

Chapter 4

The first law of thermodynamics

Definition and formulation of the first law of thermodynamics

The philosophical argument of Mayer and the experimental work of Joule led to a definite acceptance of the conservation of energy, the first law of thermodynamics. There are several definitions of the first law. A few of the accepted definitions of this law are given below:

- 1- The total amount of energy of an isolated system remains constant but may change from one form to another.
- 2- When an amount of energy of one form disappears, an equivalent amount of energy of other forms appears.
- 3- Energy cannot be created or destroyed.
- 4- Perpetual motion cannot be realized. (Perpetual – motion machine is one which runs for ever).

The first law of thermodynamics is a statement of the principle of conservation of conservation of energy.

From the principle of conservation of energy, whenever there is any net transfer of energy in wand across the boundary of a system, the energy of the system increases by an amount just equal to the net energy transferred. If U_1 represents the energy of the system at the start of a process, U_2 its energy at the end of the process, Q the net heat flowing into the system during the process, and W the net work done by the system during the process, then the increase in the energy of the system, $U_2 - U_1$, equals the difference between Q and W , or

$$U_2 - U_1 = Q - W \quad \text{-----} \quad (1)$$

This equation is one form of the first law. We call U the internal energy of the system.

The change in internal energy can be written as dU , that is, as the differential of a function of the state of the system.

Heat depends on the path

The work W may be very different when a given system is taken by different processes from one state to another. Since the change in internal energy dU is independent of the processes, it follows that heat Q is different for different processes also and that as a consequence Q is not a function of the state of the system and it is meaningless to speak of the “heat in a system”, or the “heat of a system”. It is for this reason that we have written $d'Q$, rather than dQ , to represent an infinitesimal quantity of heat flowing into a system. The symbol $d'Q$, like $d'W$, is an inexact differential. It cannot be interpreted as “a small change in Q ” since a function Q cannot be uniquely defined. Similarly, partial derivatives such as $\left(\frac{\partial Q}{\partial P}\right)_T$ have no

meaning. However, a ratio such as $\left(\frac{d'Q}{dP}\right)_T$ does have a meaning, since it is merely the ratio of a small quantity of heat flowing into a system in an isothermal process, to the corresponding change in pressure. It follows from the preceding discussion that for an infinitesimal process the first law becomes

$$dU = d'Q - d'W \quad \text{-----} \quad (2)$$

That is, although $d'Q$ and $d'W$ are both inexact differentials, their difference dU is an exact differential.

When both sides of the equation above are divided by the mass or the number of moles of a system, we get

$$du = d'q - d'w \quad \text{-----} \quad (3)$$

Heat is received (absorption):	Q is positive
Heat is rejected:	Q is negative
Heat neither received nor rejected (adiabatic):	$Q = 0$
Internal energy increases:	ΔU is positive
Internal energy decreases:	ΔU is negative
Internal energy neither increases no decreases:	$\Delta U = 0$
Work done by system (expansion):	W is positive
Work done on system (compression):	W is negative
No work done on or by system:	$W = 0$
Suppose $E =$ The total amount of energy of any system.	
$E_K =$ kinetic energy , $E_P =$ potential energy	
$U =$ other internal energy.	

$$E = U + E_k + E_p = U + \frac{1}{2}mV^2 + mgh$$

Where V = the velocity of a system from one place to another place, m = the mass of a system, g = acceleration of gravity, h = the height of a system.

$$e = \frac{E}{m} = \frac{U}{m} + \frac{\frac{1}{2}mV^2}{m} + \frac{mgh}{m} ,$$

$$e = u + \frac{1}{2}V^2 + gh \quad \text{energy per unit mass}$$

$$Q = (U_2 - U_1) + \frac{1}{2}m(V_2^2 - V_1^2) + mg(h_2 - h_1) + W \quad \text{from the first law}$$

Some special cases of the first law

1// An isothermal process

An isothermal process is a process that occurs at constant temperature. Thus, $\Delta T = 0$, then $du = 0$

$$\therefore du = d'q - d'w = 0$$

$$\therefore d'q = d'w \quad \text{-----} \quad (4)$$

2// An adiabatic process

An adiabatic process is a process that occurs without an exchange of heat between the system and its surrounding. Thus, $dq' = 0$

$$\therefore du = d'q - d'w$$

$$\therefore d'w = -du \quad \text{-----} \quad (5)$$

3// Isochoric process or isometric process

At constant volume $dv = 0$

$$d'w = PdV = 0 \quad , \quad du = d'q - d'w$$

$$\therefore du = d'q \quad \text{-----} \quad (6)$$

4// A cyclic process

The system always returns to the original state du is always equal to zero ($du = 0$) for a cyclic process.

$$du = d'q - d'w \quad \therefore d'w = d'q \quad \text{-----} \quad (7)$$

Heat capacity

A resistor in which there is a current I and across the terminals of which there is a potential difference V . In a time interval ($t_2 - t_1$), the electrical work “flowing” into the resistor is given by

$$w = \int_{t_1}^{t_2} IV dt \quad \text{-----} \quad (8)$$

Heat capacity is defined as the amount of heat required to raise the temperature of

(1 mol) of a system by (1°C) it is denoted by the symbol C .

1// Mean heat capacity: we now define the mean heat capacity of the mass (m) of fluid, over the temperature range ($T_2 - T_1$), by the equation

$$\bar{C} = \frac{Q}{T_2 - T_1} \quad \text{-----} \quad (9)$$

In mks units, heat capacity is expressed in Joules/deg.

2// True heat capacity: The true heat capacity C , at any temperature T , is defined as the limit of the ratio above, when the temperature increases from T to ($T + dT$) and the corresponding flow of heat is $d'Q$.

$$C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} = \frac{d'Q}{dT}$$

$$C = \frac{d'Q}{dT} \quad \text{-----} \quad (10)$$

Specific heat capacity

The Specific heat capacity c of a substance as the ratio of the true heat capacity of a system composed of that substance, to the mass of the system.

$$c = \frac{C}{m} = \frac{d'Q}{mdT} = \frac{d'q}{dT} \quad \text{-----} \quad (11) \quad \text{J/kgm-deg.}$$

The true molar specific heat capacity is defined as

$$c = \frac{C}{n} = \frac{d'Q}{ndT} = \frac{d'q}{dT} \quad \text{-----} \quad (12) \quad \text{J/mole-deg.}$$

The total quantity of heat Q flowing into a system when its temperature increases from T_1 to T_2 is

$$Q = \int d'Q = \int_{T_1}^{T_2} C dT \quad \text{-----} \quad (13)$$

If the system is composed of a homogeneous substance of mass m and specific heat capacity c ,

$$Q = m \int d'q = m \int_{T_1}^{T_2} c dT \quad \text{-----} \quad (14)$$

The Specific heat capacity of a substance is defined as the ratio of the heat $d'q$ flowing into the substance, per unit mass or per mole, to the rise in temperature dT . To state only the temperature increase in a process, however, does not completely define the process. For example, if a system is under a constant pressure it will, in general, increase in volume as its temperature increases. If the volume remains constant but its pressure increases. A few possibilities are shown in Fig 1, which is drawn for an ideal gas, although the same principles apply to any substance whatever.

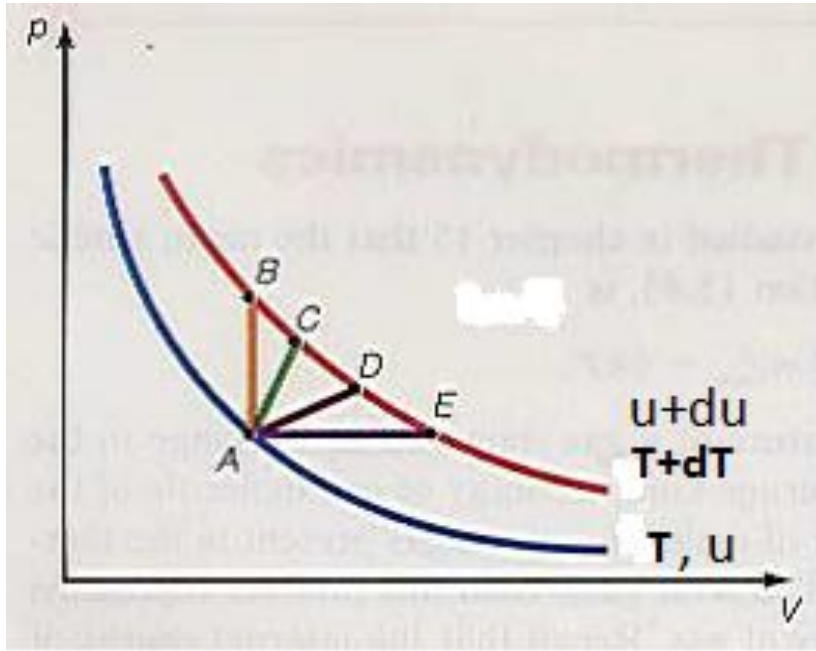


Fig. 1

The initial state of the system is represented by point (A), and the lines AB, AC, AD, and AE represent four different processes in which the temperature of the system is increased by the same amount, from (T) to (T+dT).

One finds experimentally that the heat $d'q$ supplied to the system is different in each of these processes and hence the specific heat capacity $c = \frac{d'q}{dT}$ is different in each process. Since there are obviously an infinite

number of different process, it follows that a substance has an infinite number of specific heat capacities, from a state at (T) to another state at (T+dT). The process (AE) the specific heat capacity at constant pressure c_p . The value of c_p depends, in general, on the P as well as T .

At constant pressure $dP= 0$, $\underline{d'Q = nc_p dT}$ ----- (15)

The process (AB) at constant V called the specific heat capacity at constant volume c_v , $d\nu=0$, $d'Q = nc_v dT$

$dU = d'Q - d'W$, $\therefore d'W = Pd\nu = 0$

$\therefore dU = d'Q = nc_v dT$ ----- (16)

The large stresses set up when a solid or a liquid is heated and not allowed to expand, direct experimental determinations of c_v for a solid or a liquid are difficult, and c_p is the quantity generally measured. However if c_p is known, the value of c for any other process can be calculated if we know in addition the β and K . It is therefore unnecessary to measure c for all possible processes.

$$PV=nRT, \quad PdV=nRdT=dW \quad \text{equation of state at constant P}$$

$$\text{We have } dQ = nc_p dT, \quad du = nc_v dT, \quad dW = nRdT$$

$$\text{From the first law } dU = dQ - dW$$

$$\therefore nc_v dT = nc_p dT - nRdT$$

$$\therefore c_p - c_v = R \quad \text{----- (17) for ideal gas}$$

Note

1- For all gases

- a// c_v is a function of its temperature only.
- b// c_p is a function of its temperature only and ($c_p > c_v$).
- c// $c_p - c_v = R = \text{constant}$.
- d// $\gamma = \frac{c_p}{c_v}$ is a function of its temperature only and ($\gamma > 1$).

2- For monatomic gases e.g. He, Ne, Ar

- a// c_v is remain constant for a wide range of temperature and equal to $\frac{3}{2} R$.
- b// c_p is remain constant for a wide range of temperature and equal to $\frac{5}{2} R$.
- c// γ is remain constant for a wide range of temperature and equal to $\frac{5}{3}$.

3- For diatomic gases permanent. Like CO, NO, N₂, D₂, H₂.

a// c_v is constant at normal temperature, it is equal to $\frac{5}{2} R$ and it increases with temperature.

b// c_p is constant at normal temperature, it is equal to $\frac{7}{2} R$ and it increases with temperature.

c// γ is constant at normal temperature, it is equal to $\frac{7}{5}$ and it decreases with increase the temperature.

4- For multiatoms gases and active gases, like CO_2 , NH_3 , CH_4 , Cl_2 , Br_2 .

c_v , c_p , and $\left(\frac{c_p}{c_v}\right)_v$ are changes with temperature and this changes difference from gas to another.
