By- SHAILENDRA SHUKLA SIR

THERMODYNAMICS

"The branch of chemistry which deals with the inter-conversion of different forms of energy is called thermodynamics."

Thermodynamics involves the study of all the processes occurring in nature. Hence, it is also called the chemistry of nature. Thermodynamics is totally based on human experience and is the only branch of science which has no exception.

Thermodynamics gives idea about-

(a) Favourable conditions of temperature and pressure for a process to take place.

(b) Direction and Extent of the process under given conditions of temperature and pressure.

Limitations

(1) Thermodynamics does not give any idea about the kinetics (speed) of the process.

(2) Laws of thermodynamics are only applicable on macroscopic systems i.e. on matter in bulk and are not applicable on isolated atom, ion or molecule.

Terminology

(1) System and surroundings

"The specified portion of universe which is selected for thermodynamic study is called system."

"The rest of the universe other than system is called surrounding of the system."

Both systems and surrounding remain separated from each other by some definite boundary, which may be real or imaginary.

For example, let we have to study the behavior of a mixture of alcohol and water taken in a beaker. Here, the content of the beaker is called system. Rest of the universe other than this content (system) will be the surrounding of the system. The wall of the beaker will act like real boundary between systems and its surrounding.

* Theoretically, rest of the universe other than systems is called surrounding of the system, but in practice, the limited space around the system which affects the system and which is affected by the system is called surrounding of the system.

CHEMISTRYFORCOMPETITION.COM

Types of System

Depending upon the exchange of matter and energy with their surrounding, the systems may be of following three types-

(i) Open System- Such systems which can exchange both matter and energy with their surrounding are called open systems. For example, hot water taken in an open steel flask.

(ii) Closed system- Such systems which can exchange energy with their surrounding, but cannot exchange matter are called closed systems. For example, hot water taken in a closed steel flask.

(iii) Isolated system- Such systems which cannot exchange both matter and energy with their surrounding are called isolated systems. For example, hot coffee taken in a perfectly insulated closed thermus flask.

- Universe is an isolated system.
- Human body is an open system.

(2) State of the system

The conditions of the existence of a system, when its all the macroscopic properties such as temperature, pressure, volume etc. remains unchanged, is called a state of the system.

If any of these parameters is changed, a new state is achieved.

(3) Process

"The change of a system from one state to another is called process."

The processes may be of following types-

(i) Isothermal process

"Such processes during which, the temperature of the system remains unchanged are called isothermal processes."

OR

"The processes occurring at constant temperature are called isothermal processes."

For isothermal processes, the change in temperature of the system during the process is zero. Thus, for these processes-

$$\Delta T = 0$$

These are very slow processes and are carried out in perfectly heat conducting vessels, so that, if heat is released during the process, it is transferred to the surrounding and if it is absorbed during the process, it is taken from the surrounding to keep the temperature of the system unchanged.

CHEMISTRYFORCOMPETITION.COM

Thus, during isothermal processes, there occurs free exchange of heat energy between system and surrounding and therefore, heat change of the system cannot be zero i.e.

$$q \neq 0$$

Since, internal energy (U) of the ideal gases depends only upon temperature, the change in internal energy of ideal gases during these processes is zero. Thus,

$$\Delta U = 0$$

(ii) Adiabatic process

"Such processes during which, there is no exchange of heat energy between system and their surrounding are called adiabatic processes."

Thus, for adiabatic processes, the heat change of the system during the process is zero i.e.

$$q = 0$$

These are very fast processes and are carried out in perfectly heat insulated vessels. Here, if heat is released during the process, it is not transferred to the surrounding and if it is absorbed during the process, it is not taken from the surrounding. Hence, the temperature of the system gets changed. Thus, during adiabatic processes, change in temperature of the system is not equal to zero i.e.

$$\Delta T \neq 0$$

Since, internal energy (U) of the ideal gases depends only upon temperature, it gets changed during these processes. Thus, change in internal energy of ideal gases during adiabatic processes cannot be zero. Thus,

$$\Delta U \neq 0$$

(iii) Isochoric processes

"The processes occurring at constant volume are called isochoric processes."

Thus, for isochoric processes, the change in volume of the system during the process is zero i.e.

$$\Delta V = 0$$

Here, since volume of the system remains unchanged, the pressure of system gets changed. Thus, for these processes, change in pressure of the system during the process cannot be zero i.e.

$$\Delta P \neq 0$$

(iv) Isobaric processes

"The processes occurring at constant pressure are called isobaric processes."

Thus, for isobaric processes, the change in pressure of the system during the process is zero i.e.

$$\Delta P = 0$$

CHEMISTRYFORCOMPETITION.COM

Here, since pressure of the system remains unchanged, the volume of system gets changed. Thus, for these processes, change in volume of the system during the process cannot be zero i.e.

$$\Delta V \neq 0$$

(v) Cyclic processes

"Such processes in which the systems return back to their original state moving from different states, are called cyclic processes."

In cyclic processes, the initial state of the system is also the final state of the system. Hence, change in all the state functions during these processes is always equal to zero. For example, change in internal energy (ΔU) during cyclic processes is always equal to zero i.e.

$$\Delta U = 0$$

(vi) Reversible and Irreversible processes

"Such processes in which driving and opposing forces are comparable and therefore, the direction of the process can easily be reversed at any state of the process, are called reversible processes."

For example, melting of ice at 0^0C.

Reversible processes are very slow processes.

On the other hand, such processes in which driving forces are much more larger than the opposing forces and therefore, the direction of the process cannot easily be reversed at any state of the process are called irreversible processes.

For example, free expansion of gases.

Irreversible processes are very fast processes.

(4) Extensive and Intensive properties

Such thermodynamic properties which depend upon the amount of substance contained in the system and therefore, increase with increase of amount of substance in the system, are called extensive properties of the system.

For example, mass, volume, internal energy (U), enthalpy (H), entropy (S), free energy (G) etc.

On the other hand, Such thermodynamic properties which do not depend upon the amount of substance contained in the system and therefore, do not increase with increase of amount of substance in the system, are called intensive properties of the system.

For example, melting point, boiling point, density, refractive index, viscosity, surface tension etc.

It is clear that, intensive properties are the physical constants of the system.

CHEMISTRYFORCOMPETITION.COM

- The ratio of two extensive properties may be an intensive property. For example, both mass and volume are extensive properties, but their ratio mass/volume i.e. density is an intensive properties
- If the term 'molar' is added before the name of the extensive properties, they become intensive properties. For example, mass is an extensive property, but molar mass is an intensive property. Similarly, volume is an extensive property, but molar volume is an intensive property.

(5) State functions and Path functions

Such thermodynamic quantities which depend only upon the state of the system and are independent of the path followed and agency by which the state has been attained are called state functions. For example, internal energy (U), enthalpy (H), entropy (S), free energy (G) etc.

The absolute value of state functions cannot be determined experimentally. However, the change in these quantities during a process can easily be determined. For example, absolute value of internal energy (U), cannot be determined experimentally. However, the change in internal energy (ΔU) during a process can be determined easily and is given by following expression-

$$\Delta U = U_{final} - U_{initial}$$

For a chemical reaction, the change in internal energy,

$$\Delta U = U_{products} - U_{reactants}$$

On the other hand, Such thermodynamic quantities which depend upon the path followed during the process are called path functions. For example, heat change (q) and work done (w) during a process.

- The sum of two path functions may be a state function.
  For example, both heat change (q) and work done (w) are path functions, but their sum ($q+w = \Delta U$) is a state function.

(6) Internal energy (U)

In a given state of temperature and pressure, all the substances (systems) remain associated with a definite amount of energy, which is called internal energy of the system. In fact, internal energy is the sum of all forms of kinetic and potential energies stored in the system under a given condition of temperature and pressure. Mathematically, internal energy,

$$U = K.E. + P.E$$
$$= E_{trans} + E_{vib} + E_{rot} + E_{ele} + E_{nuc} + E_{inter}$$

These constituent energies are inter-convertible. Hence, the absolute values of these constituent energies cannot be determined experimentally.

CHEMISTRYFORCOMPETITION.COM

In thermodynamics, we do not remain associated with the absolute value of the internal energy, but we remain associated with the change in internal energy during the process and it is given by following formula-

$$\Delta U = U_{final} - U_{initial}$$

For a chemical reaction, the change in internal energy

$$\Delta U = U_{products} - U_{reactants}$$

Here, the value of ΔU also depends only upon initial and final states of the system and is independent of the path followed during the process.

Sign conventions-

According to new sign conventions, any change which increases the internal energy of the system is taken to be positive while that which decreases internal energy of system is taken to be negative. Thus,

Heat absorbed by the system = +ve
Heat evolved from the system = -ve
Work done on the system = +ve
Work done by the system = -ve

First law of thermodynamics

This law was for the first time proposed by Mayer. It is, in fact, the law of conservation of energy. According to this law-

"The energy can neither be created nor be destroyed but can be transformed from one form to another during a process."

or

"Whenever one form of energy disappears, equivalent amount of another form of energy makes its appearance."

For an isolated system, this law can be defined as under-

"During all the processes occurring in an isolated system, the total energy of the system remains unchanged."

Now since, the universe is also an isolated system, from first law of thermodynamics, it can be concluded that,

"During all the processes occurring in universe, the total energy of universe remains unchanged."

CHEMISTRYFORCOMPETITION.COM

Mathematical form of first law of thermodynamics

Let, the internal energy of a system in initial state is U_1. This system absorbs q heat and w work is done on the system, so that its internal energy in final state becomes U_2, then,

$$U_2 = U_1 + q + w$$

or $$(U_2 - U_1) = q + w$$

or $$\Delta U = q + w$$

This is mathematical form o f first law of thermodynamics.

If work done is expansion work, then-

$$w = -P \Delta V$$

$$\therefore \quad \Delta U = q - P \Delta V$$

This is another form of first law of thermodynamics.

Applications

(i) Isothermal processes- For Isothermal processes, change in internal energy of the system during the process is zero i.e.

$$\Delta U = 0$$

From first law of thermodynamics-

$$\Delta U = q + w$$

or $$0 = q + w$$

or $$q = - w$$

Thus, in isothermal processes, the heat absorbed by the system is completely used up for doing work by the system and therefore, maximum work is obtained.

(ii) Adiabatic processes- For adiabatic processes, heat change of the system during the process is zero i.e.

$$q = 0$$

From first law of thermodynamics-

$$\Delta U = q + w$$

or $$\Delta U = 0 + w$$

or $$\Delta U = w$$

Thus, in adiabatic processes, increase in internal energy of the system is equal to work done on the system. In these processes, the system does work by utilization of its own internal energy.

(iii) Isochoric processes- For isochoric processes, the change in volume of the system during the process is zero i.e.

$$\Delta V = 0$$

CHEMISTRYFORCOMPETITION.COM

From first law of thermodynamics-

$$\Delta U = q + w$$

or $$\Delta U = q + P\Delta V$$

or $$\Delta U = q + 0$$

or $$\Delta U = q_v$$

Thus, in isochoric processes, the heat absorbed by the system is equal to increase in internal energy of the system.

(iv) Cyclic processes- For cyclic processes, the change in internal energy (ΔU) of the system during the process is always equal to zero i.e.

$$\Delta U = 0$$

From first law of thermodynamics-

$$\Delta U = q + w$$

or $$0 = q + w$$

or $$q = -w$$

Thus, in cyclic processes, the heat absorbed by the system is completely used up for doing work by the system and therefore, maximum work is obtained.

(**v) Isobaric processes-** First law of thermodynamics is in fact derived for isochoric processes. Hence, for these processes,

$$\Delta U = q + w$$

Physical significance of ΔU - For isochoric processes, the change in volume of the system during the process is zero i.e.

$$\Delta V = 0$$

From first law of thermodynamics-

$$\Delta U = q + w$$

$$= q + P\Delta V$$

or $$\Delta U = q + 0$$

or $$\Delta U = q_v$$

Thus, the heat change (absorbed or evolved) of the system in an isochoric processes is equal to change in internal energy of the system. This is physical significance of ΔU.

Enthalpy (H)

In isochoric processes, work done is zero. Hence, the heat change is equal to the change in internal energy of the system i.e.

$$q_v = \Delta U$$

CHEMISTRYFORCOMPETITION.COM

However, most of the processes occurring in nature are not isochoric, but are isobaric and involve change in volume of the system and therefore, work done either on the system or by the system.

Thus, in these processes, heat change is not equal to the change in internal energy of the system.

$$q_p \neq \Delta U$$

Hence, in order to express heat change in isobaric processes, a new thermodynamic function has been introduced which is called enthalpy (H) of the system. By definition,

"The sum of internal energy and pressure-volume energy of a system in a given condition of temperature and pressure is called enthalpy of the system."

Mathematically, enthalpy

$$H = U + PV$$

Enthalpy is a state function and therefore, its value depends only upon the state of the system and is independent of the path or agency by which the state has been attained. The absolute value of enthalpy cannot be determined experimentally. However, the change in enthalpy (ΔH) during a process can be determined easily and is given by following expression-

$$\Delta H = H_{final} - H_{initial}$$

For a chemical reaction, the change in enthalpy,

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

Here, the value of ΔH also depends only upon initial and final states of the system and is independent of the path followed during the process.

Relation between ΔH and ΔU-

By definition, enthalpy

$$H = U + PV$$

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

$$\text{or} \quad \Delta H = \Delta U + P\Delta V + V\Delta P \text{ ------ (1)}$$

For isobaric processes-

$$\Delta P = 0$$

$$\therefore \quad V\Delta P = 0$$

Thus, from eq. (1)-

$$\Delta H = \Delta U + P\Delta V \text{ -------- (2)}$$

This expression gives the relation between ΔH and ΔU for isobaric processes.

CHEMISTRY FOR COMPETITION.COM

From ideal gas equation-

$$PV = nRT$$

Let, V_1 and V_2 are volumes and the n_1 and n_2 are the number of gaseous moles of reactants and products respectively, then-

$$PV_1 = n_1RT$$
$$PV_2 = n_2RT$$
$$\therefore \quad P(V_2 - V_1) = (n_2 - n_1)RT$$
$$\text{or} \quad P\Delta V = \Delta n_gRT$$

Putting this value of $P\Delta V$ in eq. (2), we get-

$$\Delta H = \Delta U + \Delta n_gRT \qquad \text{------- (3)}$$

Where, $\Delta n_g = \sum n_g(\text{products}) - \sum n_g(\text{reactants})$

This expression also gives the relation between ΔH and ΔU for gaseous reactions.

Applications-

(1) The reactions in which the number of gaseous moles remains unchanged-

For example,

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$
$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Here, $\Delta n_g = 2 - 2$

$= 0$

$\therefore \quad \Delta H = \Delta U + 0 \times RT$

Thus, $\Delta H = \Delta U$

Thus, for the reactions in which total the number of gaseous moles of products is equal to that of reactants, the value of ΔH is equal to that of ΔU.

(2) The reactions in which the number of gaseous moles increases-

For example,

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

Here, $\Delta n_g = 2 - 1$

$= 1$

$\therefore \quad \Delta H = \Delta U + 1 \times RT$

or $\Delta H = \Delta U + RT$

Thus, $\Delta H > \Delta U$

Thus, for the reactions in which total the number of gaseous moles of products is more than that of reactants, the value of ΔH is greater than that of ΔU.

CHEMISTRY FOR COMPETITION.COM

(3) The reactions in which the number of gaseous moles decreases-

For example,

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

Here, $\Delta n_g = 2 - 4$

$= -2$

$\therefore \quad \Delta H = \Delta U + (-2) \times RT$

or $\Delta H = \Delta U - 2RT$

Thus, $\Delta H < \Delta U$

Thus, for the reactions in which total the number of gaseous moles of products is lesser than that of reactants, the value of ΔH is lesser than that of ΔU.

CHEMISTRYFORCOMPETITION.COM