MEASUREMENT OF ΔU AND ΔH: CALORIMETRY

Enthalpy(H) Or Heat Content

Chemical reactions are typically conducted under constant pressure conditions, often at atmospheric pressure. Therefore, it has proven valuable to introduce a new state function known as Enthalpy (H).

$$H = U + PV$$

$$\Delta H = \Delta U + \Delta(PV)$$

at constant pressure

$$\Delta H = \Delta U + P\,\Delta V \qquad \text{......(1)}$$

From First Law $\Delta U = q + w = q - PdV$

$$q = \Delta U + PdV = \Delta H \qquad \text{.....(2)}$$

combining with first law. $\Delta H = q_p$

Consequently, the transfer of heat under constant volume conditions results in a modification of the system's internal energy, whereas under constant pressure, it leads to a change in the system's enthalpy.

For a given system

$$H = f\,(T, P)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p .\, dT + \left(\frac{\partial H}{\partial T}\right)_p dP$$

For isobaric process: $dP = 0$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT$$

$$dH = C_P.\, dT$$

$$\Delta H = \int C_{p.}\, dT$$

For an ideal gas $\left(\frac{\partial H}{\partial p}\right)_T = 0$

$$dH = C_P.\, dT$$

$$\Delta H = \int C_{p.}\, dT$$

Relationship Between ΔH & ΔU

The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids)

$$\Delta H = \Delta U + \Delta(PV)$$

If substance is not undergoing chemical reaction or phase change.

$$\Delta H = \Delta U + nR\Delta T$$

In case of chemical reaction

$$\Delta H = \Delta U + (\Delta n_g)\, RT$$

Heat Capacity

The heat capacity of a system can be described as the quantity of heat necessary to increase the system's temperature by one degree. If we denote the small amount of added heat as δq and the resulting temperature rise as dT, the system's heat capacity, denoted as C, can be expressed as follows:

$$C = \frac{dq}{dT} \qquad \text{.... (i)}$$

In case of gases, we have two types of heat capacity i.e., heat capacity at constant volume and heat capacity at constant pressure.

Types of Heat Capacity:

(i) Specific Heat:

Specific heat, denoted by 'c,' refers to the amount of heat lost or gained by a 1-gram system to bring about a one-unit change in temperature. The specific heat is calculated using the formula: $c = \frac{C}{M}$,

where:

c is the specific heat,

C is the heat capacity,

M is the mass of the system.

Specific heat is considered an intensive property.

(ii) Molar Heat Capacity:

Molar heat capacity (C_m) pertains to the heat capacity for a system containing 1 mole of material. It is expressed as $C_m = \frac{C}{n}$,

where:

C is the heat capacity,

n is the number of moles.

Molar heat capacity (C_m) is an intensive property.

(iii) Heat Capacity at Constant Volume (Cv)

Molar heat capacity at constant volume is defined by the relation

$$C = \frac{dqv}{dT} \quad \text{.... (ii)}$$

For first law of thermodynamics

$$dU = dq - dw$$

But $dw = P\,dV$

$\therefore$ $dU = dq - P\,dV$ .... (iii)

At constant volume

$$dU = dq_V$$

$\therefore$ Heat capacity at constant volume C_V is given by

$$C_V = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_v$$

or $C_V = \left(\frac{\partial U}{\partial T}\right)_v$ .... (iv)

It can be defined as the rate at which the internal energy changes with respect to temperature when the volume is held constant.

(iv) Heat Capacity at Constant Pressure (C_p)

When pressure is maintained constant, equation (i) takes the form

$$C_P = \frac{\delta q_v}{dT} \quad \text{.... (v)}$$

From first law of thermodynamics

At constant pressure

$$\delta q_p = (dU + PdV) = dH$$

$$[\Delta H = U + PV \text{ At constant P, } dH = dU + PdV]$$

$\therefore$ $\delta q_p = dH$ .... (vi)

Heat capacity at constant pressure C_p is given by

$$C_p = \frac{\delta d_p}{dT} = \left(\frac{\partial H}{\partial T}\right)_p$$

or $$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{.... (vii)}$$

This is expressed as the rate of enthalpy change with temperature under constant pressure conditions. Consequently, the heat capacity of a system at constant volume, denoted as C_v, corresponds to the change in internal energy per degree of temperature increase under constant volume conditions. In a similar manner, the heat capacity at constant pressure, denoted as C_p, is numerically equivalent to the change in enthalpy per degree of temperature rise.

For one mole of gas $C_p - C_v = R$

For 'n' moles of gas $C_p - C_v = nR$

Relation between $C_{p,m}$ and $C_{v,m}$ for Ideal Gas

Given our knowledge of thermodynamics, we can express the relationship using the following equations:

$$\Delta H = \Delta E + P\Delta V \quad \text{(i)}$$

Applying the ideal gas equation,

$$P\Delta V = R\Delta T \quad \text{(ii),}$$

we can derive:

$$\Delta H = \Delta E + R\Delta T$$

Dividing both sides by ΔT, we obtain:

$$\frac{\Delta H}{\Delta T} = \frac{\Delta E}{\Delta T} + R$$

This expression is commonly written in terms of molar heat capacities:

$$C_{p,m} = C_{v,m} + R$$

Furthermore, extending this to non-molar heat capacities, we have:

$$C_p = C_v + nR$$

These equations establish the relationships between changes in enthalpy (ΔH), internal energy (ΔE), pressure (P), volume (V), temperature (T), and the gas constants (R).

Value of $C_{p,m}$ and $C_{v,m}$ for Ideal Gas

(a) For a monoatomic gas:

The internal energy change (ΔE) can be determined by the formula $\Delta E = \frac{3}{2}RT$, as it possesses three translational modes, each contributing $\frac{RT}{2}$. Consequently, the molar heat capacities are $C_{v,m} = \frac{3}{2}R$ and $C_{p,m} = \frac{5}{2}R$.

(b) For a diatomic gas:

The internal energy change (ΔE) is given by $\Delta E = \frac{5}{2}RT$, accounting for three translational modes and two rotational modes, with each contributing $\frac{RT}{2}$. Thus, the molar heat capacities are $C_{v,m} = \frac{5}{2}R$ and $C_{p,m} = \frac{7}{2}R$.

(c) For polyatomic gases:

the molecules fall into two categories: linear and non-linear.

(i) For linear molecules:

The scenario is analogous to that of diatomic molecules, resulting in $C_{v,m} = \frac{5}{2}R$ and $C_{p,m} = \frac{7}{2}R$.

(ii) For non-linear molecules:
The molar heat capacities are $C_{v,m} = 3R$ and $C_{p,m} = 4R$.

Changes in Thermodynamic Properties during the Expansion or Contraction of a Gas (w, q, ΔH, ΔE):

To assess alterations in thermodynamic properties during the expansion or compression of an ideal gas, we apply the first law of thermodynamics.

(a) **ΔE or ΔU:**
In an isothermal expansion or compression, where the system's temperature remains constant, the internal energy change (ΔU) is zero. This is a consequence of Joule's law, where $\frac{U}{V} = 0$. Thus, $dU = 0$ or $\Delta U = 0$. Substituting this into the first law of thermodynamics yields $dq - dw$ or $q = -w$. In such processes, heat is converted into work and vice versa. If heat is supplied to the system (q positive), an equivalent amount of work is done by the system (w negative), and if work is done on the system (w positive), an equivalent amount of heat is released (q negative).

(b) **ΔH:**
The enthalpy change (ΔH) is also zero,
As: $\Delta H = \Delta(U + PV) = \Delta U + \Delta(PV)$
$= \Delta U + \Delta(nRT) = \Delta U + nR(\Delta T)$
$= 0 + 0 = 0.$

(c) **Work Done:**
The magnitude of work (w) or heat (q) depends on the manner in which the expansion or compression occurs. Two distinct types of processes can be identified: reversible and irreversible. The changes in q, w, ΔU, and ΔH in these processes are delineated below.

ΔU Measurements, ΔH Measurements:

Calorimetry is the experimental technique used to measure the energy changes associated with physical or chemical processes. The heat released or absorbed during a chemical reaction is quantified using a specialized apparatus called a calorimeter.

During calorimetry, the process unfolds within a calorimeter, which is submerged in a precisely measured volume of liquid. By understanding the heat capacity of both the liquid surrounding the calorimeter and the calorimeter itself, it becomes feasible to calculate the heat generated or absorbed in the process by monitoring temperature alterations. Measurements are conducted under two distinct conditions:

(i) At constant volume, denoted as q_v,
(ii) At constant pressure, denoted as q_p.

(a) Measurements of ΔU:

To experimentally determine the heat absorbed at constant volume, i.e., the internal energy change (ΔU), a specialized apparatus called a Bomb Calorimeter is utilized. The Bomb Calorimeter consists of a robust steel vessel, referred to as the 'bomb,' designed to withstand high pressures. This vessel is submerged in a water bath to prevent any heat loss to the surroundings. A stirrer, suspended in the sealed water bath, facilitates the dissipation of heat generated from the bomb calorimeter. Additionally, a thermometer is suspended to monitor temperature changes.

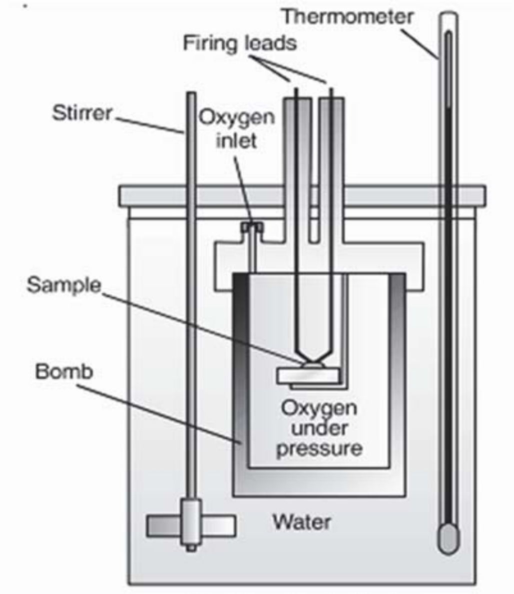


Fig.: Bomb calorimeter

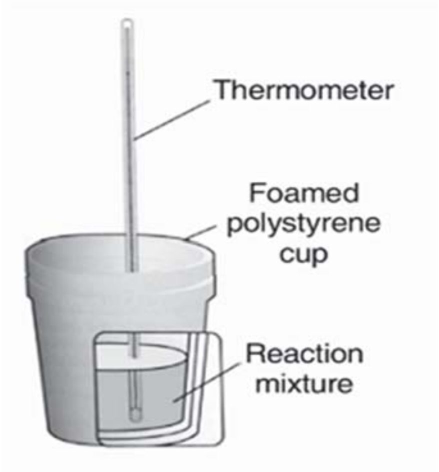
During experimentation, when a combustible substance undergoes combustion in pure dioxygen supplied within the steel bomb, the heat produced is transferred to the water surrounding the bomb. The temperature variation of the water is carefully monitored. Since the bomb calorimeter is sealed, its volume remains constant, ensuring that the energy changes associated with the reactions are measured at a constant volume.

Under these conditions, no work is performed because the reaction takes place at a constant volume within the bomb calorimeter. This holds true even for reactions involving gases, as ΔV (change in volume) equals zero. The resulting temperature change in the calorimeter, induced by the completed reaction, is then converted to qv using the known heat capacity of the calorimeter, employing the equation.

$$Q = C \times m \times \Delta T$$

(b) Measurements of ΔH:

The determination of the change in enthalpy (ΔH) during a reaction is also conducted in a calorimeter, as depicted in the figure. This measurement of heat change occurs at a constant pressure, typically under atmospheric pressure. The alteration in temperature is gauged both at the commencement and conclusion of the reaction.



Given that $\Delta H = q$ (at constant pressure p), the heat absorbed or released (q) at constant pressure is commonly referred to as the heat of reaction or the enthalpy of reaction ($\Delta_r H$).
In an exothermic reaction, where heat is released and the system loses heat to the surroundings, qp is negative, and consequently, $\Delta_r H$ is also negative. Conversely, in an endothermic reaction, where heat is absorbed and q is positive, $\Delta_r H$ is positive.