

# Nalanda Open University

## B.SC Part-1

Course : Physics (Hons)

Paper : 2

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Topic- Thermodynamics (First Law of Thermodynamics)

# First Law of Thermodynamics

As we know about it, the assumption in TD is that there are only a few numbers of macroscopic variables for a complete description of a state of a system. Definitions of physical state functions of these variables, the constraints of and relations between these state functions are the main subject of thermodynamics.

The main mathematics in TD: functions of many variables and their (partial) derivatives.

**1st law:** In an arbitrary TD transformation, let  $Q$  = net amount of heat absorbed by the system, and  $W$  = net amount of work done on the system. The 1st law states

$$\Delta E = Q + W \quad (1)$$

is the same for all transformations leading from a given initial state to a final state (Joule's law), where  $E$  is the **total energy** (or internal energy, or just energy) of the TD system. Clearly,  $E$ ,  $Q$  and  $W$  are all measured in energy unit (SI: Joule).

Mancunian James Joule (born Salford 1818, died Sale 1889, brewer and physicist) did many experiments in the 1840's to establish the equivalence of heat and work as forms of energy.

Please note: (a) Thermally isolated system: contained within adiabatic (perfectly insulated) walls. we have

$$Q = 0, \quad \Delta E = W.$$

For mechanically isolated system:  $W = 0$ . Hence  $\Delta E = Q$ , all heat turns to internal energy. (b) Internal energy  $E$  is a function of state, a macroscopic variable, but has its origin of in microscopic constituents. In general, it is simply the sum of the kinetic energies of the molecules of the system and potential energy arising from the interaction force between them.

The first law of thermodynamics is a statement of energy conservation and defines the internal energy  $E$  as an extensive state function. In an infinitesimal transformation, the first law reduces to

$$dE = \bar{d}Q + \bar{d}W \quad (2)$$

where  $dE$  is a total (exact) differential for infinitesimal transformation. However,  $\bar{d}Q$  and  $\bar{d}W$  are not exact ( $Q$  and  $W$  are not state functions);  $Q$  and  $W$  in a thermodynamics transformation are process-dependent. All these are properties of functions of more than one variables.

Since  $E$  is a state function, it depends on the TD parameters, say  $P, V$ , and  $T$ . Since the equation of state can be made to determine one of these in terms of other two, we have, for a gas,

$$E \equiv E(P, V) = E(V, T) = E(T, P) .$$

Hence

$$dE = \left( \frac{\partial E}{\partial P} \right)_V dP + \left( \frac{\partial E}{\partial V} \right)_P dV .$$

Two other similar equations can be written.

Consider a gas. In an infinitesimal, reversible transformation, for which work done by the gas  $dW = -PdV$ , the heat

$$dQ = dE + PdV. \quad (3)$$

By the definition of heat capacity at constant  $V$ ,

$$C_V \equiv \left( \frac{dQ}{dT} \right)_V = \left( \frac{\partial E}{\partial T} \right)_V \quad (4)$$

and similarly, the heat capacity at constant pressure, using Eq. (3)

$$C_P \equiv \left( \frac{dQ}{dT} \right)_P = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P . \quad (5)$$

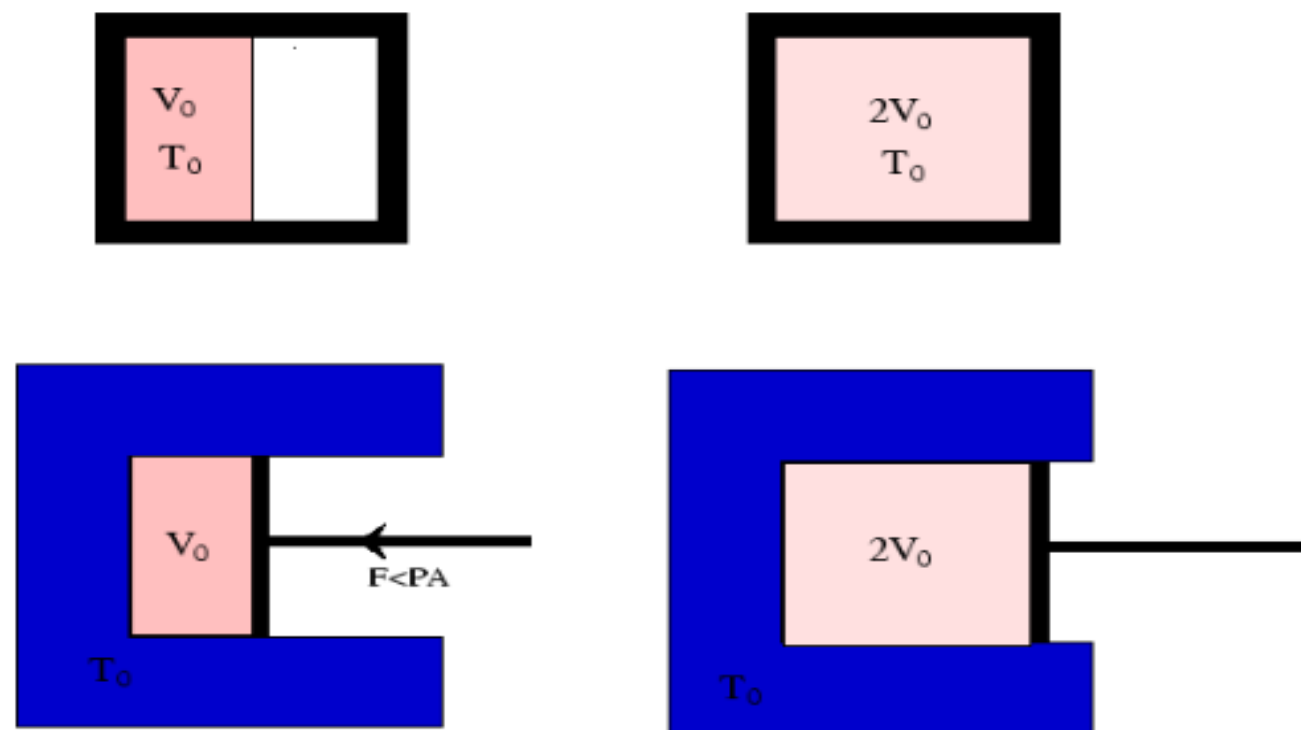
The difference between  $C_V$  and  $C_P$  clearly shows  $dQ$  is not exact, but depends on the details of the path, namely, heat  $Q$  is not a state function.

Note: Many authors use  $dW$  ( $= PdV$ ) to mean the work done by the system. We use  $dW = -PdV$  to mean work done on the system and lower case  $dw = -dW = PdV$  to mean work done by the system.

Example: Consider 2 different ways of taking a fixed mass of an ideal gas from an initial state  $(V_0, T_0)$  to a final state  $(2V_0, T_0)$ : (a) Free expansion in a container with adiabatic walls as shown in the top of Fig. 1 Clearly  $Q = 0$  and  $W = 0$ . We have

$$\Delta E = 0.$$

For ideal gas,  $E = E(T)$  (more discussion of this equation later). Hence  $T = T_0 = \text{const.}$  (b) Expansion against an external force, with  $T$  held fixed at  $T_0$  by contact with a heat bath as shown in the bottom two diagrams of Fig. 1. In this case, work is done by the gas.



**Fig. 1** (a) Free expansion (top two diagrams). (b) Expansion against an external force (bottom two diagrams).

As  $\Delta E = 0$ , we have

$$Q = -W > 0, \quad W = - \int F dx < 0.$$

Conclusion of these two examples are:  $Q$  and  $W$  are not state function but sum of them  $E$  is.

### 1.3 Real and Ideal gases: A Review

All gases which cannot be easily liquefied are found experimentally obey the following two laws:

(a) Boyles's law

$$PV = \text{const. at fixed temperature.}$$

(b) Charles's law (Gay-Lussac's law): At constant pressure, the volume of a gas varies linearly with temperature, say  $\theta$  on some arbitrary scale, e.g., Centigrade,

$$V = V_0 \left( \frac{1 + \theta}{T_0} \right) \quad \text{at fixed } P = P_0.$$

where  $T_0$  is constant (experiments show  $T_0$  nearly same for all gases. If both laws are obeyed exactly

$$PV = P_0 V_0 \left( \frac{1 + \theta}{T_0} \right) = P_0 V_0 \frac{T}{T_0}$$

where  $T = \theta + T_0$  is temperature on an absolute scale. As  $P$  and  $T$  are intensive, and  $V$  is extensive

$$\frac{PV}{T} \propto N$$

or, the ideal gas law

$$PV = Nk_B T = nRT \quad (6)$$

where  $k_B$  is the Boltzmann constant,  $R = k_B N_A$  is universal gas constant,  $N_A$  is Avogadro's number,  $n = N/N_A$  is number of mole. For the case of real gases, only the limit as  $P \rightarrow 0$  does the equation of state assume the above form.

Later in Statistical Physics, we can understand ideal gas microscopically as a gas with point-like, non-interacting molecules. All gases tend to that of an ideal gas at low enough pressure. The noble gas (e.g., helium, argon) are very close to ideal at STP; even our air at STP is quite well approximated as ideal.

For real gas in general, the internal energy  $E = E(T, P) = E(T, V)$ . For an ideal gas, this simplifies to  $E = E(T)$ , as a function of  $T$  only, as we see below. By definition, the ideal gas satisfies the equation

$$PV = nRT, \quad E = E(T) \quad \text{for ideal gas.} \quad (7)$$

Notice that for ideal gas

$$\left(\frac{\partial E}{\partial P}\right)_T = 0, \quad \left(\frac{\partial E}{\partial V}\right)_T = 0.$$

From Eq. (4), for ideal gas,

$$C_V = \frac{dE}{dT}, \quad dE = C_V dT. \quad (8)$$



In general, heat capacity may change with  $T$ . But if  $C_V = \text{constant}$ ,  $E = C_V T$ , after we define zero of energy as  $E = 0$  at  $T = 0$ .

The result of statistical mechanics (kinetic theory) show that for an ideal gas,

$$E = \frac{\nu_f}{2} N k_B T = \frac{\nu_f}{2} n R T \quad (9)$$

where  $\nu_f$  is the active degrees of freedom. The above equation states that each molecule has an average internal energy of  $\frac{1}{2} k_B T$  per active degree of freedom.

(i) Monatomic gases,  $\nu_f = 3$ ; (ii) diatomic gases,  $\nu_f = 5$  (3 translational and 2 rotational; vibrational modes are frozen out).

We can also prove

$$C_P - C_V = nR; \quad (10)$$

for ideal gas. And for reversible adiabatic process on an ideal gas

$$P V^\gamma = \text{const.}, \quad \gamma = \frac{C_P}{C_V}. \quad (11)$$

For a monatomic ideal gas,  $\gamma = 5/3$ ; for diatomic ideal gas,  $\gamma = 7/5$ .

Now we consider real gases. Many attempts exist to modify the ideal gas equation of state for real gases. Two common ones are:

(a) The hard-sphere gas: we continue to neglect the interaction except at short range where we treat the molecules as hard spheres

$$V(r) = \begin{cases} \infty, & \text{for } r \leq r_0; \\ 0, & \text{for } r > r_0. \end{cases} \quad (12)$$

Most of the ideal gas results continue to hold except  $V \rightarrow V - nb$ , where  $b$  is the "excluded volume", proportional to the volume occupied by 1 mole of gas (i.e.,  $b \propto N_A r_0^3$ ). The equation of state for a hard sphere gas becomes

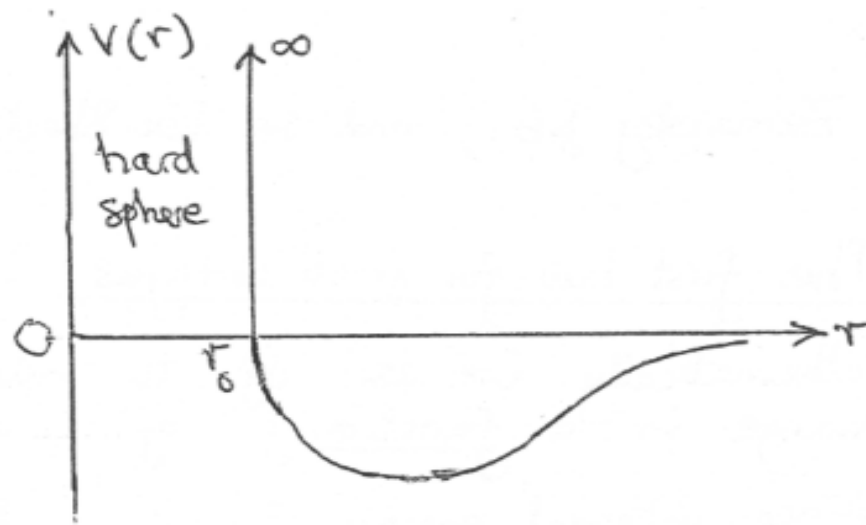
$$P(V - nb) = nRT, \quad \text{or } P(V - N\beta) = Nk_B T, \quad \beta = \frac{b}{N_A}.$$

(b) The van der Waals gas. Apart from the hard-sphere interaction at short distance, we now allow the weak intermolecular attraction at larger distances, as shown in Fig. 2. The extra attraction for  $r > r_0$  clearly reduces the pressure for a given  $V$  and  $T$ , since a molecule striking the vessel wall experiences an additional inward pull on this account. Call this intrinsic pressure  $\pi$ . So

if the observed pressure is  $P$  and that expected if there were no attraction is  $p$ ,  $p - P = \pi$ , the hard-sphere equation of state

$$P = \frac{nRT}{V - nb} \rightarrow P + \pi = \frac{nRT}{V - nb}.$$

Van der Waals argued that  $\pi$  is the result of mutual attraction between bulk of gas, i.e., the tendency of molecules forming pairs, and hence should be proportional to  $N(N - 1)/2 \propto N^2$ , or to  $N^2/V^2$  as it is intensive. Hence  $\pi = an^2/V^2$ .



**Fig. 2** A schematic diagram for the interaction potential between two molecules.

The equation of state for van der Waals gas is

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

or

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - N\beta) = Nk_B T, \quad (13)$$

where  $\beta = b/N_A$  and  $\alpha = a/N_A^2$ .