25. In a reversible cycle 100 kJ of heat is received at 500 K ; then an adiabatic expansion occurs to 400 K, at which temperature 50 kJ of heat is received, then a further adiabatic expansion to 300 K at which temperature 100 kJ of heat is rejected :

(*i*) Find the change in entropy which occurs as the system is restored to its initial state in the remainder of the cycle.

(*ii*) If during the remainder of the cycle heat is transferred only at 400 K, how much heat is transferred and in what direction ? [**Ans.** 0.008 kJ/K ; + 3.2 kJ]

26. 1 kg of air is compressed according to the law $pv^{1.25}$ = constant from 1.03 bar and 15°C to 16.45 bar. Calculate the change in entropy. [**Ans.** 0.255 kJ/kg K]

27. A quantity of gas (mean molecular weight 36.2) is compressed according to the law pv^n = constant, the initial pressure and volume being 1.03 bar and 0.98 m^3 respectively. The temperature at the start of compression is 17°C and at the end it is 115°C. The amount of heat rejected during compression is 3.78 kJ, $c_p = 0.92$. Calculate :

(*i*) Value of n, (*ii*) Final pressure, (*iii*) Change in entropy.

[**Ans.** (*i*) 1.33 ; (*ii*) 1.107 bar ; (*iii*) 0.228 kJ/kg K]

6

Availability and Irreversibility

6.1. Available and unavailable energy. 6.2. Available energy referred to a cycle. 6.3. Decrease in available energy when heat is transferred through a finite temperature difference. 6.4. Availability in non-flow systems. 6.5. Availability in steady flow systems. 6.6. Helmholtz and Gibbs functions. 6.7. Irreversibility. 6.8. Effectiveness—Highlights—Objective Type Questions—Theoretical Questions—Unsolved Examples.

6.1. AVAILABLE AND UNAVAILABLE ENERGY

There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts :

— *Available part.*

— *Unavailable part.*

'***Available energy***' is the *maximum portion of energy which could be converted into useful work by ideal processes which reduce the system to a dead state* (a state in equilibrium with the earth and its atmosphere). Because there can be only one value for maximum work which the system alone could do while descending to its dead state, it follows immediately that *'Available energy' is a property.*

A system which has a pressure difference from that of surroundings, work can be obtained from an expansion process, and if the system has a different temperature, heat can be transferred to a cycle and work can be obtained. But when the temperature and pressure becomes equal to that of the earth, transfer of energy ceases, and although the system contains internal energy, this energy is ***unavailable.***

Summarily available energy denote, the latent capability of energy to do work, and in this sense it can be applied to energy in the system or in the surroundings.

The theoretical maximum amount of work which can be obtained from a system at any state p_1 *and* T_1 *when operating with a reservoir at the constant pressure and temperature* p_0 *and* T_0 *is called* '**availability**'.

6.2. AVAILABLE ENERGY REFERRED TO A CYCLE

The ***available energy (A.E.)*** or the available part of the energy supplied is the maximum work output obtainable from a certain heat input in a cyclic heat engine (Fig. 6.1). The minimum energy that has to be rejected to the sink by the second law is called the ***unavailable energy (U.E.),*** or the unavailable part of the energy supplied.

$$\therefore \qquad Q_1 = \text{A.E.} + \text{U.E.}$$

or $$W_{max} = \text{A.E.} = Q_1 - \text{U.E.}$$

For the given values of the source temperature T_1 and sink temperature T_2, the reversible efficiency,

$$\eta_{rev.} = 1 - \frac{T_2}{T_1}$$

For a given T_1, $\eta_{rev.}$ will increase with the decrease of T_2. *The lowest practicable temperature of heat rejection is the temperature of the surroundings,* T_0.

$$\therefore \qquad \eta_{max} = 1 - \frac{T_0}{T_1}$$

and $$W_{max} = \left(1 - \frac{T_0}{T_1}\right) Q_1$$

Consider a finite process *l-m*, in which heat is supplied reversibly to a heat engine (Fig. 6.2). Taking an elementary cycle, if dQ_1 is the heat received by the engine reversibly at T_1,

Then $$dW_{max} = \frac{T_1 - T_0}{T_1} dQ_1$$

$$= dQ_1 - \frac{T_0}{T_1} dQ_1 = \text{A.E.}$$

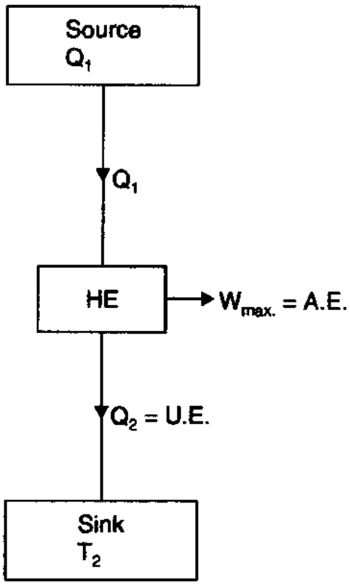


Fig. 6.1. Available and unavailable energy in a cycle.

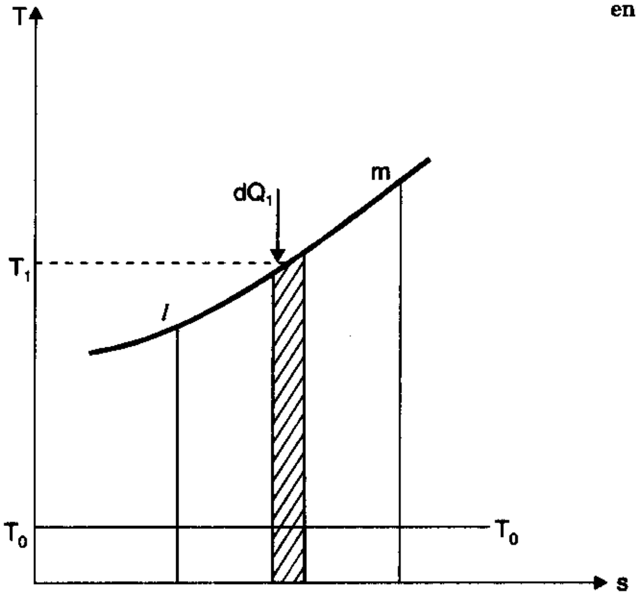


Fig. 6.2. Availability of energy.

For the heat engine receiving heat for the whole process *l-m*, and rejecting heat at T_0

$$\int_l^m dW_{max} = \int_l^m dQ_1 - \int_l^m \frac{T_0}{T_1} dQ_1$$

$$\therefore \qquad W_{max} = \text{A.E.} = Q_{l-m} - T_0 (s_l - s_m) \qquad \text{...(6.1)}$$

or unavailable energy, $$\text{U.E.} = Q_{l-m} - W_{max}$$

or $$\text{U.E.} = T_0 (s_l - s_m)$$

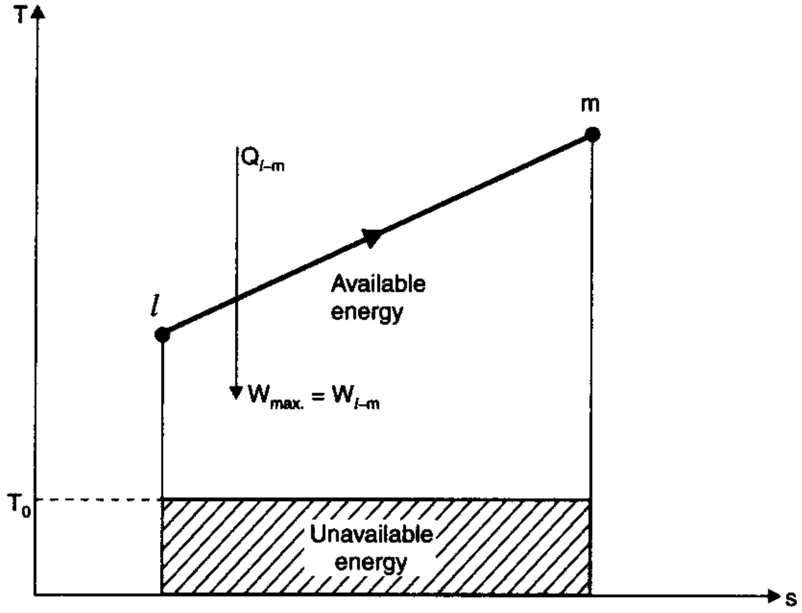


Fig. 6.3. Unavailable energy by the second law of thermodynamics.

Thus unavailable energy is the product of the lowest temperature of heat rejection, and the change of entropy of the system during the process of supplying heat (Fig. 6.3).

6.3. DECREASE IN AVAILABLE ENERGY WHEN HEAT IS TRANSFERRED THROUGH A FINITE TEMPERATURE DIFFERENCE

When transfer of heat takes place through a finite temperature difference, there is a decrease in the availability of energy so transferred. Consider a reversible heat engine operating between temperatures T_1 and T_0 (Fig. 6.4). Then

$$Q_1 = T \,.\, \Delta s \;;$$

$$Q_2 = T_0 \, \Delta s \;;$$

and $$W = \text{A.E.} = [T_1 - T_0] \, \Delta s.$$

Assume that heat Q_1 is transferred through a finite temperature difference from the reservoir or source at T_1 to the engine absorbing heat at T_1', lower than T_1 (Fig. 6.4). The availability of Q_1 as received by the engine at T_1' can be found by allowing the engine to operate reversibly in a cycle between T_1' and T_0 receiving Q_1 and rejecting Q_2'.

Now, $$Q_1 = T_1 \Delta s = T_1' \Delta s'$$

$\because$ $$T_1 > T_1'$$

$\therefore$ $$\Delta s' > \Delta s$$

$$Q_2 = T_0 \, \Delta s$$

$$Q_2' = T_0 \, \Delta s'$$

$\because$ $$\Delta s' > \Delta s$$

$\therefore$ $$Q_2' > Q_2$$

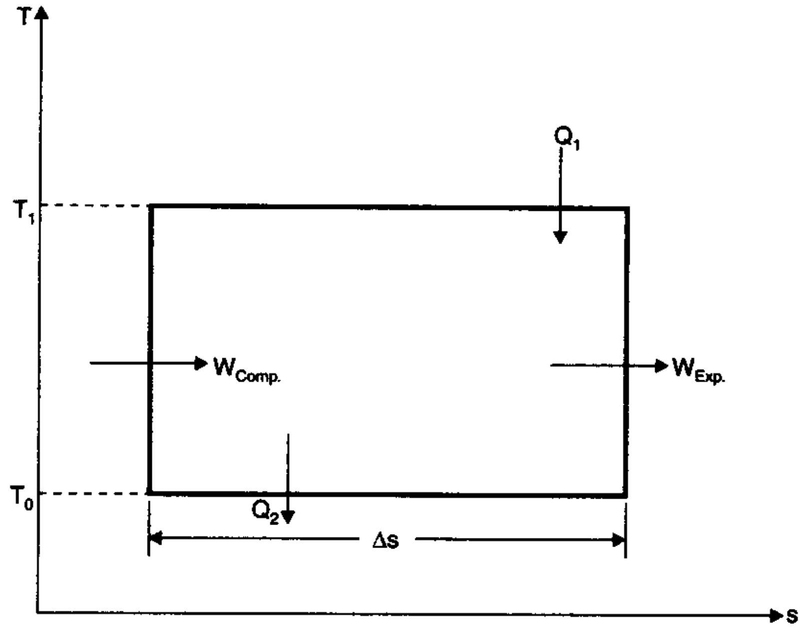


Fig. 6.4. Carnot-cycle.

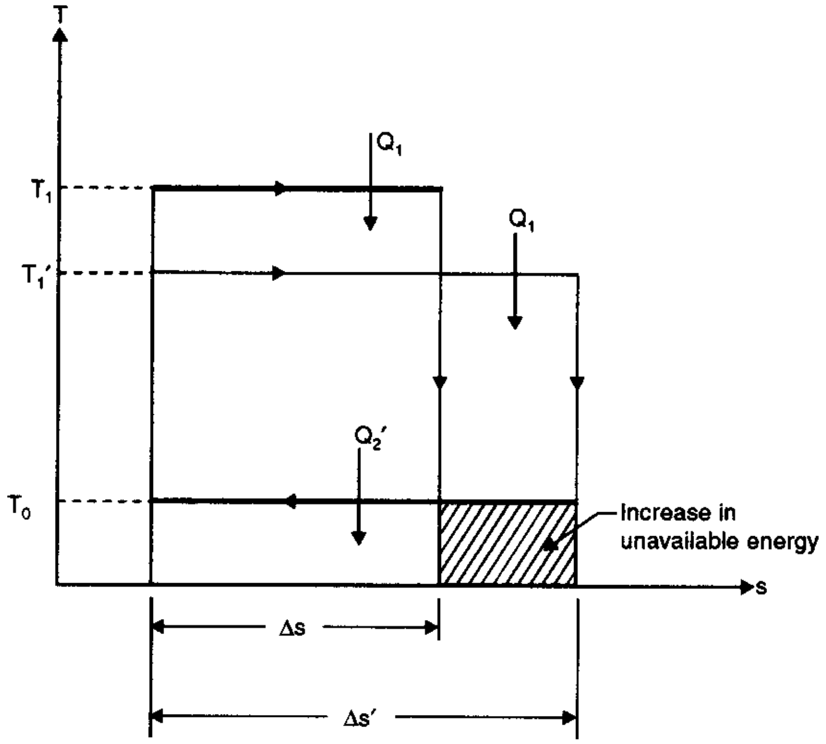


Fig. 6.5. Increase in unavailable energy due to heat transfer through a finite temperature difference.

$\therefore \qquad W' = Q_1 - Q_2' = T_1' \Delta s' - T_0 \Delta s'$

and $\qquad W = Q_1 - Q_2 = T_1 \Delta s - T_0 \Delta s$

$\therefore \qquad W' < W$, because $Q_2' > Q_2$

The *loss of available energy* due to irreversible heat transfer through finite temperature difference between the source and the working fluid during the heat addition process is given as :

$$W - W' = Q_2' - Q_2$$
$$= T_0 (\Delta s' - \Delta s)$$

i.e., Decrease in available energy, A.E.

$$= T_0 (\Delta s' - \Delta s) \qquad \text{...(6.2)}$$

Thus the decrease in A.E. is the product of the lowest feasible temperature of heat rejection and the additional entropy change in the system while receiving heat irreversibly, compared to the case of reversible heat transfer from the same source. *The greater is the temperature difference* ($T_1 - T_1'$), *the greater is the heat rejection* Q_2' *and the greater will be the unavailable part of the energy supplied* (Fig. 6.5).

Energy is said to be *degraded* each time it flows through a finite temperature difference. That is, why the second law of thermodynamics is sometimes called the *law of the degradation of energy*, and energy is said to *'run down hill'*.

6.4. AVAILABILITY IN NON-FLOW SYSTEMS

Let us consider a system consisting of a fluid in a cylinder behind a piston, the fluid expanding reversibly from initial condition of p_1 and T_1 to final atmospheric conditions of p_0 and T_0. Imagine also that the system works in conjunction with a reversible heat engine which receives heat reversibly from the fluid in the cylinder such that the working substance of the heat engine follows the cycle *O1LO* as shown in Fig. 6.6, where $s_1 = s_L$ and $T_0 = T_L$ (the only possible way in which this could occur would be if an infinite number of reversible heat engines were arranged in parallel, each operating on a Carnot cycle, each one receiving heat at a different constant temperature and each one rejecting heat at T_0). The work done by the engine is given by :

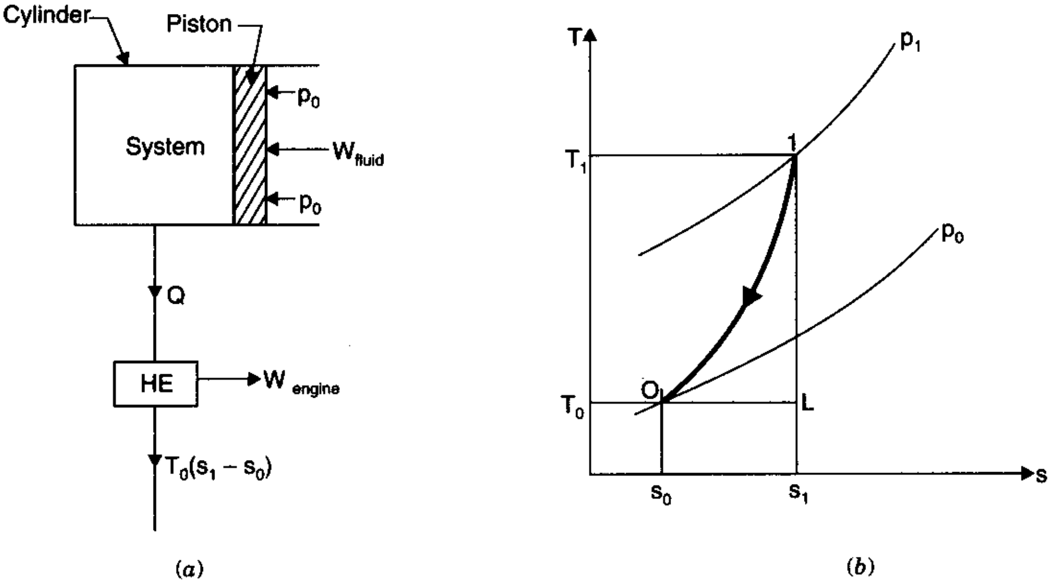


Fig. 6.6

$$W_{engine} = \text{Heat supplied} - \text{Heat rejected}$$
$$= Q - T_0 (s_1 - s_0) \quad ...(i)$$

The heat supplied to the engine is equal to the heat rejected by the fluid in the cylinder. Therefore, for the fluid in the cylinder undergoing the process 1 to 0, we have

$$-Q = (u_0 - u_1) + W_{fluid}$$

i.e.,
$$W_{fluid} = (u_1 - u_0) - Q \quad ...(ii)$$

Adding eqns. (*i*) and (*ii*), we get

$$W_{fluid} + W_{engine} = [(u_1 - u_0) - Q] + [Q - T_0 (s_1 - s_0)]$$
$$= (u_1 - u_0) - T_0 (s_1 - s_0)$$

The work done by the fluid on the piston is less than the total work done by the fluid, since there is no work done on the atmosphere which is at constant pressure p_0

i.e., Work done on atmosphere $= p_0 (v_0 - v_1)$

Hence, *maximum work available*

$$= (u_1 - u_0) - T_0 (s_1 - s_0) - p_0 (v_0 - v_1)$$

Note. When a fluid undergoes a complete cycle then the net work done on the atmosphere is zero.

$$W_{max} = (u_1 + p_0 v_1 - T_0 s_1) - (u_0 + p_0 v_0 - T_0 s_0) \quad ...(6.3)$$

$$\therefore \quad W_{max} = a_1 - a_0 \quad ...[6.3\ (a)]$$

The property, $a = u + p_0 v - T_0 s$ (per unit mass) is called the **non-flow availability function.**

6.5. AVAILABILITY IN STEADY FLOW SYSTEMS

Consider a fluid flowing steadily with a velocity C_1 from a reservoir in which the pressure and temperature remain constant at p_1 and T_1 through an apparatus to atmospheric pressure of p_0. Let the reservoir be at a height Z_1 from the datum, which can be taken at exit from the apparatus, *i.e.*, $Z_0 = 0$. For maximum work to be obtained from the apparatus the exit velocity, C_0, must be zero. It can be shown as for article 6.4 that a reversible heat engine working between the limits would reject $T_0 (s_1 - s_0)$ units of heat, where T_0 is the atmospheric temperature. Thus, we have

$$W_{max} = \left(h_1 + \frac{C_1^2}{2} + Z_1 g \right) - h_0 - T_0 (s_1 - s_0)$$

In several thermodynamic systems the kinetic and potential energy terms are negligible

i.e.,
$$W_{max} = (h_1 - T_0 s_1) - (h_0 - T_0 s_0)$$
$$= b - b_0$$

The property, $b = h - T_0 s$ (per unit mass) is called the **steady-flow availability function.**

[In the equation $b = h - T_0 s$; the function '*b*' (like the function '*a*') is a composite property of a system and its environment ; this is also known as ***Keenan function***].

Note 1. The alternative names for availability and unavailable quantity $T_0 \Delta s$ are ***energy*** and a ***energy*** respectively.

2. The only difference between $a = u + p_0 v - T_0 s$ function and $b = (h - T_0 s) = (u + pv - T_0 s)$ function is in pressure only.

6.6. HELMHOLTZ AND GIBBS FUNCTIONS

The work done in a non-flow reversible system (per unit mass) is given by :

$$W = Q - (u_0 - u_1)$$
$$= T.ds - (u_0 - u_1)$$

$$= T(s_0 - s_1) - (u_0 - u_1)$$

i.e.,
$$W = (u_1 - Ts_1) - (u_0 - Ts_0) \qquad ...(6.4)$$

The term $(u - Ts)$ is known as *Helmholtz function*. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source.

If work against atmosphere is equal to $p_0 (v_0 - v_1)$, then the maximum work available,

$$\begin{aligned} W_{max} &= W - \text{work against atmosphere} \\ &= W - p_0 (v_0 - v_1) \\ &= (u_1 - Ts_1) - (u_0 - Ts_0) - p_0 (v_0 - v_1) \\ &= (u_1 + p_0 v_1 - Ts_1) - (u_0 + p_0 v_0 - Ts_0) \\ &= (h_1 - Ts_1) - (h_0 - Ts_0) \end{aligned}$$

i.e.,
$$W_{max} = g_1 - g_0 \qquad ...(6.5)$$

where $g = h - T.s$ is known as ***Gibb's function or free energy function.***

The maximum possible available work when system changes from 1 to 2 is given by

$$W_{max} = (g_1 - g_0) - (g_2 - g_0) = g_1 - g_2 \qquad ...(6.6)$$

Similarly, for *steady flow system* the maximum work available is given by

$$W_{max} = (g_1 - g_2) + (\text{KE}_1 - \text{KE}_2) + (\text{PE}_1 - \text{PE}_2) \qquad ...(6.7)$$

where K.E. and P.E. represent the kinetic and potential energies.

It may be noted that Gibb's function $g = (h - Ts)$ is a property of the system where availability function $a = (u + p_0 v - T_0 s)$ is a composite property of the system and surroundings.

Again,
$$\begin{aligned} a &= u + p_0 v - T_0 s \\ b &= u + pv - T_0 s \\ g &= u + pv - Ts \end{aligned}$$

When state 1 proceeds to *dead state* (zero state)

$$a = b = g.$$

6.7. IRREVERSIBILITY

The actual work which a system does is always *less* than the idealized reversible work, and the difference between the two is called the *irreversibility of the process.*

Thus, Irreversibility, $I = W_{max} - W \qquad ...(6.8)$

This is also sometimes referred to as '***degradation***' or '***dissipation***'.

For a *non-flow process* between the equilibrium states, when the system exchanges heat only with environment, irreversibility (*per unit mass*),

$$\begin{aligned} i &= [(u_1 - u_2) - T_0(s_1 - s_2)] - [(u_1 - u_2) + Q] \\ &= T_0 (s_2 - s_1) - Q \\ &= T_0 (\Delta s)_{system} + T_0 (\Delta s)_{surr.} \end{aligned}$$

i.e.,
$$i = T_0 [(\Delta s)_{system} + (\Delta s)_{surr.}] \qquad ...(6.9)$$

$\therefore$
$$i \geq 0$$

Similarly, for *steady flow-process*

$$i = W_{max} - W \text{ (per unit mass)}$$

$$= \left[\left(b_1 + \frac{C_1^2}{2} + gZ_1\right) - \left(b_2 + \frac{C_2^2}{2} + gZ_2\right)\right]$$

$$- \left[\left(h_1 + \frac{C_1^2}{2} + gZ_1\right) - \left(h_2 + \frac{C_2^2}{2} + gZ_2\right) + Q\right]$$

$$= T_0 (s_2 - s_1) - Q$$

$$= T_0 (\Delta s)_{system} + T_0 (\Delta s)_{surr.}$$

i.e., $$i = T_0 (\Delta s_{system} + \Delta s_{surr.})$$

The same expression for irreversibility applies to both flow and non-flow processes.

The quantity $T_0 (\Delta s_{system} + \Delta s_{surr.})$ represents (per unit mass) an increase in unavailable energy (or energy).

6.8. EFFECTIVENESS

Effectiveness *is defined as the ratio of actual useful work to the maximum useful work.* The useful output of a system is given by the increase of availability of the surroundings.

$$\text{Effectiveness,} \quad \in = \frac{\text{Increase of availability of surroundings}}{\text{Loss of availability of the system}} \quad \text{...(6.10)}$$

For a compression or heating process the effectiveness is given by

$$\in = \frac{\text{Increase of availability of the system}}{\text{Loss of availability of the surroundings}}$$

or $$\in = \frac{W_{useful}}{W_{max\,.\,useful}} \quad \text{...[6.10 (a)]}$$

The *effectiveness of an actual process is always less than unity.* Thus effectiveness of a process is the measure of the extent to which advantage has been taken of an opportunity to obtain useful work.

Example 6.1. *One kg of air is compressed polytropically from 1 bar pressure and temperature of 300 K to a pressure of 6.8 bar and temperature of 370 K. Determine the irreversibility if the sink temperature is 293 K. Assume R = 0.287 kJ/kg K, c_p = 1.004 kJ/kg K and c_v = 0.716 kJ/kg K.*

(U.P.S.C.)

Solution. Irreversibility $I = W_{max} - W_{act}$

$$- W_{max} = \text{Change in internal energy} - T_0 \times \text{Change in entropy}$$

or $$- W_{max} = (u_2 - u_1) - T_0(s_2 - s_1) = W_{rev}$$

or $$- W_{max} = c_v(T_2 - T_1) - T_0[c_p \ln (T_2/T_1) - R \ln (p_2/p_1)]$$

$$= 0.716(370 - 300) - 293 \times [1.005 \ln (370/300) - 0.287 \ln (6.8/1)]$$

or $$W_{max} = -149.53 \text{ kJ/kg} = W_{rev}$$

(negative sign indicates that work is done on air)

The index of compression 'n' is given by

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{[(n-1)/n]}$$

or $$\frac{n-1}{n} = \frac{\ln (T_2/T_1)}{\ln (p_2/p_1)} = \frac{\ln (370/300)}{\ln (6.8/1)}$$

or $$n = 1.123$$

$$W_{actual} = \frac{mR(T_1 - T_2)}{n-1} = \frac{1 \times 0.287(300 - 370)}{1.123 - 1} = -163.33 \text{ kJ/kg}$$

$$I = W_{rev} - W_{act} = -149.53 - (-163.33) = \mathbf{13.8\ kJ/kg.} \quad \textbf{(Ans.)}$$

Example 6.2. *A system at 500 K receives 7200 kJ/min from a source at 1000 K. The temperature of atmosphere is 300 K. Assuming that the temperatures of system and source remain constant during heat transfer find out :*

(*i*) *The entropy produced during heat transfer ;*

(*ii*) *The decrease in available energy after heat transfer.*

Solution. Refer Fig. 6.7.

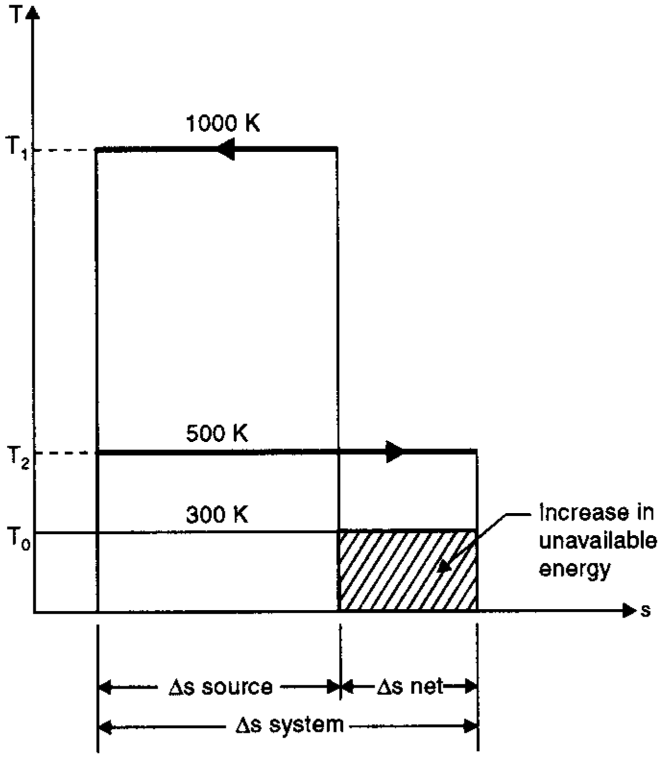


Fig. 6.7

Temperature of source, $T_1 = 1000$ K

Temperature of system, $T_2 = 500$ K

Temperature of atmosphere, $T_0 = 300$ K

Heat received by the system, $Q = 7200$ kJ/min.

(*i*) **Net change of entropy :**

Change in entropy of the *source* during heat transfer

$$= \frac{-Q}{T_1} = \frac{-7200}{1000} = -7.2 \text{ kJ/min-K}$$

Change in entropy of the *system* during heat transfer

$$= \frac{Q}{T_2} = \frac{7200}{500} = 14.4 \text{ kJ/min-K}$$

The net change of entropy, $\Delta S = -7.2 + 14.4 =$ **7.2 kJ/min-K. (Ans.)**

(*ii*) **Decrease in available energy :**

Available energy with source

$$= (1000 - 300) \times 7.2 = 5040 \text{ kJ}$$

Available energy with the system

$$= (500 - 300) \times 14.4 = 2880 \text{ kJ}$$

$\therefore$ **Decrease in available energy** = 5040 − 2880 = **2160 kJ. (Ans.)**

$$\begin{bmatrix} \text{Also, increase in available energy} \\ = T_0(S_2 - S_1) = T_0\,\Delta S \\ = 300 \times 7.2 = 2160 \text{ kJ} \end{bmatrix}$$

Example 6.3. *8 kg of air at 650 K and 5.5 bar pressure is enclosed in a closed system. If the atmosphere temperature and pressure are 300 K and 1 bar respectively, determine :*

(*i*) *The availability if the system goes through the ideal work producing process.*

(*ii*) *The availability and effectiveness if the air is cooled at constant pressure to atmospheric temperature without bringing it to complete dead state. Take* c_v = *0.718 kJ/kg K ;* c_p= *1.005 kJ/kg K.*

Solution. Mass of air, $m = 8$ kg

Temperature, $T_1 = 650$ K

Pressure, $p_1 = 5.5$ bar

Atmospheric pressure, $p_0 = 1$ bar

Atmospheric temperature, $T_0 = 300$ K

For air : $c_v = 0.718$ kJ/kg K ; $c_p = 1.005$ kJ/kg K.

(*i*) Change in available energy (for bringing the system to dead state),

$$= m[(u_1 - u_0) - T_0\Delta s]$$

Also
$$\Delta s = c_v \log_e \left(\frac{T_1}{T_0}\right) + R \log_e \frac{v_1}{v_0}$$

Using the ideal gas equation,

$$\frac{p_1 v_1}{T_1} = \frac{p_0 v_0}{T_0}$$

$$\therefore \quad \frac{v_0}{v_1} = \frac{p_1}{p_0} \cdot \frac{T_0}{T_1} = \frac{5.5}{1} \times \frac{300}{650} = 2.54$$

$$\therefore \quad \Delta s = 0.718 \log_e \left(\frac{650}{300}\right) + 0.287 \log_e \left(\frac{1}{2.54}\right)$$

$$= 0.555 + (-0.267) = 0.288 \text{ kJ/kg K}$$

$\therefore$ Change in available energy

$$= m[(u_1 - u_0) - T_0\Delta s] = m[c_v(T_1 - T_0) - T_0\Delta s]$$

$$= 8[0.718(650 - 300) - 300 \times 0.288] = 1319.2 \text{ kJ}$$

Loss of availability per unit mass during the process

$$= p_0 (v_0 - v_1) \text{ per unit mass}$$

Total loss of availability = $p_0(V_0 - V_1)$

But
$$V_1 = \frac{mRT_1}{p_1} = \frac{8 \times 287 \times 650}{5.5 \times 10^5} = 2.713 \text{ m}^3 \qquad \left[\because pV = mRT \text{ or } V = \frac{mRT}{p}\right]$$

and
$$V_0 = 2.54 \times 2.713 = 6.891 \text{ m}^3$$

$\therefore$ **Loss of availability** $= \dfrac{1 \times 10^5}{10^3}(6.891 - 2.713)$ = **417.8 kJ. (Ans.)**

(*ii*) Heat transferred during cooling (constant pressure) process

$$= m.\ c_p\ (T_1 - T_0)$$

$$= 8 \times 1.005\ (650 - 300) = 2814 \text{ kJ}$$

Change in entropy during cooling

$$\Delta s = mc_p \log_e \left(\frac{T_1}{T_0}\right)$$

$$= 8 \times 1.005 \times \log_e \left(\frac{650}{300}\right) = 6.216 \text{ kJ/K}$$

Unavailable energy $= T_0\ \Delta S$

$$= 300 \times 6.216 = 1864.8 \text{ kJ}$$

Available energy $= 2814 - 1864.8 =$ **949.2 kJ. (Ans.)**

Effectiveness, $\epsilon = \dfrac{\text{Available energy}}{\text{Change in available energy}}$

$$= \frac{949.2}{1319.2} = \mathbf{0.719.}\ \textbf{(Ans.)}$$

☞**Example 6.4.** *In a power station, the saturated steam is generated at 200°C by transferring the heat from hot gases in a steam boiler. Find the increase in total entropy of the combined system of gas and water and increase in unavailable energy due to irreversible heat transfer. The gases are cooled from 1000°C to 500°C and all the heat from gases goes to water. Assume water enters the boiler at saturated condition and leaves as saturated steam.*

Take : c_{pg} *(for gas) = 1.0 kJ/kg K,* h_{fg} *(latent heat of steam at 200°C) = 1940.7 kJ/kg.*

Atmospheric temperature = 20°C.

Obtain the results on the basis of 1 kg of water.

Solution. Refer Fig. 6.8.

Temperature of saturation steam $= 200 + 273 = 473$ K

Initial temperature of gases $= 1000 + 273 = 1273$ K

Final temperature of gases $= 500 + 273 = 773$ K

For gases : $c_{pg} = 1$ kJ/kg K

Latent heat of steam of 200°C saturation temperature, $h_{fg} = 1940.7$ kJ/kg

Atmospheric temperature $= 20 + 273 = 293$ K

Heat lost by gases = Heat gained by 1 kg saturated water when it is converted to steam at 200°C.

$$\therefore \quad m_g c_{pg}\ (1273 - 773) = 1940.7$$

[where m_g = mass of gases, c_{pg} = specific heat of gas at constant pressure]

i.e.,

$$m_g = \frac{1940.7}{1.0 \times (1273 - 773)} = 3.88 \text{ kg}$$

Change of entropy of m_g kg of gas,

$$(\Delta S)_g = m_g\ c_{pg} \log_e \left(\frac{773}{1273}\right)$$

$$= 3.88 \times 1.0 \times \log_e \left(\frac{773}{1273}\right) = -\ 1.935 \text{ kJ/K}$$

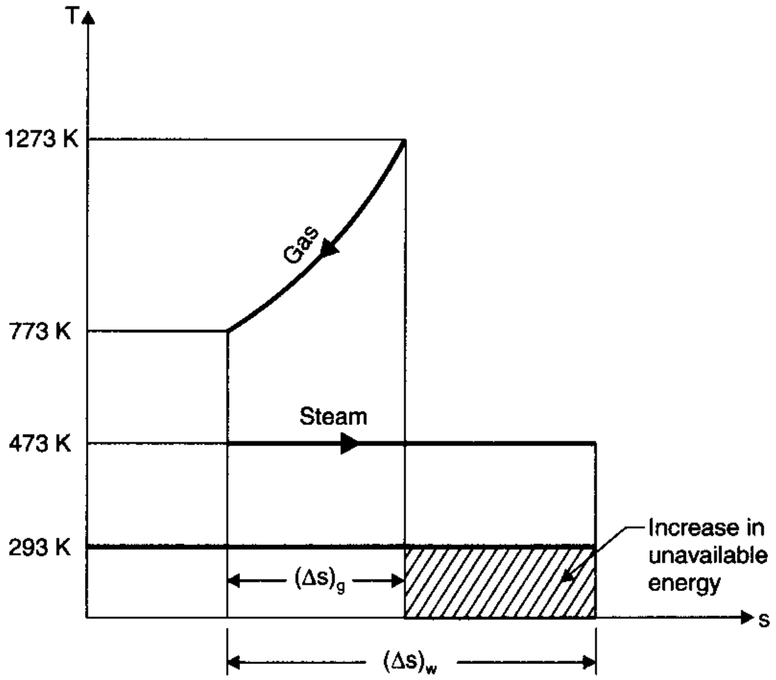


Fig. 6.8

Change of entropy of water (per kg) when it is converted into steam,

$$(\Delta s)_w = \frac{h_{fg}}{T_s} = \frac{1940.7}{(200 + 273)} = 4.103 \text{ kJ/kg K.}$$

Net change in entropy due to heat transfer

$$= -1.935 + 4.103 = \mathbf{2.168 \text{ kJ/K.}} \quad \textbf{(Ans.)}$$

Increase in unavailable energy due to heat transfer

$$= 293 \times 2.168, \text{ i.e., cross hatched area}$$

$$= \mathbf{635.22 \text{ kJ per kg of steam formed.}} \quad \textbf{(Ans.)}$$

Example 6.5. *3 kg of gas (c_v = 0.81 kJ/kg K) initially at 2.5 bar and 400 K receives 600 kJ of heat from an infinite source at 1200 K. If the surrounding temperature is 290 K, find the loss in available energy due to above heat transfer.*

Solution. Refer Fig. 6.9.

Mass of gas,	$m_g = 3$ kg
Initial pressure of gas	= 2.5 bar
Initial temperature,	$T_1' = 400$ K
Quantity of heat received by gas,	$Q = 600$ kJ
Specific heat of gas,	$c_v = 0.81$ kJ/kg K
Surrounding temperature	= 290 K
Temperature of infinite source,	$T_1 = 1200$ K

Heat received by the gas is given by,

$$Q = m_g c_v (T_2' - T_1')$$

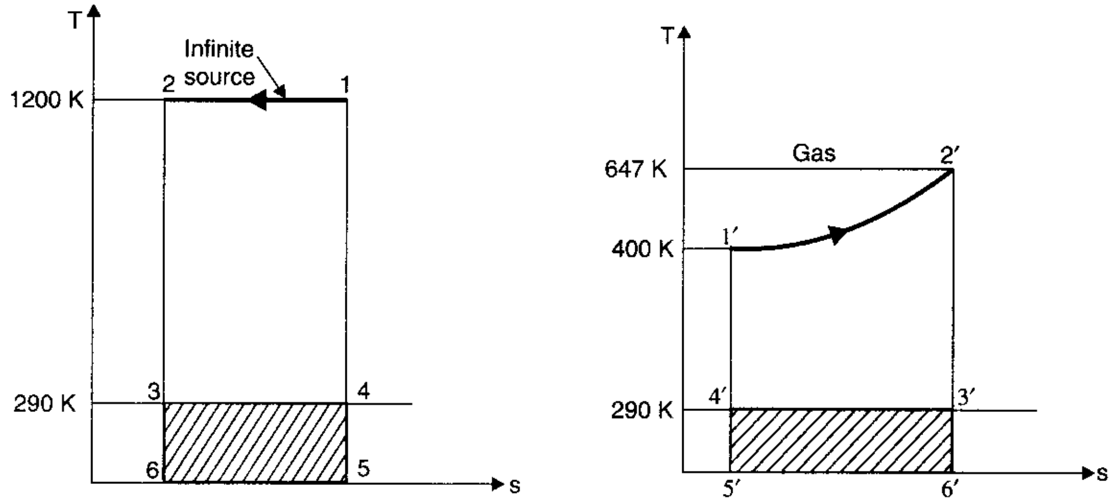


Fig. 6.9

$$600 = 3 \times 0.81\,(T_2' - 400)$$

$$\therefore \quad T_2' = \frac{600}{3 \times 0.81} + 400 = 646.9 \text{ K say } 647 \text{ K}$$

Available energy with the source

$$= \text{area } 1\text{-}2\text{-}3\text{-}4\text{-}1$$

$$= (1200 - 290) \times \frac{600}{1200} = 455 \text{ kJ}$$

Change in entropy of the gas

$$= m_g c_v \log_e \left(\frac{T_2'}{T_1'}\right) = 3 \times 0.81 \times \log_e \left(\frac{647}{400}\right) = 1.168 \text{ kJ/K}$$

Unavailability of the gas $= \text{area } 3'\text{-}\ 4'\text{-}\ 5'\text{-}\ 6'\text{-}\ 3'$

$$= 290 \times 1.168 = 338.72 \text{ kJ}$$

Available energy with the gas

$$= 600 - 338.72 = 261.28 \text{ kJ}$$

∴ **Loss in available energy due to heat transfer**

$= 455 - 261.28 =$ **193.72 kJ. (Ans.)**

☞**Example 6.6.** *Calculate the unavailable energy in 60 kg of water at 60°C with respect to the surroundings at 6°C, the pressure of water being 1 atmosphere.*

Solution. Refer Fig. 6.10.

Mass of water, $m = 60$ kg

Temperature of water, $T_1 = 60 + 273 = 333$ K

Temperature of surroundings, $T_0 = 6 + 273 = 279$ K

Pressure of water, $p = 1$ atm.

If the water is cooled at a constant pressure of 1 atm. from 60°C to 6°C the heat given up may be used as a *source for a series of Carnot engines each using the surroundings as a sink.* It is assumed that the amount of energy received by any engine is small relative to that in the source and temperature of the source does not change while heat is being exchanged with the engine.

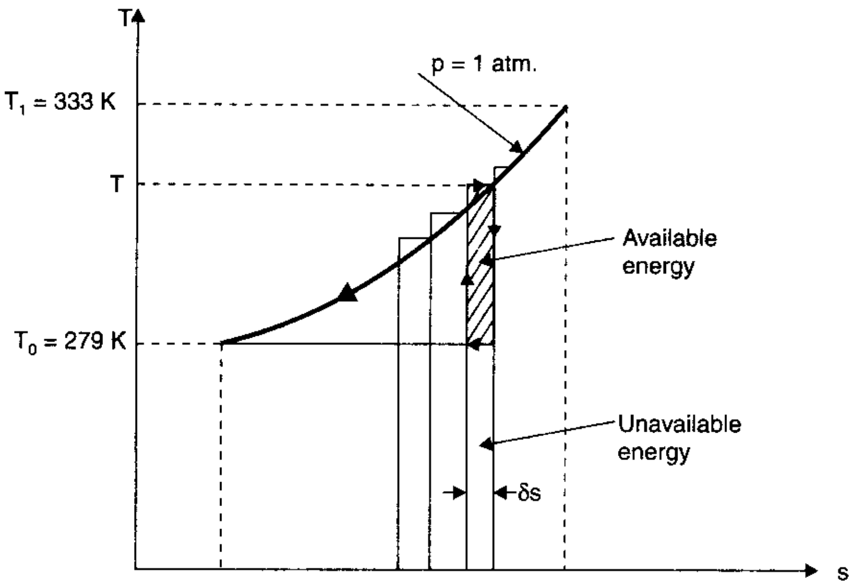


Fig. 6.10

Consider that the source has fallen to temperature T, at which level there operates a Carnot engine which takes in heat at this temperature and rejects heat at T_0 = 279 K. If δs is the entropy change of water, the work obtained is

$$\delta W = -\, m(T - T_0)\, \delta s$$

where δs is negative.

$$\therefore \qquad \delta W = -\, 60\, (T - T_0)\, \frac{c_p \delta T}{T} = -\, 60\, c_p \left(1 - \frac{T_0}{T}\right) \delta T$$

With a very great number of engines in the series, the total work (maximum) obtainable when the water is cooled from 333 K to 279 K would be

$$\begin{aligned} W_{max} &= \text{Available energy} \\ &= -\,\lim. \sum_{333}^{279} 60\, c_p \left(1 - \frac{T_0}{T}\right) \delta T \\ &= \int_{279}^{333} 60\, c_p \left(1 - \frac{T_0}{T}\right) dT \\ &= 60\, c_p \left[(333 - 279) - 279 \log_e \left(\frac{333}{279}\right)\right] \\ &= 60 \times 4.187\, (54 - 49.36) = 1165.7 \text{ kJ} \end{aligned}$$

Also, $$Q_1 = 60 \times 4.187 \times (333 - 279) = 13565.9 \text{ kJ}$$

∴ **Unavailable energy** = $Q_1 - W_{max}$

= 13565.9 – 1165.7 = **12400.2 kJ. (Ans.)**

Example 6.7. *15 kg of water is heated in an insulated tank by a churning process from 300 K to 340 K. If the surrounding temperature is 300 K, find the loss in availability for the process.*

Solution. Mass of water, m = 15 kg

Temperature, T_1 = 340 K

Surrounding temperature, $T_0 = 300$ K

Specific heat of water, $c_p = 4.187$ kJ/kg K

Loss in availability :

Work added during churning

= Increase in enthalpy of the water

= 15 × 4.187 × (340 – 300) = 2512.2 kJ

Now the energy in the water = 2512.2 kJ

The availability out of this energy is given by

$$m[(u_1 - u_0) - T_0\ \Delta s]$$

where $$\Delta s = c_p \log_e \left(\frac{T_1}{T_0}\right)$$

$\therefore$ $$\Delta s = 4.187 \log_e \left(\frac{340}{300}\right) = 0.524 \text{ kJ/kg K}$$

$\therefore$ Available energy

$= m\ [c_v\ (T_1 - T_0) - T_0\ \Delta s]$

$= 15\ [4.187\ (340 - 300) - 300 \times 0.524] = 158.7$ kJ

$\therefore$ **Loss in availability**

= 2508 – 158.7 = **2349.3 kJ. (Ans.)**

This shows that *conversion of work into heat is highly irreversible process* (since out of 2512.2 kJ of work energy supplied to increase the temperature, only 158.7 kJ will be available again for conversion into work).

Example 6.8. *5 kg of air at 550 K and 4 bar is enclosed in a closed system.*

(i) Determine the availability of the system if the surrounding pressure and temperature are 1 bar and 290 K respectively.

(ii) If the air is cooled at constant pressure to the atmospheric temperature, determine the availability and effectiveness.

Solution. Mass of air, $m = 5$ kg

Temperature, $T_1 = 550$ K

Pressure, $p_1 = 4 \text{ bar} = 4 \times 10^5 \text{ N/m}^2$

Temperature, $T_2 = T_0 = 290$ K

Pressure, $p_2 = p_0 = 1 \text{ bar} = 1 \times 10^5 \text{ N/m}^2$.

(*i*) **Availability of the system :**

Availability of the system is

$$= m[(u_1 - u_0) - T_0(s_1 - s_0)] = m[c_v(T_1 - T_0) - T_0\ \Delta s]$$

$$\Delta s = c_p \log_e \frac{T_1}{T_0} - R \log_e \left(\frac{p_1}{p_0}\right)$$

$$= 1.005 \log_e \left(\frac{550}{290}\right) - 0.287 \log_e \left(\frac{4}{1}\right)$$

$= 0.643 - 0.397 = 0.246$ kJ/kg K

$\therefore$ **Availability of the system**

$= m\ [c_v\ (T_1 - T_0) - T_0\Delta s]$

$= 5[0.718\ (550 - 290) - 290 \times 0.246] =$ **576.7 kJ. (Ans.)**

(*ii*) Heat transferred during cooling

$$Q = m \times c_p \times (T_1 - T_0)$$
$$= 5 \times 1.005 \times (550 - 290)$$
$$= 1306.5 \text{ kJ} \quad \text{...... heat lost by the system}$$

Change of entropy during cooling

$$\Delta S = m \times c_p \times \log_e \left(\frac{T_1}{T_0}\right)$$
$$= 5 \times 1.005 \times \log_e \left(\frac{550}{290}\right) = 3.216 \text{ kJ/K}$$

Unavailable portion of this energy

$$= T_0 \, . \, (\Delta S) = 290 \times 3.216 = 932.64 \text{ kJ}$$

∴ **Available energy** $= 1306.5 - 932.64 =$ **373.86 kJ. (Ans.)**

Effectiveness, $\epsilon = \dfrac{\text{Available energy}}{\text{Availability of the system}} = \dfrac{373.86}{576.7}$

$= \mathbf{0.648}$ **or 64.8%. (Ans.)**

Example 6.9. *Air at the rate of 25 kg/min is compressed in a centrifugal air compressor from 1 bar to 2 bar. The temperature increases from 15°C to 100°C during compression. Determine actual and minimum power required to run the compressor. The surrounding air temperature is 15°C.*

Neglect the heat interaction between the compressor and surroundings and changes in potential and kinetic energy.

Take for air, $c_p = 1.005$ *kJ/kg K,* $R = 0.287$ *kJ/kg K.*

Solution. Rate of flow of air, $m = 25$ kg/min.

Initial pressure, $p_1 = 1$ bar

Final pressure, $p_2 = 2.0$ bar

Initial temperature, $T_1 = T_0 = 15 + 273 = 288$ K

Final temperature, $T_2 = 100 + 273 = 373$ K.

Applying energy equation to compressor,

$$W_{actual} = h_2 - h_1 \qquad [\text{as } Q = 0,\ \Delta PE = 0,\ \Delta KE = 0]$$
$$= c_p (T_2 - T_1) = 1.005 (373 - 288) = 85.4 \text{ kJ/kg}$$

Total actual work done/min

$$= 25 \times 85.4 = 2135 \text{ kJ/min}$$
$$= \frac{2135}{60} = 35.58 \text{ kJ/s} = 35.58 \text{ kW}$$

The *minimum work required is given by the increase in availability of the air stream.*

$$W_{min} = b_2 - b_1 = (h_2 - h_1) - T_0 (s_2 - s_1)$$
$$s_2 - s_1 = c_p \log_e \left(\frac{T_2}{T_1}\right) - R \log_e \left(\frac{p_2}{p_1}\right) \quad \text{...per unit mass}$$
$$= 1.005 \log_e \left(\frac{373}{288}\right) - 0.287 \log_e \left(\frac{2.0}{1}\right)$$
$$= 0.2599 - 0.1989 = 0.061 \text{ kJ/kg K}$$

∴ $W_{min} = (h_2 - h_1) - T_0(s_2 - s_1)$

$$= 85.4 - 288 \times 0.061 = 67.8 \text{ kJ/kg}$$

∴ **Minimum work required**

$$\frac{25 \times 67.8}{60} = 28.25 \text{ kJ/s} = \mathbf{28.25\ kW.}\ \textbf{(Ans.)}$$

Example 6.10. *1 kg of oxygen at 1 bar and 450 K is mixed with 1 kg of hydrogen at the same temperature and pressure by removing the diaphragm as shown in Fig. 6.11. Determine the loss in availability if the surrounding temperature is 290 K.*

Assume that the system is fully isolated.

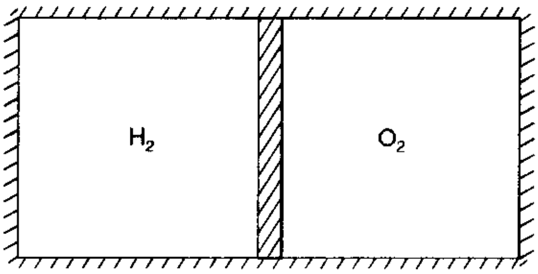


Fig. 6.11

Solution. Mass of oxygen, $m_{O_2} = 1$ kg

Mass of hydrogen, $m_{H_2} = 1$ kg

Pressure, $p = 1 \text{ bar} = 1 \times 10^5 \text{ N/m}^2$

Temperature, $T_{O_2} = T_{H_2} = 450$ K

Surrounding temperature = 290 K

Characteristic gas constant of O_2,

$$R_{O_2} = \frac{R_0}{M_{O_2}} = \frac{8314}{32} = 259.6 \text{ J/kg K}$$

Now to find volume of O_2 using the relation,

$$pv = mRT$$

$$v = \frac{mRT}{p} = \frac{1 \times 259.6 \times 450}{1 \times 10^5} = 1.168 \text{ m}^3$$

i.e., $v_{O_2} = 2.336 \text{ m}^3$

Characteristic gas constant of H_2,

$$R_{H_2} = \frac{R_0}{M_{H_2}} = \frac{8314}{2} = 4157 \text{ J/kg K}$$

Volume of H_2, $v_{H_2} = \dfrac{1 \times 4157 \times 450}{1 \times 10^5} = 18.706 \text{ m}^3$

Total volume after mixing

$$= v_{O_2} + v_{H_2} = 1.168 + 18.706$$

$$= 19.874 \text{ m}^3$$

The partial pressure of each gas changes after the mixing even though the temperature is the same due to increase in volume.

Change in entropy of *oxygen*

$$= R_{O_2} \log_e \frac{v_2}{v_1}$$

$$= 259.6 \log_e \left(\frac{19.874}{1.168}\right) = 735.7 \text{ J/K}$$

Change in entropy of hydrogen

$$= R_{H_2} \log_e \frac{v_2}{v_1} = 4157 \log_e \left(\frac{19.874}{18.706}\right)$$

$$= 251.78 \text{ J/K}$$

Net change in entropy,

$$\Delta S = 735.7 + 251.78 = 987.48 \text{ J/K}$$

Loss in availability

$$= T_0 \Delta S = 290 \times 987.48 \text{ J} = \frac{290 \times 987.48}{10^3} \text{ kJ} = 286.36 \text{ kJ}$$

i.e., **Loss in availability = 286.36 kJ. (Ans.)**

☞**Example 6.11.** *Calculate the decrease in available energy when 20 kg of water at 90°C mixes with 30 kg of water at 30°C, the pressure being taken as constant and the temperature of the surroundings being 10°C.*

Take c_p of water as 4.18 kJ/kg K.

Solution. Temperature of surrounding, $T_0 = 10 + 273 = 283$ K

Specific heat of water, $c_p = 4.18$ kJ/kg K

The available energy of a system of mass *m*, specific heat c_p, and at temperature *T*, is given by,

$$\text{Available energy, A.E.} = mc_p \int_{T_0}^{T} \left(1 - \frac{T_0}{T}\right) dT$$

Now, available energy of 20 kg of water at 90°C,

$$(\text{A.E.})_{20 \text{ kg}} = 20 \times 4.18 \int_{(10+273)}^{(90+273)} \left(1 - \frac{283}{T}\right) dT$$

$$= 83.6 \left[(363 - 283) - 283 \log_e \left(\frac{363}{283}\right)\right]$$

$$= 83.6\ (80 - 70.45) = 798.38 \text{ kJ}$$

Available energy of 30 kg of water at 30°C,

$$(\text{A.E.})_{30 \text{ kg}} = 30 \times 4.18 \int_{(10+273)}^{(30+273)} \left(1 - \frac{283}{T}\right) dT$$

$$= 30 \times 4.18 \left[(303 - 283) - 283 \log_e \left(\frac{303}{283}\right)\right]$$

$$= 125.4\ (20 - 19.32) = 85.27 \text{ kJ}$$

Total available energy,

$$(\text{A.E.})_{\text{total}} = (\text{A.E.})_{20 \text{ kg}} + (\text{A.E.})_{30 \text{ kg}}$$

$$= 798.38 + 85.27 = 883.65 \text{ kJ}$$

If t°C is the final temperature after mixing, then

$$20 \times 4.18 \times (90 - t) = 30 \times 4.18\ (t - 30)$$

or $$20(90 - t) = 30\,(t - 30)$$

$$\therefore \quad t = \frac{20 \times 90 + 30 \times 30}{20 + 30} = 54°\text{C}$$

Total mass after mixing = 20 + 30 = 50 kg

Available energy of 50 kg of water at 54°C

$$(\text{A.E.})_{50\text{ kg}} = 50 \times 4.18 \left[(327 - 283) - 283 \log_e\left(\frac{327}{283}\right)\right]$$

$$= 209\,(44 - 40.89) = 649.99 \text{ kJ}$$

∴ **Decrease in available energy due to mixing**

= Total energy before mixing – Total energy after mixing

= 883.65 – 649.99 = **233.66 kJ. (Ans.)**

☞ **Example 6.12.** *In an heat exchanger (parallel flow type) waters enter at 50°C and leaves at 70°C while oil (specific gravity = 0.82, specific heat = 2.6 kJ/kg K) enters at 240°C and leaves at 90°C. If the surrounding temperature is 27°C determine the loss in availability on the basis of one kg of oil per second.*

Solution. Refer Fig. 6.12.

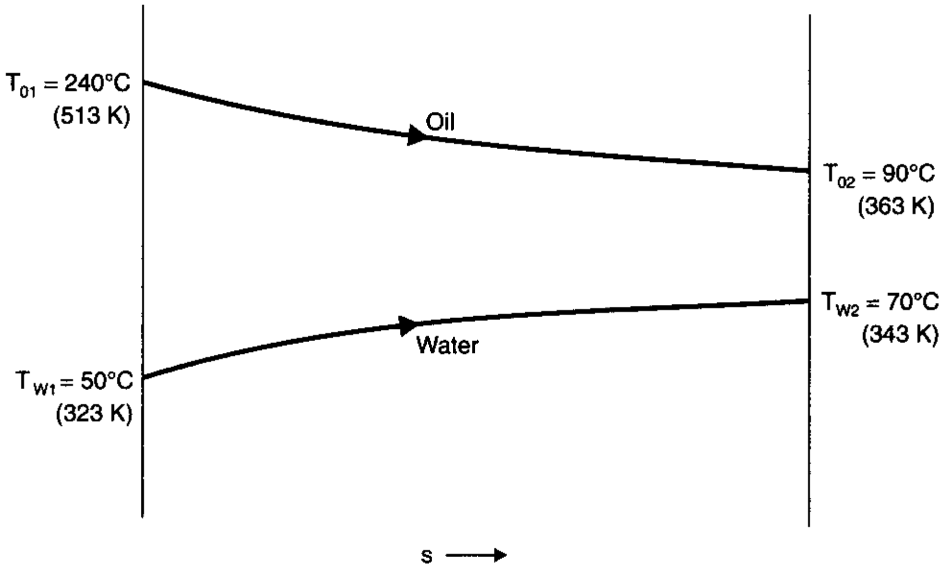


Fig. 6.12

Inlet temperature of water, T_{w_1} = 50°C = 323 K

Outlet temperature of water, T_{w_2} = 70°C = 343 K

Inlet temperature of oil, T_{o_1} = 240°C = 513 K

Outlet temperature of oil, T_{o_2} = 90°C = 363 K

Specific gravity of oil = 0.82

Specific heat of oil = 2.6 kJ/kg K

Surrounding temperature, T_0 = 27 + 273 = 300 K.

Loss in availability :

Consider one kg of oil.

Heat lost by oil = Heat gained by water

$$m_0 \times c_{po} \times (T_{o_1} - T_{o_2}) = m_w \times c_{pw} \times (T_{w_2} - T_{w_1})$$

where c_{po} = Specific heat of oil (2.6 kJ/kg K),

c_{pw} = Specific heat of water (4.18 kJ/kg K), and

m_o = Mass of oil (= 1 kg).

m_w = Mass of water (= ?)

$$\therefore \quad 1 \times 2.6 \times (513 - 363) = m_w \times 4.18 \times (343 - 323)$$

or

$$390 = 83.6\, m_w \text{ or } m_w = 4.66 \text{ kg}$$

Entropy change of water

$$= m_w\, c_{pw} \log_e \frac{T_{w_2}}{T_{w_1}} = 4.66 \times 4.18 \times \log_e \left(\frac{343}{323}\right) = 1.17 \text{ kJ/K}$$

Entropy change of oil

$$= m_o c_{po} \log_e \left(\frac{T_{o_2}}{T_{o_1}}\right) = 1 \times 2.6 \log_e \left(\frac{363}{513}\right) = -\, 0.899 \text{ kJ/K}$$

Change in availability of water

$$= m_w[c_{pw}(T_{w_2} - T_{w_1})] - T_o\,(\Delta S)_w$$

$$= 4.66[(4.18\,(343 - 323)] - 300 \times 1.17 = 38.57 \text{ kJ}$$

+ve sign indicates an *increase in availability*

Change in availability of oil

$$= m_o[c_{po}(T_{o_2} - T_{o_1})] - T_0\,(\Delta S)_0]$$

$$= 1[2.6(363 - 513)] - 300 \times (-\,0.899) = -\,120.3 \text{ kJ/K}$$

∴ **Loss in availability**

$$= -\,120.3 + 38.57 = -\,\mathbf{81.73\ kJ.}\quad \textbf{(Ans.)}$$

(–ve sign indicates the **loss**).

Example 6.13. *1 kg of ice at 0°C is mixed with 12 kg of water at 27°C. Assuming the surrounding temperature as 15°C, calculate the net increase in entropy and unavailable energy when the system reaches common temperature :*

Given : Specific heat of water = 4.18 kJ/kg K ; specific heat of ice = 2.1 kJ/kg K and enthalpy of fusion of ice (latent heat) = 333.5 kJ/kg.

Solution. Mass of ice, $m_{ice} = 1$ kg

Temperature of ice, $T_{ice} = 0 + 273 = 273$ K

Mass of water, $m_{water} = 12$ kg

Temperature of water, $T_{water} = 27 + 273 = 300$ K

Surrounding temperature, $T_0 = 15 + 273 = 288$ K

Specific heat of water = 4.18 kJ/kg K

Specific heat of ice = 2.1 kJ/kg K

Latent heat of ice = 333.5 kJ/kg

Let T_c = *common temperature* when heat flows between ice and water stops.

Heat lost by water = Heat gained by ice

i.e., $$12 \times 4.18(300 - T_c) = 4.18(T_c - 273) + 333.5$$

or $$15048 - 50.16T_c = 4.18T_c - 1141.14 + 333.5$$

or $$54.34\ T_c = 15855.64$$

$$\therefore \quad T_c = 291.8 \text{ K or } 18.8°\text{C}.$$

Change of entropy of water $= 12 \times 4.18 \log_e \left(\dfrac{291.8}{300}\right) = -1.39$ kJ/K

Change of entropy of ice $= 1 \times 4.18 \log_e \left(\dfrac{291.8}{273}\right) + \dfrac{333.5}{273} = 1.499$ kJ/K

Net change of entropy, $\Delta S = -1.39 + 1.499 = 0.109$ kJ/K

Hence, **net increase in entropy = 0.109 kJ/K. (Ans.)**

Increase in unavailable energy = $T_0 \Delta S = 288 \times 0.109 =$ **31.39 kJ. (Ans.)**

☞**Example 6.14.** *A vapour, in a certain process, while condensing at 400°C, transfers heat to water at 200°C. The resulting steam is used in a power cycle which rejects heat at 30°C.*

What is the fraction of the available energy in the heat transferred from the process vapour at 400°C that is lost due to the irreversible heat transfer at 200°C ?

Solution. Refer Fig. 6.13.

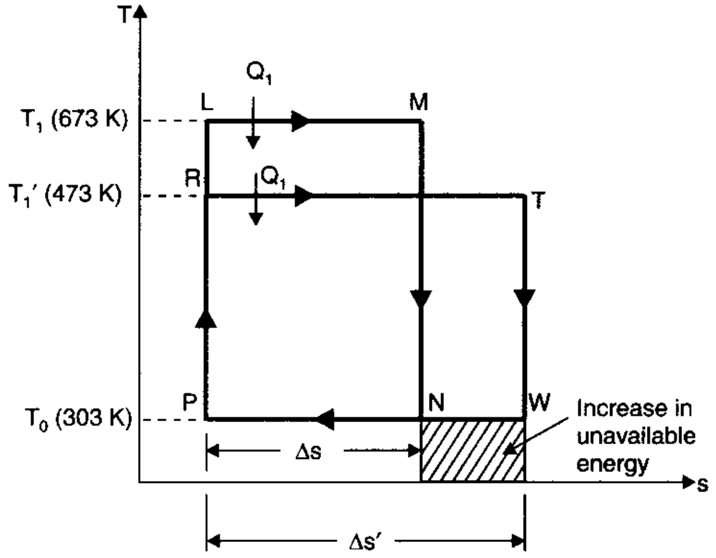


Fig. 6.13

Temperature of vapour, $T_1 = 400 + 273 = 673$ K

Temperature of water, $T_2 = 200 + 273 = 473$ K

Temperature at which heat is rejected, $T_0 = 30 + 273 = 303$ K.

LMNP (Fig. 6.13) would have been the power cycle, if there was no temperature difference between the vapour condensing and the vapour evaporating, and the area under *NP* would have been the unavailable energy. *RTWP* is the power cycle when the vapour condenses at 400°C and the water evaporates at 200°C. The unavailable energy becomes the area under *PW*. Therefore, the increase in unavailable energy due to irreversible heat transfer is represented by the area under *NW*.

Now, $$Q_1 = T_1\Delta s = T_1'\Delta s'$$

$$\frac{\Delta s'}{\Delta s} = \frac{T_1}{T_1'}$$

W = Work done in cycle *LMNP*

$= (T_1 - T_0)\,\Delta s$ ...per unit mass

W' = Work done in cycle *RTWP*

$= (T_1 - T_0)\,\Delta s'$ ...per unit mass

The fraction of energy that becomes unavailable due to irreversible heat transfer,

$$\frac{W - W'}{W} = \frac{(T_1 - T_0)\Delta s - (T_1 - T_0)\Delta s'}{(T_1 - T_0)\Delta s} = \frac{T_0\,(\Delta s' - \Delta s)}{(T_1 - T_0)\Delta s}$$

$$= \frac{T_0\left(\frac{\Delta s'}{\Delta s} - 1\right)}{(T_1 - T_0)} = \frac{T_0\left(\frac{T_1}{T_1'} - 1\right)}{(T_1 - T_0)}$$

$$= \frac{T_0\,(T_1 - T_1')}{T_1'\,(T_1 - T_0)} = \frac{303(673 - 473)}{473(673 - 303)} = 0.346$$

Hence **the fraction of energy that becomes unavailable = 0.346 or 34.6%. (Ans.)**

Example 6.15. *A liquid is heated at approximately constant pressure from 20°C to 80°C by passing it through tubes which are immersed in a furnace. The furnace temperature is constant at 1500°C. Calculate the effectiveness of the heating process when the atmospheric temperature is 15°C.*

Take specific heat of liquid as 6.3 kJ/kg K.

Solution. Initial temperature of fluid, $T_1 = 20 + 273 = 293$ K

Final temperature of fluid, $T_2 = 80 + 273 = 353$ K

Temperature of the furnace, $T_f = 1500 + 273 = 1773$ K

Atmospheric temperature, $T_0 = 15 + 273 = 288$ K

Specific heat of liquid, $c_{pl} = 6.35$ kJ/kg K

Increase of availability of the liquid

$$= b_2 - b_1 = (h_2 - h_1) - T_0(s_2 - s_1)$$

i.e., $$b_2 - b_1 = c_{pl}\,(T_2 - T_1) - T_0 \times c_{pl}\log_e \frac{T_2}{T_1}$$

$$= 6.3\,(353 - 293) - 288 \times 6.3 \times \log_e\left(\frac{353}{293}\right) = 39.98 \text{ kJ/kg}$$

Now, the heat rejected by the furnace = Heat supplied to the liquid, $(h_2 - h_1)$.

If this quantity of heat were supplied to a heat engine operating on the Carnot cycle its thermal efficiency would be,

$$\eta_{th} = \left(1 - \frac{T_0}{T_f}\right) = \left(1 - \frac{288}{1773}\right) = 0.837 \text{ (or 83.7\%)}$$

∴ Work which could be obtained from a heat engine

= Heat supplied × Thermal efficiency

i.e., Possible work of heat engine = $(h_2 - h_1) \times 0.837$

The possible work from a heat engine is a measure of the loss of availability of the furnace.

$\therefore$ Loss of availability of surroundings

$$= (h_2 - h_1) \times 0.837 = c_{pl}\,(T_2 - T_1) \times 0.837$$
$$= 6.3\,(353 - 293) \times 0.837 = 316.38 \text{ kJ/kg}$$

Then, *effectiveness of the heating process*,

$$\epsilon = \frac{\text{Increase of availability of the liquid}}{\text{Loss of availability of surroundings}}$$
$$= \frac{39.98}{316.38} = \mathbf{0.1263} \text{ or } \mathbf{12.63\%}. \quad \textbf{(Ans.)}$$

Note. *The very low value of effectiveness reflects the irreversibility of the transfer of heat through a large temperature difference.* If the furnace temperature were much lower then process would be much more effective, although the heat transferred to the liquid would remain the same.

Example 6.16. *Air at 20°C is to be heated to 50°C by mixing it in steady flow with a quantity of air at 100°C. Assuming that the mixing process is adiabatic and neglecting changes in kinetic and potential energy, calculate :*

(*i*) *The ratio of mass flow of air initially at 100°C to that initially at 20°C.*

(*ii*) *The effectiveness of heating process, if the atmospheric temperature is 20°C.*

Solution. (*i*) Let, x = ratio of mass flows.

Stream 1 = air at 20°C ($T_1 = 20 + 273 = 293$ K)

Stream 2 = air at 100°C ($T_2 = 100 + 273 = 373$ K)

Stream 3 = air at 50°C ($T_3 = 50 + 273 = 323$ K)

If, c_p = Specific heat of air constant pressure

Then $\quad c_pT_1 + xc_pT_2 = (1 + x)c_pT_3$

or $\quad c_pT_1 + xc_pT_2 = c_pT_3 + xc_pT_3$

or $\quad xc_p(T_2 - T_3) = c_p(T_3 - T_1)$

i.e., $\quad xc_p(373 - 323) = c_p(323 - 293)$

$$\therefore \quad x = \frac{30}{50} = \mathbf{0.6}. \quad \textbf{(Ans.)}$$

(*ii*) Let the system considered be a stream of air of unit mass, heated from 20°C to 50°C.

Increase of availability of system

$$= b_3 - b_1 = (h_3 - h_1) - T_0(s_3 - s_1) = c_p(T_3 - T_1) - T_0(s_3 - s_1)$$
$$= 1.005(323 - 293) - 293(s_3 - s_1) \qquad [\because \; T_0 = 20 + 273 = 293 \text{ K}]$$

Also, $\quad s_3 - s_1 = c_p \log_e \dfrac{T_3}{T_1} = 1.005 \log_e \dfrac{323}{293} = 0.0979$ kJ/kg K

$\therefore$ *Increase of availability of system*

$$= 1.005 \times 30 - 293 \times 0.0979 = 1.465 \text{ kJ/kg.}$$

The system, which is the air being heated, is 'surrounded' by the air stream being cooled. Therefore, the loss of availability of the surroundings is given by, $x(b_2 - b_3)$.

i.e., *Loss of availability of surroundings*

$$= x[(h_2 - h_3) - T_0(s_2 - s_3)] = 0.6[c_p(T_2 - T_3) - T_0(s_2 - s_3)]$$
$$= 0.6\left[1.005\,(373 - 323) - 293 \times 1.005 \log_e \left(\frac{373}{323}\right)\right]$$

$$= 0.6[50.25 - 42.38] = 4.722 \text{ kJ/kg}$$

$$\therefore \quad \textit{Effectiveness} = \frac{\text{Increase of availability of system}}{\text{Loss of availability of surroundings}}$$

$$= \frac{1.465}{4.722} = \mathbf{0.31} \quad \text{or} \quad \mathbf{31\%.} \quad \textbf{(Ans.)}$$

The *low* figure for the effectiveness is an indication of the *highly irreversible nature of the mixing process.*

☞**Example 6.17.** *2.5 kg of air at 6 bar, 90°C expands adiabatically is a closed system until its volume is doubled and its temperature becomes equal to that of the surroundings which is at 1 bar, 5°C. For this process determine :*

(*i*) *The maximum work ;*

(*ii*) *The change in availability ;*

(*iii*) *The irreversibility.*

For air take : $c_v = 0.718$ *kJ/kg K,* $R = 0.287$ *kJ/kg K.*

Solution. Mass of air, $m = 2.5$ kg

Initial pressure of air, $p_1 = 6 \text{ bar} = 6 \times 10^5 \text{ N/m}^2$

Ratio of final to initial volume, $\frac{V_2}{V_1} = 2$

Initial temperature of air, $T_1 = 90 + 273 = 363$ K

Final pressure of air, $p_2 = 1 \text{ bar} = 1 \times 10^5 \text{ N/m}^2$

Final temperature of air, $T_2 = T_0 = 5 + 273 = 278$ K

From the property relation

$$TdS = dU + pdV$$

or

$$dS = \frac{dU}{T} + \frac{pdV}{T}$$

$$dS = \frac{mc_v dT}{T} + \frac{mRdV}{V} \quad \left[\because u = c_v \, dT \text{ and } pV = mRT \text{ or } \frac{p}{T} = \frac{mR}{V}\right]$$

$\therefore$ The entropy change of air between the initial and final states is

$$\int_1^2 dS = \int_1^2 \frac{mc_v dT}{T} + \int_1^2 \frac{mRdV}{V}$$

or

$$S_2 - S_1 = mc_v \log_e \frac{T_2}{T_1} + mR \log_e \frac{V_2}{V_1}$$

(*i*) **The maximum work,** $\mathbf{W_{max}}$ **:**

Also,
$$W_{max} = (U_1 - U_2) - T_0(S_1 - S_2)$$

$$= m\left[c_v(T_1 - T_2) + T_0\left(c_v \log_e \frac{T_2}{T_1} + R \log_e \frac{v_2}{v_1}\right)\right]$$

$$= 2.5\left[0.718(363 - 278) + 278\left(0.718 \log_e \left(\frac{278}{363}\right) + 0.287 \log_e 2\right)\right]$$

$$= 2.5[61.03 + 278(-0.1915 + 0.1989)] = 157.7 \text{ kJ}$$

Hence, **maximum work = 157.7 kJ. (Ans.)**

(*ii*) **The change in availability :**

The change in availability is given by,

$$A_1 - A_2 = (U_1 - U_2) - T_0(S_1 - S_2) + p_0(V_1 - V_2)$$

$$= W_{max} + p_0\,(V_1 - V_2)$$

$$= 157.7 + p_0\,(V_1 - 2V_1) = 157.7 - P_0V_1 \qquad \left[\begin{array}{l} p_1V_1 = mRT_1 \\ \because\ V_1 = \dfrac{mRT_1}{p_1} \end{array}\right]$$

$$= 157.7 - \frac{1 \times 10^5}{10^3}\left[\frac{2.5 \times (0.287 \times 1000) \times 363}{6 \times 10^5}\right] = 114.29 \text{ kJ}$$

Hence **change in availability = 114.29 kJ. (Ans.)**

(*iii*) **The irreversibility ; I :**

The irreversibility is given by

$$I = W_{max.\ useful} - W_{actual}$$

From the first law of thermodynamics,

$$W_{actual} = Q - \Delta U = -\Delta U = U_1 - U_2 \qquad [\because\ Q = 0 \text{ ... adiabatic process}]$$

$$I = (U_1 - U_2) - T_0(S_1 - S_2) - (U_1 - U_2)$$

$$= T_0(S_2 - S_1)$$

$$= T_0(\Delta S)_{system}$$

For adiabatic process, $(\Delta S)_{surr.} = 0$

$$I = T_0\left[mc_v \log_e \frac{T_2}{T_1} + mR \log_e \frac{v_2}{v_1}\right]$$

$$= 278 \times 2.5\left(0.718 \log_e\left(\frac{278}{363}\right) + 0.287 \log_e 2\right)$$

$$= 695(-\,0.1915 + 0.1989) = 5.143 \text{ kJ}$$

Hence, **the irreversibility = 5.143 kJ. (Ans.)**

☞**Example 6.18.** *In a turbine the air expands from 7 bar, 600°C to 1 bar, 250°C. During expansion 9 kJ/kg of heat is lost to the surroundings which is at 1 bar, 15°C. Neglecting kinetic energy and potential energy changes, determine per kg of air :*

(*i*) *The decrease in availability ;*

(*ii*) *The maximum work ;*

(*iii*) *The irreversibility.*

For air, take : $c_p = 1.005$ *kJ/kg K,* $h = c_pT$, *where* c_p *is constant.*

Solution. Mass of air considered = 1 kg

Pressure, $p_1 = 7 \text{ bar} = 7 \times 10^5 \text{ N/m}^2$

Temperature, $T_1 = 600 + 273 = 873 \text{ K}$

Pressure, $p_2 = 1 \text{ bar} = 1 \times 10^5 \text{ N/m}^2$

Temperature, $T_2 = 250 + 273 = 523 \text{ K}$

Surrounding temperature, $T_0 = 15 + 273 = 288 \text{ K}$

Heat lost to the surroundings during expansion,

$$Q = 9 \text{ kJ/kg.}$$

(*i*) From the property relation,

$$TdS = dH - Vdp$$

$$dS = \frac{dH}{T} - \frac{Vdp}{T}$$

$$= \frac{m.c_p dT}{T} - \frac{mRdp}{p}$$

or

$$\int_1^2 dS = \int_1^2 \frac{m.c_p dT}{T} - \int_1^2 \frac{mRdp}{p}$$

or

$$S_2 - S_1 = mc_p \log_e \frac{T_2}{T_1} - mR \log_e \frac{p_2}{p_1}$$

$$\left\{ \begin{array}{l} \because h = c_p T, dh = c_p dT \\ dH = mc_p dT \text{ and } pV = mRT \\ \text{or } V = \dfrac{mRT}{p} \end{array} \right\}$$

For 1 kg of air

$$s_2 - s_1 = c_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}$$

Now, the change in availability is given by

$$b_1 - b_2 = (h_1 - T_0 s_1) - (h_2 - T_0 s_2)$$

$$= (h_1 - h_2) - T_0(s_1 - s_2)$$

$$= c_p (T_1 - T_2) - T_0 \left(R \log_e \frac{p_2}{p_1} - c_p \log_e \frac{T_2}{T_1} \right)$$

$$= 1.005(873 - 523) - 288 \left[0.287 \log_e \left(\frac{1}{7} \right) - 1.005 \log_e \left(\frac{523}{873} \right) \right]$$

$$= 351.75 - 288(-0.5585 + 0.5149) = 364.3 \text{ kJ/kg}$$

i.e., **Decrease in availability = 364.3 kJ/kg. (Ans.)**

(*ii*) **The maximum work,**

W_{max} = Change in availability = **364.3 kJ/kg. (Ans.)**

(*iii*) From steady flow energy equation,

$$Q + h_1 = W + h_2$$

$$W = (h_1 - h_2) + Q$$

$$= c_p (T_1 - T_2) + Q$$

$$= 1.005(873 - 523) + (-9) = 342.75 \text{ kJ/kg}$$

The irreversibility,

$$I = W_{max} - W$$

$$= 364.3 - 342.75 = \mathbf{21.55 \text{ kJ/kg. (Ans.)}}$$

Alternatively, $I = T_0 (\Delta S_{system} + \Delta S_{surr.})$

$$= 288 \left[1.005 + \log_e \left(\frac{523}{873} \right) - 0.287 \log_e \left(\frac{1}{7} \right) + \frac{9}{288} \right]$$

$$= 288 [-0.5149 + 0.5585 + 0.03125]$$

$$= 21.55 \text{ kJ/kg.}$$

Example 6.19. *1 kg of air undergoes a polytropic compression from 1 bar and 290 K to 6 bar and 400 K. If the temperature and pressure of the surroundings are 290 K and 1 bar respectively, determine :*

(i) The irreversibility ;

(ii) The effectiveness.

Take for air : $c_p = 1.005$ *kJ/kg K,* $c_v = 0.718$ *kJ/kg K,* $R = 0.287$ *kJ/kg K.*

Solution. Mass of air, $m = 1$ kg

Initial temperature, $T_1 = T_0 = 290$ K

Final temperature, $T_2 = 400$ K

Initial pressure, $p_1 = p_0 = 1$ bar

Final pressure, $p_2 = 6$ bar.

(*i*) **The irreversibility, I :**

We know that reversible work,

$$W_{rev.} = \text{Change in internal energy} - T_0 \times \text{Change in entropy}$$

$$= (u_2 - u_1) - T_0 \left[c_p \log_e \left(\frac{T_2}{T_1} \right) - R \log_e \left(\frac{p_2}{p_1} \right) \right]$$

$$= c_v (T_2 - T_1) - T_0 \left[c_p \log_e \left(\frac{T_2}{T_1} \right) - R \log_e \left(\frac{p_2}{p_1} \right) \right]$$

$$= 0.718 (400 - 290) - 290 \left[1.005 \log_e \left(\frac{400}{290} \right) - 0.287 \log_e \left(\frac{6}{1} \right) \right]$$

$$= 78.98 - 290 (0.3232 - 0.5142)$$

$$= 134.37 \text{ kJ/kg } (-)$$ [–ve sign indicates that work is done on the air]

Actual work is given by

$$W_{actual} = \frac{mR(T_1 - T_2)}{n - 1} = \frac{R(T_1 - T_2)}{n - 1} \text{ as } m = 1 \text{ kg.}$$

The index n for the compression is given by :

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}}$$

$$\therefore \quad \frac{400}{290} = \left(\frac{6}{1} \right)^{\frac{n-1}{n}} \quad \text{or} \quad 1.379 = (6)^{\frac{n-1}{n}}$$

$$\log_e 1.379 = \left(\frac{n-1}{n} \right) \log_e 6 \quad \text{or} \quad 0.3213 = 1.7917 \left(\frac{n-1}{n} \right)$$

$$\therefore \quad \frac{n-1}{n} = \frac{0.3213}{1.7917} = 0.1793 \quad \text{or} \quad n = 1.218$$

$$\therefore \quad W_{actual} = \frac{0.287 (290 - 400)}{(1.218 - 1)} = -144.8 \text{ kJ}$$

(–ve sign means that the work is done on the air)

Now, **irreversibility** $= W_{rev} - W_{actual}$

$= -134.37 - (-144.8) =$ **10.43 kJ. (Ans.)**

(*ii*) **The effectiveness, ϵ :**

$$\epsilon = \frac{W_{rev.}}{W_{actual}} = \frac{-134.37}{-144.8}$$ = **0.928** or **92.8%. (Ans.)**

Example 6.20. *A flywheel whose moment of inertia is 0.62 kg m² rotates at a speed 2500 r.p.m. in a large heat insulated system, the temperature of which is 20°C.*

(i) If the K.E. of the flywheel is dissipated as frictional heat at the shaft bearings which have a water equivalent of 1.9 kg, find the rise in the temperature of the bearings when the flywheel has come to rest.

(ii) Calculate the greatest possible amount of the above heat which may be returned to the flywheel as high-grade energy, showing how much of the original K.E. is now unavailable. What would be the final r.p.m. of the flywheel, if it is set in motion with this available energy ?

Solution. Moment of inertia of the flywheel, $I = 0.62$ kg m²

Initial angular velocity of the flywheel, $\omega_1 = \frac{2\pi N_1}{60} = \frac{2\pi \times 2500}{60}$

$= 261.8$ rad/s.

Temperature of insulated system, $T_0 = 20 + 273 = 293$ K

Water equivalent of shaft bearings $= 1.9$ kg

(*i*) Initial available energy of the flywheel,

$$(\text{K.E.})_{initial} = \frac{1}{2} I \omega_1^2$$

$$= \frac{1}{2} \times 0.62 \times (261.8)^2 = 2.12 \times 10^4 \text{ N.m} = 21.2 \text{ kJ}.$$

When this K.E. is dissipated as frictional heat, if Δt is the temperature rise of the bearings, we have

Water equivalent of bearings × rise in temperature = 21.2

i.e., $(1.9 \times 4.18)\ \Delta t = 21.2$

or $$\Delta t = \frac{21.2}{1.9 \times 4.18} = 2.67°\text{C}$$

Hence, **rise in temperature of bearings = 2.67°C. (Ans.)**

∴ **Final temperature of the bearings = 20 + 2.67 = 22.67°C.**

(*ii*) *The maximum amount of energy which may be returned to the flywheel as high-grade energy is,*

$$\text{A.E.} = 1.9 \times 4.18 \int_{293}^{295.67} \left(1 - \frac{293}{T}\right) dT$$

$$= 1.9 \times 4.18 \left[(295.67 - 293) - 293 \log_e \left(\frac{295.67}{293}\right)\right] = \mathbf{0.096\ kJ.}\ \mathbf{(Ans.)}$$

The amount of energy rendered unavailable is

$$\text{U.E.} = (\text{A.E.})_{\text{initial}} - (\text{A.E.})_{\text{returnable as high grade energy}}$$

$$= 21.2 - 0.096 = 21.1 \text{ kJ}.$$

Since the amount of energy returnable to the flywheel is 0.096 kJ, if ω_2 is the final angular velocity, and the flywheel is set in motion with this energy, then

$$0.096 \times 10^3 = \frac{1}{2} \times 0.62 \times \omega_2^2$$

$$\therefore \quad \omega_2^2 = \frac{0.096 \times 10^3 \times 2}{0.62} = 309.67 \quad \text{or} \quad \omega_2 = 17.59 \text{ rad/s}.$$

If N_2 is the final r.p.m. of the flywheel, then

$$\omega_2 = \frac{2\pi N_2}{60} \quad \text{or} \quad N_2 = \frac{17.59 \times 60}{2\pi} = 168 \text{ r.p.m.}$$

i.e., **Final r.p.m. of the flywheel = 168 r.p.m. (Ans.)**

☞**Example 6.21.** *The air, in a steady flow, enters the system at a pressure of 8 bar and 180°C with a velocity of 80 m/s and leaves at 1.4 bar and 20°C with a velocity of 40 m/s. The temperature of the surroundings is 20°C and pressure is 1 bar. Determine :*

(i) Reversible work and actual work assuming the process to be adiabatic ;

(ii) Irreversibility and effectiveness of the system on the basis of 1 kg of air flow.

Take for air : c_p = 1.005 kJ/kg K ; R = 0.287 kJ/kg K.

Solution. Initial pressure of air, $p_1 = 8$ bar

Initial temperature of air, $T_1 = 180 + 273 = 453$ K

Final pressure of air, $p_2 = 1.4$ bar

Final temperature, $T_2 = T_0 = 20 + 273 = 293$ K

Surroundings' pressure, $p_0 = 1$ bar

Mass of air = 1 kg

Initial velocity of air, $C_1 = 80$ m/s

Final velocity of air, $C_2 = 40$ m/s.

(*i*) **Reversible work and actual work :**

Availability of air at the inlet

$$= (h_1 - h_0) - T_0 (s_1 - s_0) + \frac{C_1^2}{2}$$

$$= c_p (T_1 - T_0) - T_0 (s_1 - s_0) + \frac{C_1^2}{2}$$

$$(s_1 - s_0) = c_p \log_e \left(\frac{T_1}{T_0}\right) - R \log_e \left(\frac{p_1}{p_0}\right)$$

$$= 1.005 \log_e \left(\frac{453}{293}\right) - 0.287 \log_e \left(\frac{8}{1}\right)$$

$$= 0.437 - 0.596 = -0.159 \text{ kJ/kg K}$$

∴ Availability of air at the inlet

$$= 1.005 (453 - 293) - 293 (-0.159) + \frac{80^2}{2 \times 10^3}$$

$$= 160.8 + 46.58 + 3.2 = 210.58 \text{ kJ}$$

Availability at the exit

$$= (h_2 - h_0) - T_0 (s_2 - s_0) + \frac{C_2^2}{2}$$

$$= -T_0 (s_2 - s_0) + \frac{C_2^2}{2}$$

as $h_2 = h_0$ because $T_2 = T_0 = 293$ K

Now $s_2 - s_0 = -R \log_e \left(\frac{p_2}{p_0}\right) = -0.287 \log_e \left(\frac{1.4}{1}\right) = -0.09656$ kJ/kg K

∴ Availability at the exit

$$= -293 (-0.09656) + \frac{40^2}{2 \times 10^3} = 29.09 \text{ kJ/kg}$$

Reversible/theoretical work which must be available,

$$W_{rev} = 210.58 - 29.09 = \mathbf{181.49\ kJ.}\ \textbf{(Ans.)}$$

Actual work developed can be calculated by using the energy equation for adiabatic steady flow process as follows :

$$W_{actual} = (h_1 - h_2) + \left(\frac{C_1^2 - C_2^2}{2}\right)$$

$$= c_p (T_1 - T_2) + \left(\frac{C_1^2 - C_2^2}{2}\right)$$

$$= 1.005(453 - 293) + \left(\frac{80^2 - 40^2}{2 \times 10^3}\right)$$

$$= 160.8 + 2.4 = \mathbf{163.2\ kJ/kg.}\quad \textbf{(Ans.)}$$

(*ii*) **Irreversibility and effectiveness :**

Irreversibility, $I = W_{rev} - W_{actual}$

$$= 181.49 - 163.2 = \mathbf{18.29\ kJ/kg.}\quad \textbf{(Ans.)}$$

Effectiveness, $\epsilon = \dfrac{W_{actual}}{W_{rev}} = \dfrac{163.2}{181.49}$

$$= \mathbf{0.899}\ \text{or}\ \mathbf{89.9\%}.\quad \textbf{(Ans.)}$$

Example 6.22. *Steam expands adiabatically in a turbine from 20 bar, 400°C to 4 bar, 250°C. Calculate :*

(*i*) *The isentropic efficiency of the process ;*

(*ii*) *The loss of availability of the system assuming an atmospheric temperature of 20°C ;*

(*iii*) *The effectiveness of the process ;*

The changes in K.E. and P.E. may be neglected.

Solution. Initial pressure of steam, $p_1 = 20$ bar

Initial temperature of steam, $t_1 = 400°C$

Final pressure of steam, $p_2 = 4$ bar

Final temperature of steam, $t_2 = 250°C$

Atmospheric temperature, $= 20°C\ (= 293\ K)$.

Initial state 1 : 20 bar, 400°C ; From steam tables,

$$h_1 = 3247.6\ \text{kJ/kg}\ ;\ s_1 = 7.127\ \text{kJ/kg K}$$

Final state 2 : 4 bar 250°C ; From steam tables,

$$h_2' = 2964.2\ \text{kJ/kg},\ s_2' = 7.379\ \text{kJ/kg K}$$

The process is shown as 1 to 2′ in Fig. 6.14

$$s_1 = s_2 = \mathbf{7.127\ kJ/kg\ K}$$

Hence, interpolating,

$$h_2 = 2752.8 + \left(\frac{7.127 - 6.930}{7.171 - 6.930}\right)(2860.5 - 2752.8)$$

$$= 2752.8 + \frac{0.197}{0.241} \times 107.7 = 2840.8\ \text{kJ/kg}.$$

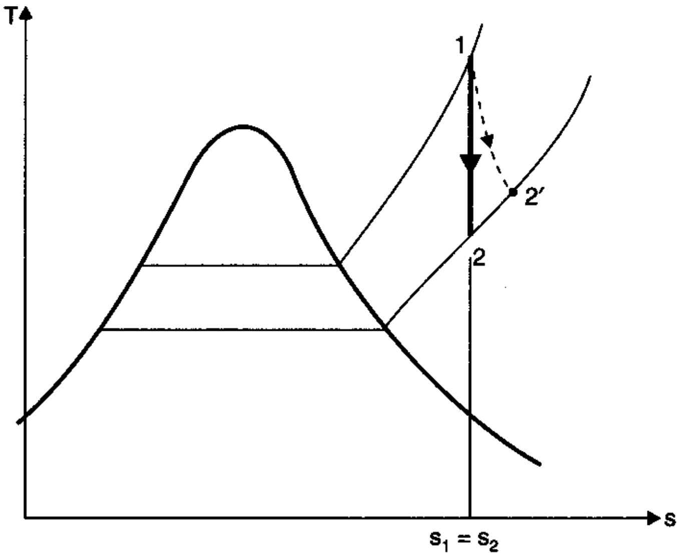


Fig. 6.14

(*i*) **Isentropic efficiency :**

$$\eta_{isen.} = \frac{\text{Actual work output}}{\text{Isentropic work}}$$

$$= \frac{h_1 - h_2'}{h_1 - h_2} = \frac{3247.6 - 2964.2}{3247.6 - 2840.8}$$

$$= \frac{283.4}{406.8} = \mathbf{0.6966} \text{ or } \mathbf{69.66\%}. \quad \textbf{(Ans.)}$$

(*ii*) **Loss of availability :**

Loss of availability $= b_1 - b_2$

$= h_1 - h_2' + T_0 (s_2' - s_1')$

$= 3247.6 - 2964.2 + 293 (7.379 - 7.127)$

$= 283.4 + 73.83 =$ **357.23 kJ/kg. (Ans.)**

(*iii*) **Effectiveness :**

Effectiveness, $\epsilon = \dfrac{W}{b_1 - b_2'} = \dfrac{h_1 - h_2'}{b_1 - b_2'}$

$$= \frac{3247.6 - 2964.2}{357.9} = \mathbf{0.7918 \text{ or } 79.18\%}. \quad \textbf{(Ans.)}$$

HIGHLIGHTS

1. '*Available energy*' is the maximum portion of the energy which could be converted into useful work by ideal processes which reduce the system to a dead state.
2. The theoretical maximum amount of work which can be obtained from a system at any state p_1 and T_1 when operating with a reservoir at the constant pressure and temperature p_0 and T_0 is called '*availability*'.

3. Energy is said to be *degraded* each time it flows through a finite temperature difference. That is, why the second law of thermodynamics is sometimes called the *law of the degradation of energy*, and energy is said to *'run down hill'*.
4. In non-flow systems :

   Maximum work available,

$$W_{max} = (u_1 - u_0) - T_0(s_1 - s_0) - p_0(v_0 - v_1)$$
$$= (u_1 + p_0v_1 - T_0s_1) - (u_0 + p_0v_0 - T_0s_0)$$
$$= a_1 - a_0 \quad \text{...per unit mass}$$

   The property $a = u + p_0v - T_0s$ is called the *non-flow availability function*.
5. In steady-flow systems :

   Maximum work available,

$$W_{max} = (h_1 - T_0s_1) - (h_0 - T_0s_0)$$
$$= b - b_0 \quad \text{...per unit mass}$$

   The property, $b = h - T_0s$ is called the *steady-flow availability function*.
6. It may be noted that Gibb's function $g = (h - Ts)$ is a property of the system where availability function $a = u + p_0v - T_0s$ is a composite property of the system and surroundings.

   Again,

$$a = u + p_0v - T_0s$$
$$b = u + pv - T_0s$$
$$g = u + pv - Ts$$

   When state 1 proceeds to dead state (zero state)

$$a = b = g.$$

7. The actual work which a system does is always less than the idealized reversible work, and the difference between the two is called the *irreversibility of the process*. This is also sometimes referred to as *degradation* or *dissipation*.

   Effectiveness is defined as the ratio of actual useful work to the maximum useful work.

OBJECTIVE TYPE QUESTIONS

Choose the correct answer :

1. Gibb's function is expressed as
   (a) $(u + pv - Ts)$ (b) $(u + pv - Tds)$
   (c) $(u + pdv - Tds)$ (d) $(u + pv - sdT)$.
2. Availability function is expressed as
   (a) $a = (u + p_0v - T_0s)$ (b) $a = (u + p_0dv + T_0ds)$
   (c) $a = (du + p_0dv - T_0ds)$ (d) $a = (u + p_0v + T_0s)$.
3. To increase work capacity of energy transferred by heat transfer from high temperature to low temperature
   (a) lower temperature should be lowered keeping temperature difference same
   (b) higher temperature should be increased keeping temperature difference same
   (c) temperature difference should be increased (d) temperature difference should be decreased.
4. Helmholtz function is expressed as
   (a) $(u - Ts)$ (b) $(h - Ts)$
   (c) $(- sdT + vdp)$ (d) $(u + pv)$.
5. If a heat source at temperature T_1 transfers heat to a system at temperature $T_2 (T_1 > T_2)$, state which of the following statements is *not true* ?
   (a) Δ_{system} decreases (b) Δ_{source} decreases
   (c) $(\Delta_{system} + \Delta_{source})$ decreases (d) $(\Delta_{system} + \Delta_{source})$ increases.

Answers

1. (*a*)	2. (*a*)	3. (*d*)	4. (*a*)	5. (*d*).

THEORETICAL QUESTIONS

1. Explain the concept of available and unavailable energy. When does the system become dead ?
2. Define the term 'availability'.
3. Is the availability function same for a non-flow and a flow process ?
4. Define availability function and find the relationship between availability function and change in availability.
5. How are the concepts of entropy and unavailable energy related to each other ?
6. Derive an expression for availability in non-flow systems.
7. Derive an expression for availability in steady flow systems.
8. Differentiate between availability function and Gibb's energy function.
9. Derive an expression for decrease in available energy when heat is transferred through a finite temperature difference.
10. Derive a general expression for irreversibility in (*i*) non-flow process, (*ii*) steady flow process.
11. What is the effectiveness of a system and how does it differ from efficiency ?

UNSOLVED EXAMPLES

1. A system receives 10000 kJ of heat at 500 K from a source at 1000 K. The temperature of the surroundings is 300 K. Assuming that the temperature of the system and source remains constant during heat transfer, find :

   (*i*) The entropy production due to above mentioned heat transfer ;

   (*ii*) Decrease in available energy. **[Ans.** (*i*) 10 kJ/K ; (*ii*) 3000 kJ]
2. In a power station, saturated steam is generated at 252°C by transferring heat from the hot gases generated in the combustion chamber. The gases are cooled from 1100°C to 550°C during transferring the heat for steam generation. Determine the increase in total entropy of the combined system of gas and steam and increase in unavailable energy on the basis of one kg of steam generated. Assume water enters the boiler at saturated condition and leaves as saturated steam. **[Ans.** 1.99 kJ/K ; 597 kJ/kg of steam formed]
3. Air at 15°C is to be heated to 40°C by mixing it in steady flow with a quantity of air at 90°C. Assuming that the mixing process is adiabatic and neglecting changes in kinetic and potential energy, calculate the ratio of the mass flow of air initially at 90°C to that initially at 15°C. Calculate also the effectiveness of the heating process, if the atmospheric temperature is 15°C. **[Ans.** 0.5, 0.327 or 32.7%]
4. A liquid of specific heat 6.3 kJ/kg K is heated at approximately constant pressure from 15°C to 70°C by passing it through tubes which are immersed in a furnace. The furnace temperature is constant at 1400°C. Calculate the effectiveness of the heating process when the atmospheric temperature is 10°C. **[Ans.** 0.121 or 12.1%]
5. 500 kJ of heat from an infinite source at 1000 K is supplied to 2 kg of gas initially at 2 bar and 350 K in a closed tank. Find the loss in available energy due to above heat transfer. Take : c_v (gas) = 0.8 kJ/kg K and surrounding temperature = 300 K. **[Ans.** 157.5 kJ]
6. In an heat exchanger of parallel flow type, water enters at 60°C and leaves at 80°C while oil of specific gravity 0.8 enters at 250°C and leaves at 100°C. The specific heat of oil is 2.5 kJ/kg K and surrounding temperature is 300 K. Determine the loss in availability on the basis of one kg of oil flow per second. **[Ans.** – 59.9 kJ]
7. 1 kg of ice at 0°C is mixed with 10 kg of water at 30°C. Determine the net increase in the entropy and unavailable energy when the system reaches common temperature. Assume that surrounding temperature is 10°C. Take, specific heat of water = 4.18 kJ/kg K ; specific heat of ice = 2.1 kJ/kg K ; latent heat of ice = 333.5 kJ/kg. **[Ans.** 0.114 kJ/K, 32.30 kJ]

8. 1000 kJ of heat leaves hot gases at 1400°C from a fire box of a boiler and goes to steam at 250°C. Atmospheric temperature is 20°C. Divide the energy into available and unavailable portions :
   (*i*) As it leaves the hot gases.
   (*ii*) As it enters the steam. **[Ans.** (*i*) 825 kJ, 175 kJ ; (*ii*) 440 kJ, 580 kJ]
9. In a certain process, a vapour, while condensing at 420°C, transfers heat to water evaporating at 250°C. The resulting steam is used in a power cycle which rejects heat at 35°C. What is the fraction of the available energy in the heat transferred from the process vapour at 420°C that is lost due to the irreversible heat transfer at 250°C. **[Ans.** 0.26]
10. In a steam boiler, hot gases from a fire transfer heat to water which vapourizes at constant temperature. In certain case, the gases are cooled from 1100°C to 550°C while the water evaporates at 220°C. The specific heat of gases is 1.005 kJ/kg K, and the latent heat of water at 220°C is 1858.5 kJ/kg. All the heat transferred from the gases goes to the water. How much does the total entropy of the combined system of gas and water increase as a result of irreversible heat transfer ? Obtain the result on the basis of 1 kg of water evaporated. If the temperature of the surroundings is 30°C find the increase in unavailable energy due to irreversible heat transfer. **[Ans.** 2.045 kJ/K, 620 kJ]
11. Calculate the unavailable energy in 40 kg of water at 75°C with respect to the surroundings at 5°C, the pressure being 1 atmosphere. **[Ans.** 10420 kJ]
12. Calculate the decrease in available energy when 25 kg of water at 95°C mixes with 35 kg of water at 35°C, the pressure being taken as constant and the temperature of the surroundings being 15°C.
    Take c_p of water = 4.18 kJ/kg K. **[Ans.** 281.81 kJ]
13. 2 kg of air at 5 bar, 80°C expands adiabatically in a closed system until its volume is doubled and its temperature becomes equal to that of the surroundings which is at 1 bar, 5°C. For this process, determine :
    (*i*) The maximum work ;
    (*ii*) The change in availability ;
    (*iii*) The irreversibility.
    For air take : $c_v = 0.718$ kJ/kg K, $u = c_vT$, where c_v is constant and $pV = mRT$, where p is in bar, V volume in m^3, m mass in kg, R is constant equal to 0.287 kJ/kg K, and T temperature in K.
    [Ans. (*i*) 122.72 kJ ; (*ii*) 82.2 kJ ; (*iii*) 15.2 kJ]
14. One kg of air at a pressure p, and temperature 900 K is mixed with 1 kg of air at the same pressure and 500 K.
    Determine the loss in availability if the surrounding temperature is 300 K. **[Ans.** 54 kJ]
15. 10 kg of water is heated in an insulated tank by a churning process from 300 K to 350 K. Determine the loss in availability for the process if the surrounding temperature is 300 K. **[Ans.** 1968 kJ]
16. A closed system contains 10 kg of air at 600 K and 5 bar. Determine the availability of the system if the surrounding pressure and temperature are 1 bar and 300 K respectively.
    If the air is cooled at constant pressure to the atmospheric temperature, determine the availability and effectiveness. **[Ans.** 1464 kJ ; 921 kJ ; 0.63]
17. In a turbine air expands from 5 bar, 520°C to 1 bar, 300°C. During expansion 10 kJ/kg of heat is lost to the surroundings which is at 0.98 bar, 20°C. Neglecting kinetic and potential energy changes, determine per kg of air :
    (*i*) The decrease in availability ;
    (*ii*) The maximum work ;
    (*iii*) The irreversibility.
    For air take : $c_p = 1.005$ kJ/kg K ; $h = c_pT$, where c_p is constant.
    [Ans. (*i*) 260.7 kJ/kg ; (*ii*) 260.7 kJ/kg ; (*iii*) 49.6 kJ/kg]
18. A centrifugal air compressor compresses air at the rate of 20 kg/min from 1 bar to 2 bar. The temperature increases from 20°C to 120°C during the compression. Determine actual and minimum power required to run the compressor. The surrounding air temperature is 20°C.
    Neglect the heat interaction between the compressor and surroundings and changes in potential and kinetic energy. **[Ans.** 24.2 kW]

19. 1 kg of air is compressed polytropically from 1 bar and 300 K to 7 bar and 380 K. Determine the irreversibility and effectiveness, assuming temperature and pressure as 300 K and 1 bar.

Take for air : $c_p = 1.005$ kJ/kg K, $c_p = 0.718$ kJ/kg K, $R = 0.287$ kJ/kg K. [**Ans.** 1.25 kJ ; 0.924]

20. The moment of inertia of a flywheel is 0.54 kg-m^2 and it rotates at a speed of 3000 r.p.m. in a large heat insulated system, the temperature of which is 15°C. If the kinetic energy of the flywheel is dissipated as frictional heat at the shaft bearings which have a water equivalent of 2 kg, find the rise in the temperature of the bearings when the flywheel has come to rest.

Calculate the greatest possible amount of the above heat which may be returned to the flywheel as high-grade energy, showing how much of the original kinetic energy is now unavailable. What would be the final r.p.m. of the flywheel, if it is set in motion with this available energy ?

[**Ans.** 3.19°C ; 0.1459 kJ ; 222 r.p.m.]

21. In a steady flow air enters the system at a pressure of 10 bar and 200°C with a velocity of 100 m/s and leaves at 1.5 bar and 25°C with a velocity of 50 m/s. The temperature of the surroundings is 25°C and pressure is 1 bar. Determine reversible work and actual work assuming the process to be adiabatic.

Determine also the irreversibility and effectiveness of the system on the basis of one kg of air flow.

Take for air : $c_p = 1$ kJ/kg K ; $R = 287$ J/kg K. [**Ans.** 200.65 kJ ; 178.75 kJ/kg, 21.90 kJ/kg ; 0.894]

7

Thermodynamic Relations

7.1. General aspects. 7.2. Fundamentals of partial differentiation. 7.3. Some general thermodynamic relations. 7.4. Entropy equations (*Tds* equations). 7.5. Equations for internal energy and enthalpy. 7.6. Measurable quantities : Equation of state, co-efficient of expansion and compressibility, specific heats, Joule-Thomson co-efficient 7.7. Clausius-Claperyon equation—Highlights—Objective Type Questions—Exercises.

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 :

$$f(x, y, z) = 0 \qquad ...(i)$$

$$x = x(y, z) \qquad ...(ii)$$

$$y = y(x, z) \qquad ...(iii)$$

$$z = z(x, y) \qquad ...(iv)$$

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

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

Then the differential of the dependent variable x is given by

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

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

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

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

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

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

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

then from these two relations, we have

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

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

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

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

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

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

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

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

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

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

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,

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

Combining these equations, we get

$$Tds = du + pdv$$

or

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

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,

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

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

Gibb's free energy function,

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

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 :

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

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

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

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

Also,

$$\boxed{\begin{aligned}\left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial p}{\partial s}\right)_v & \text{...(7.18)}\\ \left(\frac{\partial T}{\partial p}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_p & \text{...(7.19)}\\ \left(\frac{\partial p}{\partial T}\right)_v &= \left(\frac{\partial s}{\partial v}\right)_T & \text{...(7.20)}\\ \left(\frac{\partial v}{\partial T}\right)_p &= -\left(\frac{\partial s}{\partial p}\right)_T & \text{...(7.21)}\end{aligned}}$$

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

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

But for a reversible constant volume change

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

or

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

But,

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

[Maxwell's eqn. (7.20)]

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

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

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

Similarly, writing

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

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

where $$c_p = T\left(\frac{\partial s}{\partial T}\right)_p \qquad \text{...(7.26)}$$

Also $$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \qquad \text{[Maxwell's eqn. (7.21)]}$$

whence, substituting in eqn. (7.25)

$$\boxed{Tds = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp} \qquad \text{...(7.27)}$$

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 $u = f(T, v)$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = c_v\, dT + \left(\frac{\partial u}{\partial v}\right)_T dv \qquad \text{...(7.28)}$$

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

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

or $$\left(\frac{\partial u}{\partial v}\right)_T = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial v}\right)_T + \left(\frac{\partial u}{\partial v}\right)_s$$

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

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

This is sometimes called the **energy equation.**

From equation (7.28), we get

$$\boxed{du = c_v dT + \left\{T\left(\frac{\partial p}{\partial T}\right)_v - p\right\} dv} \qquad \text{...(7.30)}$$

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

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

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

$$= c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp \qquad \text{...(7.31)}$$

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

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

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

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

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

From eqn. (7.31), we get

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

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

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

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 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 $\left(\frac{\partial v}{\partial T}\right)_p$. 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,

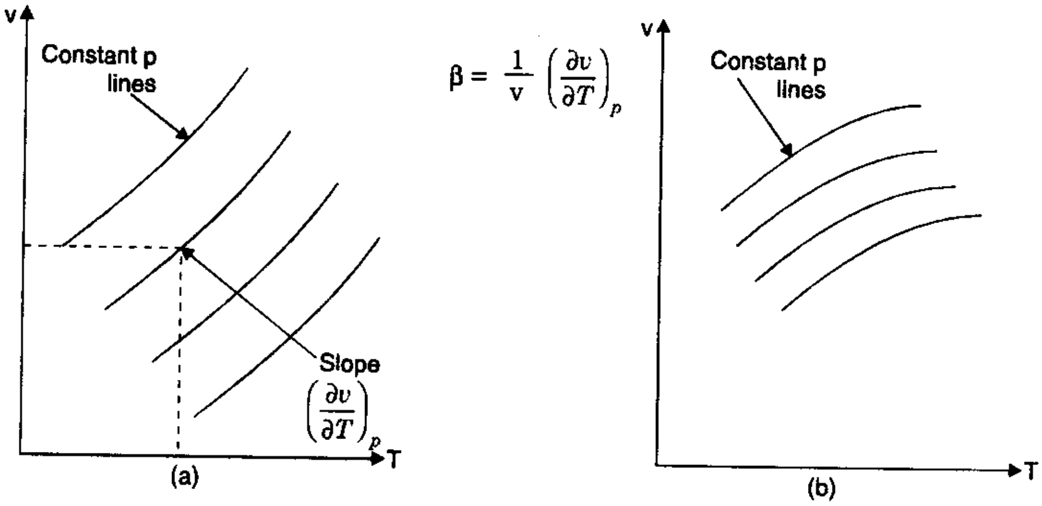


Fig. 7.1. Determination of co-efficient of expansion from *p-v-T* data.

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

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

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

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 $\left(\frac{\partial v}{\partial p}\right)_T$. 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

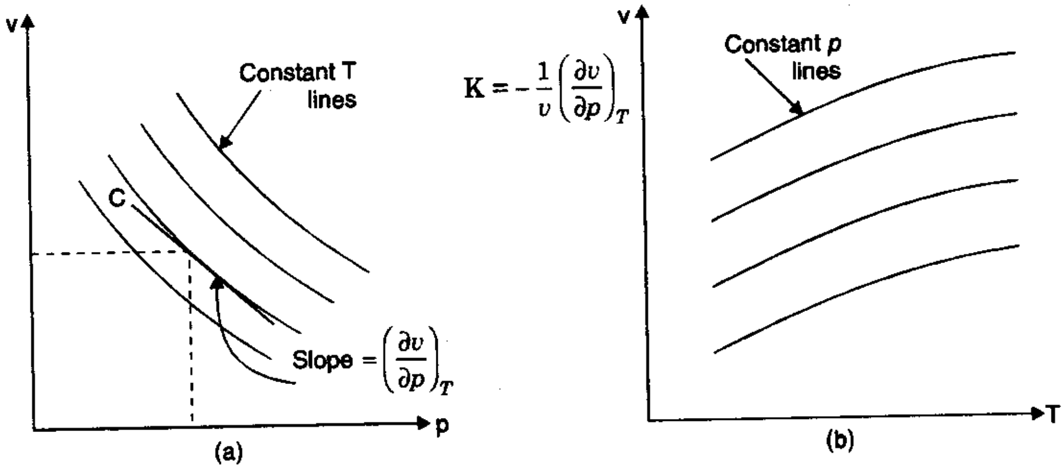


Fig. 7.2. Determination of compressibility from p-T data.

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

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.*,

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

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

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

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.

Consider the first quantity $\left(\frac{\partial u}{\partial T}\right)_v$. 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 : $\left(\frac{\Delta u}{\Delta T}\right)_v = \left(\frac{Q}{\Delta T}\right)_v$. 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 $\left(\frac{\partial u}{\partial T}\right)_v$, and the *true specific heat at constant volume* is defined by $c_v = \left(\frac{\partial u}{\partial T}\right)_v$. 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, $\left(\frac{\Delta h}{\Delta T}\right)_p = \left(\frac{Q}{\Delta T}\right)_p$ 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 $c_p = \left(\frac{\partial h}{\partial T}\right)_p$. 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

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

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

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

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

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

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

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

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

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

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

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

Alternative Expressions for Internal Energy and Enthalpy

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

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

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

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

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

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

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

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

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

(*ii*) Since $$u = h - pv$$

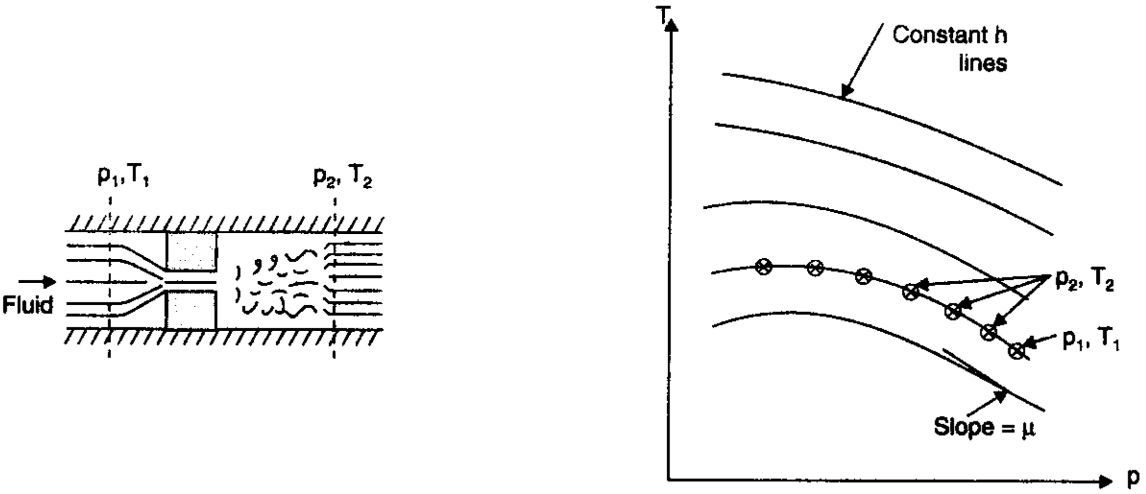
or $$\left(\frac{\partial u}{\partial p}\right)_T = \left(\frac{\partial h}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T - v$$
$$= v - v\beta T + pKv - v$$

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 $\left(\frac{\partial T}{\partial p}\right)_h$. 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.



(*a*) (*b*)

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

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

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

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

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

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

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

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

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

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

Let $h = f(p, T)$

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

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

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

For throttling process, $dh = 0$

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

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

$\left(\frac{\partial h}{\partial p}\right)_T$ 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.

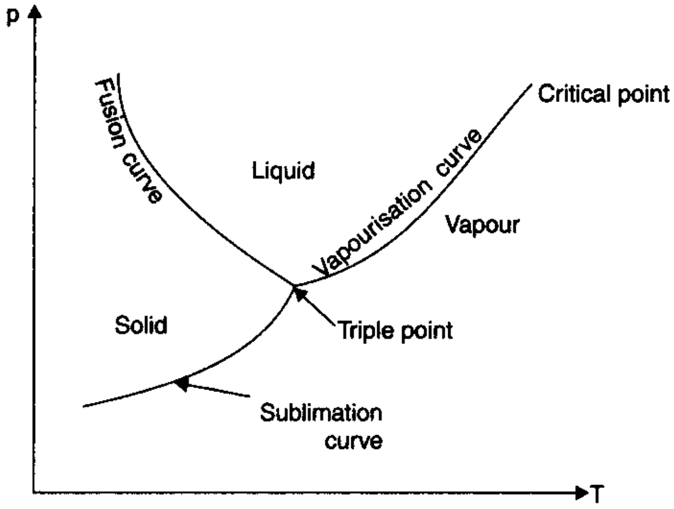


Fig. 7.4. p-T diagram.

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, $$s_g - s_f = s_{fg} = \frac{h_{fg}}{T}$$

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

where s_{fg} = Increase in specific entropy,

v_{fg} = Increase in specific volume, and

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

$$\therefore \qquad \frac{dp}{dT} = \frac{s_g - s_f}{v_g - v_f} = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{T \,.v_{fg}} \qquad ...(7.50)$$

This is known as **Clausius-Claperyon or Claperyon equation** for *evaporation of liquids*. The derivative $\frac{dp}{dT}$ 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

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

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

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

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

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

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 :

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

As per second law of thermodynamics,

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

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

$$Tds = du + pdv$$

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

$\therefore \quad dh = du + pdv + vdp = Tds + vdp$

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

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

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

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

$\therefore$ The above equation becomes,

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

or

$$= pv\beta + v\beta\left(\frac{\partial u}{\partial v}\right)_T$$ **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 $\left(\frac{\partial u}{\partial T}\right)_p$. 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

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

or

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

Also,

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

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

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

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

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

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

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

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

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

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

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

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

(*ii*) **Change in enthalpy :**

The change in enthalpy is given by

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

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

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

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

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

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

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

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

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

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

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

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

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

For Van der Waals equation

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

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

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

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

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

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

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

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

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

(*iii*) **Change in entropy :**

The change in entropy is given by

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

For Van der Waals equation,

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

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

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

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

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.

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

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

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

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

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

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

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

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 $$p = \frac{RT}{v} \qquad \text{...(Given)}$$

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

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

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

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

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

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

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

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

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

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

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

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 :

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

(1) Using the cyclic relation

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

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

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

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

Using the chain rule,

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

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

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

This is *Maxwell Third relation.*

(2) Again using the cyclic relation

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

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

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

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

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

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

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

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

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

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

This is *Maxwell fourth relation.*

Example 7.9. *Derive the following relations :*

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

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

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

g = *Gibbs function (per unit mass).*

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

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

Also $da = -pdv - sdT$

Comparing the co-efficients of dT, we get

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

Also $a = u - Ts$

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

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

(*ii*) Let $g = f(p, T)$

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

Also $dg = vdp - sdT$

Comparing the co-efficients of dT, we get

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

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

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

(*iii*) From eqn. (7.23), we have

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

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

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

From eqns. (*i*) and (*ii*), we get

$$c_v = -T\left(\frac{\partial^2 a}{\partial T^2}\right)_v . \quad \textbf{(Ans.)}$$

(*iv*) From eqn. (7.26), we have

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

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

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

From eqns. (*i*) and (*ii*), we get

$$c_p = -\mathrm{T}\left(\frac{\partial^2 g}{\partial T^2}\right)_p . \quad \textbf{(Ans.)}$$

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

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT - \left(\frac{\partial v}{\partial T}\right)_p . dp \qquad ...(i)$$

The enthalpy is given by

$$dh = c_p dT = Tds + vdp$$

Dividing by dT at constant pressure

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

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

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

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

Substituting this in eqn. (*ii*), we get

$$\boxed{ds = c_p \frac{dT}{T} - \beta v dp} \quad \textbf{(Ans.)}$$

Example 7.11. *Derive the following relations :*

$$(i)\ \left(\frac{\partial T}{\partial p}\right)_s = \frac{Tv\beta}{c_p} \qquad (ii)\ \left(\frac{\partial T}{\partial v}\right)_s = -\frac{T\beta}{c_v K}.$$

where β = *Co-efficient of cubical expansion, and*

K = *Isothermal compressibility.*

Solution. (*i*) Using the Maxwell relation (7.19), we have

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

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

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

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{\beta v T}{c_p}$$

i.e., $\left(\frac{\partial T}{\partial p}\right)_s = \frac{Tv\beta}{c_p}$. **(Ans.)**

(*ii*) Using the Maxwell relation (7.18)

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

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

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

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

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

i.e., $\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{1}{-vK}\right)\beta v = \frac{\beta}{K}$

$$\therefore \qquad \left(\frac{\partial T}{\partial v}\right)_s = \frac{-T\beta}{c_v K}. \quad \textbf{(Ans.)}$$

☞**Example 7.12.** *Derive the third Tds equation*

$$Tds = c_v \left(\frac{\partial T}{\partial p}\right)_v dp + c_p \left(\frac{\partial T}{\partial v}\right)_p dv$$

and also show that this may be written as :

$$Tds = \frac{c_v}{\beta} Kdp + \frac{c_p}{\beta v} dv.$$

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

Then

$$ds = \left(\frac{\partial s}{\partial p}\right)_v dp + \left(\frac{\partial s}{\partial v}\right)_p dv$$

or

$$Tds = T\left(\frac{\partial s}{\partial p}\right)_v dp + T\left(\frac{\partial s}{\partial v}\right)_p dv$$

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

But

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T} \quad \text{and} \quad \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$$

Hence

$$\mathbf{Tds} = \mathbf{c_v}\left(\frac{\partial \mathbf{T}}{\partial \mathbf{p}}\right)_{\mathbf{v}} \mathbf{dp} + \mathbf{c_p}\left(\frac{\partial \mathbf{T}}{\partial \mathbf{v}}\right)_{\mathbf{p}} \mathbf{dv} \qquad \textbf{...Proved.}$$

Also

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

and

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

Substituting these values in the above *Tds* equation, we get

$$\mathbf{Tds} = \frac{\mathbf{c_v K}}{\beta} \mathbf{dp} + \frac{\mathbf{c_p}}{\beta \mathbf{v}} \mathbf{dv} \qquad \textbf{...Proved.}$$

Example 7.13. *Using Maxwell relation derive the following Tds equation*

$$Tds = c_p\, dT - T\left(\frac{\partial v}{\partial T}\right)_p dp. \qquad \textbf{(U.P.S.C. 1988)}$$

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

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

where $c_p = T\left(\frac{\partial s}{\partial T}\right)_p$

Also,

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

Substituting these in eqn. *(i)*, we get

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

Example 7.14. *Derive the following relations*

$$\left(\frac{\partial T}{\partial v}\right)_u = \frac{T\left(\frac{\partial p}{\partial T}\right)_v - p}{c_v}.$$

Solution. $\left(\frac{\partial T}{\partial v}\right)_u$ can be expressed as follows :

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

Also $\qquad Tds = du + pdv$

or $\qquad du = Tds - pdv$

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

or $\qquad \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - p \qquad$ ...(*i*)

or $\qquad \left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v \qquad$ ...(*ii*)

Dividing eqn. (*i*) by eqn. (*ii*), we get

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

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

and $\qquad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad$ ... Maxwell relation

Substituting these value in eqn. (*iii*), we get

$$\left(\frac{\partial T}{\partial v}\right)_u = \frac{T\left(\frac{\partial p}{\partial T}\right)_v - p}{c_v}$$ ...**Proved.**

☞**Example 7.15.** *Prove that for any fluid*

(*i*) $\left(\frac{\partial h}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T + T\left(\frac{\partial p}{\partial T}\right)_v \qquad$ (*ii*) $\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$

Show that for a fluid obeying van der Waal's equation

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

where R, a and b are constants

$$h \text{ (enthalpy)} = \frac{RTb}{v-b} - \frac{2a}{v} + f(T)$$

where f(T) is arbitrary.

Solution. We know that

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

Also $$dh = Tds + vdp = T\left[\frac{c_v}{T}dT + \left(\frac{\partial p}{\partial T}\right)_v dv\right] + vdp$$

i.e., $$dh = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v + dv + vdp$$

Putting $dT = 0$, we get

$$\left(\frac{\partial \mathbf{h}}{\partial \mathbf{v}}\right)_\mathbf{T} = \mathbf{T}\left(\frac{\partial \mathbf{p}}{\partial \mathbf{T}}\right)_\mathbf{v} + \mathbf{v}\left(\frac{\partial \mathbf{p}}{\partial \mathbf{v}}\right)_\mathbf{T} \quad \textbf{...Proved.}$$

(*ii*) $$\left(\frac{\partial h}{\partial p}\right)_T = \left(\frac{\partial h}{\partial v}\right)_T\left(\frac{\partial v}{\partial p}\right)_T = \left[T\left(\frac{\partial p}{\partial T}\right)_v + v\left(\frac{\partial p}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial p}\right)_T$$

i.e., $$\left(\frac{\partial h}{\partial p}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial p}\right)_T + v \qquad ...(i)$$

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

∴ Eqn. (*i*) becomes

$$\left(\frac{\partial \mathbf{h}}{\partial \mathbf{p}}\right)_\mathbf{T} = \mathbf{v} - \mathbf{T}\left(\frac{\partial \mathbf{v}}{\partial \mathbf{T}}\right)_\mathbf{p} \quad \textbf{...Proved.}$$

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

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

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

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

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

$$= \frac{-RTv + RT(v-b)}{(v-b)^2} + \frac{2a}{v^2} = \frac{-RTv + RTv - RTb}{(v-b)^2} + \frac{2a}{v^2}$$

i.e., $$\left(\frac{\partial h}{\partial v}\right)_T = \frac{-RTb}{(v-b)^2} + \frac{2a}{v^2}$$

or $$\mathbf{h} = \frac{\mathbf{RTb}}{\mathbf{v-b}} - \frac{\mathbf{2a}}{\mathbf{v}} + \mathbf{f(T)} \quad \textbf{...Proved.}$$

This shows h depends on T and v.

Example 7.16. *Derive the following relations :*

(*i*) $\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p = -c_p\left(\frac{\partial T}{\partial p}\right)_h$ (*ii*) $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$

With the aid of eqn. (ii) show that

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

The quantity $c_p\left(\frac{\partial T}{\partial p}\right)_h$ *is known as Joule-Thomson cooling effect. Show that this cooling effect for a gas obeying the equation of state* $(v - b) = \frac{RT}{p} - \frac{C}{T^2}$ *is equal to* $\left(\frac{3C}{T^2}\right) - b$.

Solution. We know that

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

Also $$\mu = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \qquad \text{...[Eqn. (7.46)]}$$

$\therefore$ $$\left(\frac{\partial h}{\partial p}\right)_T = -\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = v - T\left(\frac{\partial v}{\partial T}\right)_p \qquad \text{... \textbf{Proved.}}$$

Also $$\mu = \left(\frac{\partial T}{\partial p}\right)_h$$

$\therefore$ $$\left(\frac{\partial h}{\partial p}\right)_T = -c_p\left(\frac{\partial T}{\partial p}\right)_h.$$

(*ii*) Let $u = f(T, v)$

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

$$= c_v\, dT + \left(\frac{\partial u}{\partial v}\right)_T dv \qquad \text{...(i)}$$

Also $du = Tds - pdv$

Substituting the value of Tds [from eqn. 7.24], we get

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

$$= c_v\, dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv \qquad \text{...(ii)}$$

From (*i*) and (*ii*), we get

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

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

or $$\left(\frac{\partial u}{\partial p}\right)_T = \left(\frac{\partial v}{\partial p}\right)_T\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]$$

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

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

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

Also $\left(\frac{\partial u}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T$ ...Already proved.

and $\mu = \frac{1}{c_p}\left[T\left(\frac{\partial u}{\partial T}\right)_p - v\right]$ ...[Eqn. (7.46)]

Now $v - b = \frac{RT}{p} - \frac{C}{T^2}$ ...[*Given*]

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + \frac{2C}{T^3}$$

Substituting this value in the expression of μ above, we get

$$\mu = \frac{1}{c_p}\left[T\left(\frac{R}{p} + \frac{2C}{T^3}\right) - v\right]$$

or $\mu c_p = T\left(\frac{R}{p} + \frac{2C}{T^3}\right) - \frac{RT}{p} + \frac{C}{T^2} - b = \frac{3C}{T^2} - b$

or $c_p\left(\frac{\partial T}{\partial p}\right)_h = \frac{3C}{T^2} - b$ ...**Proved.**

Example 7.17. *The pressure on the block of copper of 1 kg is increased from 20 bar to 800 bar in a reversible process maintaining the temperature constant at 15°C. Determine the following :*

(*i*) *Work done on the copper during the process,*

(*ii*) *Change in entropy,* (*iii*) *The heat transfer,*

(*iv*) *Change in internal energy, and* (*v*) $(c_p - c_v)$ *for this change of state.*

Given : β *(Volume expansivity* $= 5 \times 10^{-5}$ */K, K (thermal compressibility)* $= 8.6 \times 10^{-12}$ m^2/N *and v (specific volume)* $= 0.114 \times 10^{-3}$ m^3/kg.

Solution. (*i*) **Work done on the copper, W :**

Work done during isothermal compression is given by

$$W = \int_1^2 p\,dv$$

The isothermal compressibility is given by

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

$\therefore$ $dv = -K(v.dp)_T$

$\therefore$ $W = -\int_1^2 pKv.dp = -vK\int_1^2 p\,dp$

Since v and K remain essentially constant

$\therefore$ $W = -\frac{vK}{2}(p_2^2 - p_1^2)$

$$= -\frac{0.114 \times 10^{-3} \times 8.6 \times 10^{-12}}{2}\left[(800 \times 10^5)^2 - (20 \times 10^5)^2\right]$$

$$= -\frac{0.114 \times 8.6 \times 10^{-15}}{2} \times 10^{10}\,[(800)^2 - (20)^2]$$

$$= -\frac{0.114 \times 8.6 \times 10^{-5}}{2}\,(640000 - 400) = -\,\mathbf{3.135\ J/kg.} \quad \textbf{(Ans.)}$$

The *negative sign indicates that the work is done on the copper block.*

(*ii*) **Change in entropy :**

The change in entropy can be found by using the following Maxwell relation :

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p = -\frac{v}{v}\left(\frac{\partial v}{\partial T}\right)_p = -v\beta \text{ as } \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \beta$$

$$\therefore \quad (ds)_T = -v\beta\,(dp)_T$$

Integrating the above equation, assuming v and β remaining constant, we get

$$\mathbf{s_2 - s_1} = -v\beta\,(p_2 - p_1)_T$$

$$= -0.114 \times 10^{-3} \times 5 \times 10^{-5}\,[800 \times 10^5 - 20 \times 10^5]$$

$$= -0.114 \times 10^{-3} \times 5\,(800 - 20) = -\,\mathbf{0.446\ J/kg\ K.} \quad \textbf{(Ans.)}$$

(*iii*) **The heat transfer, Q :**

For a reversible isothermal process, the heat transfer is given by :

$$\mathbf{Q} = T(s_2 - s_1) = (15 + 273)(-0.4446) = -\,\mathbf{128\ J/kg.} \quad \textbf{(Ans.)}$$

(*iv*) **Change in internal energy, du :**

The change in internal energy is given by :

$$\mathbf{du} = Q - W$$

$$= -128 - (-3.135) = -\,\mathbf{124.8\ J/kg.} \quad \textbf{(Ans.)}$$

(*v*) $\mathbf{c_p - c_v}$ **:**

The difference between the specific heat is given by :

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

$$= \frac{(5 \times 10^{-5})^2 \times (15 + 273) \times 0.114 \times 10^{-3}}{8.6 \times 10^{-12}} = \mathbf{9.54\ J/kg\ K.} \quad \textbf{(Ans.)}$$

Example 7.18. *Using Clausius-Claperyon's equation, estimate the enthalpy of vapourisation. The following data is given :*

At 200°C : $v_g = 0.1274\ m^3/kg\ ;\ v_f = 0.001157\ m^3/kg\ ;\ \left(\frac{dp}{dT}\right) = 32\ kPa/K.$

Solution. Using the equation

$$\left(\frac{dp}{dT}\right) = \frac{h_{fg}}{T_s(v_g - v_f)}$$

where, h_{fg} = Enthalpy of vapourisation.

Substituting the various values, we get

$$32 \times 10^3 = \frac{h_{fg}}{(200 + 273)(0.1274 - 0.001157)}$$

$$\therefore \quad \mathbf{h_{fg}} = 32 \times 10^3\,(200 + 273)(0.1274 - 0.001157)\ J$$

$$= 1910.8 \times 10^3\ J/kg = \mathbf{1910.8\ kJ/kg.} \quad \textbf{(Ans.)}$$

Example 7.19. *An ice skate is able to glide over the ice because the skate blade exerts sufficient pressure on the ice that a thin layer of ice is melted. The skate blade then glides over this thin melted water layer. Determine the pressure an ice skate blade must exert to allow smooth ice skate at – 10°C.*

The following data is given for the range of temperatures and pressures involved :

$$h_{fg(ice)} = 334 \text{ kJ/kg} \; ; \; v_{liq.} = 1 \times 10 \text{ m}^3\text{/kg} \; ; \; v_{ice} = 1.01 \times 10^3 \text{ m}^3/\text{kg}.$$

Solution. Since it is a problem of phase change from solid to liquid, therefore, we can use Clausius-Claperyon equation given below :

$$\frac{dp}{dT} = \frac{h_{fg}}{v_{fg}} \cdot \frac{1}{T}$$

Multiplying both the sides by dT and integrating, we get

$$\int_{p_1}^{p_2} dp = \frac{h_{fg}}{v_{fg}} \int_{T_1}^{T_2} \frac{dT}{T}$$

or
$$(p_2 - p_1) = \frac{h_{fg}}{v_{fg}} \log_e \left(\frac{T_2}{T_1}\right) \qquad \text{...}(i)$$

But at $\quad p_1 = 1 \text{ atm.}, \; t_1 = 0°\text{C}$

Thus, $\quad p_1 = 1.013 \text{ bar}, \; T_1 = 0 + 273 = 273 \text{ K}$

$$p_2 = ?, \; T_2 = -10 + 273 = 263 \text{ K}$$

Substituting these values in eqn. (i), we get

$$(p_2 - 1.013 \times 10^5) = \frac{334 \times 10^3}{(1 - 1.01)} \times \log_e \left(\frac{263}{273}\right)$$

$$= \frac{334 \times 10^3}{0.01} \times \log_e \left(\frac{273}{263}\right) = 12.46 \times 10^5 \text{ N/m}^2$$

or
$$p_2 = 12.46 \times 10^5 + 1.013 \times 10^5$$

$$= 13.47 \times 10^5 \text{ N/m}^2 \text{ or } \mathbf{13.47 \text{ bar.}} \quad \textbf{(Ans.)}$$

This pressure is considerably high. It can be achieved with ice skate blade by having only a small portion of the blade surface in contact with the ice at any given time. If *the temperature drops lower than – 10°C, say – 15°C, then it is not possible to generate sufficient pressure to melt the ice and conventional ice skating will not be possible.*

Example 7.20. *For mercury, the following relation exists between saturation pressure (bar) and saturation temperature (K) :*

$$\log_{10} p = 7.0323 - 3276.6/T - 0.652 \log_{10} T$$

Calculate the specific volume v_g *of saturation mercury vapour at 0.1 bar.*

Given that the latent heat of vapourisation at 0.1 bar is 294.54 kJ/kg.

Neglect the specific volume of saturated mercury liquid.

Solution. Latent heat of vapourisation, h_{fg} = 294.54 kJ/kg (at 0.1 bar) ...(given)

Using Clausius-Claperyon equation

$$\frac{dp}{dT} = \frac{h_{fg}}{v_{fg}T} = \frac{h_{fg}}{(v_g - v_f)T} \qquad \text{...}(i)$$

Since v_f is neglected, therefore eqn. (i) becomes

$$\frac{dp}{dT} = \frac{h_{fg}}{v_g T}$$

Now, $\quad \log_{10} p = 7.0323 - \dfrac{3276.6}{T} - 0.652 \log_{10} T$