The following is an experimental observation:

For any cyclic process of a CLOSED SYSTEM, the net work output of the system is equal to the net heat input:

$$\oint \delta W = \oint \delta Q$$

This is a statement of the first law of thermodynamics. It is an observation; it can not be deduced or proven from any other principal of nature.

First Law for a process:

For a process:



Note that for a process:

$$\int_{1}^{2} \left(\delta Q - \delta W \right) \neq 0$$

But, for a cycle:

$$\oint (\delta Q - \delta W) = 0$$

Consider a cycle consisting of a process *A* (state 1 to state 2) and a process *B* (state 2 to state 1)

For the cycle consisting of process *A* + process *B*:

$$\int_{1}^{2} \left(\delta Q - \delta W \right) + \int_{2}^{1} \left(\delta Q - \delta W \right) = 0$$

A B

Consider next the cycle consisting of process A (as above) and another process C (state 2 to state 1) different from process B between the same states 1 and 2.

For the cycle consisting now of process A + process C:

$$\int_{1}^{2} \left(\delta Q - \delta W \right) + \int_{2}^{1} \left(\delta Q - \delta W \right) = 0$$

A C



Substituting for process A in the above equation, we obtain

$$-\int_{2}^{1} \left(\delta Q - \delta W \right) + \int_{2}^{1} \left(\delta Q - \delta W \right) = 0$$

C B

or

$$\int_{2}^{1} (\delta Q - \delta W) = \int_{2}^{1} (\delta Q - \delta W)$$

$$C \qquad B$$

Since paths *C* and *B* are two arbitrary paths between states 2 and 1, the integral is the <u>same</u> for <u>all</u> other <u>paths</u> between these two states, hence the integral

$$\int_{2}^{1} (\delta Q - \delta W) \longrightarrow \text{does not depend on the path}$$

$$\longrightarrow \text{depends only on end states}$$

$$\longrightarrow \text{therefore it represents a property of the system}$$

Let
$$\int_{1}^{2} \left(\delta Q - \delta W \right) = \int_{1}^{2} dE = E_{2} - E_{1} = \Delta E$$

where E is a state variable. We can now write

$$dE = \delta Q - \delta W$$

This is a statement of the FIRST LAW OF THERMODYNAMICS for a CLOSED SYSTEM (a system whose mass is constant and only heat and work can cross the boundaries).

Since Q and W are forms of energy, E also represents energy.

Note, that since *E* represents a state variable its differential quantity is indicated by the letter *d* (representing an exact differential) instead of the Greek symbol δ (representing an inexact differential whose integral represents a path function).

Additionally

From
$$\int_{1}^{2} dE = \int_{1}^{2} \delta Q - \int_{1}^{2} \delta W$$

we can also write $\Delta E = E_2 - E_1 = Q_{12} - W_{12}$

Note that thermodynamics tells us that there exist an energy function E, however it provides no information of its value, it provides information only for energy difference, ΔE , and not E itself.

Note that for no energy exchange with the surroundings, Q = 0 and W = 0; the system is said to be <u>isolated</u> and $(\Delta E)_{\text{isolated system}} = 0$.

Note: $E \longrightarrow$ stored energy, property of the system

- *W intransit* due to mechanical interaction between the system and its surroundings
- Q → energy in transit due to the thermal interaction (temperature difference between the system and its surroundings, or phase change for a pure substance).

Note, there are three related ideas contained in the FIRST LAW:

- 1. CONSERVATION OF ENERGY
- 2. THE EXISTANCE OF AN ENERGY FUNCTION, A STATE VARIABLE CALLED ENERGY
- 3. DEFINITION OF HEAT AS ENERGY IN TRANSIT

<u>A further note on the energy E</u>

We have defined previously mechanical forms of energy

POTENTIAL ENERGY (energy associated with the position of the system as whole in the earth's gravitational field)

$$\Delta E_{POTENTIAL} = \int_{1}^{2} mgdz = mg(z_2 - z_1) = \Delta(PE)$$

KINETIC ENERGY (energy associated with the motion of the system as a whole relative to an external fixed coordinate reference frame)

$$\Delta E_{KINETIC} = \int mV dV = \frac{1}{2} mV_{2}^{2} - \frac{1}{2} mV_{1}^{2} = \Delta (KE)$$

In engineering thermodynamics we consider a third form of energy on a macroscopic scale, called the INTERNAL ENERGY, *U*. All forms of energy, other than kinetic energy and potential energy are lumped together in the internal energy of the system.

POTENTIAL ENERY (*PE*) KINETIC ENERGY (*KE*) INTERNAL ENERGY (*U*)

E is the total energy of a system and is represented as

$$E = PE + KE + U$$

Note that on a microscopic scale the internal energy, U, represents the translational, rotational, vibrational energy of molecules, chemical changes, nuclear reactions, etc.

The common expression for the total energy in this class will be:

$$E = U + \frac{1}{2}mV^2 + mgz$$
 this represents an extensive variable

In terms of an intensive energy variable (e = E/m)

$$e = \frac{E}{m} = u + \frac{1}{2}V^2 + gz$$

For a stationary system, $\Delta PE = 0$ and $\Delta KE = 0$ and the first law for a closed system is written as:

$$\Delta U = Q - W$$

The first law can also be expressed on a time rate basis:

In differential form

$$dE = \delta Q - \delta W$$

For time rate substitute change by rate of change and take it in the limit as the time interval goes to zero:

$$Lim_{\Delta t \to 0} \left\{ \frac{\Delta E}{\Delta t} = \frac{Q}{\Delta t} - \frac{W}{\Delta t} \right\}$$
$$\frac{dE}{dt} = \dot{Q} - \dot{W}$$

Note, in the "dot" notation

$$\dot{Q} = Lim_{\Delta t \to o} \frac{Q}{\Delta t}, \qquad \dot{W} = Lim_{\Delta t \to o} \frac{W}{\Delta t}$$

The units of Q and W are *Joules* and of \dot{Q} and \dot{W} are *Joules/sec* or *Watt*