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THERMODYNAMICS-2

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6.2 Some basic concepts

6.2.1 Thermodynamic system

A *thermodynamic system* is a certain portion of the universe selected for the purpose of investigation and is thus distinct, being set apart from everything else, and is essentially macroscopic. The system may be a gas such as air, a vapour such as steam, a vapour in contact with its liquid such as liquid ammonia and ammonia vapour, a mixture such as air and gasoline vapour etc. In addition to these systems relevant to engineering in particular, there may be such thermodynamic systems as a stretched wire, electric capacitors, thermocouples, magnetic materials, surface films and electric cells which are of more relevance in physics. Plainly, a thermodynamic system is perceptible by our senses.

A system may be simple or complex. It may also be *homogeneous* or *heterogeneous* where each component can exist in different *phases*. A gas enclosed in a cylinder fitted with a frictionless gas-tight piston is a *simple homogeneous system*, but a phenol-water mixture is an example of a *complex heterogeneous system*. Whatever be the system, it is always finite.

6.2.2 Surroundings and boundary

By *surroundings* of a system is meant everything outside it that can influence its behaviour. The *boundary* of a system is the envelope that encloses the system and thereby separates it from its surroundings. This is illustrated in Fig.6.1. The importance of the boundary lies in visualising the system distinctly and it may be real or imaginary.

The boundary of a system may or may not allow it to interact with its surroundings. The boundary that does *not* allow any exchange of matter and energy between the system and its surroundings is called an *isolating boundary*. A system bounded by an isolating boundary is termed an *isolated system* and is not of much importance thermodynamically. A system with a boundary that permits exchange of matter between the system and the surroundings is called an *open system*. The system, however, is said to be a *closed system* if its boundary allows exchange of energy, but prevents exchange of matter between the system and the surroundings. A closed system, however, is not an isolated system. The exchange of energy between the system and the surroundings may take place either *thermally* or *by doing work on the system*. The surface or boundary that prevents thermal interaction with surroundings is called *adiabatic*, and the system is *thermally isolated*. If, however, heat exchange can occur through the boundary, it is said to be *diathermic*. A system with a diathermic boundary will necessarily be in *thermal contact* with the surroundings.

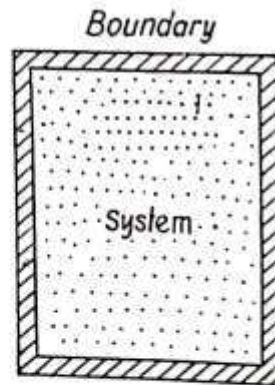


Fig.6.1 Thermodynamic system and boundary

6.2.3 State of a system and thermodynamic variables

In mechanics, the motion of a system is described by solving its equation of motion, the solution giving information relating to time-variation of the position vector associated with the system. In a like manner, in thermodynamics, the *state of a system* at any instant is represented by its condition at that instant, the condition being completely specified by a set of experimentally measurable quantities, called *variables of state* or *thermodynamic variables*. For example, to a stretched wire correspond the thermodynamic variables tension and length; for a surface film the variables are the surface tension and the area; for a capacitor they are e.m.f and the charge; for a hydrostatic system the variables are pressure and volume; and so on. The thermodynamic variables are also termed *thermodynamic coordinates*. A particularly simple condition of state of a system is the *equilibrium state* in which the variables specifying the state are time-independent, that is, do not change with time and are reproducible (Read Art. 6.2.4).

The thermodynamic variables may be of two different kinds: *intensive* and *extensive*. *Intensive* variables of a system in a given state are those which are *independent of its mass or the number of particles*. *Extensive* variables, on the other hand, are *proportional to the mass or, to the number of particles* in the system. Tension, surface tension, e.m.f., in the above examples are intensive variables; length, area, charge are extensive variables. Pressure and temperature are intensive, while volume is an extensive variable.

We give below the thermodynamic variables of some important thermodynamic systems.

Table 6.1 : Thermodynamic variables

System	Intensive variable	Extensive variable
1. Hydrostatic system	pressure, p	volume, V
2. Surface film	surface tension, S	area, A
3. Stretched wire	tension, F	length, L
4. Electric cell	potential difference, E	charge, Z
5. Paramagnetic substance	magnetic intensity, H	dipole moment, M

If y be a macroscopic parameter characterizing the state of a homogeneous system and if the system be divided, by a partition, into two parts or sub-systems having y -values y_1 and y_2 respectively, then

- (i) y is extensive, if $y = y_1 + y_2$
- (ii) y is intensive, if $y = y_1 = y_2$

If x, y be two arbitrary intensive variables, then $xy, y/x, \partial y/\partial x, x + y$ are also intensive. If X, Y are two arbitrary extensive variables, then $X + Y$ is also extensive, but $Y/X, \partial Y/\partial X$ are intensive. Similarly, if x is intensive and X extensive, then $xX, X/x, \partial X/\partial x$ will be extensive. Extensive variables when referred to their *specific values*, that is, the *value per unit mass* of the system are known as *specific variables*. Interestingly, a specific variable corresponding to any extensive variable becomes, by definition, mass-independent and is thus an intensive variable.

It is customary to designate the extensive variables by capital letters and their specific values by the corresponding small letters. For example, if V be the total volume of the system, v will represent the specific volume.

6.2.5 Thermodynamic processes

A system is said to undergo a *thermodynamic process*, when the values of its thermodynamic variables or coordinates change from one equilibrium state to another.

To analyse a thermodynamic process, the variation of one thermodynamic variable is plotted with respect to another and the plot is known as *indicator diagram* (Fig.6.2). On such a diagram the state of a system is determined uniquely by a point. And a process means a line connecting a series of such points. In the adjacent diagram, the initial state of the system is represented by the point (p_1, V_1) , the system undergoes an expansion, and the final state of the system is defined by the point (p_2, V_2) . The process is represented by the curve shown in Fig.6.2. Indicator diagram here is p - V diagram.

It is worth noting that joining the initial and final points by a line has an *important implication* in that the intermediate states are also equilibrium states. And this at once imposes some restrictions as regards the evolution of the thermodynamic process. Since the intermediate states are uniquely defined, they being all equilibrium states, a thermodynamic process can be made to retrace its original path to reach back the initial state. How to execute the retracting (that is, what conditions need be satisfied) however is a separate story. If retracing is possible, the process is said to be *reversible*, if not it is said to be *irreversible*. All natural processes are irreversible. We shall discuss reversibility later in greater detail.

The concept of reversibility facilitates the mathematical formulation of thermodynamics. But how to analyse a natural process within the framework of such a formulation? The problem has been overcome by introducing what may be termed a *quasi-static process*, discussed in a separate sub-section (6.2.9) that follows. Essentially, when a process is carried out extremely slowly such that every state through which the system passes departs only infinitesimally from equilibrium, the process is said to be *quasi-static*. A quasistatic process is thus a *succession of thermodynamic equilibrium states*. For finite departures from equilibrium, the process becomes *non-quasistatic* where system variables do not define the states through which the system passes. They cannot also describe the processes the system undergoes. Consequently, a non-quasistatic process cannot be represented by a line on the indicator diagram.

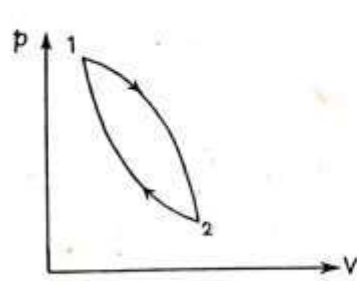


Fig.6.3 A cyclic process represented on p - V diagram

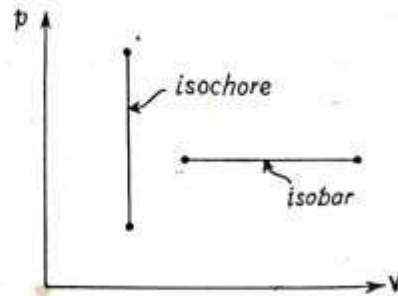


Fig.6.4 An isochoric and an isobaric process on p - V diagram

If the series of processes undergone by a system leads to its reversal back to the initial state, the series constitutes a *cyclic process* and is represented by a closed path on the indicator diagram (Fig.6.3). Some processes, again, are so characterised that a thermodynamic coordinate

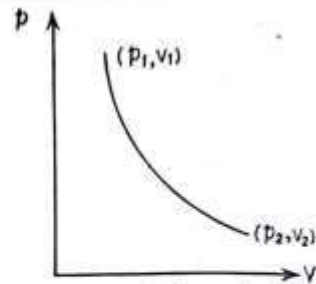


Fig.6.2 An indicator diagram

of the system remains constant throughout. A process in which volume is so kept constant is called *isochoric*, represented on the indicator diagram by a straight line parallel to the p -axis (Fig.6.4). A process where pressure remains constant is called *isobaric* represented by a line parallel to V -axis (Fig.6.4) on the indicator diagram. Similarly, a process in which temperature remains constant is called *isothermal* and one in which there is no thermal interaction (exchange) taking place between the system and its surroundings is called *adiabatic*.

6.2.6 Change in state in an infinitesimal process

If a system undergoes a small change of state in making transition from an initial equilibrium state to another state very near to the former, all the coordinates in general, undergo small changes. If the *change in volume* is small compared to V , but quite large compared to the volume occupied by few molecules, we may denote it by differential dV . Since V is a macroscopic coordinate, ' dV ' will be meaningful when it is large enough to accommodate quite a large number of molecules. Similarly, *change of pressure* is small compared to p , but large in the sense of molecular fluctuation, and is denoted by dp .

So the infinitesimals in thermodynamics are characterised as small compared to the quantity itself but large with reference to the behaviour of few molecules. As already stated in kinetic theory, it makes no sense in stating the temperature, volume and pressure of a few molecules.

It is obvious from the foregoing that the equation of state can be used to calculate the physical parameters of the system like volume expansivity, bulk modulus etc. as has been shown in Art. 6.2.7.

6.3 First law of thermodynamics : Background and formulation

The first law of thermodynamics is a mathematical formulation of the quantitative aspect of the law of conservation and transformation of energy.

The classical experiments of Davy, Rumford, Mayer and Joule led to the discovery of the equivalence of heat and work. To arrive at the formulation of the first law we consider a system completely surrounded by adiabatic envelope but coupled to the surroundings so that work may be done. It is possible to visualise many adiabatic paths connecting the initial and the final states of the system. They are accompanied by non-static dissipative processes. The amount of work done along different adiabatic paths indicated by indirect experiments is the same along all the paths.

The generalised statement of this result is known as the *first law of thermodynamics*.

If a thermally insulated system is caused to change from an initial state to a final state, the amount of work done is the same for all adiabatic paths connecting the state.

The dependence of the adiabatic work on only the initial and final states of the system and its invariance with respect to the path of transformation enables us to invoke a *single-valued function* of state variables of the thermodynamic system, such that the value of the function in the final state minus that at the initial state is equal to the adiabatic work. This function is the *internal energy function* U of the system and is therefore.

$$-W_{i \rightarrow f}|_{\text{ad}} = U_f - U_i$$

the negative sign is in conformity with the signature of work.

For the work done by the system, $W_{i \rightarrow f}$ is positive so that $U_f < U_i$, that is, the internal energy of the system decreases, consistent with the principle of conservation of energy. Similarly, when work is done upon the system, $W_{i \rightarrow f}$ is negative, $U_f > U_i$, the internal energy of the system increases as expected from the principle of conservation of energy. So in order to measure the change in internal energy of a system, experiments involving adiabatic work must be performed. In the laboratory, such experiments are difficult to carry out.

6.4 Mathematical formulation of the first law

The equation (i) of the previous Art. 6.3 may be written for an infinitesimal process as

$$\bar{d}Q = dU + \bar{d}W \quad (\text{i})$$

For a chemical system undergoing quasi-static process

$$\bar{d}Q = dU + pdV \quad (\text{ii})$$

For a system of stretched wire (*elastic system*)

$$\bar{d}Q = dU - FdL \quad (\text{iii})$$

F and L being the tension and length respectively.

For a *magnetic system*

$$\bar{d}Q = dU - HdM \quad (\text{iv})$$

where H is the magnetic intensity and M , the magnetic moment.

From the foregoing analysis, we may conclude that the first law of thermodynamics is more than a statement of the principle of conservation of energy. The formulation leads to the existence of '*internal energy*' function U as a single-valued function of state variables specifying the configuration of the thermodynamic system and defines 'heat' as *energy during transit* by virtue of temperature difference.

6.5 Applications of the first law

The first law of thermodynamics has been successfully applied to a number of physical and chemical processes, both in the laboratory and outside in nature. We shall discuss in this section some of those applications.

Heat capacities: For an infinitesimal quasistatic process performed by one gm. mol. of a chemical system

$$\bar{d}Q = dU + p dV \quad (i)$$

$\bar{d}Q$ being not an exact differential, but dU and dV are; U and V being functions of coordinates defining the equilibrium state of the system.

Let us assume that U is a function of two independent variables T and V of the system.

$$\begin{aligned} \therefore U &= U(T, V) \\ \therefore dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \end{aligned} \quad (ii)$$

Substituting (ii) in (i), we obtain

$$\bar{d}Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} dV \quad (iii)$$

For a process where $V = \text{const.}$, $dV = 0$ (isochoric process). So, from (iii),

$$C_V = \left(\frac{\bar{d}Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (iv)$$

C_V being the heat capacity at constant volume. Since we have taken one gm. mol., it is also the molar specific heat at constant volume.

Similarly, expressing both U and V as functions of temperature T and pressure p , for an infinitesimal quasistatic process

$$\bar{d}Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp + p \left\{ \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \right\} \quad (v)$$

For a process where $p = \text{const.}$, $dp = 0$ (isobaric process). So from (v), we get

$$C_p = \left(\frac{\bar{d}Q}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \quad (vi)$$

where C_p is the heat capacity at constant pressure. Here also it is the molar specific heat at constant pressure.

For an isothermal quasistatic process, $dT = 0$. We obtain from (iii) and (v)

$$\left(\frac{\bar{d}Q}{dV}\right)_T = p + \left(\frac{\partial U}{\partial V}\right)_T = L_V, \text{ say.} \quad (vii)$$

$$\text{and } \left(\frac{\bar{d}Q}{dp}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T + p \left(\frac{\partial V}{\partial p}\right)_T = L_p, \text{ say.} \quad (viii)$$

We define L_V , the latent heat of expansion, as the amount of heat required to increase the volume of unit mass (or 1 gm. mol.) of the substance quasi-statically, temperature remaining

constant. Similarly, L_p is the heat required to increase the pressure of unit mass of the system at constant temperature.

From (vii) and (viii), using (i), we respectively have

$$\bar{d}Q = C_V dT + L_V dV \quad (ix)$$

$$\text{and } \bar{d}Q = C_p dT + L_p dp \quad (x)$$

Difference between specific heats: $C_p - C_V$: From eq. (iii) we obtain

$$C_p = \left(\frac{\bar{d}Q}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} \left(\frac{\partial V}{\partial T}\right)_p \quad (xi)$$

$$= C_V + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} \left(\frac{\partial V}{\partial T}\right)_p \quad (xii)$$

$$\therefore C_p - C_V = \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} \left(\frac{\partial V}{\partial T}\right)_p$$

The first term in the bracket on the right gives the amount of work done in pushing back the surroundings at constant pressure, while the second term tells how the internal energy changes with volume, being associated with the work done against intermolecular forces.

Introducing the volume expansivity, $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$, eq. (xii) may be written as

$$C_p - C_V = \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} \beta V = L_V \beta V \quad (xiii)$$

where L_V is the latent heat of expansion, already defined.

Special cases - For a perfect gas, $pV = RT$ so that $p(\partial V/\partial T)_p = R$. Also, since there is no intermolecular attraction, its internal energy is wholly kinetic and remains unchanged in free expansion (see later). Thus, $(\partial U/\partial V)_T = 0$.

$$\therefore \text{From (xii)} \quad C_p - C_V = R \quad (xiv)$$

$$\text{For } n \text{ gm. mol, it takes the form } C_p - C_V = nR \quad (xiva)$$

This is known as Mayer's relation.

For a real gas, however, the internal energy changes with volume, for work has to be done against the intermolecular forces. Taking the van der Waals' model of real gases,

$$(p + a/V^2)(V - b) = RT$$

We shall see later that $(\partial U/\partial V)_T = a/V^2$, so that from (xii)

$$C_p - C_V = \frac{RT}{V - b} \left(\frac{\partial V}{\partial T}\right)_p \quad (xv)$$

Differentiating van der Waals' equation

$$\left\{p + \frac{a}{V^2} - (V - b) \frac{2a}{V^3}\right\} \left(\frac{\partial V}{\partial T}\right)_p = R$$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p + \frac{a}{V^2} - \frac{2a}{V^3}(V - b)} = \frac{R(V - b)}{RT - \frac{2a}{V^3}(V - b)^2}$$

$$\therefore \frac{1}{V - b} \left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T \left\{1 - \frac{2a}{RTV^3}(V - b)^2\right\}} = \frac{1}{T} \left\{1 + \frac{2a}{RTV^3}(V - b)^2\right\}$$

expanding binomially and retaining terms up to first order in a which is very small.

∴ From (xv), we thus obtain

$$C_p - C_v = R \left\{ 1 + \frac{2a}{RTV^3} (V - b)^2 \right\} \quad (xvi)$$

Comparing (xvi) with (xiv), it is observed that the difference is more for a real gas. For large molecular separations, the second term in the bracket of (xvi) is ignorable and the result is one with the perfect gas. Fig.6.7 shows that the plot of $(C_p - C_v)/R$ vs. V for a van der Waals' gas. It is observed that the ideal gas value is attained only at a large value of V .

Free expansion: In their experiments on free expansion of a gas, Joule and Mayer observed that the temperature of the gas remains unaltered.

In the free expansion, a gas is kept in one part of the vessel by a partition, the other part evacuated. On removing the partition, the gas is allowed to expand against vacuum and fills the whole vessel (Fig.6.8). Free expansion is a non-static process and takes place under thermal isolation. Since the gas expands against vacuum, no external work is done by the gas.

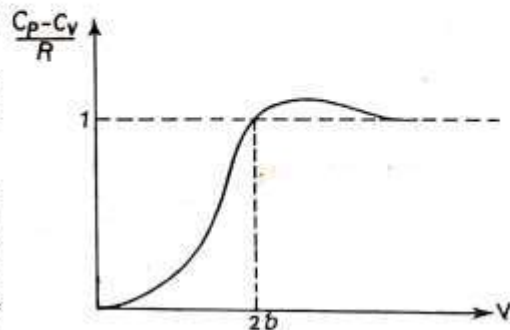


Fig.6.7 Plot of $(C_p - C_v)/R$ vs. V of a van der Waals' gas

$$\therefore \bar{d}Q = 0, \quad \bar{d}W = 0$$

Hence, from the first law, $dU = 0$.

If U is assumed to depend on T and V ,

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

Since $dT = 0$ (as was observed by Joule and Mayer), and also $dU = 0$, we obtain

$$\left(\frac{\partial U}{\partial V} \right)_T = 0, \quad \text{since } dV \neq 0.$$

Similarly, taking U as a function of T and p , we would get

$$\left(\frac{\partial U}{\partial p} \right)_T = 0$$

The internal energy of such a system depends on temperature T only and is independent of p and V . The results on change of temperature are valid only for an ideal gas, although Joule and Mayer performed experiments on real gases. The thermometers used by them for measurement of temperature after free expansion were of low precision and they considered the gases used to obey the Boyle's and Charles' laws (ideal gases).



Fig.6.8 Joule expansion (Free expansion)

6.9 Work in quasi-static processes

1. (a) Isothermal expansion or compression of an ideal gas, the initial volume V_i changing finally to V_f . The work

$$\begin{aligned} W_{iso} &= \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV \quad (\because pV = nRT) \\ &= nRT \int_{V_i}^{V_f} \frac{dV}{V} \\ &= nRT \ln \frac{V_f}{V_i} \end{aligned}$$

2. Adiabatic expansion or compression of an ideal gas, the initial volume V_i changing finally to V_f . The work W_{ad} is given by

$$\begin{aligned} W_{ad} &= \int_{V_i}^{V_f} p dV = k \int_{V_i}^{V_f} V^{-\gamma} dV \quad (\because pV^\gamma = k \text{ (const.)}) \\ &= \frac{k}{\gamma - 1} [V^{1-\gamma}]_{V_i}^{V_f} = \frac{k}{\gamma - 1} (V_i^{1-\gamma} - V_f^{1-\gamma}) \\ &= \frac{p_i V_i - p_f V_f}{\gamma - 1} \quad (\because p_i V_i^\gamma = k = p_f V_f^\gamma) \end{aligned} \quad (ii)$$

$$= \frac{R}{\gamma - 1} (T_i - T_f) \quad (\because p_i V_i = RT_i; \quad p_f V_f = RT_f) \quad (iii)$$

$$= C_V (T_i - T_f) \quad (\because \gamma = C_p/C_V \text{ and } R = C_p - C_V) \quad (iv)$$

The relations (ii), (iii) and (iv) constitute the different expression for the adiabatic work done by an ideal gas. The corresponding expressions for a van der Waals' gas are given elsewhere.

6.2.7 Some deductions from equation of state

The equation of state in the parametric form may be used to study the behaviour of a system under different conditions.

Consider a hydrostatic system with the equation of state

$$f(p, V, T) = 0$$

$$\text{or, } p = p(V, T)$$

$$\therefore dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT \quad (\text{i})$$

where dp is an infinitesimal change in p . The $(\partial p/\partial V)_T$ expresses the rate of change of pressure with volume when the temperature is constant, that is, in an *isothermal* process; $(\partial p/\partial T)_V$ is the rate of change of pressure with temperature when the volume is kept constant, that is, for an *isochoric* process.

For an *isobaric* process, $dp = 0$ and eq. (i) becomes

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \quad (\text{ii})$$

To attribute physical meaning to (ii), we note that *volume expansivity* β of a material, in an isobaric process, is given by

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad (\text{iii})$$

and *isothermal elasticity*, E_T , reciprocal of *isothermal compressibility* K_T , of a material is defined as

$$E_T = \frac{1}{K_T} = -V \left(\frac{\partial p}{\partial V}\right)_T \quad (\text{iv})$$

Combining (ii), (iii) and (iv), we obtain

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta V E_T}{V} = \beta E_T \quad (\text{v})$$

Thus, for a given change in temperature, the increase in pressure will be more when expansivity and also elasticity are large (compressibility small) and conversely.

Using (v), we get from (i)

$$dp = -\frac{E_T}{V} dV + \beta E_T dT \quad (\text{vi})$$

For an *isochoric* process, (vi) reduces to

$$dp = \beta E_T dT \quad (\text{vii})$$

For a finite change in pressure, the change in temperature is

$$\int_{p_1}^{p_2} dp = \int_{T_1}^{T_2} \beta E_T dT$$

$$\text{or, } p_2 - p_1 = \beta E_T (T_2 - T_1) \quad (\text{viii})$$

assuming β and E_T constant in the temperature range considered.

Thus, if β and E_T are experimentally determined, eq. (viii) provides the final pressure, in an isochoric process, for a given rise in temperature.