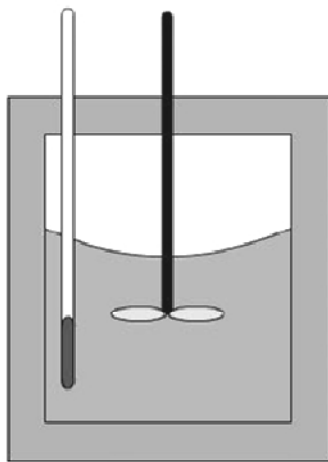




The First Law of Thermodynamics

Joule experiment

James P. Joule carried out his famous experiment, he placed known amounts of water, oil, and mercury in an insulated container and agitated the fluid with a rotating stirrer. The amounts of work done on the fluid by the stirrer were accurately measured, and the temperature changes of the fluid were carefully noted. He found for each fluid that a fixed amount of work was required per unit mass for every degree of temperature rise caused by the stirring, and that the original temperature of the fluid could be restored by the transfer of heat through simple contact with a cooler object. In this experiment you can conclude there is a relationship between heat and work or in other words heat is a form of energy.



- Work added to system
no Heat escaped
- Temperature rises
as water is stirred
- Energy is conserved

Internal Energy

Through the Joule experiment, what happens to energy between the time it is added to water as work, and the time it is extracted to heat? Logic suggests that this energy contained in the water is in another form, which is called **internal energy**.

Internal energy refers to the energy of molecules of a substance, which are in ceaseless motion and possess kinetic energy. The addition of heat to a substance increases this molecular activity, and thus causes an increase in its internal energy. Work done on the substance can have the same effect, as was shown by Joule. Internal energy cannot be directly measured; there are no internal-energy meters. As a result, absolute values are unknown. However, this is not a disadvantage in thermodynamic analysis, because only changes in internal energy are required.



$$U = f(T, V)$$

$$\partial u = \left(\frac{\partial U}{\partial T} \right)_V \partial T + \left(\frac{\partial U}{\partial V} \right)_T \partial V$$

$$\int_{U_1}^{U_2} \partial U = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T} \right)_V \partial T + \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V} \right)_T \partial V$$

$$\Delta U = \int_{T_1}^{T_2} C_v dT + \int_{V_1}^{V_2} \left(\frac{\partial U}{\partial V} \right)_T \partial V$$

In case of case ideal gas $\left(\frac{\partial U}{\partial V} \right)_T = 0$, and this lead to

$$\Delta U = \int_{T_1}^{T_2} C_v dT$$

Internal Energy

- ❖ Motion & bonding of molecules
- ❖ Kinetic energy of molecules
- ❖ Potential energy of molecules
- ❖ Bonding energy

Important factors influencing

- ❖ Temperature
- ❖ State of aggregation ; solid liquid and gas
- ❖ Chemical composition

- Energy
 - Kinetic energy, E_k
associated with "motion"
 - Potential energy, E_p
associated with "position"
 - Internal energy, U
associated with "atomic motion & bonding"



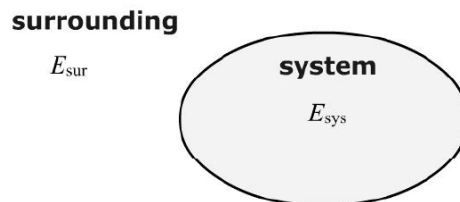
THE FIRST LAW OF THERMODYNAMICS

Heat and internal energy as form of energy makes possible a generalization of law of conservation of mechanical energy. Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms. Energy cannot be created or destroyed .you can only change it from one form to another , or you can only add it to the system from the surrounding.

System : the part in which the process occurs or the part of the universe that we choose to study .The system may be of any size depending on the application, and its boundaries may be real or imaginary, rigid or flexible .

Surroundings : The rest of the universe

Boundary :The surface dividing the system from the surroundings



The first law applies to the system and surroundings, and not to the system alone. In its most basic form, the first law requires:

$$\Delta (\text{energy of system}) + \Delta (\text{energy of surroundings}) = 0$$

The system may change in its internal energy, in its potential or kinetic energy, and in the potential or kinetic energy of its finite parts. Since attention is focused on the system, the nature of energy changes in the surroundings is not of interest.

ENERGY BALANCE FOR CLOSED SYSTEMS

System can be

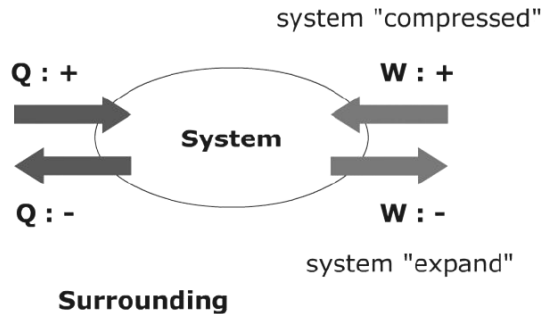
- Open: mass and energy can transfer between the system and surroundings
- Closed :energy can transfer between system and surroundings, but **NOT** mass
- Isolated :neither mass nor energy can transfer between the system and surroundings.

Since no streams enter or leave a closed system, no internal energy is transported across All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work.



$$\Delta (\text{Energy of the surroundings}) = \pm Q \pm W \quad (2-1)$$

Sign of Q and W depends on which direction of transfer



The energy of system : $\Delta(\text{energy of the system}) = \Delta U + \Delta E_k + \Delta E_p \quad (2-2)$

By equating equations (2-1) and (2-2) : $\Delta U + \Delta E_k + \Delta E_p = \pm Q \pm W \quad (2-3)$

Closed systems often undergo processes that cause no change in the system other than in its *internal energy*. For such processes :

$$\Delta U^t = Q - W \quad \text{Or} \quad dU^t = dQ - dW \quad (2-4)$$

Hint

Properties, such as volume V^t and internal energy U^t depend on the quantity of material in a system; such properties are said to be *extensive*. In contrast, temperature and pressure, the principal thermodynamic coordinates for homogeneous fluids, are independent of the quantity of material, and are known as *intensive* properties. An alternative means of expression for the extensive properties of a homogeneous system, such as V^t and U^t , is:

$$V^t = m V \quad \text{or} \quad V^t = n V, \quad \text{and} \quad U^t = m U \quad \text{or} \quad U^t = n U$$

Although V^t and U^t for a homogeneous system of arbitrary size are extensive properties, specific and molar volume V (or density) and specific and molar internal energy U are intensive.

For closed system of n moles

$$\Delta (n U) = n \Delta U = Q - W \quad \text{or} \quad d(n U) = n dU = dQ - dW$$

In this form, these equations show explicitly the amount of substance comprising the system

Ex: Water flows over waterfall 100 m in height, take 1 kg of water as the system and assume that it does not exchange energy with its surroundings.



- a) What is the potential energy of water at the top of falls with respect to the base of the falls?
- b) What is the kinetics energy of water just before it strikes bottom ?
- c) After 1 Kg of water enters the river below the falls , what change has occurred in its state?

THERMODYNAMIC STATE AND STATE FUNCTIONS

In thermodynamics , there are two types of quantities ; those which depend on path and those are not. there are many examples of quantities which do not depend on path , e.g. temperature , pressure , specific volume. They depend only on present conditions, however reached. Such quantities are known as *state functions*. We know from experience that for a homogeneous pure substance fixing two of these properties automatically fixes all the others, and thus determines its thermodynamic state. When two of them are held at fixed values for a homogeneous pure substance, the thermodynamic state of the substance is fully determined. This means that a state function, such as specific internal energy, is a property that always has a value; it may therefore be expressed mathematically as a function of other thermodynamic properties, such as temperature and pressure, or temperature and density, and its values may be identified with points on a graph.



The differential of a state function represents an infinitesimal change in its value. Integration of such a differential results in a finite difference between two of its values, e.g.:

$$\int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P$$

Work and heat ,on the other hand are not state function ,since they depend on path they cannot identify with points on a graph but they represented by areas, The differentials of heat and work are not changes, but are infinitesimal amounts. When integrated, these differentials give not finite changes, but finite amounts. Thus,

$$\int dQ = Q$$

State function represents a property of a system and always has value , while work and heat appear only when changes are caused in system by process , which required time.

There are two classes of properties

- a) Extensive ; depend on quantity of material involved (U ,H , ..)
- b) Intensive ; independent of quantity of material (T , p ,..)

Ex : when a system is taken from state *a* to state *b* in the below figure along *acb* , 100 J of heat flows into the system and the system does 40 J of work

- a) How much heat flows into the system along path *aeb* if the work done by the system is 20 J?
- b) The system returns from *b* to *a* along path *bda* . If the work done on the system is 30 J , does the system adsorb or liberate heat? How much ?

