7

Thermodynamic Relations

7.1. GENERAL ASPECTS

In this chapter, some important thermodynamic relations are deduced ; principally those which are useful when tables of properties are to be compiled from limited experimental data, those which may be used when calculating the work and heat transfers associated with processes undergone by a liquid or solid. It should be noted that the relations only apply to a substance in the solid phase when the stress, i.e. the pressure, is uniform in all directions ; if it is not, a single value for the pressure cannot be alloted to the system as a whole.

Eight properties of a system, namely pressure (p), volume (v), temperature (T), internal energy (u), enthalpy (h), entropy (s), Helmholtz function (f) and Gibbs function (g) have been introduced in the previous chapters. h, f and g are sometimes referred to as **thermodynamic potentials**. Both f and g are useful when considering chemical reactions, and the former is of fundamental importance in statistical thermodynamics. The Gibbs function is also useful when considering processes involving a change of phase.

Of the above eight properties only the first three, i.e., p, v and T are directly measurable. We shall find it convenient to introduce other combination of properties which are relatively easily measurable and which, together with measurements of p, v and T, enable the values of the remaining properties to be determined. These combinations of properties might be called 'thermodynamic gradients' ; they are all defined as the rate of change of one property with another while a third is kept constant.

7.2. FUNDAMENTALS OF PARTIAL DIFFERENTIATION

Let three variables are represented by x, y and z. Their functional relationship may be expressed in the following forms :

$$f(x, y, z) = 0 \qquad \qquad \text{...(i)}$$
$$x = x(y, z) \qquad \qquad \text{...(ii)}$$
$$y = y(x, z) \qquad \qquad \text{...(iii)}$$
$$z = z(x, y) \qquad \qquad \text{...(iv)}$$

Let x is a function of two independent variables y and z

$$x = x(y, z) \qquad \qquad \text{...(7.1)}$$

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Then the differential of the dependent variable x is given by

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \qquad \qquad ...(7.2)$$

where dx is called an **exact differential**.

If $\left(\frac{\partial x}{\partial y}\right)_z = M$ and $\left(\frac{\partial x}{\partial z}\right)_y = N$

Then $\qquad\qquad\qquad\qquad dx = Mdy + Ndz \qquad\qquad\qquad ...(7.3)$

Partial differentiation of M and N with respect to z and y, respectively, gives

$$\frac{\partial M}{\partial z} = \frac{\partial^2 x}{\partial y \partial z} \qquad \text{and} \qquad \frac{\partial N}{\partial y} = \frac{\partial^2 x}{\partial z \partial y}$$

or $\qquad\qquad\qquad\qquad \dfrac{\partial M}{\partial z} = \dfrac{\partial N}{\partial y} \qquad\qquad\qquad ...(7.4)$

dx is a perfect differential when eqn. (7.4) is satisfied for any function x.

Similarly if $\qquad y = y(x, z)$ and $z = z(x, y)$ $\qquad\qquad ...(7.5)$

then from these two relations, we have

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \qquad\qquad ...(7.6)$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad\qquad ...(7.7)$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\right]$$

$$= \left[\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y\right] dx + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$= \left[\left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y\right] dx + dy$$

or $\qquad\qquad \left(\dfrac{\partial y}{\partial x}\right)_z + \left(\dfrac{\partial y}{\partial z}\right)_x \left(\dfrac{\partial z}{\partial x}\right)_y = 0$

or $\qquad\qquad \left(\dfrac{\partial y}{\partial z}\right)_x \left(\dfrac{\partial z}{\partial x}\right)_y = - \left(\dfrac{\partial y}{\partial x}\right)_z$

or $\qquad\qquad \left(\dfrac{\partial x}{\partial y}\right)_z \left(\dfrac{\partial z}{\partial x}\right)_y \left(\dfrac{\partial y}{\partial z}\right)_x = -1 \qquad\qquad ...(7.8)$

In terms of p, v and T, the following relation holds good

$$\boxed{\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial v}{\partial T}\right)_p = -1} \qquad\qquad ...(7.9)$$

7.3. SOME GENERAL THERMODYNAMIC RELATIONS

The first law applied to a closed system undergoing a reversible process states that

$$dQ = du + pdv$$

According to second law,

$$ds = \left(\frac{dQ}{T}\right)_{rev.}$$

Combining these equations, we get

$$Tds = du + pdv$$

or

$$du = Tds - pdv \qquad\qquad ...(7.10)$$

The properties h, f and g may also be put in terms of T, s, p and v as follows :

$$dh = du + pdv + vdp = Tds + vdp$$

Helmholtz free energy function,

$$df = du - Tds - sdT \qquad\qquad ...(7.11)$$

$$= - pdv - sdT \qquad\qquad ...(7.12)$$

Gibb's free energy function,

$$dg = dh - Tds - sdT = vdp - sdT \qquad\qquad ...(7.13)$$

Each of these equations is a result of the two laws of thermodynamics.

Since du, dh, df and dg are the exact differentials, we can express them as

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv,$$

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp,$$

$$df = \left(\frac{\partial f}{\partial v}\right)_T dv + \left(\frac{\partial f}{\partial T}\right)_v dT,$$

$$dg = \left(\frac{\partial g}{\partial p}\right)_T dp + \left(\frac{\partial g}{\partial T}\right)_p dT.$$

Comparing these equations with (7.10) to (7.13) we may equate the corresponding co-efficients. For example, from the two equations for du, we have

$$\left(\frac{\partial u}{\partial s}\right)_v = T \text{ and } \left(\frac{\partial u}{\partial v}\right)_s = - p$$

The complete group of such relations may be summarised as follows :

$$\left(\frac{\partial u}{\partial s}\right)_v = T = \left(\frac{\partial h}{\partial s}\right)_p \qquad\qquad ...(7.14)$$

$$\left(\frac{\partial u}{\partial v}\right)_s = - p = \left(\frac{\partial f}{\partial v}\right)_T \qquad\qquad ...(7.15)$$

$$\left(\frac{\partial h}{\partial p}\right)_s = v = \left(\frac{\partial g}{\partial p}\right)_T \qquad\qquad ...(7.16)$$

$$\left(\frac{\partial f}{\partial T}\right)_v = - s = \left(\frac{\partial g}{\partial T}\right)_p \qquad\qquad ...(7.17)$$

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Also,

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v \qquad \text{...(7.18)}$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p \qquad \text{...(7.19)}$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \qquad \text{...(7.20)}$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \qquad \text{...(7.21)}$$

The equations (7.18) to (7.21) are known as **Maxwell relations**.

It must be emphasised that eqns. (7.14) to (7.21) do not refer to a process, but simply express relations between properties which must be satisfied when any system is in a state of equilibrium. Each partial differential co-efficient can itself be regarded as a property of state. The state may be defined by a point on a three dimensional surface, the surface representing all possible states of stable equilibrium.

7.4. ENTROPY EQUATIONS (Tds Equations)

Since entropy may be expressed as a function of any other two properties, e.g. temperature T and specific volume v,

$$s = f(T, v)$$

i.e.,

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

or

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv \qquad \text{...(7.22)}$$

But for a reversible constant volume change

$$dq = c_v (dT)_v = T(ds)_v$$

or

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v \qquad \text{...(7.23)}$$

But,

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad \text{[Maxwell's eqn. (7.20)]}$$

Hence, substituting in eqn. (7.22), we get

$$Tds = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \qquad \text{...(7.24)}$$

This is known as the **first form of entropy equation** or the **first Tds equation**.
Similarly, writing

$$s = f(T, p)$$

$$Tds = T\left(\frac{\partial s}{\partial T}\right)_p dT + T\left(\frac{\partial s}{\partial p}\right)_T dp \qquad \text{...(7.25)}$$

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where $\quad c_p = T\left(\dfrac{\partial s}{\partial T}\right)_p$ $\hspace{6cm}$ ...(7.26)

Also $\hspace{2.5cm}\left(\dfrac{\partial s}{\partial p}\right)_T = -\left(\dfrac{\partial v}{\partial T}\right)_p$ $\hspace{3cm}$ [Maxwell's eqn. (7.21)]

whence, substituting in eqn. (7.25)

$$Tds = c_p dT - T\left(\dfrac{\partial v}{\partial T}\right)_p dp$$ $\hspace{3cm}$ ...(7.27)

This is known as the second form of entropy equation or the second Tds equation.

7.5. EQUATIONS FOR INTERNAL ENERGY AND ENTHALPY

(i) Let $\hspace{3cm} u = f(T, v)$

$$du = \left(\dfrac{\partial u}{\partial T}\right)_v dT + \left(\dfrac{\partial u}{\partial v}\right)_T dv = c_v\, dT + \left(\dfrac{\partial u}{\partial v}\right)_T dv$$ $\hspace{1.5cm}$ ...(7.28)

To evaluate $\left(\dfrac{\partial u}{\partial v}\right)_T$ $\quad$ let $u = f(s, v)$

Then $\hspace{3cm} du = \left(\dfrac{\partial u}{\partial s}\right)_v ds + \left(\dfrac{\partial u}{\partial v}\right)_s dv$

or $\hspace{3cm} \left(\dfrac{\partial u}{\partial v}\right)_T = \left(\dfrac{\partial u}{\partial s}\right)_v\left(\dfrac{\partial s}{\partial v}\right)_T + \left(\dfrac{\partial u}{\partial v}\right)_s$

But $\hspace{3cm} \left(\dfrac{\partial u}{\partial s}\right)_v = T, \ \left(\dfrac{\partial s}{\partial v}\right)_T = \left(\dfrac{\partial s}{\partial T}\right)_v, \left(\dfrac{\partial u}{\partial v}\right)_s = -p$

Hence $\hspace{2.5cm} \left(\dfrac{\partial u}{\partial v}\right)_T = T\left(\dfrac{\partial p}{\partial T}\right)_v - p$ $\hspace{3cm}$ ...(7.29)

This is sometimes called the energy equation.
From equation (7.28), we get

$$du = c_v dT + \left\{T\left(\dfrac{\partial p}{\partial T}\right)_v - p\right\} dv$$ $\hspace{3cm}$ ...(7.30)

(ii) To evaluate dh we can follow similar steps as under

$$h = f(T, p)$$

$$dh = \left(\dfrac{\partial h}{\partial T}\right)_p dT + \left(\dfrac{\partial h}{\partial p}\right)_T dp$$

$$= c_p dT + \left(\dfrac{\partial h}{\partial p}\right)_T dp$$ $\hspace{3cm}$ ...(7.31)

To find $\left(\dfrac{\partial h}{\partial p}\right)_T$;   let h = f(s, p)

Then, $dh = \left(\dfrac{\partial h}{\partial s}\right)_p ds + \left(\dfrac{\partial h}{\partial p}\right)_s dp$

$\left(\dfrac{\partial h}{\partial p}\right)_T = \left(\dfrac{\partial h}{\partial s}\right)_p \left(\dfrac{\partial s}{\partial p}\right)_T + \left(\dfrac{\partial h}{\partial p}\right)_s$

But $\left(\dfrac{\partial h}{\partial s}\right)_p = T, \left(\dfrac{\partial s}{\partial p}\right)_T = -\left(\dfrac{\partial v}{\partial p}\right)_p , \left(\dfrac{\partial h}{\partial p}\right)_s = v$

Hence

$$\boxed{\left(\dfrac{\partial h}{\partial p}\right)_T = v - T\left(\dfrac{\partial v}{\partial T}\right)_p}$$ ...(7.32)

From eqn. (7.31), we get

$$\boxed{dh = c_p\, dT + \left\{v - T\left(\dfrac{\partial v}{\partial T}\right)_p\right\} dp}$$ ...(7.33)

7.6. MEASURABLE QUANTITIES

Out of eight thermodynamic properties, as earlier stated, only p, v and T are directly measurable. Let us now examine the information that can be obtained from measurements of these primary properties, and then see what other easily measurable quantities can be introduced.

The following will be discussed :

 (i) Equation of state
 (ii) Co-efficient of expansion and compressibility
 (iii) Specific heats
 (iv) Joule-Thomson co-efficient.

7.6.1. Equation of State

Let us imagine a series of experiments in which the volume of a substance is measured over a range of temperatures while the pressure is maintained constant, this being repeated for various pressures. The results might be represented graphically by a three-dimensional surface, or by a family of constant pressure lines on a v-T diagram. It is useful if an equation can be found to express the relation between p, v and T, and this can always be done over a limited range of states. No single equation will hold for all phases of a substance, and usually more than one equation is required even in one phase if the accuracy of the equation is to match that of the experimental results. Equations relating p, v and T are called equations of state or characteristic equations. Accurate equations of state are usually complicated, a typical form being

$$pv = A + \frac{B}{v} + \frac{C}{2} + \text{ .....}$$

where A, B, C, ... are functions of temperature which differ for different substances.

An equation of state of a particular substance is an empirical result, and it cannot be deduced from the laws of thermodynamics. Nevertheless the general form of the equation may be

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predicted from hypotheses about the microscopic structure of matter. This type of prediction has been developed to a high degree of precision for gases, and to a lesser extent for liquids and solids. The simplest postulates about the molecular structure of gases lead to the concept of the perfect gas which has the equation of state pv = RT. Experiments have shown that the behaviour of real gases at low pressure with high temperature agrees well with this equation.

7.6.2. Co-efficient of Expansion and Compressibility

From p-v-T measurements, we find that an equation of state is not the only useful information which can be obtained. When the experimental results are plotted as a series of constant pressure lines on a v-T diagrams, as in Fig. 7.1 (a), the slope of a constant pressure line at any given state is $\left(\dfrac{\partial v}{\partial T}\right)_p$. If the gradient is divided by the volume at that state, we have a value of a property of the substance called its co-efficient of cubical expansion β. That is,

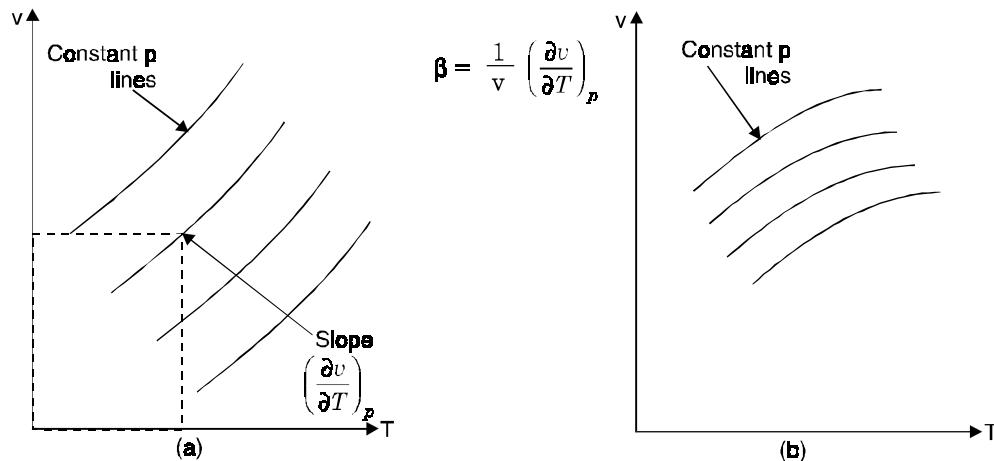$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

Fig. 7.1. Determination of co-efficient of expansion from p-v-T data.

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \qquad \qquad ...(7.34)$$

Value of β can be tabulated for a range of pressures and temperatures, or plotted graphically as in Fig. 7.2 (b). For solids and liquids over the normal working range of pressure and temperature, the variation of β is small and can often be neglected. In tables of physical properties β is usually quoted as an average value over a small range of temperature, the pressure being atmospheric. This average co-efficient may be symbolised by β and it is defined by

$$\beta = \frac{v_2 - v_1}{v_1 (T_2 - T_1)} \qquad \qquad ...(7.35)$$

Fig. 7.2 (a) can be replotted to show the variation of volume with pressure for various constant values of temperature. In this case, the gradient of a curve at any state is $\left(\dfrac{\partial v}{\partial p}\right)_T$. When this gradient is divided by the volume at that state, we have a property known as the compressibility K of the substance. Since this gradient is always negative, i.e., the volume of a substance always decreases with increase of pressure when the temperature is constant, the compressibility is usually made a positive quantity by defining it as
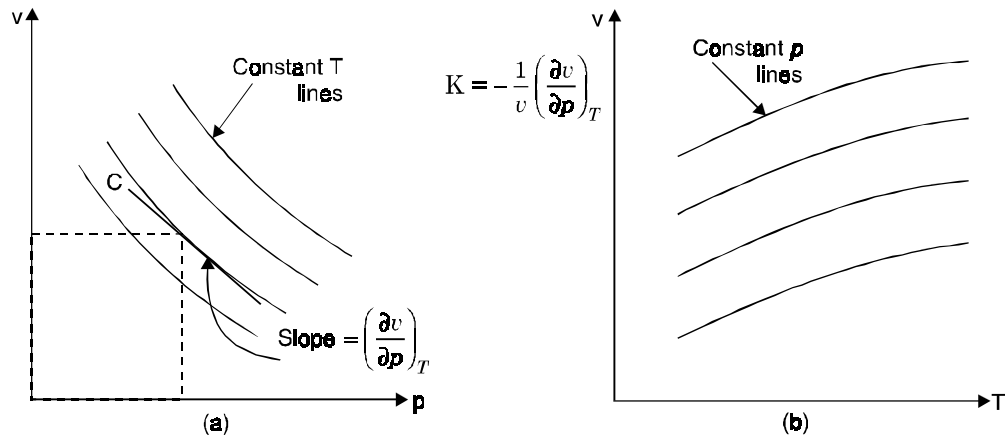
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Fig. 7.2. Determination of compressibility from p-T data.

$$K = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad \qquad ...(7.36)$$

K can be regarded as a constant for many purposes for solids and liquids. In tables of properties it is often quoted as an average a value over a small range of pressure at atmospheric temperature, i.e.,

$$\overline{K} = -\frac{v_2 - v_1}{v_1(p_2 - p_1)}$$

When β and K are known, we have

$$\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_p\left(\frac{\partial v}{\partial p}\right)_T = -1$$

Since

$$\left(\frac{\partial v}{\partial T}\right)_p = \beta v \quad \text{and} \quad \left(\frac{\partial v}{\partial p}\right)_T = -Kv,$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{\beta}{K} \qquad \qquad ...(7.37)$$

When the equation of state is known, the co-efficient of cubical expansion and compressibility can be found by differentiation. For a perfect gas, for example, we have

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} \quad \text{and} \quad \left(\frac{\partial v}{\partial p}\right)_T = \frac{RT}{p^2}$$

Hence

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{pv} = \frac{1}{T},$$

and

$$K = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{RT}{p^2 v} = \frac{1}{p}.$$

7.6.3. Specific Heats

Following are the three differential co-efficients which can be relatively easily determined experimentally.

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Consider the first quantity $\left(\dfrac{\partial u}{\partial T}\right)_v$. During a process at constant volume, the first law informs us that an increase of internal energy is equal to heat supplied. If a calorimetric experiment is conducted with a known mass of substance at constant volume, the quantity of heat Q required to raise the temperature of unit mass by ΔT may be measured. We can then write : $\left(\dfrac{\Delta u}{\Delta T}\right)_v = \left(\dfrac{Q}{\Delta T}\right)_v$. The quantity obtained this way is known as the mean specific heat at constant volume over the temperature range ΔT. It is found to vary with the conditions of the experiment, i.e., with the temperature range and the specific volume of the substance. As the temperature range is reduced the value approaches that of $\left(\dfrac{\partial u}{\partial T}\right)_v$, and the true specific heat at constant volume is defined by $c_v = \left(\dfrac{\partial u}{\partial T}\right)_v$. This is a property of the substance and in general its value varies with the state of the substance, e.g., with temperature and pressure.

According to first law of thermodynamics the heat supplied is equal to the increase of enthalpy during a reversible constant pressure process. Therefore, a calorimetric experiment carried out with a substance at constant pressure gives us, $\left(\dfrac{\Delta h}{\Delta T}\right)_p = \left(\dfrac{Q}{\Delta T}\right)_p$ which is the mean specific heat at constant pressure. As the range of temperature is made infinitesimally small, this becomes the rate of change of enthalpy with temperature at a particular state defined by T and p, and this is true specific heat at constant pressure defined by $c_p = \left(\dfrac{\partial h}{\partial T}\right)_p$. c_p also varies with the state, e.g., with pressure and temperature.

The description of experimental methods of determining c_p and c_v can be found in texts on physics. When solids and liquids are considered, it is not easy to measure c_v owing to the stresses set up when such a substance is prevented from expanding. However, a relation between c_p, c_v, β and K can be found as follows, from which c_v may be obtained if the remaining three properties have been measured.

The First Law of Thermodynamics, for a reversible process states that

$$dQ = du + p\, dv$$

Since we may write $u = \phi(T, v)$, we have

$$du = \left(\dfrac{du}{\partial T}\right)_v dT + \left(\dfrac{\partial u}{\partial v}\right)_T dv$$

$\therefore$
$$dQ = \left(\dfrac{\partial u}{\partial T}\right)_v dT + \left\{p + \left(\dfrac{\partial u}{\partial v}\right)_T\right\} dv = c_v\, dT + \left\{p + \left(\dfrac{\partial u}{\partial v}\right)_T\right\} dv$$

This is true for any reversible process, and so, for a reversible constant pressure process,

$$dQ = c_p(dT)_p = c_v(dT)_p + \left\{p + \left(\dfrac{\partial u}{\partial v}\right)_T\right\} (dv)_p$$

Hence
$$c_p - c_v = \left\{p + \left(\dfrac{\partial u}{\partial v}\right)_T\right\} \left(\dfrac{\partial v}{\partial T}\right)_p$$

Also
$$\left(\dfrac{\partial p}{\partial T}\right)_v = \left(\dfrac{\partial s}{\partial v}\right)_T = \dfrac{1}{T}\left\{p + \left(\dfrac{\partial u}{\partial v}\right)_T\right\}, \text{ and therefore}$$

$$c_p - c_v = T\left(\dfrac{\partial p}{\partial T}\right)_v \left(\dfrac{\partial v}{\partial T}\right)_p$$

Now, from eqns. (7.34) and (7.37), we have

$$c_p - c_v = \frac{\beta^2 T v}{K} \qquad \qquad ...(7.38)$$

Thus at any state defined by T and v, c_v can be found if c_p, β and K are known for the substance at that state. The values of T, v and K are always positive and, although β may sometimes be negative (e.g., between 0° and 4°C water contracts on heating at constant pressure), β^2 is always positive. It follows that c_p is always greater than c_v.

The other expressions for c_p and c_v can be obtained by using the equation (7.14) as follows :

Since
$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v$$

We have
$$c_v = T \left(\frac{\partial s}{\partial T}\right)_v \qquad \qquad ...(7.39)$$

Similarly,
$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = \left(\frac{\partial h}{\partial s}\right)_p \left(\frac{\partial s}{\partial T}\right)_p$$

Hence,
$$c_p = T \left(\frac{\partial s}{\partial T}\right)_p \qquad \qquad ...(7.40)$$

Alternative Expressions for Internal Energy and Enthalpy

(i) Alternative expressions for equations (7.29) and (7.32) can be obtained as follows :

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p \qquad \qquad ...(7.29)$$

But
$$\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right) \left(\frac{\partial v}{\partial p}\right)_T = -1$$

or
$$\left(\frac{\partial p}{\partial T}\right)_v = - \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T = + \frac{\beta v}{K v} = \frac{\beta}{K}$$

Substituting in eqn. (7.29), we get

$$\boxed{\left(\frac{\partial u}{\partial v}\right)_T = T \frac{\beta}{K} - p} \qquad \qquad ...(7.41)$$

Thus,
$$\boxed{du = c_v dT + \left(\frac{T\beta}{K} - p\right) dv} \qquad \qquad ...[7.28\ (a)]$$

Similarly,
$$\left(\frac{\partial h}{\partial p}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_p \qquad \qquad ...(7.32)$$

But by definition, $\left(\frac{\partial u}{\partial T}\right)_p = \beta v$

Hence
$$\boxed{\left(\frac{\partial h}{\partial p}\right)_T = v(1 - \beta T)} \qquad \qquad ...(7.42)$$

Thus

$$dh = c_p \, dT + v(1 - \beta T) \, dp \qquad ...[7.31 \, (a)]$$

(ii) Since

$$u = h - pv$$

or

$$\left(\frac{\partial u}{\partial p}\right)_T = \left(\frac{\partial h}{\partial p}\right)_T - p \left(\frac{\partial v}{\partial p}\right)_T - v$$

$$= v - v\beta T + pKv - v$$

Hence

$$\left(\frac{\partial u}{\partial p}\right)_T = pKv - v\beta T \qquad ...(7.43)$$

7.6.4. Joule-Thomson Co-efficient

Let us consider the partial differential co-efficient $\left(\dfrac{\partial T}{\partial p}\right)_h$. We know that if a fluid is flowing through a pipe, and the pressure is reduced by a throttling process, the enthalpies on either side of the restriction may be equal.

The throttling process is illustrated in Fig. 7.3 (a). The velocity increases at the restriction, with a consequent decrease of enthalpy, but this increase of kinetic energy is dissipated by friction, as the eddies die down after restriction. The steady-flow energy equation implies that the enthalpy of the fluid is restored to its initial value if the flow is adiabatic and if the velocity before restriction is equal to that downstream of it. These conditions are very nearly satisfied in the following experiment which is usually referred to as the Joule-Thomson experiment.
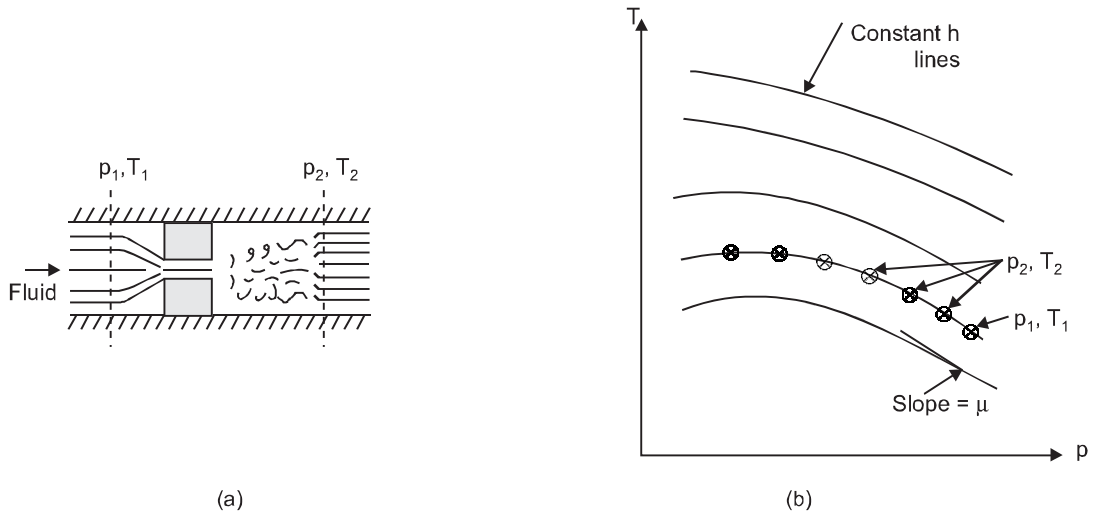

Fig. 7.3. Determination of Joule-Thomson co-efficient.

Through a porous plug (inserted in a pipe) a fluid is allowed to flow steadily from a high pressure to a low pressure. The pipe is well lagged so that any heat flow to or from the fluid is negligible when steady conditions have been reached. Furthermore, the velocity of the flow is kept low, and any difference between the kinetic energy upstream and downstream of the plug is negligible. A porous plug is used because the local increase of directional kinetic energy, caused by the restriction, is rapidly converted to random molecular energy by viscous friction in fine passages of the plug. Irregularities in the flow die out in a very short distance downstream of the plug, and

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temperature and pressure measurements taken there will be values for the fluid in a state of thermodynamic equilibrium.

By keeping the upstream pressure and temperature constant at p_1 and T_1, the downstream pressure p_2 is reduced in steps and the corresponding temperature T_2 is measured. The fluid in the successive states defined by the values of p_2 and T_2 must always have the same value of the enthalpy, namely the value of the enthalpy corresponding to the state defined by p_1 and T_1. From these results, points representing equilibrium states of the same enthalpy can be plotted on a T-s diagram, and joined up to form a curve of constant enthalpy. The curve does not represent the throttling process itself, which is irreversible. During the actual process, the fluid undergoes first a decrease and then an increase of enthalpy, and no single value of the specific enthalpy can be ascribed to all elements of the fluid. If the experiment is repeated with different values of p_1 and T_1, a family of curves may be obtained (covering a range of values of enthalpy) as shown in Fig. 7.3 (b).

The slope of a curve [Fig. 7.3 (b)] at any point in the field is a function only of the state of the fluid, it is the Joule-Thomson co-efficient μ, defined by $\mu = \left(\dfrac{\partial T}{\partial p}\right)_h$. The change of temperature due to a throttling process is small and, if the fluid is a gas, it may be an increase or decrease. At any particular pressure there is a temperature, the temperature of inversion, above which a gas can never be cooled by a throttling process.

Both c_p and μ, as it may be seen, are defined in terms of p, T and h. The third partial differential co-efficient based on these three properties is given as follows :

$$\left(\frac{\partial h}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_h \left(\frac{\partial T}{\partial h}\right)_p = -1$$

Hence

$$\left(\frac{\partial h}{\partial p}\right)_T = -\mu c_p \qquad \qquad ...(7.44)$$

μ may be expressed in terms of c_p, p, v and T as follows :

The property relation for dh is dh = T ds + v dp

From second T ds equation, we have

$$Tds = c_p\, dT - T \left(\frac{\partial v}{\partial T}\right)_p dp$$

$\therefore$
$$dh = c_p\, dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] dp \qquad \qquad ...(7.45)$$

For a constant enthalpy process dh = 0. Therefore,

$$0 = (c_p\, dT)_h + \left[\left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\} dp\right]_h$$

or
$$(c_p\, dT)_h = \left[\left\{T\left(\frac{\partial v}{\partial T}\right)_p - v\right\} dp\right]_h$$

$\therefore$
$$\mu = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \qquad \qquad ...(7.46)$$

For an ideal gas, $\qquad\qquad$ pv = RT ; $\quad v = \dfrac{RT}{p}$

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or
$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} = \frac{v}{T}$$

∴
$$\mu = \frac{1}{c_p}\left(T \times \frac{v}{T} - v\right) = 0.$$

Therefore, if an ideal gas is throttled, there will not be any change in temperature.

Let
$$h = f(p, T)$$

Then
$$dh = \left(\frac{\partial h}{\partial p}\right)_T dp + \left(\frac{\partial h}{\partial T}\right)_p dT \qquad ...(7.47)$$

But
$$\left(\frac{\partial h}{\partial T}\right)_p = c_p$$

∴
$$dh = \left(\frac{\partial h}{\partial p}\right)_T dp + c_p dT$$

For throttling process, dh = 0

∴
$$0 = \left(\frac{\partial h}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_h + c_p \qquad ...(7.48)$$

or
$$c_p = -\frac{1}{\mu}\left(\frac{\partial h}{\partial p}\right)_T \qquad ...(7.49)$$

$\left(\dfrac{\partial h}{\partial p}\right)_T$ is known as the constant temperature co-efficient.

7.7. CLAUSIUS-CLAPERYON EQUATION

Clausius-Claperyon equation is a relationship between the saturation pressure, temperature, the enthalpy of evaporation, and the specific volume of the two phases involved. This equation provides a basis for calculations of properties in a two-phase region. It gives the slope of a curve separating the two phases in the p-T diagram.
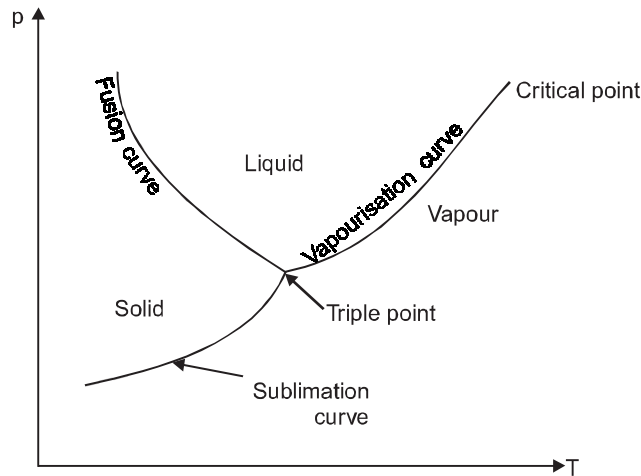

Fig. 7.4. p-T diagram.

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The Clausius-Claperyon equation can be derived in different ways. The method given below involves the use of the Maxwell relation [eqn. (7.20)]

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

Let us consider the change of state from saturated liquid to saturated vapour of a pure substance which takes place at constant temperature. During the evaporation, the pressure and temperature are independent of volume.

$$\therefore \qquad \left(\frac{dp}{dT}\right) = \frac{s_g - s_f}{v_g - v_f}$$

where, s_g = Specific entropy of saturated vapour,

s_f = Specific entropy of saturated liquid,

v_g = Specific volume of saturated vapour, and

v_f = Specific volume of saturated liquid.

Also, $\qquad s_g - s_f = s_{fg} = \dfrac{h_{fg}}{T}$

and $\qquad v_g - v_f = v_{fg}$

where $\quad s_{fg}$ = Increase in specific entropy,

v_{fg} = Increase in specific volume, and

h_{fg} = Latent heat added during evaporation at saturation temperature T.

$$\therefore \qquad \frac{dp}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{s}{v_{fg}} = \frac{h}{T \cdot v_{fg}} \qquad \qquad ...(7.50)$$

This is known as Clausius-Claperyon or Claperyon equation for evaporation of liquids. The derivative $\dfrac{dp}{dT}$ is the slope of vapour pressure versus temperature curve. Knowing this slope and the specific volume v_g and v_f from experimental data, we can determine the enthalpy of evaporation, $(h_g - h_f)$ which is relatively difficult to measure accurately.

Eqn. (7.50) is also valid for the change from a solid to liquid, and from solid to a vapour.

At very low pressures, if we assume $v_g \simeq v_{fg}$ and the equation of the vapour is taken as $pv = RT$, then eqn. (7.50) becomes

$$\frac{dp}{dT} = \frac{h}{Tv_g} = \frac{h_{fg}\, p}{RT^2} \qquad \qquad ...(7.51)$$

or $$\qquad h_{fg} = \frac{RT^2}{p}\frac{dp}{dT} \qquad \qquad ...(7.52)$$

Eqn. (7.52) may be used to obtain the enthalpy of vapourisation. This equation can be rearranged as follows :

$$\frac{dp}{p} = \frac{h_{fg}}{R} \cdot \frac{dT}{T^2}$$

Integrating the above equation, we get

$$\int \frac{dp}{p} = \frac{h_{fg}}{R} \int \frac{dT}{T^2}$$

$$\ln \frac{p_2}{p_1} = \frac{h_{fg}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \qquad ...(7.53)$$

Knowing the vapour pressure p_1 at temperature T_1 we can find the vapour pressure p_2 corresponding to temperature T_2 from eqn. (7.53).

From eqn. (7.50), we see that the slope of the vapour pressure curve is always +ve, since $v_g > v_f$ and h_{fg} is always +ve. Consequently, the vapour pressure of any simple compressible substance increases with temperature.

— It can be shown that the slope of the sublimation curve is also +ve for any pure substance.

— However, the slope of the *melting curve could be +ve or –ve*.

— *For a substance that contracts on freezing, such as water, the slope of the melting* curve will be negative.

☞Example 7.1. For a perfect gas, show that

$$c_p - c_v = \left[p + \left(\frac{\partial u}{\partial v} \right)_T \right]\left(\frac{\partial v}{\partial T} \right)_p = pv\beta + v\beta\left(\frac{\partial u}{\partial v} \right)_T$$

where β is the co-efficient of cubical/volume expansion.

Solution. The first law of thermodynamics applied to a closed system undergoing a reversible process states as follows :

$$dQ = du + pdv \qquad \qquad ...(i)$$

As per second law of thermodynamics,

$$ds = \left(\frac{dQ}{T} \right)_{rev.} \qquad \qquad ...(ii)$$

Combining these equations (i) and (ii), we have

$$Tds = du + pdv$$

Also, since $\qquad \qquad h = u + pv$

∴ $\qquad \qquad dh = du + pdv + vdp = Tds + vdp$

Thus, $\qquad \qquad Tds = du + pdv = dh - vdp$

Now, writing relation for u taking T and v as independent, we have

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

$$= c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

Similarly, writing relation for h taking T and p as independent, we have

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp$$

$$= c_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp$$

In the equation for Tds, substituting the value of du and dh, we have

$$c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv + pdv = c_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp - vdp$$

or $\qquad c_v dT + \left[p + \left(\frac{\partial u}{\partial v} \right)_T \right] dv = c_p dT - \left[v - \left(\frac{\partial h}{\partial p} \right)_T \right] dp$

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Since the above equation is true for any process, therefore, it will also be true for the case when dp = 0 and hence

$$(c_p - c_v)\,(dT)_p = \left[p + \left(\frac{\partial u}{\partial v}\right)_T\right](dv)_p$$

or

$$(c_p - c_p) = \left[p + \left(\frac{\partial u}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_p$$

By definition, $\qquad \beta = \dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_p$

∴ The above equation becomes,

$$c_p - c_v = \left[p + \left(\frac{\partial u}{\partial v}\right)_T\right]v\beta$$

or

$$= pv\beta + v\beta\left(\frac{\partial u}{\partial v}\right)_T \qquad \text{Proved.}$$

☞Example 7.2. Find the value of co-efficient of volume expansion β and isothermal *compressibility K for a Van der Waals' gas obeying*

$$\left(p + \frac{a}{v^2}\right)(v - b) \;=\; RT.$$

Solution. Van der Waals equation is

$$\left(p + \frac{a}{v^2}\right)(v - b) \;=\; RT$$

Rearranging this equation, we can write

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

Now for β we require $\left(\dfrac{\partial u}{\partial T}\right)_p$. This can be found by writing the cyclic relation,

$$\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_v\left(\frac{\partial p}{\partial v}\right)_T = -1$$

Hence

$$\left(\frac{\partial v}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T}$$

From the Van der Waals equation,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b}$$

Also

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v - b)^2} + \frac{2a}{v^3}$$

Hence

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{v}\left[-\frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T}\right]$$

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or
$$\beta = \frac{1}{v}\left[-\frac{\dfrac{R}{v-b}}{\dfrac{-RT}{(v-b)^2}+\dfrac{2a}{v^3}}\right] \cdot \frac{Rv^2\,(v-b)}{RTv^3-2a(v-b)^2} \quad \text{(Ans.)}$$

Also,
$$K = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\frac{1}{v}\left[\frac{1}{\dfrac{2a}{v^3}-\dfrac{RT}{(v-b)^2}}\right] = \frac{v^2\,(v-b)^2}{RTv^3-2a(v-b)^2} \cdot \text{(Ans.)}$$

Example 7.3. Prove that the internal energy of an ideal gas is a function of temperature alone.

Solution. The equation of state for an ideal gas is given by

$$p = \frac{RT}{v}$$

But
$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \qquad\qquad\qquad \text{[Eqn. (7.29)]}$$

$$= T\,\frac{R}{v} - p = p - p = 0.$$

Thus, if the temperature remains constant, there is no change in internal energy with volume (and therefore also with pressure). Hence internal energy (u) is a function of temperature (T) alone. ...Proved.

Example 7.4. Prove that specific heat at constant volume (c_v) *of a Van der Waals' gas is a function of temperature alone.*

Solution. The Van der Waals equation of state is given by,

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

or
$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b}$$

or
$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$$

Now
$$\left(\frac{dc_v}{dv}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

Hence
$$\left(\frac{\partial c_v}{\partial v}\right)_T = 0$$

Thus c_v of a Van der Waals gas is independent of volume (and therefore of pressure also). Hence it is a function of temperature alone.

☞Example 7.5. *Determine the following when a gas obeys Van der Waals' equation,*

$$\left(p+\frac{a}{v^2}\right)(v-b) = RT$$

(i) Change in internal energy ; (ii) Change in enthalpy ;

(iii) Change in entropy.

Solution. (i) Change in internal energy :

The change in internal energy is given by

$$du = c_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv$$

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But,
$$\left(\frac{\partial p}{\partial T}\right)_v = \left[\frac{\partial}{\partial T}\left\{\frac{RT}{v-b} - \frac{a}{v^2}\right\}\right]_v = \frac{R}{v-b}$$

$\therefore$
$$\int_1^2 du = c_v \int_1^2 dT + \int_1^2\left[T\left(\frac{R}{v-b}\right) - p\right]dv$$

$$= c_v \int_1^2 dT + \int_1^2\left[T\left(\frac{R}{v-b}\right) - \left\{\frac{RT}{v-b} - \frac{a}{v^2}\right\}\right]dv$$

$$= c_v \int_1^2 dT + \int_1^2\left[\frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2}\right]dv$$

$$= c_v \int_1^2 dT + \int_1^2 \frac{a}{v^2}.dv$$

$\therefore$
$$u_2 - u_1 = c_v(T_2 - T_1) + a\left(\frac{1}{v_1} - \frac{1}{v_2}\right). \quad \text{(Ans.)}$$

(ii) Change in enthalpy :

The change in enthalpy is given by

$$dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]dp$$

$$\left(\frac{\partial h}{\partial p}\right)_T = 0 + v - T\left(\frac{\partial v}{\partial T}\right)_p \qquad \qquad ...(1)$$

Let us consider $p = f(v, T)$

$\therefore$
$$dp = \left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT$$

$\therefore$
$$(dp)_T = \left(\frac{\partial p}{\partial v}\right)_T dv + 0 \quad \text{as } dT = 0 \qquad \qquad ...(2)$$

From equation (1),

$$(dh)_T = \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right](dp)_T.$$

Substituting the value of $(dp)_T$ from eqn. (2), we get

$$(dh)_T = \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]\left(\frac{\partial p}{\partial v}\right)_T dv$$

$$= \left[v\left(\frac{\partial p}{\partial v}\right)_T - T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial v}\right)_T\right]dv \qquad \qquad ...(3)$$

Using the cyclic relation for p, v, T which is

$$\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_v\left(\frac{\partial p}{\partial v}\right)_T = -1$$

$\therefore$
$$\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_v$$

Substituting this value in eqn. (3), we get

$$(dh)_T = \left[v \left(\frac{\partial p}{\partial v} \right)_T + T \left(\frac{\partial p}{\partial T} \right)_v \right] dv \qquad \ldots(4)$$

For Van der Waals equation

$$\left(\frac{\partial p}{\partial v} \right)_T = \frac{\partial}{\partial v} \left[\left(\frac{RT}{v-b} \right) - \frac{a}{v^2} \right]_T$$

$$= - \frac{RT}{(v-b)^2} + \frac{2a}{v^3} \qquad \ldots(5)$$

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{\partial}{\partial T} \left[\left(\frac{RT}{v-b} - \frac{a}{v^2} \right) \right]_v = \frac{R}{v-b} \qquad \ldots(6)$$

Substituting the values of eqns. (5) and (6) in equation (1), we get

$$(dh)_T = \left[v \left\{ - \frac{RT}{(v-b)^2} + \frac{2a}{v^3} \right\} + T \left(\frac{R}{v-b} \right) \right] dv$$

$$\therefore \qquad \int_1^2 (dh)_T = - RT \int_1^2 \frac{v}{(v-b)^2} \, dv + 2a \int_1^2 \frac{dv}{v^2} + RT \int_1^2 \frac{dv}{(v-b)}$$

$$\therefore \qquad (h_2 - h_1)_T = - RT \left[\log_e \left(\frac{v_2-b}{v_1-b} \right) - b \left\{ \frac{1}{v_2-b} - \frac{1}{v_1-b} \right\} \right]$$

$$- 2a \left(\frac{1}{v_2} - \frac{1}{v_1} \right) + RT \, \log_e \left(\frac{v_2-b}{v_1-b} \right)$$

$$= bRT \left[\frac{1}{(v_2-b)} - \frac{1}{(v_1-b)} \right] - 2a \left[\frac{1}{v_2} - \frac{1}{v_1} \right]. \quad \text{(Ans.)}$$

(iii) Change in entropy :

The change in entropy is given by

$$ds = c_p \frac{dT}{T} + \left(\frac{\partial p}{\partial T} \right)_v \cdot dv$$

For Van der Waals equation,

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v-b} \qquad \ldots \text{as per eqn. (6)}$$

$$\therefore \qquad ds = c_v \frac{dT}{T} + \frac{R}{v-b} \, dv$$

$$\therefore \qquad \int_1^2 ds = c_v \int_1^2 \left[\frac{dT}{T} \right] + R \int_1^2 \frac{dv}{(v-b)}$$

$$\therefore \qquad s_2 - s_1 = c_v \, \log_e \left[\frac{T_2}{T_1} \right] + R \, \log_e \left[\frac{v_2-b}{v_1-b} \right]. \quad \text{(Ans.)}$$

Example 7.6. The equation of state in the given range of pressure and temperature is given by

$$v = \frac{RT}{p} - \frac{C}{T^3}$$

where C is constant.

Derive an expression for change of enthalpy and entropy for this substance during an isothermal process.

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Solution. The general equation for finding dh is given by

$$dh = c_p \, dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$$

$$\int_1^2 dh = 0 + \int_1^2 \left[\left\{ v - T \left(\frac{\partial v}{\partial T} \right)_p \right\} \right]_T$$

as $dT = 0$ for isothermal change.

From the given equation of state, we have

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p} + \frac{3C}{T^4} \qquad\qquad ...(i)$$

$$\therefore \qquad h_2 - h_1 = \int_1^2 \left[\left\{ \left(\frac{RT}{p} - \frac{C}{T^3} \right) - \frac{RT}{p} - \frac{3C}{T^3} \right\} dp \right]_T$$

$$= \left[\int_1^2 \left(-\frac{4C}{T^3} \right) dp \right]_T = -\frac{4C}{T^3} [(p_2 - p_1)]_T$$

The general equation for finding ds is given by

$$ds = c_p \, \frac{dT}{T} - \left(\frac{\partial v}{\partial T} \right)_p dp$$

$$\int_1^2 ds = \left[-\int_1^2 \left(\frac{\partial v}{\partial T} \right)_p dp \right]_T$$

as $dT = 0$ for isothermal change.

Substituting the value from eqn. (**i**), we get

$$(s_2 - s_1) = \left[\int_1^2 -\left(\frac{R}{p} + \frac{3C}{T^4} \right) dp \right]_T$$

$$= -R \, \log_e \left(\frac{2}{p_1} \right) - \left(\frac{3C}{T^4} \right) (p_2 - \mathbf{p_1}) \quad \text{(Ans.)}$$

Example 7.7. For a perfect gas obeying $pv = RT$, show that c_v and c_p are independent of pressure.

Solution. Let $s = f(T, v)$

Then
$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv$$

Also
$$u = f(T, v)$$

Then
$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv = c_v \, dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

Also,
$$du = Tds - pdv$$

$$Tds - pdv = c_v \, dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

$$ds = c_v \, \frac{dT}{T} + \frac{1}{T} \left[\left(\frac{\partial u}{\partial v} \right)_T + p \right] dv$$

Equating the co-efficients of dT in the two equations of ds, we have

$$\frac{c_v}{T} = \left(\frac{\partial s}{\partial T}\right)_v$$

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\frac{\partial^2 s}{\partial T \partial v}$$

From eqn. (7.20),

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

$$\frac{\partial^2 s}{\partial v \partial T} = \left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v$$

Also $\qquad\qquad p = \dfrac{RT}{v}$ $\qquad\qquad\qquad\qquad$ ...(Given)

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0 \qquad \text{or} \qquad \left(\frac{\partial c_v}{\partial v}\right)_T = 0$$

This shows that c_v is a function of T alone, or c_v is independent of pressure.

Also, $\qquad\qquad c_p = T\left(\dfrac{\partial s}{\partial T}\right)_p$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = T\frac{\partial^2 s}{\partial T \partial p}$$

From eqn. (7.21), $\qquad \left(\dfrac{\partial s}{\partial p}\right)_T = -\left(\dfrac{\partial v}{\partial T}\right)_p$

$$\frac{\partial^2 s}{\partial p \partial T} = -\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

Again, $\qquad\qquad v = \dfrac{R}{p}$ $\qquad\qquad\qquad\qquad$ ...(Given)

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$$

and $\qquad\qquad \left(\dfrac{\partial^2 v}{\partial T^2}\right)_p = 0 \; ; \qquad \left(\dfrac{\partial c_p}{\partial p}\right)_T = 0$

This shows that c_p is a function of T alone or c_p is independent of pressure.

Example 7.8. Using the first Maxwell equation, derive the remaining three.

Solution. The first Maxwell relation is as follows :

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$$

...(i) (Eqn. 7.18)

(1) Using the cyclic relation

$$\left(\frac{\partial T}{\partial v}\right)_s \cdot \left(\frac{\partial v}{\partial s}\right)_T \cdot \left(\frac{\partial s}{\partial T}\right)_v = -1$$

$$\therefore \qquad \left(\frac{\partial s}{\partial v}\right)_T = -\left(\frac{\partial T}{\partial v}\right)_s \cdot \left(\frac{\partial s}{\partial T}\right)_v$$

...(ii)

Substituting the value from eqn. (i) in eqn. (ii), we get

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial s}\right)_v \cdot \left(\frac{\partial s}{\partial T}\right)_v$$

...(iii)

Using the chain rule,

$$\left(\frac{\partial p}{\partial s}\right)_v \cdot \left(\frac{\partial s}{\partial T}\right)_v \cdot \left(\frac{\partial T}{\partial p}\right)_v = 1$$

...(iv)

Substituting the value of eqn. (iv) in eqn. (iii), we get

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

This is Maxwell Third relation.

(2) Again using the cyclic relation

$$\left(\frac{\partial s}{\partial p}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_s \cdot \left(\frac{\partial v}{\partial s}\right)_p = -1$$

$$\therefore \qquad \left(\frac{\partial v}{\partial s}\right)_p = -\left(\frac{\partial p}{\partial s}\right)_v \cdot \left(\frac{\partial v}{\partial p}\right)_s$$

...(v)

Substituting the value from eqn. (i) into eqn. (v)

$$\left(\frac{\partial v}{\partial s}\right)_p = \left(\frac{\partial T}{\partial v}\right)_s \cdot \left(\frac{\partial v}{\partial p}\right)_s$$

...(vi)

Again using the chain rule,

$$\left(\frac{\partial T}{\partial v}\right)_s \cdot \left(\frac{\partial v}{\partial p}\right)_s \cdot \left(\frac{\partial p}{\partial T}\right)_s = 1$$

Substituting the value of (vi) into (v), we get

$$\left(\frac{\partial v}{\partial s}\right)_p = \left(\frac{\partial T}{\partial p}\right)_s$$

This is Maxwell second relation.

(3) $$\left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial p}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T = -1$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial v}{\partial p}\right)_T$$

$$= -\left(\frac{\partial p}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial s}{\partial p}\right)_T \left(\frac{\partial v}{\partial s}\right)_T$$

Substituting the value from eqn. (**i**), we get

$$\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial s}{\partial p}\right)_T \left(\frac{\partial v}{\partial s}\right)_T$$

$$= \left\{\left(\frac{\partial T}{\partial v}\right)_s \cdot \left(\frac{\partial v}{\partial s}\right)_T \cdot \left(\frac{\partial s}{\partial T}\right)_v\right\}\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial s}{\partial p}\right)_T$$

$$\therefore \qquad \boxed{\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T}$$

This is Maxwell fourth relation.

Example 7.9. Derive the following relations :

(i) $u = a - T\left(\dfrac{\partial a}{\partial T}\right)_v$
　　　　　　　　　　　(ii) $h = g - T\left(\dfrac{\partial g}{\partial T}\right)_p$

(iii) $c_v = -T\left(\dfrac{\partial^2 a}{\partial T^2}\right)_v$
　　　　　　　　　　(iv) $c_p = -T\left(\dfrac{\partial^2 g}{\partial T^2}\right)_p$

where　a = Helmholtz function (per unit mass), and

　　　　g = Gibbs function (per unit mass).

Solution. (i) Let a = f(v, T)

Then $\qquad\qquad da = \left(\dfrac{\partial a}{\partial v}\right)_T dv + \left(\dfrac{\partial a}{\partial T}\right)_v dT$

Also $\qquad\qquad da = -pdv - sdT$

Comparing the co-efficients of dT, we get

$$\left(\frac{\partial a}{\partial T}\right)_v = -s$$

Also $\qquad\qquad a = u - Ts$

or $\qquad\qquad u = a + Ts = a - T\left(\dfrac{\partial a}{\partial T}\right)_v$

Hence $\qquad\qquad u = a - T\left(\dfrac{\partial a}{\partial T}\right)_v.$　(Ans.)

(ii) Let $\qquad\qquad g = f(p, T)$

Then $\qquad\qquad dg = \left(\dfrac{\partial g}{\partial p}\right)_T dp + \left(\dfrac{\partial g}{\partial T}\right)_p dT$

Also $\qquad\qquad dg = vdp - sdT$

Comparing the co-efficients of dT, we get

$$\left(\frac{\partial g}{\partial T}\right)_p = -s$$

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Also
$$h = g + Ts = g - T\left(\frac{\partial g}{\partial T}\right)_p$$

Hence
$$h = g - T\left(\frac{\partial g}{\partial T}\right)_p. \quad \text{(Ans.)}$$

(iii) From eqn. (7.23), we have
$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v \qquad \qquad \qquad ...(i)$$

Also
$$\left(\frac{\partial a}{\partial T}\right)_v = -s$$

or
$$\left(\frac{\partial s}{\partial T}\right)_v = -\left(\frac{\partial^2 a}{\partial T^2}\right)_v \qquad \qquad \qquad ...(ii)$$

From eqns. (i) and (ii), we get
$$c_v = -T\left(\frac{\partial^2 a}{\partial T^2}\right)_v. \quad \text{(Ans.)}$$

(iv) From eqn. (7.26), we have
$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p \qquad \qquad \qquad ...(i)$$

Also
$$\left(\frac{\partial g}{\partial T}\right)_p = -s$$

or
$$\left(\frac{\partial s}{\partial T}\right)_p = -\left(\frac{\partial^2 g}{\partial T^2}\right)_p \qquad \qquad \qquad ...(ii)$$

From eqns. (i) and (ii), we get
$$c_p = -T\left(\frac{\partial^2 g}{\partial T^2}\right)_p. \quad \text{(Ans.)}$$

Example 7.10. Find the expression for ds in terms of dT and dp.
Solution. Let $s = f(T, p)$

Then
$$ds = \left(\frac{\partial s}{\partial T}\right)_p . dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

As per Maxwell relation (7.21)
$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

Substituting this in the above equation, we get
$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT - \left(\frac{\partial v}{\partial T}\right)_p . dp \qquad \qquad \qquad ...(i)$$

The enthalpy is given by
$$dh = c_p dT = Tds + vdp$$

Dividing by dT at constant pressure
$$\left(\frac{\partial h}{\partial T}\right)_p = c_p = T\left(\frac{\partial s}{\partial T}\right)_p + 0 \qquad \text{(as dp = 0 when pressure is constant)}$$

Now substituting this in eqn. (i), we get

$$ds = c_p \, \frac{dT}{T} - \left(\frac{\partial s}{\partial T}\right)_p \cdot dp \qquad \qquad \qquad ...(ii)$$

But

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$

Substituting this in eqn. (ii), we get

$$\boxed{ds = c_p \, \frac{dT}{T} - \beta v \, dp} \qquad \text{(Ans.)}$$