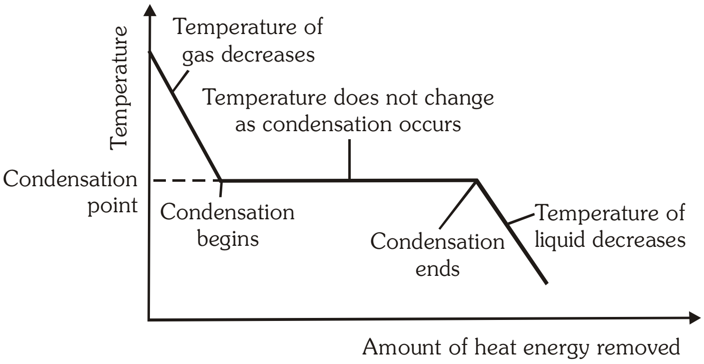


Fig.10 Changing gas to liquid by removal of heat energy

Evaporation

Vaporisation that occurs at the surface of a liquid is called 'evaporation'

[see fig 11].

Evaporation occurs during boiling and at temperatures below the boiling point. All the particles in a material do not have same speeds, they move at different speeds. Some particles at the liquid's surface are moving much faster than other particles. Some of these particles are moving so fast that the attractive forces are not strong enough to keep them at the surface of the liquid. These fast moving particles escape into the space above the liquid. Above the liquid, the particles are far apart and the attractive forces between them are weak. These particles move independently and are in the gas state.

During evaporation, the fastest particles leave the surface of the liquid. The particles that remain have less speeds. This means that the heat energy of the liquid decreases. As a result, the liquid cools as evaporation occurs. You experience this cooling effect when perspiration evaporates from your skin.

Fig.12 shows a complete graph that explains how a solid finally converts to its vapour form.

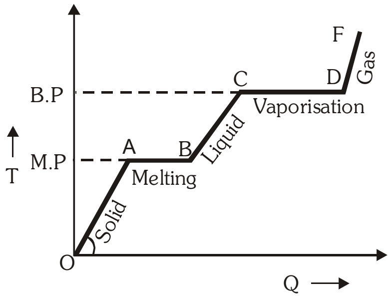


Fig.12 Conversion of a solid into vapour

Latent heat

Latent heat is energy transferred during phase changes. The word latent means “lying hidden within a person or thing”. Here, the word latent is used because the energy absorbed by the material during phase change looks “hidden” since there is no change in temperature.

☞ The energy per unit mass that is transferred during a phase change of a substance is called **latent heat**.

There are two types of latent heat :

(1) **Latent heat of fusion :** The heat per unit mass for the solid-liquid phase change is called the latent heat of fusion.

(2) **Latent heat of vaporisation :** The heat per unit mass for the liquid-gas phase change is called the latent heat of fusion.

Formula for latent heat, $Q = m L$

Where, m = mass of the substance undergoing phase change and L is the latent heat.

Latent heat of fusion of ice is 80 cal/g or 3.36×10^5 J/kg. The latent heat of vaporisation of water is 540 cal/g or 2.27×10^6 J/kg.

Specific latent heat of melting and fusion

In equation $Q = mL$, if $m = 1$ then $Q = L$, thus

The specific latent heat of melting of a substance is defined as the heat energy required to convert unit mass of the substance from solid to liquid state without the change in temperature.

On the other hand, the specific latent heat of fusion of a substance is the heat energy released when a unit mass of substance converts from liquid to solid state without the change in temperature.

For a pure substance, the specific latent heat of fusion is same as the specific latent heat of melting.

Unit of specific latent heat : The S.I. unit of specific latent heat is J kg^{-1}. other common units are cal g^{-1} and kilo-calorie kg^{-1}. They are related as :

1 kilo-cal kg^{-1} = 1 cal g^{-1}

1 cal g^{-1} = 4.2 K g^{-1}

or 1 cal g^{-1} = 4.2×10^3 J kg^{-1}

Specific latent heat of fusion of ice

For ice, the specific latent heat of fusion is 33600 J kg^{-1} (= 80 cal g^{-1}). It means that 1 kg of ice at 0°C absorbs 336000 J (or 1 g of ice at 0°C absorbs 80 cal) of heat energy to convert into water at 0°C.

In other words, 1 kg of water at 0°C will liberate 336000 J or 1 g of water at 0°C will liberate 80 cal) of heat energy ot convert into ice at 0°C.

Obviously 1 g water at 0°C has 336 J (or 80 cal) heat energy more than 1 g ice at 0°C.

☞ Specific latne heat can be found by electrical method also $L = \frac{pt}{m}$

NUMERICAL ABILITY

1. 5 g of water at 30 °C and 5 g of ice at – 20 °C are mixed together in a vessel. Find the final temperature of the mixture. Heat absorbed by the vessel is negligible. Given, specific heat of ice = 0.5 Cal/g/°C ; latent heat of ice is 80 cal/g.

Solution

Let the entire ice melts and final temperature be t.

$Q_{water} = Q_{ice}$

or $5 \times 1 \times (30 - t) = 5 \times 0.5 \times (20) + 5 \times 80 + 5 \times 1 \times (t - 0)$

or $150 - 5t = 50 + 400 + 5t$

or $-10t = 450 - 150 = 300$

or $\mathbf{t = -30\ °C}$

This is not possible because final temperature must lie between – 20 °C and 30 °C. This means entire ice will not melt, therefore **final temperature will be 0°C**.

Firstly, a whole mass (5 g) of ice will come to 0 °C and then a part of this ice will melt. Let m be the mass of ice that melted. Again,

$Q_{water} = Q_{ice}$

or $5 \times 1 \times (30 - 0) = 5 \times 0.5 \times 20 + m \times 80$ or $150 = 50 + m \times 80$

or m = 100/80 = 1.25 g i.e., **only 1.25 g of ice will melt**.

2. 5 g of ice at 0 °C is dropped in a beaker containing 20 g of water at 40 °C. What will be the final temperature ?

Solution

Let final temperature be 't'.

Heat absorbed by ice = $m_iL + m_ic_i\,\Delta T_i = 5 \times 80 + 5 \times 1 \times (t - 0) = 400 + 5t$

Heat released by water = $m_wc_w\Delta T_w = 20 \times 1 \times (40 - t) = 800 - 20t$

According to the principle of calorimetry,

heat absorbed by the cold body = heat released by hot body

or $400 + 5t = 800 - 20t$ or $25\,t = 400$

or $t = 400/25 = \mathbf{16\ °C}$

3. When 0.15 kg of ice of 0 °C mixed with 0.30 kg of water at 50 °C in a container, the resulting temperature is 6.7 °C. Calculate the heat of fusion of ice. (sp. heat of water = 4186 J kg^{-1} K^{-1})

Solution

Heat lost by 0.3 kg of water is equal to the heat gained by 0.15 kg of ice in melting plus heat gained by 0.15 kg of water formed by melting of ice to reach final temperature (6.7 °C).

$Q_{water} = Q_{ice} + Q'_{water}$

[Q'_{water} is the heat gained by 0.15 kg of water formed by melting of ice]

or $m_w C_w \Delta T_w = m_i L + m_i C_w \Delta T'_w$

or $0.3 \times 4186 \times (50 - 6.7) = 0.15 \times L + 0.15 \times 4186 \times (6.7 - 0)$

or $0.3 \times 4186 \times 43.3 = 0.15 \times L + 0.15 \times 4186 \times 6.7$

or $0.15 \times L = 0.3 \times 4186 \times 43.3 - 0.15 \times 4186 \times 6.7 = 4186 \times 0.3 \times (43.3 - 0.5 \times 6.7)$

or $0.15 \times L = 4186 \times 0.3 \times (43.3 - 3.35) = 4186 \times 0.3 \times 39.95$

or $L = (4186 \times 0.3 \times 39.95)/\ 0.15 = 334461.4$ J/kg

$= \mathbf{3.345 \times 10^5\ J/kg}$

4. 1 g of steam at 100 °C can melt how much ice at 0 °C? Given, specific heat of water = 1 cal/g°C ; latent heat of ice = 80 cal/g ; latent heat of steam = 540 cal/g.

Solution

Heat required by ice for melting of m g of ice = $mL_f = m \times 80$

Heat possessed by 1 gram of steam to get condensed and then brought to 0 °C = $mL_v + m\,C\,\Delta t = 1 \times 540 + 1 \times 1 \times 100 = 640$ cal

Now, $m \times 80 = 640$

or $m = \dfrac{640}{80}$ = **8 grams**

POINTS TO REVISE

- **Calorimetry :** The branch of physics that deals with determination of specific heats, heat absorbed or released during a process, calorific values of combustible substances is called calorimetry.
  - **Specific heat (c) :** The amount of heat required for a unit increase in the temperature of unit mass of a substance is called its specific heat.

    Heat absorbed or released by a substance, $\mathbf{Q = m\,c\,\Delta t}$

    where, m = mass of the substance ; c = specific heat of the substance ;

    Δt = change in temperature of the substance.
    - **Unit of specific heat :** J/kgK or J/kg°C
    - Specific heat depends on the state of substance i.e., solid, liquid or gas. For example, specific heats of water, ice and steam are different.

	Cal g^{-1} °C^{-1}	J kg^{-1} °C^{-1}
Specific heat of ice	0.5	2100
Specific heat of water	1.0	4200
Specific heat of steam	0.47	1970

    - Specific heat signifies the resistance (opposition) of a substance to a change in its temperature.
    - Sand heats up (or cools down) faster than water because the sand on a beach has a lower specific heat than water.
    - The tendency on the part of water to resist changes in temperature improves the climate in many locations.
  - **Thermal capacity (heat capacity) :** Amount of heat needed to increase the temperature of a substance of any mass by 1°C is called thermal capacity of that substance.

    Thermal capacity = (mass of body) × (specific heat) or $\mathbf{H_C = mc}$
    - **Unit of heat capacity** : J/K or J/°C.
    - Water has a much higher capacity for storing energy than most of the common materials hence water is a very useful cooling agent used in the cooling systems of automobiles and other engines.
  - **Molar heat capacity (molar specific heat)**

    $\mathbf{C = M_0 c}$ where, M_0 = molar mass (in kg) ; c = specific heat in J/kg °C

    $\mathbf{Q = \mu\,C\,\Delta t}$ where, Q = heat absorbed or released ; μ = number of moles.

    or $C = \dfrac{Q}{\mu \Delta t}$
    - **Unit of molar heat capacity :** J/mol K or J/mol °C.
- **Principle of calorimetry :** When one body is kept in contact with another body, the body at higher temperature loses heat and the body at lower temperature gains heat such that finally both of them have same temperature. Such a temperature is called **equilibrium temperature**.
  - According to principle of calorimetry, when two bodies at different temperatures are mixed together or kept in direct contact, heat will be transferred from body at higher temperature to the body at lower temperature till they acquire same temperature; heat lost by hot body is equal to the heat gained by the cold body.

- Let two substances of specific heats c_1, c_2 ; temperatures t_1, t_2 and masses m_1, m_2 respectively are kept in contact with each other. Let $t_1 > t_2$, after some time both the substances attain a final temperature t_e, then $t_1 > t_e > t_2$. According to principle of calorimetry,

  heat gained by cold body = heat lost by hot body

  $$m_2c_2(t_e - t_2) = m_1c_1(t_1 - t_e)$$

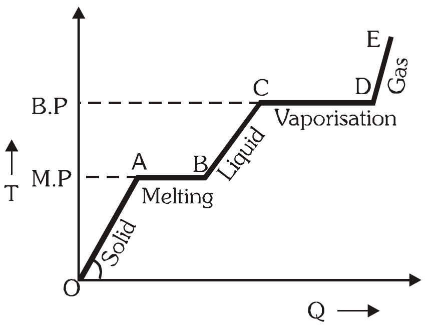
  On solving, we get, $$\boxed{t_e = \frac{m_1c_1t_1 + m_2c_2t_2}{m_1c_1 + m_2c_2}}$$

- **Change of phase :** A substance changes its phase i.e. from solid to liquid or liquid to gas at constant temperature. A substance changes its state from solid to liquid at its '**melting point**'. Similarly, a substance changes its state from liquid to gas at its '**boiling point**'.

- **Latent heat :** It is the amount of heat absorbed or released per unit mass of a body during the change of state at constant temperature. There are two types of latent heat :
  - **Latent heat of fusion :** The heat per unit mass for the solid-liquid phase change is called the latent heat of fusion. Latent heat of fusion of ice is 80 Cal/g or 3.36×10^5 J/kg.
  - **Latent heat of vaporisation :** The heat per unit mass for the liquid-gas phase change is called the latent heat of vaporisation. The latent heat of vaporisation of water is 540 Cal/g or 2.27×10^6 J/kg.
  - Formula for latent heat : **Q = m L**

    Where, m = mass of the substance undergoing phase change and L is the latent heat.

- **Melting :** Melting occurs when a solid changes into a liquid. The **melting point** of a material is the temperature at which the material changes from a solid to a liquid.
- **Freezing :** Freezing occurs when a liquid changes into a solid. The **freezing point** is the temperature at which the liquid changes to a solid.
- **Vaporisation :** The change from a liquid to a gas is called '**vaporization**'. Vaporization can occur within a liquid and at the surface of a liquid. Vaporization that occurs within a liquid is called '**boiling**'.
- **Condensation :** The change from a gas to a liquid is called '**condensation**'. The **condensation point** is the temperature at which the gas changes to a liquid.



Conversion of a solid into vapour

- **Evaporation :** Vaporisation that occurs at the surface of a liquid is called '**evaporation**'. Evaporation occurs during boiling and at temperatures below the boiling point. During evaporation, the fastest particles leave the surface of the liquid. The particles that remain have less speeds. The liquid cools as evaporation occurs. You experience this cooling effect when perspiration evaporates from your skin.

INTRODUCTION :

Thermo (Heat/energy) + Dynamics (Flow/motion)

Thermodynamics is the branch of science which deals with the energy changes taking place in all physical and chemical processes but **Chemical thermodynamics** is the branch of thermodynamics which deals with the study of energy changes taking place in chemical processes.

Advantages of thermodynamics :

(i) It gives information about various **thermodynamic laws.**

(ii) It helps us to predict whether a given **chemical reaction will take place or not** under the given set of conditions.

(iii) It gives information about various **energy changes**.

Limitations of thermodynamics :

(i) Thermodynamics deals with the properties like temperature, pressure, volume, etc of matter in bulk but doesn't tell us anything about the individual properties of atoms or molecules.

or

Thermodynamics deals with **macroscopic system** but not with **microscopic system.**

(ii) It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the **rate of reaction.**

SOME IMPORTANT TERMS :

- **System** : A system is defined as a specific part of universe or specified portion of the matter which is under experimental investigation
- **Surrounding** : The rest part of the universe excluding the system is called surrounding.

  Universe = System + Surrounding
- **Boundary** : Anything which separates system and surrounding is called boundary.

  Types of boundary :

  (i) Boundary can be conducting or non-conducting.

  (ii) Boundary can be rigid or non-rigid.

  (iii) Boundary can be real or imaginary.

For example :

A reaction is carried out in a beaker. The contents of beaker constitute the system, beaker serves as boundary and anything which is outside the beaker is called surroundings.

TYPES OF SYSTEM :

System are of 3 types :

Open system : This type of system can exchange energy as well as matter with the surrounding. The boundary is neither sealed nor insulated. Total mass will not remain constant.

Eg.1 Coffee in open glass. Hot water in open glass.

Eg.2 All living systems. human being, plants, animals.

Eg.3 Classroom, earth.

Closed system : This type of systems can exchange energy, (in the form of heat, work or radiations) but not matter with its surroundings. The boundary is sealed but not insulated. Amount of the system will remain constant.

Eg.1 Coffee in closed vessel. Hot water in closed vessel.

Eg.2 Glowing bulb, tube light.

Eg.3 A satellite in orbit.

Isolated system : This type of system are perfectly insulated systems and cannot interact in any way with its surrounding i.e. neither matter nor energy can be exchanged with the surrounding. The boundary is sealed and insulated. Universe can be considered as an isolated system.

Eg.1 Coffee in thermosflask.

STATE OF THE SYSTEM :

- Properties which define state of any system are called its state variables or thermodynamic variables or thermodynamic quantities.
- The state of the system is defined by their measurable properties like temperature, pressure, volume etc.
- If any of these properties change, state of the system is said to be changed.

State Function :

- Those state variables which depend only upon initial and final state of the system but doesn't depend upon the path or mechanism followed by the system to achieve final state are called state function.
- State functions are denoted by capital letters.

Ex. E, H, S, G, T, P, V etc.

Path function :

- Properties of the system which depend upon the initial and final state of the system as well as the path or mechanism followed by the system to achieve final state are called path function.
- Path functions are denoted by small letters.

Eg. Work done (w), heat (q)

Thermodynamic properties :

(i) **Intensive properties** : The properties of the system which are independent of matter (size and mass) present in system are called intensive properties.

(ii) **Extensive properties** : The properties of the system which are dependent on matter (size and mass) present in system are called extensive properties

Extensive Properties	**Intensive Properties**
Volume (V)	Molar volume (V_m)
Number of moles (n)	Density (d)
Mass (m)	Gibb's energy per mole (G_m)
Gibb's Energy (G)	Specific heat
Entropy (S)	Pressure (P)
Enthalpy (H)	Temperature (T)
Internal energy (E or U)	All concentration terms (M,N)
Heat capacity (C)	Boiling point, freezing point (T_b, T_f)
Force (F)	Cell potential (E_{cell})
Surface Area (A)	Specific conductance (κ)
	Refractive index
	Surface tension, Viscosity
	pH value
	Vapour pressure

Special Points :

(i) The ratio of two extensive properties indicates the intensive property Eg. $d = \frac{\text{mass}}{\text{volume}}$

(ii) An extensive property can be converted into intensive property when it is defined for unit amount of the substance.

Eg. Mass per unit volume = density; $\left(d = \frac{m}{V}\right)$

(iii) Intensive properties of a substance are non-additive in nature while extensive properties are additive in nature.

	$\boxed{H_2O}$	$\boxed{H_2O}$	On adding		
Vessel	**A**	**B**			
Mass	m_1	m_2	$m_1 + m_2$	(Total mass)	Extensive
Moles	n_1	n_2	$n_1 + n_2$	(Total moles)	
Volume	V_1	V_2	$V_1 + V_2$	(Total volume)	
Density	d	d	Remains same	(d)	Intensive
Boiling point	T	T	Remains same	(T)	

TYPES OF THERMODYNAMIC PROCESSES :

When a system changes from one state to another, the operation is called a thermodynamic process.

Thermodynamic processes may be in form of expansion or compression.

(a) Isothermal Process (n,T = constant)

Isothermal processes are those processes in which

(a) Temperature of system during entire process remains constant i.e. $\Delta T = 0$

(b) Heat is exchanged with surroundings

(c) Volume and pressure are variable

- For ideal gas in Isothermal process $\Delta E = 0$ and $\Delta H = 0$
- All phase transitions are isothermal process but $\Delta E \neq 0$ and $\Delta H \neq 0$

(b) Isobaric Process (n,P=constant) :

Isobaric processes are those processes in which

(a) Pressure of system during entire process remains const i.e. $\Delta P = 0$

(b) Volume and temperature are variable.

(c) Process in open system is isobaric in nature.

(c) Isochoric Process (n,V = constant) :

Isochoric processes are those processes in which

(a) Volume remains constant i.e. $\Delta V = 0$

(b) Pressure and temperature are variable

(c) Work, $w = -P\Delta V$, $\because \Delta V = 0$, $\therefore w = 0$ (Zero)

(d) Process in closed system is isochoric in nature.

(d) Adiabatic Process (n = constant, q = 0)

Adiabatic processes are those processes in which

(a) No exchange of heat between system and surrounding takes place durint entire process i.e. $q = 0$

(b) The temperature pressure, volume of the system varies.

(c) The system is thermally insulated by keeping the system in an insulated container.

(e) Cyclic Process :

When a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.

In cyclic process change in all state function will be zero. i.e. $\Delta E = 0$, $\Delta H = 0$, $\Delta P = 0$, $\Delta T = 0$

(f) Reversible Process (quasi-static) :

(1) Process in which all changes occuring at any part of the system are exactly reversed when small changes in variables are carried out in opposite direction.

(2) Driving force should be infinitesimally greater than opposing force.

(3) Process takes place in infinitesimal small steps or in many steps and takes infinite time to complete the process.

(4) It is an ideal process.

(5) Work obtained in expansion is maximum.

(6) System is in virtual equilibrium at any state.

(7) $P_{ext} = P_{int} \pm dP$; P_{ext} is variable.

Irreversible Process :

(1) Process in which direction of change cannot be reversed by small changes in variables.

(2) Driving force is much greater than opposing force.

(3) It takes finite time and finite/usually single step.

(4) Process takes place in short time

(5) All natural processes are irreversible

(6) System is in equilibrium only at initial and final state

(7) $P_{ext} = P_{int} \pm \Delta P$; P_{ext} is constant.

WORK AND HEAT :

(A) Work : Product of force and displacement is known as work.

$$\text{work (w)} = \text{force (F)} \times \text{displacement } (\ell)$$

Consider a gas enclosed in a cylinder fitted with a frictionless piston.

Suppose area of cross section of cylinder = A and pressure on the piston = P

Initial volume of the gas = V_1 and final volume of the gas = V_2

(By expansion) displacement of piston = ℓ

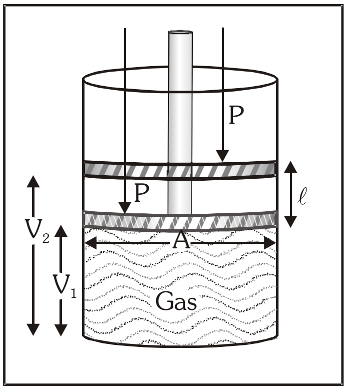
work done by the gas (in expansion) = $w = F.\ell$

$$\because P = \frac{F}{A} \qquad \therefore F = P \times A$$

$w = P \times A \times \ell$ (change in volume = $A \times \ell = V_2 - V_1$)

$w = P \times (V_2 - V_1)$

$w = P\Delta V$ (According to Physics)



In general $\boxed{w = -P_{external}\, DV}$ (According to Chemistry)

SIGN CONVENSIONS :

- According to latest sign conventions

  (a) Work done is taken negative if it is done by the system since energy of system is decreased.

  Eg. Expansion of gas.

  $\because V_2 > V_1$; ΔV = positive; w = negative

  (b) Work done is taken positive if it is done on the system, since energy of system is increased.

  Eg. Compression work.

  $\because V_1 > V_2$; ΔV = negative ; w = positive

(B) Heat exchange (q) :

Heat is defined as the energy that flow in or out of a system because of a difference in temprature between the thermodynamic system and its surrounding. It is a path function.

According to IUPAC convention, heat given by the system is expressed with negative sign and heat given to the system is expressed with positive sign.

- Heat always flows from high temperature to low temprature.
- Heat flowing into the system q = positive
- Heat flowing out of the system q = negative

Units of heat & work :

Calorie : It is defined as the quantity of heat required to raise the temperature of 1 g of water by 1°C (14.5 to 15.5°C)

$1 \text{ cal} = 4.184 \text{ J} \simeq 4.2 \text{ J}$

$1 \text{ L-atm} = 101.3 \text{ J} = 24.206 \text{ cal} = 101.3 \times 10^7 \text{ erg}$

$\boxed{1 \text{ L-atm} > 1 \text{ Cal} > 1 \text{ J} > 1 \text{ erg}}$

POINTS TO REVISE

- Molar properties like ΔH_m, ΔG_m, ΔS_m, ΔU_m are intensive properties.
- In cyclic process change in all state function will be equal to zero.
  $\Delta E = 0$; $\Delta H = 0$ $\Delta P = 0$, $\Delta T = 0$ etc.
- For ideal gases $\Delta E = 0$ (For isothermal process)
- All natural process are irreversible in nature.
- Both q and w are (+) **to** system.
- Both q and w are (–) **by** the system.

INTERNAL ENERGY (E/U) :

Internal energy of a system is defined as the sum of different energies associated with its atoms and molecules like Potential energy, Kinetic energy (due to translatory, rotatory and vibratory motion), electronic energy, nuclear energy etc.

$E = E_{PE} + E_T + E_R + E_V + E_e + E_N$

(i) Internal energy is an **extensive property**.

(ii) We can **never find out the absolute value** of internal energy (E) of system.

We can only calculate the change in internal energy of the system (ΔE) by using an instrument which is called as Bomb calorimeter. In Bomb calorimeter reactions are carried out at constant volume.

(iii) Internal energy is a **state function**.

$\Delta E = E_f - E_i$

(In reaction) $\Delta E = E_P - E_R$

ΔE is + ve if $E_f > E_i$

ΔE is – ve if $E_f < E_i$

LAWS OF THERMODYNAMICS :

GENERAL POINT :

Laws of thermodynamics are based on human experiences there is no formal proof for them.

FIRST LAW OF THERMODYNAMICS (FLOT) :

- This law is based on law of conservation of energy and was given by **Robert Mayer and Helmholtz.**
- Energy can neither be created nor destroyed but can be transformed from one form to another.
- The total energy of the universe is always constant. i.e. total energy of an isolated system is always conserved.
- The mathematical form of first law of thermodynamics can be expressed as follows

$\boxed{\Delta E = q + w}$: where q, w are path function and E is state function.

Here q is the energy given to the system and w is the work done on the system ; ΔE is change in internal energy.

Note :- Put the value of q and w with proper sign.

CONCLUSIONS FROM THE FIRST LAW OF THERMODYNAMICS :

(a) During isothermal process of an ideal gas :

During an isothermal process the temperature of the system remains constant and hence

$\Delta E = 0$

Therefore FLOT : $\Delta E = q + w$

$\therefore \boxed{+q = -w}$ or $-q = +w$

In isothermal process –

(I) Heat absorbed by the system is equal to work done by the system.

OR

(II) Heat evolved by the system is equal to work done on the system.

(b) During isochoric process :

At constant volume $V_1 = V_2$ i.e. $\Delta V = 0$

Hence $W = -P\Delta V = 0$ .... No work done at constant volume therefore,

FLOT: $\Delta E = q + w \ \boxed{\Delta E = q_v}$

(i) In isochoric process

- At constant volume, heat absorbed by the system is equal to increase in internal energy of the system.

OR

- At constant volume, heat evolved by the system is equal to decrease in internal energy of the system.

(ii) Heat at constant volume $(q_v) = \Delta E$

(iii) **In isochoric process heat is idependent of path.**

(c) During adiabatic process :

During adiabatic process the system acts an isolated system and hence **q = 0** in such cases. Therefore

FLOT : $\Delta E = q + w$ $\because q = 0$ $\boxed{\Delta E = w}$

(i) Work done on the system is equal to increase in internal energy of the system i.e., when a gas is compressed adiabatically its internal energy increases.

OR

Work done by the system is equal to decrease in internal energy of the system, i.e., when a gas is expanded adiabatically its internal energy decreases.

(ii) **In adiabatic process work is independent of path.**

(d) During Cyclic Process :

$\Delta E = 0$ FLOT ; $\Delta E = q + w$ $\boxed{+q = -w}$

In cyclic process.

(I) Work done by the system is equal to heat absorbed by the system.

OR

(II) Work done on the system is equal to heat evolved by the system.

(e) During Isobaric process :

P – constant

FLOT : $\Delta E = q + W$

$\Delta E = q + (-P\Delta V)$

$q_P = \Delta E + P\Delta V$

$q_P = (E_2 - E_1) + P(V_2 - V_1)$

$q_P = (E_2 + PV_2) - (E_1 + PV_1)$

$\because$ Enthalpy $H = E + PV$

$\therefore$ $q_P = H_2 - H_1$ $\boxed{q_P = \Delta H}$

(i) **In isobaric process :**

- At constant pressure, heat absorbed by the system is equal to increase in enthalpy of the system.

OR

- At constant pressure, heat evolved by the system is equal to decrease in enthalpy of the system.

(ii) Heat at constant pressure (q_p) = ΔH

(iii) **In isobaric process heat is idependent of path.**

ENTHALPY (H) :

Mathematically it is heat contained in the system measured at constant pressure.

The sum of internal energy and pressure volume (PV) energy is known as enthalpy.

$$\boxed{H = E + PV}$$

- It is impossible to determine absolute value of enthalpy so we determine change in enthalpy (ΔH).

  $\Delta H = H_{final} - H_{initial}$
- Enthalpy is an extensive property because E and V are extensive properties.
- It is a state function because E, P and V are state functions.

$\because H = E + PV$

$$\therefore \quad \boxed{\Delta H = \Delta E + \Delta(PV)} \quad ...(i)$$

(when P, V and T are variables)

At constant pressure : $\boxed{\Delta H = \Delta E + P.\Delta V}$ ...(ii)

At constant volume : $\boxed{\Delta H = \Delta E + V.\Delta P}$ ...(iii)

For chemical reactions at constant temprature and pressure $\because P.\Delta V = \Delta n_g RT$

So from equation (i) $\boxed{\Delta H = \Delta E + \Delta n_g RT}$ ...(iv)

where $\Delta H = q_p$; at constant P ; $\Delta E = q_v$; at constant V

So equation (iv) can be also written as $\boxed{q_p = q_v + \Delta n_g RT}$ ...(v)

POINTS TO REVISE

- If, $\Delta n_g = 0 \rightarrow \boxed{\Delta H = \Delta E}$ eg. $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- If, $\Delta n_g > 0 \rightarrow \boxed{\Delta H > \Delta E}$ eg. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
- If, $\Delta n_g < 0 \rightarrow \boxed{\Delta H < \Delta E}$ eg. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

HEAT CAPACITY / MOLAR HEAT CAPACITY / SPECIFIC HEAT CAPACITY :

(i) **Heat capacity (C) :** Amount of heat required to raise the temperature of given amount of a substance by 1°C or 1K is called heat capacity.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temp.}}$$

$$\boxed{C = \frac{dq}{dT}}$$

Units :- JK^{-1}, Cal K^{-1}, J $°C^{-1}$, Cal $°C^{-1}$

- Heat capacity is extensive property.

(ii) **Molar heat capacity (C_m) :** Amount of heat required to raise the temperature of 1 mole of substance by 1°C or 1 K is called as molar heat capacity.

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{mole of substance}} \Rightarrow \boxed{C_m = \frac{C}{n}}$$

Units :- $Jmol^{-1}\,K^{-1}$, Cal $mol^{-1}\,K^{-1}$, J $mol^{-1}\,°C^{-1}$, Cal $mol^{-1}\,°C^{-1}$

- Molar heat capacity is an intensive property.

(iii) **Spcific heat capacity (c) :** Amount of heat required to raise the temperature of 1 g of substance by 1°C or 1K is called as specific heat capacity.

$$\boxed{c = \frac{C_m}{\text{molecular weight}}}$$

Units :- $Jg^{-1}\,K^{-1}$, Cal $g^{-1}\,K^{-1}$, J $g^{-1}\,°C^{-1}$, Cal $g^{-1}\,°C^{-1}$

- Specific heat capacity is an intensive property.

- If heat is suppplied at constant pressure, then $C_p = \left(\frac{dq}{dT}\right)_P = \frac{dH}{dT}$ ...(i)
- If heat is supplied at cosntatn volume, then $C_V = \left(\frac{dq}{dT}\right)_V = \frac{dE}{dT}$ ...(ii)

From equation (i) and (ii) :

From equation (i)	**Unit**	**From equation (ii)**
• $\Delta H = C_p dT$ [Here C_P is heat capacity at constant P]	JK^{-1}	$\Delta E = C_V dT$ [Here C_V is heat capacity at constant V]
• For n moles $\Delta H = nC_p dT$ [Here C_P is molar heat capacity at constant P]	$J\ mol^{-1}K^{-1}$	$\Delta E = nC_V dT$ [Here C_V is molar heat capacity at constant V]
• For m gram $\Delta H = mC_p dT$ [Here C_P is gram specific heat (specific heat capacity) at constant P]	$J\ g^{-1}\ K^{-1}$	$\Delta E = mC_V dT$ [Here C_V is gram specific heat (specific heat capacity) at constant V]

Relation between C_P and C_V for 1 mole of an ideal gas :

$\because \quad H = E + PV$

for ideal gas,

$PV = nRT$

$PV = RT$ for 1 mole

$\therefore \quad H = E + RT$ differentiate w.r.t. temperature

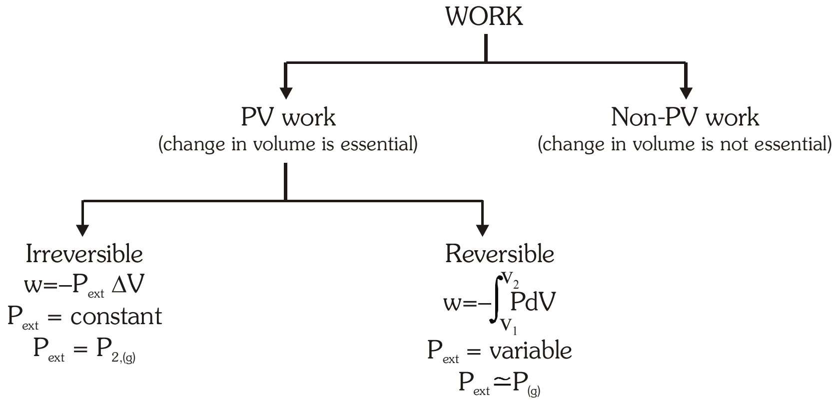
$$\left(\frac{dH}{dT}\right) = \left(\frac{dE}{dT}\right) + R$$

$$C_P = C_V + R$$

(i) $\boxed{C_P - C_V = R}$ Mayer's formula

(ii) $\boxed{\frac{C_P}{C_V} = \gamma}$, γ = Poisson's ratio

WORK DONE IN DIFFERENT PROCESS :



Here $P_{2(g)}$ = Pressure of gas outside piston.

$P_{(g)}$ = Pressure of gas inside piston.

(a) Work done in reversible isothermal process :

P_{external} = Variable

For reversible process

$P_{\text{ext}} = P_{\text{gas}} \pm dP$

$$\because \quad w_{\text{rev.}} = -\int_{V_1}^{V_2} P_{\text{ext.}} dV$$

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} (P_{\text{gas}} \pm dP).dV$$

Both dP and dV are very small so, (dP.dV) is negligible.

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} P_{\text{gas}}.dV$$

$$w_{\text{rev.}} = -\int_{V_1}^{V_2} \frac{nRT}{V}.dV$$

$$w_{\text{rev.}} = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

$$w_{\text{rev.}} = -nRT\ell n\left(\frac{V_2}{V_1}\right)$$

or, $$\boxed{w_{\text{rev.}} = -2.303nRT\log_{10}\left(\frac{V_2}{V_1}\right)} \quad ...(i)$$

according to Boyle's law at constant temperature $P \propto \frac{1}{V}$ or PV = constant

$$\therefore \quad P_1V_1 = P_2V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\boxed{w_{\text{rev.}} = -2.303nRT\log\left(\frac{P_1}{P_2}\right)} \quad ...(ii)$$

(b) Work done in reversible adiabatic process :

In adiabatic process q = 0

FLOT : $\Delta E = q + w$

$$\Rightarrow \boxed{w = \Delta E} \Rightarrow w = nC_V\Delta T$$

$$\boxed{w = nC_V(T_2 - T_1)} \quad ......(i)$$

$$\because \quad C_P - C_V = R$$

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\gamma - 1 = \frac{R}{C_V} \quad \left(\because \gamma = \frac{C_P}{C_V}\right) \Rightarrow C_V = \frac{R}{\gamma - 1} \quad ....(ii)$$

From equation (i) and (ii) $$\boxed{w = \frac{nR}{\gamma - 1}(T_2 - T_1)} = \boxed{w = \frac{P_2V_2 - P_1V_1}{(\gamma - 1)}}$$

State equations of reversible adiabatic processes are :

PV^{γ} = constant

$TV^{\gamma-1}$ = constant

$T^{\gamma}P^{1-\gamma}$ = constant

POINTS TO REVISE

- Work in closed vessel is zero because volume remains constant.
- Work during free expansion of an ideal gas in vacuum is zero, because P_{ext} is zero.
- Work in a chemical reaction $w = -P\Delta V = -\Delta n_g.RT$

SPONTANEOUS PROCESS AND NON–SPONTANEOUS PROCESS :

(i) Spontaneous process :

- The process which has a natural tendency to occur in a particular direction either of its own or after proper initiation under the given set of conditions.
- All natural processes are ir-reversible and spontaneous processes. The natural processes take place of their own in one direction only.

(ii) Non–spontaneous process :

- The process which does not occur of its own in a particular direction i.e. a process which does not have a natural tendency to occur in a particular direction either of its own or after initiation is called as non-spontaneous process.
- Non-spontaneous process may be made to occur when energy from some external source is supplied continuously throughout the process.

Examples of spontaneous process that need no initiation :

Ex. Flow of water from high level to low level.
Flow of heat from hot body to cold body.
Flow of charge from high potential to low potential.
Flow of gas from high pressure to low pressure.

Ex. Melting of ice at 25° C
Evapouration of water at 25° C
Dissolution of common salt in water.

Ex. Mixing of different non reacting gases

Examples of spontaneous process that need initiation :

Ex. Burning of fuel (coal, petrol)

$$C(s) + O_2 \longrightarrow CO_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Ex. Lighting of candle

Criteria for a process to be spontaneous :

(i) Tendency to attain minimum energy or maximum stability (Energy Factor).
(ii) Tendency to attain maximum randomness (Entropy Factor)

ENTROPY (S) :

(i) The thermodynamic quantity, which is used to measure **degree of randomness** or **disorderness** of the system is called as entropy.

Entropy (s) $\propto$ Randomness or disorderness

(ii) More is the disorderness, higher is the entropy.

(iii) The ratio of heat absorbed by the system in isothermal and reversible manner to the temperature at which heat is absorbed is equals to the change in entropy.

$$\boxed{\Delta S = \frac{q_{rev}}{T}}$$

Where q_{rev}= heat absorbed by the system in a reversible manner at the temperature T

Unit : J K^{-1} or Cal K^{-1}

(iv) $\Delta S = S_{final} - S_{inital}$

If $S_{final} > S_{initial}$: Then ΔS = positive

If $S_{final} < S_{initial}$: Then ΔS = negative

(v) Entropy is an extensive property and state function.

(vi) Entropy change in a chemical reaction $\boxed{\Delta S = \Sigma S_{product} - \Sigma S_{reactant}}$

(vii) Entropy change for a process : $\Delta S = \frac{q_{rev}}{T}$ $\boxed{\Delta S = nC_V \ell n \frac{T_2}{T_1} + nR\ln \frac{V_2}{V_1}}$ or $\boxed{\Delta S = nC_P \ell n \frac{T_2}{T_1} + nR\ln \frac{P_1}{P_2}}$

Case I : For an ideal gas reversible isothermal process; : $T_2 = T_1$

$$\boxed{\Delta S = nR\ln \frac{V_2}{V_1} = nR\ln \frac{P_1}{P_2}}$$

$$\boxed{\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 nR \log \frac{P_1}{P_2}}$$

Case II : For an isochoric process $V_2 = V_1$

$$\boxed{\Delta S = nC_V \ln \frac{T_2}{T_1}} \; ; \; \boxed{\Delta S = 2.303\ nC_v \log \frac{T_2}{T_1}}$$

(viii) **For reversible adiabatic process :**

Entropy remains constant so process is also known as **isoentropic process**.

Factors affecting entropy of system :

(I) If $\Delta n_g > 0$ then $\Delta S > 0$

If $\Delta n_g < 0$ then $\Delta S < 0$

(II) Physical state : $S_{solid} < S_{liquid} < S_{gas}$

(III) On increasing gaseous moles entropy increases.

(IV) On increasing temperature, S will increase.

Ex. $\underset{300K}{Fe(s)} \rightarrow \underset{400K}{Fe(s)}$: ΔS=positive

(V) On decreasing pressure, S increases.

Ex. $\underset{5atm}{N_2(g)} \rightarrow \underset{2\ atm}{N_2(g)} : \Delta S$ = positive

(VI) Mixture : $\left.\begin{array}{l} \text{Solid + solid} \\ \text{liquid + liquid} \\ \text{gas + gas} \end{array}\right\} S \uparrow$

Entropy change during phase transition :

(I) **Entropy of fusion $[(\Delta S)_f]$ mole :**

The entropy change, when 1 mol solid changes into liquid at its melting point temperature.

$$\text{solid} \rightleftharpoons \text{liquid}$$

$$(\Delta S)_f = \frac{\Delta H_{fusion}}{T}$$

(II) Entropy of vapourisation [$(\Delta S)_{vap}$] mole :

The entropy change, when 1 mol liquid changes into vapour at its boiling point temperature.

$$\text{liquid} \rightleftharpoons \text{vapour}$$

$$(\Delta S)_{vap} = \frac{\Delta H_{vap}}{T}$$

(III) Entropy of sublimation [$(\Delta S)_{sub}$] mole :

The entropy change, when 1 mol solid changes into vapour at a particular temperature.

$$\text{solid} \rightleftharpoons \text{vapour}$$

$$(\Delta S)_{sub} = \frac{\Delta H_{sub}}{T}$$

Some famous or extra ordinary examples of entropy change :

(i) Entropy of graphite > Entropy of diamond.

(ii) In rusting of iron entropy increases.

(iii) $NH_4Cl(s) + aq \longrightarrow NH_4^+(aq) + Cl^-(aq)$

In this process NH_4^+ and Cl^- ions are free to move in solution where as they are not free to move in solid NH_4Cl. Hence ΔS is positive for this type of dissolution process.

(iv) On addition of HCl in the aqueous solution of Ag^+ ions entropy decreases due to precipitation of AgCl.

(v) **On boiling of egg :** Denaturation of proteins occur. Thus entropy increases.

(vi) **Stretching of rubber :** During stretching of rubber band its long flexible macromolecules get uncoiled. The uncoiled form has more specific geometry and more ordered arrangement. Thus entropy decreases.

Total entropy change in reversible process :

In reversible process, at every step system and surroundings remain in thermal equilibrium with each other.

Let a system, releases q heat to the surroundings at temperature T.

$$\Delta S_{system} = \frac{-q}{T}; \qquad \Delta S_{surroundings} = \frac{+q}{T}$$

$$\because \quad \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{total} = \frac{-q}{T} + \frac{q}{T} \Rightarrow \boxed{\Delta S_{total} = 0}$$

Total entropy change in irreversible process :

Let a system is at high temperature T_1 and surroundings are at low temperature T_2.

Let q amount of heat is released by the system.

$$\Delta S_{system} = \frac{-q}{T_1}, \qquad \Delta S_{surroundings} = \frac{+q}{T_2}$$

$$\because \quad \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = \frac{-q}{T_1} + \frac{q}{T_2}$$

$$\therefore \quad \boxed{\Delta S_{total} = +ve} \qquad (\because T_1 > T_2)$$

Total entropy change for irreversible spontaneous process is always greater than zero.

Spontaneity of a process in terms of total entropy change :

If, $\Delta S_{total} = +ve \Rightarrow$ spontaneous process

If, $\Delta S_{total} = -ve \Rightarrow$ non spontaneous process

If, $\Delta S_{total} = 0 \Rightarrow$ process is at equilibrium

SECOND LAW OF THERMODYNAMICS (SLOT) :

(i) It states about the direction of flow of heat

(ii) All natural processes in universe are ir-reversible process or natural processes are spontaneous process.

(iii) Due to spontaneous process entropy of universe is increasing continuously i.e. entropy of an isolated system increases.

$$(\Delta S)_T = +\ ve \quad \text{or} \quad (\Delta S)_T > 0 \quad \text{or} \quad (\Delta S)_{system} + (\Delta S)_{surr.} > 0$$

GIBB'S ENERGY (G or F) :

- Gibb's energy is defined at constant temperature and pressure to predict spontaneity of a process.
- Gibb's energy is a thermodynamic quantity which is used to measure the capacity of system to do useful work or Gibb's energy is that part of the total energy of system which can be converted into useful work.
- The term Gibbs energy was introduced to explain criteria of spontaneity in terms of system.

• Since ; energy = useful work + randomness energy

$$H = G + TS$$

$$\boxed{G = H - TS} \quad \ldots(i)$$

So the function that takes both enthalpy and entropy of system into account is called Gibbs energy.

• Gibbs energy is an extensive property and state function.

• Absolute value of G can't be measured but change can be measured, So we discuss (ΔG)

$$\Delta G = G_{final} - G_{initial}$$

From eq. (i) $\boxed{\Delta G = \Delta H - T\Delta S}$

Where ΔG = Change in Gibb's energy

ΔH = Change in enthalpy

ΔS = Change in entropy

Relation between Gibb's energy change and non expansion work or useful work :

FLOT : $\Delta E = q + W$

If, work is done by the system, then, $\Delta E = q - W$ ....(i)

According to Gibb's, system does both expansion and non expansion work.

$\therefore$ $W = W_{expansion} + W_{non\ expansion}$

$W = P\Delta V + W_{non\ expansion}$

Put W in equation (i)

$\Rightarrow$ $\Delta E = q - (P\Delta V + W_{non\ expansion})$

$q = \Delta E + P\Delta V + W_{non\ expansion}$

$q = \Delta H + W_{non\ expansion}$ $(\because \Delta H = \Delta E + P\Delta V)$

$T\Delta S = \Delta H + W_{non\ expansion}$ $(\because \Delta S = q/T)$

$W_{non\ expansion} = T.\Delta S - \Delta H$ $(\because \Delta G = \Delta H - T\Delta S)$

$\Rightarrow$ $\boxed{W_{non\,expansion} = -\Delta G}$ or $\boxed{W_{useful} = -\Delta G}$

The decrease in Gibb's energy of system is equal to the non expansion work or useful work.

Relation in between ΔG of system and ΔS_{total} or Gibb's energy change and spontaneity :

$\because$ $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

Let system releases heat at constant temperature T and pressure P.

$\therefore$ $q = q_P = \Delta H$

$q_{system} = -q_{surroundings}$

$$\Rightarrow \quad \Delta H_{\text{system}} = -\,\Delta H_{\text{surroundings}}$$

$$\Delta S_{\text{surr.}} = \frac{\Delta H_{\text{surr.}}}{T}$$

$$\Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{sys.}}}{T}$$

$$\because \quad \Delta S_{\text{total}} = \Delta S_{\text{sys.}} + \left(\frac{-\Delta H_{\text{sys.}}}{T}\right)$$

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys.}} - \Delta H_{\text{sys.}}$$

$$T\Delta S_{\text{total}} = -(\Delta H_{\text{sys.}} - T\Delta S_{\text{sys.}})$$

$$T\Delta S_{\text{total}} = -\Delta G_{\text{sys.}}$$

or $\boxed{\Delta G_{\text{sys.}} = -T\Delta S_{\text{total}}}$

(i) If, $\Delta S_{\text{total}} = +ve \Rightarrow \Delta G_{\text{system}} = -ve \Rightarrow$ spontaneous process

(ii) If, $\Delta S_{\text{total}} = -ve \Rightarrow \Delta G_{\text{system}} = +ve \Rightarrow$ non spontaneous process

(iii) If, $\Delta S_{\text{total}} = 0 \Rightarrow \Delta G_{\text{system}} = 0 \Rightarrow$ process is at equilibrium.

$\Delta_r H^{-}$	$\Delta_r S^{-}$	$\Delta_r G^{-}$	**Description**
–	+	–	Reaction spontaneous at all temperature
–	–	–	(at low T) Reaction spontaneous at low temperature
–	–	+	(at high T) Reaction nonspontaneous at high temperature
+	+	+	(at low T) Reaction nonspontaneous at low temperature
+	+	–	(at high T) Reaction spontaneous at high temperature
+	–	+	(at all T) Reaction nonspontaneous at all temperatures

Relationship between standard Gibb's energy change ($\Delta G°$) and Equilibrium constant (K_{eq}) :-

For a reaction $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$\Delta G = \Delta G° + RT\,\ell nQ$$

At equilibrium – $\Delta G = 0$ and $Q = K_{eq}$

$$0 = \Delta G° + RT\,\ell n\,K_{eq}$$

$$\therefore \quad \boxed{\Delta G° = -RT\ell n K_{eq}} \qquad \ldots\text{(i)}$$

$$\text{or} \quad \boxed{\Delta G° = -2.303RT\log_{10} K_{eq}} \qquad \ldots\text{(ii)}$$

from equation (i)

$$\log K_{eq} = -\frac{\Delta G°}{RT}$$

$$\therefore \quad \boxed{K_{eq} = e^{-\Delta G°/RT}} \qquad \ldots\text{(iii)}$$

THIRD LAW OF THERMODYNAMICS (TLOT)

At zero kelvin (absolute zero temperature), the entropy of pure perfect crystalline solid is taken as zero.

Exceptions :

(i) NO, N_2O (ii) CO, CO_2 (iii) Mixture of isotopes (iv) Ice

THERMOCHEMISTRY

INTRODUCTION :

Thermochemistry is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or chemical reaction takes place within the system.

Depending upon the conditions under which the reaction is carried out, the quantity of heat transferred is related to energy or enthalpy change due to changes of states which occur in the system.

In this chapter we will introduced enthalpies of some specific reaction. Like, Enthalpy of formation (ΔH_f), Enthalpy of combustion (ΔH_{comb}), Bond dissociation enthalpy (ΔH_{BDE}) & Enthalpy of Neutralisation ($\Delta H_{neutralization}$)

THERMOCHEMICAL REACTION :

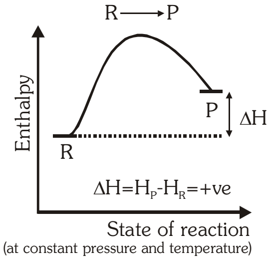
The balanced chemical reaction which give information about the physical states of reactants & products and heat change is called as thermo chemical reaction.

eg. $2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}, \Delta H = +\text{ xcal}$

Thermo chemical reaction are of 2 types.

(i) Endothermic reaction :

The reaction which absorbs heat is called as endothermic reaction.



$\boxed{\Delta H = +ve}$

$\Delta H = H_P - H_R = +ve$ i.e. $\boxed{H_P > H_R}$

(a) Stability of reactant > Stability of product because more heat is required to break the bonds of reactant.

(b) The product formed in the endothermic reaction is called endothermic compound.

(c) If more heat is absorbed then the product formed in the reaction will be less stable or the reactant is more stable.

Representation of endothermic reaction :

$A + B + xCal \longrightarrow C + D$ (endo)

$A + B \longrightarrow C + D - xcal$ (endo)

$A + B \longrightarrow C + D, \Delta H = +\text{ xcal}$ (endo)

Examples :

(I) Dissociation reactions (mostly)

(II) Fusion reactions

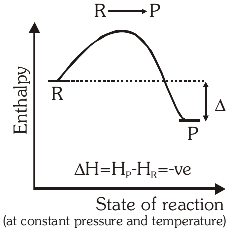
(III) Vaporization reactions

(IV) Sublimation reactions

(V) Photosynthesis $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$, $\Delta H = +ve$

(ii) Exothermic reaction :

The reaction which evolves heat is called as exothermic reaction.



$\boxed{\Delta H = -ve}$ $\Delta H = H_P - H_R = -ve$ i.e. $\boxed{H_P < H_R}$

(a) Stability of reactant < Stability of product because less heat is required to break the bonds of reactant.

(b) The product formed in the exothermic reaction is called exothermic compound.

(c) If more heat is released then the product formed in the reaction will be more stable or the reactant is less stable.

Representation of exothermic reaction.

$A + B \longrightarrow C + D + xcal$ (exo)

$A + B - xcal \longrightarrow C + D$ (exo)

$A + B \longrightarrow C + D, \quad \Delta H = -\, xcal$ (exo)

Examples :

(I) Combustion reactions (II) Neutralisation reactions

(III) Respiration reaction **eg.** $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

(IV) Formation reaction $<\begin{matrix}\text{endo}\\ \text{exo (generally)}\end{matrix}$

Exceptions of formation reaction :

$$\left[\begin{array}{l} C + 2S \longrightarrow CS_2 \\ \frac{1}{2}N_2 + \frac{3}{2}Cl_2 \longrightarrow NCl_3 \\ N_2 + O_2 \longrightarrow NO/N_2O/NO_2/N_2O_4 \\ O_2 + F_2 \longrightarrow OF_2/O_2F_2 \end{array}\right] \Delta H = +ve \text{ (endothermic)}$$

POINTS TO REVISE

(i) If conditions are not given then, ΔH is considered to be ΔH°.

(ii) If thermochemical reaction is multiplied by a coefficient then, ΔH of reaction is also multiplied by that coefficient.

e.g. $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O\ (\ell)$ $\Delta H = -285\ kJ\ mol^{-1}$

$2H_2(g) + O_2 \longrightarrow 2H_2O\ (\ell)$ $\Delta H = -2 \times 285\ kJ$

(iii) If reaction is reversed then numerical value of ΔH remains same but sign is changed.

$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O\ (\ell)$ $\Delta H = -285\ kJ\ mol^{-1}$

$H_2O\ (\ell) \longrightarrow H_2(g) + \frac{1}{2} O_2(g)$ $\Delta H = +285\ kJ\ mol^{-1}$

HEAT OF REACTION OR (ENTHALPLY OF REACTION) OR (ΔH_R) :

The amount of heat evolved or absorbed when number of moles of the reactant according to the balanced chemical reaction had completely reacted is called as heat of reaction.

Example : $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)},$ $\Delta H_R = ✓$

$H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{(g)},$ $\Delta H_R = ✗$

$H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{2\,(g)},$ $\Delta H_R = ✓$

Note : Heat of reaction at constant pressure is ΔH and heat of reaction at constant volume is ΔE.

Factors affecting heat of reaction :

(i) Reaction condition :

(a) The chemical reactions are carried out at constant temperature with either pressure or volume constant.

At constant pressure $q_p = \Delta H_{reactin}$

At constant volume $q_v = \Delta E_{reaction}$

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

(ii) Quantity of reactant :

Example : $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)}$ $\quad \Delta H_1 = -x \text{ lCal mol}^{-1}$

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\quad \Delta H_2 = 2 \times (-x \text{ Kcal})$

If equation is multiplied by coefficient then value of Δ H is also multiplied by that coefficient.

(iii) Physical state of products and reactants :

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(\ell)}, \qquad \Delta H = -285.8 \text{ kJ mole}^{-1}$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)}, \qquad \Delta H = -\ 242 \text{ kJ/mole}^{-1}$$

If the physical state of product is different then the value of ΔH is different.

Note : For H_2O (liq.), ΔH is more negative in comparison to the formation of H_2O(vap.) because when vapours convert into liquid then some heat is released.

(iv) Allotropic form : (Physical nature of reactant)

$$C_{\text{graphite}} + O_2 \longrightarrow CO_2, \qquad \Delta H_R = -\ 393.5 \text{ kJ mole}^{-1}$$

$$C_{\text{diamond}} + O_2 \longrightarrow CO_2, \qquad \Delta H_R = -\ 399.5 \text{ kJ mole}^{-1}$$

(v) Temperature :

Effect of temperature on heat of reaction is given by **Kirchoff equation**

(i) at constant pressure : $\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_{Pm}$

$\Delta C_{Pm} = \Sigma(C_{Pm})_P - \Sigma(C_{Pm})_R$

ΔH_{T_1} = Heat of reaction at T_1 temperature

ΔH_{T_2} = Heat of reaction at T_2 temperature

(ii) at constant volume : $\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_{Vm}$

$\Delta C_{Vm} = \Sigma(C_{Vm})_P - \Sigma(C_{Vm})_R$

TYPES OF HEAT OF REACTION :

(A) Heat of formation, Enthalpy of formation (ΔH_f) or (Δ_f H) :

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states).

The reference state of oxygen, carbon and sulphur are O_2 gas, C_{graphite} and S_{rhombic} , respectively some reactions with standard molar enthalpies of formation are :

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f \quad ✓$$

$$\frac{1}{2} H_{2(g)} + \frac{1}{2} N_{2(g)} + \frac{3}{2} O_{2(g)} \longrightarrow \underset{1\text{mole}}{HNO_3} \qquad \Delta H_f \quad ✓$$

$$Na_{(s)} + \frac{1}{2} O_{2(g)} + \frac{1}{2} H_{2(g)} \longrightarrow \underset{1\text{mole}}{NaOH} \qquad \Delta H_f \quad ✓$$

APPLICATION OF ΔH_f :

Calculation of ΔH of any general reaction.

Let us considered a general reaction aA + bB → cC + dD

$$\Delta H_{\text{reaction}} = \Sigma \Delta H_{f(\text{products})} - \Sigma \Delta H_{f(\text{reactant})} = \left[c\Delta H_{f(C)} + d\Delta H_{f(D)}\right] - \left[a\Delta H_{f(A)} + b\Delta H_{f(B)}\right]$$

POINTS TO REVISE

- Standard condition means, P = 1 atm, T = 25°C or 298 K
  Standard heat of formation is represent by ΔH_f°.
- If no condition is given then value of ΔH_f is considerd as ΔH_f°.
- Standard heat of formation of all the elements in stable standard state is taken to be zero.
- The reference state of commonly used elements are

Elements	**Reference state**	
C	$C_{(graphite)}$	
S	$S_{8(Rhombic)}$	(Rhombic sulphur is energy wise more stable as compared to monoclinic sulphur)
P	$P_{4(white)}$	
O	$O_{2(g)}$	
H	$H_{2(g)}$	
Br	$Br_{2(\ell)}$	
Metal	$M_{(s)}$[except $Hg_{(\ell)}$]	

- The formation reaction may be exothermic or endothermic.

(B) Heat of combustion (ΔH_{comb}) :

Amount of heat evolved when 1 mole of substance is completely burnt (or oxidised) in excess of oxygen.

Example :

$\underset{1mole}{C_{graphite}} + O_2 \longrightarrow CO_2, \Delta H_{comb}$ ✓ and ΔH_f ✓

$\underset{1mole}{C_{diamond}} + O_2 \longrightarrow CO_2, \Delta H_{comb}$ ✓ and ΔH_f ×

$\underset{1mole}{C} + \frac{1}{2}O_2 \longrightarrow CO, \quad \Delta H_{comb}$ × and ΔH_f ✓

$\underset{1mole}{CO} + \frac{1}{2}O_2 \longrightarrow CO_2, \quad \Delta H_{comb}$ ✓ and ΔH_f ×

Note :

(I) Heat of combustion reaction is always exothermic

(II) If conditions are not given then ΔH_{comb} considered as ΔH°_{comb}.

(III) If in a reaction heats of combustion of reactants and products are given then heat of that reaction can be measured as follows

$$\boxed{\Delta H = \Sigma\,(\Delta H_{comb})_R - \Delta(\Delta H_{comb})_P}$$

APPLICATION OF HEAT OF COMBUSTION :

Calorific value or fuel value (C.V.) :

The amount of heat evolved when 1 g of a substance (food or fuel) is completely burnt (or oxidised)

$$\boxed{\text{Calorific value} = \frac{\Delta H_{comb}}{\text{Molecular weight}}}$$

Unit :- kJ g^{-1} or kCal g^{-1}

POINTS TO REVISE

- Heat of combustion reaction is always exothermic
- If conditions are not given then ΔH_{comb} is considered as ΔH°_{comb}.
- Maximum value of calorific value = Maximum efficiency or best fuel
- H_2 has the highest calorific value (150 kJ/g) but it is not used as domestic or industrial fuel due to some technical problems.

(C) Heat of neutralisation (ΔH_{neut}) :

The heat evolved when one equivalent of an acid is completely neutralised by one equivalent of a base in dilute solution is called as heat of neutralisation.

$$\mathrm{SA + SB \longrightarrow Salt + Water}$$

$$\mathrm{HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl + H_2O}$$

$$\mathrm{H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O}$$

$$\boxed{\mathrm{H^+ + OH^- \longrightarrow H_2O}}$$

Note :

(i) When one equivalent of SA is neutralised by one equivalent of SB then evolve heat remain constant and its value is – 13.7 kCal/equivalent or – 57.2 kJ equivalent^{-1}.

eg.	SA		SB		
	HCl (aq)	+	NaOH (aq)	$\longrightarrow$	NaCl + H_2O + 13.7 kCal
	NV = 1 eq.		NV = 1 eq.	$\longrightarrow$	$\Delta H = -13.7$ kCal
	NV = 2 eq.		NV = 2 eq.	$\longrightarrow$	$\Delta H = 2\ (-13.7)$ kCal
	NV = 3 eq.		NV = 3 eq.	$\longrightarrow$	$\Delta H = 3\ (-13.7)$ kCal
	NV = 4 eq.		NV = 5 eq. = (4 + 1) eq.	$\longrightarrow$	$\Delta H = 4\ (-13.7)$ kCal
	NV = 5 eq. = (3+2)eq		NV = 3 eq.	$\longrightarrow$	$\Delta H = 3\ (-13.7)$ kCal

(ii) If one of the acid or base or both are weak then heat of neutralization is usually less than –13.7 KCal eq^{-1} or –57.3 kJ eq^{-1} because some part of the heat released in neutralization is absorbed to dissociate the weak electrolyte completely.

eg. $\overset{\text{WA}}{\mathrm{CH_3COOH(aq)}} + \overset{\text{SB}}{\mathrm{NaOH(aq)}} \rightarrow \mathrm{CH_3COONa(aq) + H_2O}; \Delta H = -13.4$ kCal eq^{-1}

Exception :

For a reaction $\mathrm{HF + NaOH \rightarrow NaF + H_2O}$; $\Delta H = -16.7$ Kcal; this is because of hydration of F^- ion.

(D) Heat of hydrogenation ($\Delta H_{Hydrogenation}$) :

The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.

Unsaturated organic compound $\xrightarrow{\text{Change}}$ Saturated organic compound

(= or ≡ Bond) **(– Bond)**

$C_2H_2 + 2H_2 \longrightarrow C_2H_6$, ΔH_{hydro} ✓

$C_2H_2 + H_2 \longrightarrow C_2H_4$, ΔH_{hydro} ×

$C_2H_4 + H_2 \longrightarrow C_2H_6$, ΔH_{hydro} ✓

Note : Heat of hydrogenation is exothermic process.

(E) Heat of atomization (ΔH_{atom}) :

The amount of heat required to dissociate 1 mol substance into gaseous atoms is called as heat of atomization.

Example : $\frac{1}{2}H_{2(g)} \longrightarrow 1\,H_{(g)}$ $\quad \Delta H_{atom}$ ×

$H_{2(g)} \longrightarrow 2\,H_{(g)}$ $\quad \Delta H_{atom}$ ✓

$\frac{1}{2}Cl_{2(g)} \longrightarrow 1\,Cl_{(g)}$ $\quad \Delta H_{atom}$ ×

$Cl_{2(g)} \longrightarrow 2Cl_{(g)}$ $\quad \Delta H_{atom}$ ✓

Note : It is an endothermic reaction.

(F) HEAT OF TRANSFORMATION :

(i) Heat of fusion ($\Delta\ H_{fusion}$) : The required amount of heat to convert 1 mole solid into liquid at its melting point is called as heat of fusion.

Example : $1\ H_2O_{(s)} \longrightarrow H_2O_{(l)}$ $\quad \Delta\ H_{fusion}$ ✓

Note : Heat of fusion is always endothermic reaction i.e. ($\Delta\ H = +$ ve)

(ii) Heat of vapourization ($\Delta\ H_{Vapour}$) : The required amount of heat to convert 1 mole liquid into gas at its boiling point is called as heat of vapourization.

Example : $1\ H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$ $\quad \Delta\ H_{Vapour}$ ✓

Note : Heat of vapourization is always endothermic reaction i.e. ($\Delta\ H = +$ve)

(iii) Heat of sublimation ($\Delta\ H_{Sub}$) :

The required amount of heat to convert 1 mole solid into gas at a certain termperature is called as heat of sublimation.

Example : $H_2O_{(s)} \longrightarrow H_2O_{(g)}$, $\quad \Delta\ H_{Sub}$ ✓

Note : Heat of sublimation is always endothermic reaction i.e. ($\Delta H = +$ ve)

(G) Heat of hydration (ΔH_{hydra}) :

Amount of heat evolved when **one mole** of anhydrous salt combines with fixed number of water molecules to convert into its specific hydrated crystal is called as heat of hydration.

Example :

- $1\ CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4 .5\ H_2O(s) \quad \Delta H = -$ ve

  anhydrous salt hydrated salt
- $1\ MgSO_4(s) + 7H_2O\ (\ell) \longrightarrow MgSO_4.7H_2O(s) \quad \Delta H = -$ ve

  anhydrous salt hydrated salt
- $1\ CaCl_2(s) + 6H_2O(\ell) \longrightarrow CaCl_2 .6\ H_2O(s) \quad \Delta H = -$ ve

  anhydrous salt hydrated salt

Special Note : Heat of hydration is exothermic

(H) Heat of solution ($\Delta H_{sol.}$) :

Amount of heat absorbed or evolved when **one mol** of substance is dissolved in such a large volume of solvent that further addition of solvent does not produce any more heat change is called as **'Heat of solution'**.

Example 1: $1\ CuSO_{4(s)} + aq \longrightarrow CuSO_4(aq)$ $\Delta H_{solution}$ ✓

$1\ CuSO_{4(s)} + 5H_2O\ (\ell) \longrightarrow CuSO_4.5H_2O(s)$ $\Delta H_{hydration}$ ✓

Example 2: $MgSO_{4(s)} + 7H_2O\ (\ell) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

$MgSO_4.7H_2O(s) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

Sp. Note : Heat of solution may be endothermic or exothermic.

(I) Bond energy / Bond dissociation energy :

The required amount of energy to dissociate **one mole gaseous bond** into separate **gaseous atoms** is called as **bond dissociation energy.**

Example : $1H-H_{(g)} \longrightarrow 2H_{(g)}$ ΔH_{H-H} ✓

$1Cl-Cl_{(g)} \longrightarrow 2Cl_{(g)}$ ΔH_{Cl-Cl} ✓

$1H-Cl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)}$ ΔH_{H-Cl} ✓

$1H-Cl_{(g)} \longrightarrow H^+_{(g)} + Cl^-_{(g)}$ ΔH_{H-Cl} ×

$1H-Cl_{(g)} \longrightarrow \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)},$ ΔH_{H-Cl} ×

$1H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)}$ ΔH_{H-O} ×

POINTS TO REVISE

- The **bond energy** may be defined as the **average** amount of energy required to dissociate one mole gaseous bond into separate gaseous atoms.
- Bond dissociation process is an endothermic process.
- If bond energy of various bonds present in the reactants and products are given then ΔH of that reaction can be calculate as follows.

$$\boxed{\Delta H = \Sigma\ (B.E.)_R - \Sigma\ (B.E.)_P}$$

- **In the case of poly atomic molecule** we calculate the average bond energy.

$$\boxed{(BE)_{av} = \text{Average bond energy} = \frac{\text{Total energy required with all bonds}}{\text{Number of bond dissociation}}}$$

Example : $H-O-H_{(g)} + 112\ KJ \longrightarrow H-O_{(g)} + H_{(g)}$

$H-O_{(g)} + 108\ KJ \longrightarrow H_{(g)} + O_{(g)}$

$$(BE)_{av} = \text{Average bond energy} = \frac{112+108}{2} = 110\ \text{kJ mol}^{-1}$$

LAWS OF THERMOCHEMISTRY :

(I) LAVOISIER AND LAPLACE LAW :

Enthalpy of formation of compound is **numerically equal** to the enthalpy of decomposition of that compound with **opposite sign**.

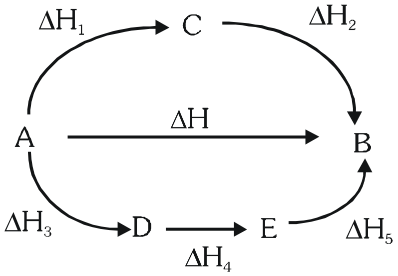
Example : $C + O_2 \longrightarrow CO_2,$ $\Delta H = -94$ kCal

$CO_2 \longrightarrow C + O_2,$ $\Delta H = +94$ kCal

(II) HESS LAW OF CONSTANT HEAT SUMMATION :

The heat change in a complete chemical reaction always remain same whether reaction completes in one step or more.

Example

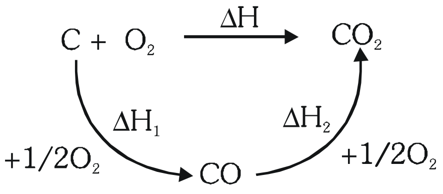


$\Delta H = \Delta H_1 + \Delta H_2$

or $\Delta H = \Delta H_3 + \Delta H_4 + \Delta H_5$

or $\mathbf{\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5}$

Example



$\mathbf{\Delta H = \Delta H_1 + \Delta H_2}$

POINTS TO REVISE

- Heat change of a reaction does not depend on the **number of steps** used in the reaction.
- Heat change of a reaction does not depend on **intermediate position**, it depend only on initial and final state.
- Heat change of a chemical reaction does not depend on **time of reaction**.