First Law of Thermodynamics

The first law of thermodynamics states that energy can neither be created nor destroyed, It can be only transformed from one form to another. This law is also known as conservation of energy.

let us suppose that there is no such equivalance between heat and work Then it may be possible first time to convert certain amount of heat (x) joules into a certain amount of mechanical work and then in the revese process transformation of the same amount of mechanical work into heat producing (y) joules of heat.

Where $y > x$

Thus the original condition will have been restored, But the heat equivalent to ($y-x$) joules will have been created and in this way prepitual motion machine can be created.

But according to human experience there must be equivalence of heat and work. It is well know fact that energy can be created by destruction of Mass. Thus these two quatities may be related as

$$E = mc^2 \quad \text{(Eistein eq}^n\text{)}$$

where E = energy, m = mass & c = velocity

The modified law states that the total mass and energy of an isolated system remains constant & the term system explains the ideal gas always

Every substace is associated with definit amount of energy which depends upon its chemical nature as well as its temp. Volume and Pressure this energy is known as intrisic energy.

The internal energy of a system is a state fuction it does not depends upon the path; Hence change in internal energy depends on its final and initial state so it is exact or perfect differential.

Interlnal energy is represeted by U or E

let U_A be the energy of the system in state A and U_B be the energy of the system in state B.

$$\therefore \Delta U = U_B - U_A$$

If a system is going under change from state A to state B. Then heat taken by the system is q and work done is w

$$\therefore \Delta U = q - W$$

If in a given process, the quantity of heat transferred from the surrounding to the system is q and work done in the process is 'w' then the change in internal energy ΔU is given by

$$\Delta U = q + W$$

If work is done by the surrounding on the system (compression of gas) the w is taken as (+) positive sign

$$\text{So, } \Delta U = q + W$$

On the otherhand If work is done by the system on the surrounding (expansion of gas) W is taken as negative (−) sign

$$\text{So, } \Delta U = q - W$$

First law eqn ($\Delta U = q + W$) where ΔU is a definite Quantity. Thus energy, Pressure, temperature, Volume are state function. On the Other hand W and q are not state fuction.

In terms of mathematics we can say that differential of energy dU is an exact differential and heat and work has Inexact differentials.

So, the exact differentials can be integrated between the appropriate limits, But it can not be done in case of inexact differentials.

Hence, $\int_{U_1}^{U_2} du = U_2 - U_1$

But $\int_{q_1}^{q_2} dq \neq q_2 - q_1$ and $\int_{W_1}^{W_2} dw \neq W_2 - W_1$

Limitations of 1st Law :—

) It gives definit relation between heat absorbed and work done but it puts no restriction of the direction of flow of heat

) Energy of an isolated system remains constant during specified Change of state but it does not tells the reaction or change occurs sponteneously.

The first law does not indicates whether a transformation of energy would at all occur and if occur to what extent.

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First law equation ($\Delta U = q + w$). ΔU is a definite quantity.
Thus energy, Pressure, temperature, Volume are state functions. On the other hand w and q are not state function. In terms of mathematics we can say that differential of energy dU is an exact differential and the differential of heat and work i.e dq and dw are inexact differentials. So the exact differentials can be integrated between the appropriate limits, But it can not be done in case of inexact differentials.

$$\text{Hence} \quad \int_{U_1}^{U_2} du = U_2 - U_1$$

$$\text{But} \quad \int_{q_1}^{q_2} dq \neq q_2 - q_1$$

$$\text{and Also,} \quad \int_{w_1}^{w_2} dw \neq W_2 - W_1$$

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What is Euler Reciprocal Relation?

Let Z is a state function of two independent variables x and y of the system
i.e $\quad Z = f(x,y)$

$$\text{so,} \quad dz = \left(\frac{\partial z}{\partial x}\right)_y \cdot dx + \left(\frac{\partial z}{\partial y}\right)_x \cdot dy$$

$$= M(x,y)\,dx + N(x,y)\,dy$$

where $M(x,y) = \left(\frac{\partial z}{\partial x}\right)_y$ & $N(x,y) = \left(\frac{\partial z}{\partial y}\right)_x$

$$\text{Again} \quad \left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y\, \partial x} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x\, \partial y}$$

$$\text{Since} \quad \frac{\partial^2 z}{\partial y\, \partial x} = \frac{\partial^2 z}{\partial x\, \partial y}$$

$$\text{Hence} \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \text{——— A}$$

This eq^n is called Euler Reciprocal relation. It is applicable to state function only.

Since Z is a state function when a system passed from initial state A to final state B finite change ΔZ is given by

$$\Delta Z = Z_B - Z_A$$

Also $\oint dz = 0$ where $\oint$ (cyclic integral) means that the system is in the same state at the end of its path i.e It has traversed a closed path.
Thus dz is an exact differential.