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Physical Chemistry

First Law Of Thermodynamics

THERMODYNAMICS
FIRST LAW

Definition of thermodynamics — Thermo means heat and dynamics means flow. So we can say that thermodynamics is a quantitative relation between heat and other forms of energy. We shall explain here the first law of thermodynamics. The law is based on human experience and has no theoretical proof but nothing contrary to the law has been found so far. Further it deals with matter in bulk (macroscopic system) and is independent of behaviour of matter at microscopic level i.e. atomic and molecular level.

Common thermodynamic terms —

1. System and surroundings — The part of universe which is under consideration is called a system. Everything outside the system is called surroundings.

2. Types of system — A thermodynamic system may exchange energy, matter or both with the surroundings. There are three types of system —

   (a) open system — This system can exchange both matter and energy with the surroundings. eg. A reaction taking place in an open vessel.

(b) Closed System – This system can exchange only energy but not the matter with the surroundings. eg A reaction taking place in a cylinder enclosed by a piston.

(c) Isolated System – This system can neither exchange matter nor energy with the surroundings. eg, water placed in a vessel which is closed as well as insulated.

3. Thermodynamic State – The state of a thermodynamic system is defined by specifying temperature, pressure and composition so that other parameters are automatically fixed. There are two types of functions which specify the state of a system.

(a) State function – A thermodynamic property is called a state function when the change in its value depends only upon initial and final states and not on its past history eg, mass, temperature, internal energy etc.

(b) Path function – If the change in the value of thermodynamic property depends upon the path followed, it is called state function eg, heat and work.

State functions are called exact differentials and represented by capital letter whereas path functions are inexact differentials and shown by small letter. Let Z is a state function which depends on two independent variables x and y ie. $Z = f(x,y)$ Then Z will be exact differential when,

$$\frac{\partial^2 Z}{\partial y \partial x} = \frac{\partial^2 Z}{\partial x \partial y}$$

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4. Extensive and intensive properties – Extensive property depends upon the amount of substance present in the system. eg, mass, volume and energy.
Intensive property is independent of the amount of the substance present in the system. eg density, specific heat, refractive index etc.
It should be noted that ratio of two extensive property may be intensive property eg density (mass/volume)

5. Thermodynamic processes – A process refers to the mode of affecting a change. Certain processes are –

(a) Reversible process – Here the change in the system and surroundings is conducted in such a way that it can be restored back to its original condition.
(b) Irreversible process – Here the change takes place in such a way that the system cannot be restored back in original condition.
(c) Isothermal process – In such process, temperature remains same throughout the process.
(d) Adiabatic process – Here no heat enters or leaves the system during any stage of the process.
(e) Isobaric process – Here the pressure of system does not change when the process occurs.
(f) Isochoric process – Here the volume of system does not change during any stage of process.
A reversible process is almost impossible because it would require infinite time for completion but the concept of reversible process is quite important.

First Law Of Thermodynamics

The law is simply law of conservation of energy ie energy can neither be created nor destroyed although it can be converted from one form to the other. Other statements are -

(i) It is impossible to construct a perpetual motion machine which can work continuously without consuming energy.

(ii) The energy of an isolated system remains constant.

Mathematical formula of first law of thermodynamics -

Let E_1 is the initial internal energy of a system. We can increase the internal energy of the system by supplying heat q to the system and by doing work w on the system. Let the final internal energy is E_2. Then we can write $E_2 = E_1 + q + w$

or $E_2 - E_1 = q + w$ or $\Delta E = q + w$ ------(1)

The equation (1) is the mathematical form of first law of thermodynamics. According to convention heat given and work done on the system are given positive sign whereas heat taken from system and work done by the system are given negative sign. In most processes the heat is given to the system and system performs the work. So equation (1) takes the form $\Delta E = q - w$ ----(2)

Internal Energy - The internal energy of a system is associated is associated with its molecular motion as well as molecular constitution. It depends upon the quantity of substance in the system ie extensive property. It is exact differential ie. state function. Although q and w are path function but ΔE is state function. Internal energy of ideal gas is a function of temperature only. Hence in isothermal process (T = Constant) we have $\Delta E = 0$.

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which means there is no change in internal energy.

Enthalpy – Let the change of state of a system is brought at constt. pressure. So there will be change in volume. Let it increases from V_1 to V_2 at constant pressure P. Then work done by the system $w = -P(V_2 - V_1)$

Using first law of thermodynamics, $\Delta E = q - P(V_2 - V_1)$

or $E_2 - E_1 = q - P(V_2 - V_1)$ or $(E_2 + PV_2) - (E_1 + PV_1) = q$

Here the quantity $(E + PV)$ is called enthalpy H of the system and defined as total energy stored in the system.

$H = E + PV$ Since E, P and V are definite properties which define the state of a system. Hence H is also a definite property depending upon the state of a system i.e. state function.

Physical and chemical processes are often carried out at constant volume or constant pressure.

Let volume is kept constant then $\Delta V = 0$ since $w = P.\Delta V$

So from first law of thermodynamics $\Delta E = q_V$

which shows that entire heat supplied to the system at constant volume will increase the internal energy of the system i.e. ΔE is the heat of reaction at constt. volume.

Further change in enthalpy at constant pressure can be written as, $\Delta H = \Delta E + P.\Delta V$

From first law of thermodynamics $\Delta E = q - w = q - P.\Delta V$

So that $\Delta H = q_P$, hence enthalpy change for a system is the heat absorbed by the system at constt. pressure. So ΔH is the heat of reaction at constt. pressure. Enthalpy is the energy stored in the system which can be converted into heat hence enthalpy is also called heat content of the system.

First law of thermodynamics and life process – $\Delta E = q - w$

During growth period the child takes more food (q) and performs minimum work (w). So the difference ($q-w$) is added to internal energy and child grows in a healthy manner.

After a certain age we must balance in taking food (q) and performing physical work (w) so that ΔE remains the same otherwise accumulation of ΔE will produce obesity and many health problems. So $+q$ and $-w$ should be balanced. This explains necessity of physical work.

During prolong fasts $+q$ is zero. So $\Delta E = -w$ or we can say that our life depends on the reserve energy. So our weight goes down and internal energy becomes down and down.

During illness, certain processes of our body become very fast. So heat energy accumulates and temperature rises. The rate of energy loss is increased and internal energy is again lost. We become very weak.

Merit and Demerit of thermodynamics – It provides the criteria for predicting the feasibility of a process (second law) under given condition. It determines the extent to which a process can proceed before attainment of equilibrium. It helps in deduction of most of generalisations of physical chemistry.

Otherhand thermodynamics apply only to matter in bulk and not to individual molecules. It does not tell anything about the rate at which a given process may proceed. It concerns only with the Initial and final states of the system and not concerned with the path by which the change is brought about which means that there is no light on the mechanism of process.