Often the pipe velocities in throttling are so low that the K.E. terms are also negligible. So

$$h_1 = h_2 \tag{5.16}$$

or the enthalpy of the fluid before throttling is equal to the enthalpy of the fluid after throttling.

5.4.3 Turbine and Compressor

Turbines and engines give positive power output, whereas compressors and pumps require power input.

For a turbine (Fig. 5.6) which is well insulated, the flow velocities are often small, and the K.E. terms can be neglected. The S.F.E.E. then becomes

$$h_1 = h_2 + \frac{\text{đ}W_x}{dm} \quad \text{or} \quad \frac{W_x}{m} = (h_1 - h_2)$$

It is seen that work is done by the fluid at the expense of its enthalpy.

Similarly, for an adiabatic pump or compressor, work is done upon the fluid and W is negative. So the S.F.E.E. becomes

$$h_1 = h_2 - \frac{W_x}{m} \quad \text{or} \quad \frac{W_x}{m} = h_2 - h_1$$

The enthalpy of the fluid increases by the amount of work input.

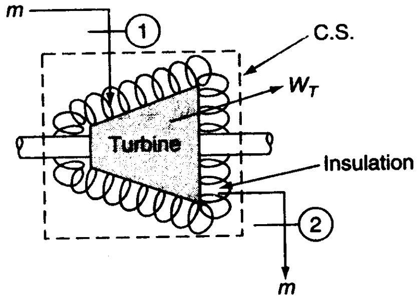


Fig. 5.6 *Flow through a turbine*

5.4.4 Heat Exchanger

A heat exchanger is a device in which heat is transferred from one fluid to another. Figure 5.7 shows a steam condenser, where steam condensers outside the tubes and cooling water flows through the tubes. The S.F.E.E. for the C.S. gives

$$w_c h_1 + w_s h_2 = w_c h_3 + w_s h_4 \quad \text{or} \quad w_s (h_2 - h_4) = w_c(h_3 - h_1)$$

Here the K.E. and P.E. terms are considered small, there is no external work done, and energy exchange in the form of heat is confined only between the two fluids, i.e., there is no external heat interaction or heat loss.

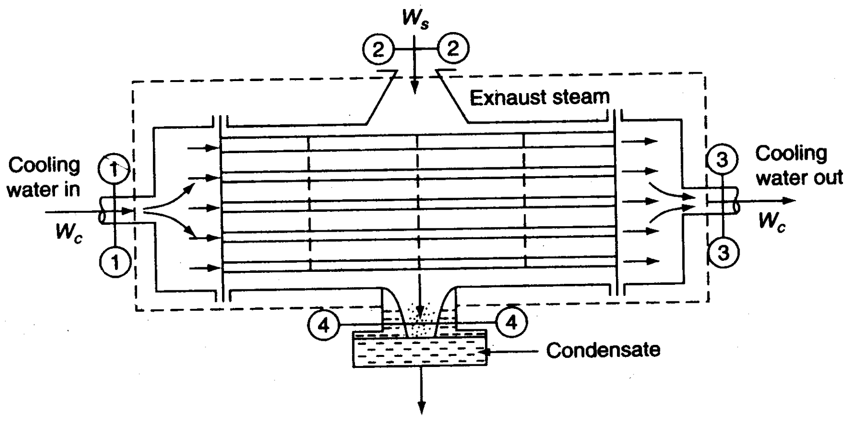


Fig. 5.7 *Steam condenser*

Figure 5.8 shows a steam desuperheater where the temperature of the superheated steam is reduced by spraying water. If w_1, w_2, and w_3 are the mass flow rates of the injected water, of the steam entering, and of the steam leaving, respectively, and h_1, h_2, and h_3 are the corresponding enthalpies, and if K.E. and P.E. terms are neglected as before, the S.F.E.E. becomes

$$w_1 h_1 + w_2 h_2 = w_3 h_3$$

and the mass balance gives

$$w_1 + w_2 = w_3$$

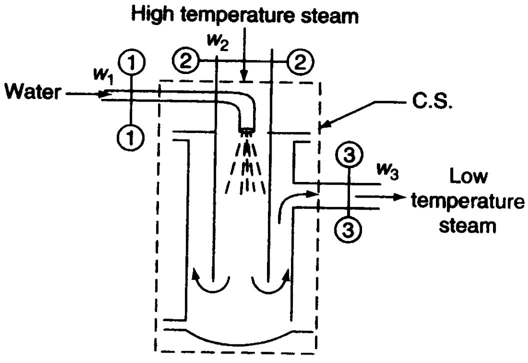


Fig. 5.8 *Steam desuperheater*

5.5 COMPARISON OF S.F.E.E. WITH EULER AND BERNOULLI EQUATIONS

The steady flow energy Eq. (5.8) can be written as

$$\frac{\text{đ}Q}{dm} = (h_2 - h_1) + \frac{\bar{V}_2^2 - \bar{V}_1^2}{2} + (Z_2 - Z_1)\,g + \frac{dW_x}{dm}$$

In the differential form the S.F.E.E. becomes

$$\text{đ}Q = dh + \bar{V}d\bar{V} + gdZ + dW_x \tag{5.17}$$

where $\text{đ}Q$ and $\text{đ}W_x$ refer to unit mass of the substance. Since $h = u + pv$ and $\text{đ}Q = \text{đ}u + pdv$ (for a quasi-static path involving only pdv-work), Eq. (5.17) can be written as

$$du + pdV = du + pdV + Vdp + VdV + gdZ + \text{đ}W_x$$

For an inviscid frictionless fluid flowing through a pipe

$$Vdp + VdV + gdZ = 0 \tag{5.18}$$

This is the *Euler equation*. If we integrate between two sections 1 and 2 of the pipe

$$\int_1^2 vdp + \int_1^2 VdV + \int_1^2 gdZ = 0$$

For an incompressible fluid, v = constant

$$\therefore \quad v(p_2 - p_1) + \frac{V_2^2}{2} - \frac{V_1^2}{1} + g(Z_2 - Z_1) = 0 \tag{5.19}$$

Since the specific volume v is the reciprocal of the density ρ, we have

$$\frac{p_1}{\rho} + \frac{V_1^2}{2} + Z_1 g = \frac{p_2}{\rho} + \frac{V_2^2}{2} + Z_2 g \tag{5.20}$$

or

$$\frac{p}{\rho} + \frac{V^2}{2} + Zg = \text{constant} \tag{5.21}$$

This is known as the *Bernoulli equation*, which is valid for an inviscid incompressible fluid. It can also be expressed in the following form

$$\Delta\left(pv + \frac{V^2}{2} + gZ\right) = 0 \tag{5.22}$$

where v is constant and Δ (...) means 'increase in ...

The S.F.E.E. as given by Eq. (5.18) or Eq. (5.17) can be written with $(u + pv)$ substituted for h, as follows:

$$Q - W_x = \Delta\left(u + pv + \frac{V^2}{2} + gZ\right) \tag{5.23}$$

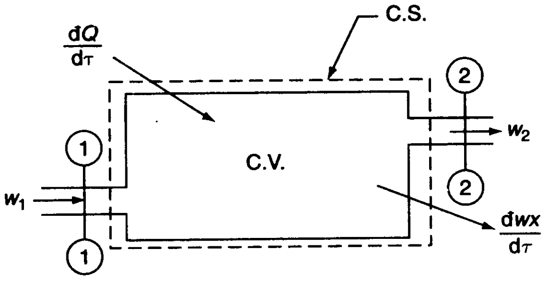
A comparison of Eqs (5.22) and (5.23) shows that they have several terms in common. However, while the Bernoulli equation is restricted to frictionless incompressible fluids, the S.F.E.E. is not, and is valid for viscous compressible fluids as well. The Bernoulli equation is, therefore, a special limiting case of the more general steady flow energy equation.

5.6 VARIABLE FLOW PROCESSES

Many flow processes, such as filling up and evacuating gas cylinders, are not steady. Such processes can be analyzed by the control volume technique. Consider a device through which a fluid is flowing under non-steady state conditions (Fig. 5.9). The rate at which the mass of fluid within the control volume is accumulated is equal to the net rate of mass flow across the control surface, as given below

$$\frac{dm_V}{d\tau} = w_1 - w_2 = \frac{dm_1}{d\tau} - \frac{dm_2}{d\tau} \tag{5.24}$$

where m_V is the mass of fluid within the control volume at any instant.



Variable flow process

Over any finite period of time

$$\Delta m_V = \Delta m_1 - \Delta m_2 \tag{5.25}$$

The rate of accumulation of energy within the control volume is equal to the net rate of energy flow across the control surface. If E_V is the energy of fluid within the control volume at any instant.

Rate of energy increase = Rate of energy inflow – Rate of energy outflow

$$\frac{dE_V}{d\tau} = w_1\left(h_1 + \frac{V_1^2}{2} + Z_1 g\right) + \frac{\text{đ}Q}{d\tau} - w_2\left(h_2 + \frac{V_2^2}{2} + Z_2 g\right) - \frac{\text{đ}W_x}{d\tau} \tag{5.26}$$

Now

$$E_V = \left(U + \frac{mV^2}{2} + mgZ\right)_V$$

where m is the mass of fluid in the control volume at any instant.

$$\therefore \quad \frac{dE_V}{d\tau} = \frac{d}{d\tau}\left(U + \frac{mV^2}{2} + mgZ\right)_V = \left(h_1 + \frac{V_1^2}{2} + Z_1 g\right)\frac{dm_1}{d\tau} + \frac{\text{đ}Q}{d\tau} - \left(h_2 + \frac{V_2^2}{2} + Z_2 g\right)\frac{dm_2}{d\tau} - \frac{\text{đ}W_x}{d\tau} \tag{5.27}$$

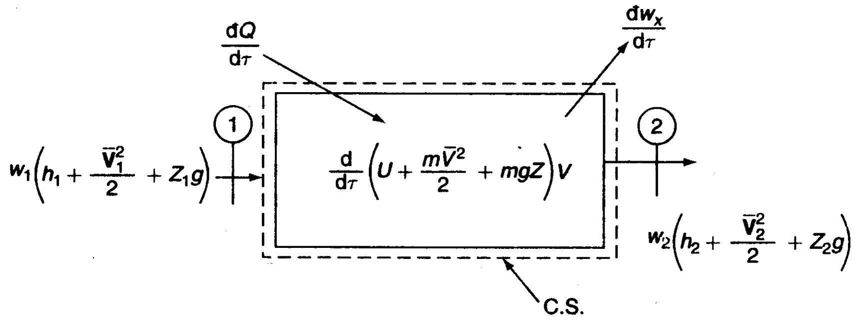


Fig. 5.10 *Energy fluxes in an unsteady system*

Figure 5.10 shows all these energy flux quantities. For any finite time interval, Eq. (5.27) becomes

$$\Delta E_V = Q - W_x + \int \left(h_1 + \frac{V_1^2}{2} + Z_1 g \right) dm_1 - \int \left(h_2 + \frac{V_2^2}{2} + Z_2 g \right) dm_2 \tag{5.28}$$

Equation (5.26) is the *general energy equation*. For steady flow,

$$\frac{dE_V}{d\tau} = 0,$$

and the equation reduces to Eq. (5.7). For a closed system $w_1 = 0$, $w_2 = 0$, then from Eq. (5.26),

$$\frac{dE_V}{d\tau} = \frac{đQ}{d\tau} - \frac{đW_x}{d\tau} \quad \text{or} \quad dE_V = đQ - đW_x \quad \text{or,} \quad đQ = dE + đW_x$$

as obtained earlier.

5.7 EXAMPLE OF A VARIABLE FLOW PROBLEM

Variable flow processes may be analyzed either by the system technique or the control volume technique, as illustrated below.

Consider a process in which a gas bottle is filled from a pipeline (Fig. 5.11). In the beginning the bottle contains gas of mass m_1 at state p_1, t_1, v_1, h_1 and u_1. The valve is opened and gas flows into the bottle till the mass of gas in the bottle is m_2 at state p_2, t_2, v_2, h_2 and u_2. The supply to the pipeline is very large so that the state of gas in the pipeline is constant at p_p, t_p, v_p, h_p, u_p, and V_p.

System Technique Assume an envelope (which is extensible) of gas in the pipeline and the tube which would eventually enter the bottle, as shown in Fig. 5.11.

Energy of the gas before filling

$$E_1 = m_1 u_1 + (m_2 - m_1) \left(\frac{V_p^2}{2} + u_p \right)$$

where $(m_2 - m_1)$ is the mass of gas in the pipeline and tube which would enter the bottle.

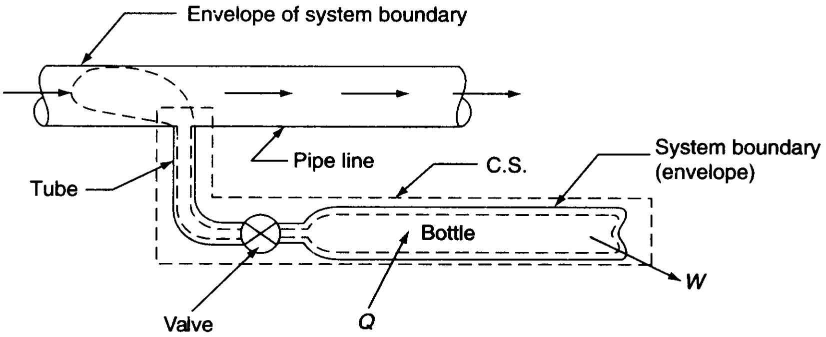


Fig. 5.11 Bottle-filling process

Energy of the gas after filling

$$E_2 = m_2u_2$$

$$\Delta E = E_2 - E_1 = m_2u_2 - \left[m_1u_1 + (m_2 - m_1)\left(\frac{\mathbf{V}_p^2}{2} + u_p\right)\right] \tag{5.29}$$

The P.E. terms are neglected: The gas in the bottle is not in motion, and so the K.E. terms have been omitted.

Now, there is a change in the volume of gas because of the collapse of the envelope to zero volume. Then the work done

$$W = p_p(V_2 - V_1) = p_p[0 - (m_2 - m_1)v_p] = -(m_2 - m_1)p_pv_p$$

∴ Using the first law for the process

$$Q = \Delta E + W$$

$$= m_2u_2 - m_1u_1 - (m_2 - m_1)\left(\frac{\mathbf{V}_p^2}{2} + u_p\right) - (m_2 - m_1)p_pv_p$$

$$= m_2u_2 - m_1u_1 - (m_2 - m_1)\left(\frac{\mathbf{V}_p^2}{2} + h_p\right) \tag{5.30}$$

which gives the energy balance for the process.

Control Volume Technique Assume a control volume bounded by a control surface, as shown in Fig. 5.11. Applying the energy Eq. (5.27) to this case, the following energy balance may be written on a time rate basis

$$\frac{dE_V}{d\tau} = \frac{đQ}{d\tau} + \left(h_p + \frac{\mathbf{V}_p^2}{2}\right)\frac{dm}{d\tau}$$

Since h_p and V_p are constant, the equation is integrated to give for the total process

$$\Delta E_V = Q + \left(h_p + \frac{\mathbf{V}_p^2}{2}\right)(m_2 - m_1)$$

Now $$\Delta E_V = U_2 - U_1 = m_2u_2 - m_1u_1$$

∴ $$Q = m_2u_2 - m_1u_1 - \left(h_p + \frac{\mathbf{V}_p^2}{2}\right)(m_2 - m_1)$$

This equation is the same as Eq. (5.30).

If $m_1 = 0$, i.e., the bottle is initially evacuated,

Again, if $Q = 0$ and $h_p \gg \frac{V_p^2}{2}$, $\quad Q = m_2u_2 - m_2\left(h_p + \frac{V_p^2}{2}\right) \quad 0 = m_2u_2 - m_2h_p$

or $\quad u_2 = h_p = u_p + p_pv_p$

Thus, flow work (p_pv_p) is converted to an increase in molecular internal energy ($u_2 - u_p$).

If the gas is assumed ideal,

$$c_vT_2 = c_pT_p \quad \text{or} \quad T_2 = \gamma\, T_p$$

If $T_p = 27 + 273 = 300$ K, then for air

$$T_2 = 1.4 \times 300 = 420 \text{ K} \quad \text{or} \quad t_2 = 147°\text{C}$$

Therefore, in adiabatically filling a bottle with air at 27°C, the gas temperature rises to 147°C due to the flow work being converted to internal energy increase.

5.8 DISCHARGING AND CHARGING A TANK

Let us consider a tank discharging a fluid into a supply line (Fig. 5.12). Since $đ W_x = 0$ and $dm_{in} = 0$, applying first law to the control volume,

$$dU_V = đ Q + \left(h + \frac{V^2}{2} + gz\right)_{out} dm_{out} \tag{5.31}$$

Assuming K.E. and P.E. of the fluid to be small and $đ Q = 0$

$$d(mu) = h dm$$

$$m du + u dm = u dm + pv\, dm$$

$$\frac{dm}{m} = \frac{du}{pv} \tag{5.32}$$

Again $\quad V = vm = \text{const.}$

$$v dm + m dv = 0$$

or $$\frac{dm}{m} = -\frac{dv}{v} \tag{5.33}$$

From Eqs (5.32) and 5.33),

$$\frac{du}{pv} = -\frac{dv}{v}$$

$$d(u + pv) = 0 \quad \text{or} \quad đ Q = 0$$

which shows that the process is adiabatic and quasi-static.

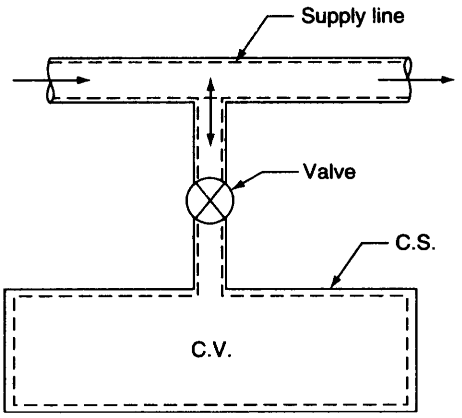
For charging the tank

$$\int (h dm)_{in} = \Delta U_V = m_2u_2 - m_1u_1 \tag{5.34}$$

$$m_ph_p = m_2u_2 - m_1u_1$$

where the subscript p refers to the constant state of the fluid in the pipeline. If the tank is initially empty, $m_1 = 0$.

$$m_ph_p = m_2u_2$$



Charging and discharging a tank

Since

$$m_p = m_2$$

$$h_p = u_2$$

Enthalpy is converted to internal energy.

If the fluid is an ideal gas, the temperature of the gas in the tank after it is charged is given by

$$c_p T_p = c_v T_2$$

or

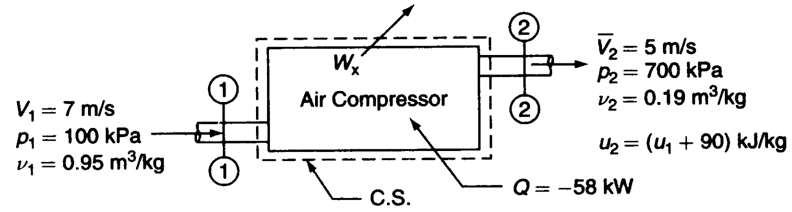
$$T_2 = \gamma T_p \tag{5.35}$$

Solved Examples

Example 5.1

Air flows steadily at the rate of 0.5 kg/s through an air compressor, entering at 7 m/s velocity, 100 kPa pressure, and 0.95 m³/kg volume, and leaving at 5 m/s, 700 kPa, and 0.19 m³/kg. The internal energy of the air leaving is 90 kJ/kg greater than that of the air entering. Cooling water in the compressor jackets absorbs heat from the air at the rate of 58 kW. (a) Compute the rate of shaft work input to the air in kW. (b) Find the ratio of the inlet pipe diameter to outlet pipe diameter.

Solution Figure Ex. 5.1 shows the details of the problem.



(a) Writing the steady flow energy equation, we have

$$w\left(u_1 + p_1\nu_1 + \frac{V_1^2}{2} + Z_1 g\right) + \frac{\bar{d}Q}{d\tau} = w\left(u_2 + p_2\nu_2 + \frac{V_2^2}{2} + Z_2 g\right) + \frac{\bar{d}W_x}{d\tau}$$

$$\therefore \quad \frac{\bar{d}W_x}{d\tau} = -w\left[(u_2 - u_1) + (p_2\nu_2 - p_1\nu_1) + \frac{V_2^2 - V_1^2}{2} + (Z_2 - Z_1)g\right] + \frac{\bar{d}Q}{d\tau}$$

$$\therefore \quad \frac{\bar{d}W_x}{d\tau} = -0.5\frac{\text{kg}}{\text{s}}\left[90\frac{\text{kJ}}{\text{kg}} + (7 \times 0.19 - 1 \times 0.95)100\frac{\text{kJ}}{\text{kg}} + \frac{(5^2 - 7^2) \times 10^{-3}}{2}\frac{\text{kJ}}{\text{kg}} + 0\right] - 58 \text{ kW}$$

$$= -0.5\,[90 + 38 - 0.012] \text{ kJ/s} - 58 \text{ kW}$$

$$= -122 \text{ kW}$$

Ans. (a)

Rate of work input is 122 kW.

(b) From mass balance, we have

$$w = \frac{A_1\mathbf{V}_1}{\nu_1} = \frac{A_2\mathbf{V}_2}{\nu_2}$$

$$\therefore \quad \frac{A_1}{A_2} = \frac{\nu_1}{\nu_2}\cdot\frac{\mathbf{V}_2}{\mathbf{V}_1} = \frac{0.95}{0.19}\times\frac{5}{7} = 3.57$$

$$\therefore \quad \frac{d_1}{d_2} = \sqrt{3.57} = 1.89$$

Ans. (b)

Example 5.2

In a steady flow apparatus, 135 *kJ of work is done by each kg of fluid. The specific volume of the fluid, pressure, and velocity at the inlet are* 0.37 *m*^{3}*/kg,* 600 *kPa, and* 16 *m/s. The inlet is* 32 *m above the floor, and the discharge pipe is at floor level. The discharge conditions are* 0.62 *m*^{3}*/kg,* 100 *kPa, and* 270 *m/s. The total heat loss between the inlet and discharge is* 9 *kJ/kg of fluid. In flowing through this apparatus, does the specific internal energy increase or decrease, and by how much?*

Solution Writing the steady flow energy equation for the control volume, as shown in Fig. Ex. 5.2.

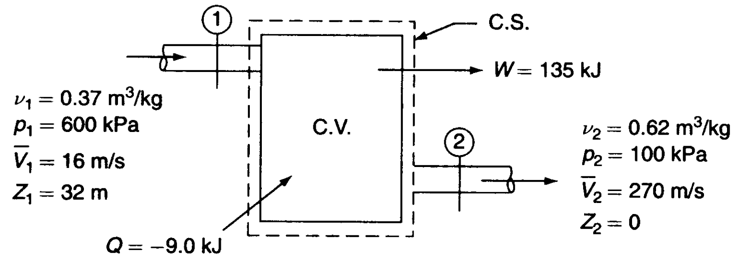


Fig. Ex. 5.2

$$u_1 + p_1\nu_1 + \frac{\mathbf{V}_1^2}{2} + Z_1 g + \frac{đQ}{\mathrm{d}m} = u_2 + p_2\nu_2 + \frac{\mathbf{V}_2^2}{2} + Z_2 g + \frac{đW_x}{\mathrm{d}m}$$

$$\therefore \quad u_1 - u_2 = (p_2\nu_2 - p_1\nu_1) + \frac{\mathbf{V}_2^2 - \mathbf{V}_1^2}{2} + (Z_2 - Z_1)g + \frac{đW_x}{\mathrm{d}m} - \frac{đQ}{\mathrm{d}m}$$

$$= (1\times 0.62 - 6\times 0.37)\times 10^2 + \frac{\left(270^2 - 16^2\right)\times 10^{-3}}{2}$$

$$+ (-32\times 9.81\times 10^{-3}) + 135 - (-9.0)$$

$$= -160 + 36.45 - 0.314 + 135 + 9 = 20.136 \text{ kJ/kg}$$

Specific internal energy decreases by 20.136 kJ.

Example 5.3

In a steam power station, steam flows steadily through a 0.2 *m diameter pipeline from the boiler to the turbine. At the boiler end, the steam conditions are found to be:* p = 4 *MPa,* t = 400°*C,* h = 3213.6 *kJ/kg, and* ν = 0.073 *m*^{3}*/kg. At the turbine end, the conditions are found to be:* p = 3.5 *MPa,* t = 392°*C,* h = 3202.6 *kJ/kg, and* ν = 0.084 *m*^{3}*/kg. There is a heat loss of* 8.5 *kJ/kg from the pipeline. Calculate the steam flow rate.*

Solution Writing the steady flow energy equation for the control volume as shown in Fig. Ex. 5.3

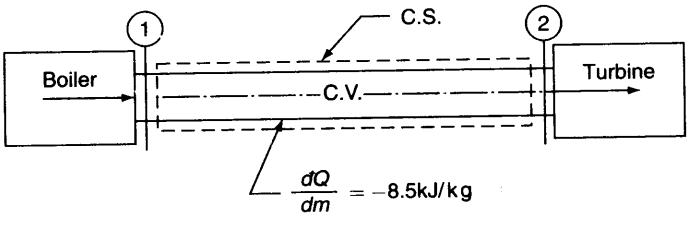


Fig. Ex. 5.3

$$h_1 + \frac{\mathbf{V}_1^2}{2} + Z_1 g + \frac{\text{đ}Q}{\text{d}m} = h_2 + \frac{\mathbf{V}_2^2}{2} + Z_2 g + \frac{\text{đ}W_x}{\text{d}m}$$

Here, there is no change in datum, so change in potential energy will be zero.

Now $$\frac{A_1\mathbf{V}_1}{\nu_1} = \frac{A_2\mathbf{V}_2}{\nu_2}$$

$\therefore$ $$\mathbf{V}_2 = \frac{A_1\mathbf{V}_1}{\nu_1} \cdot \frac{\nu_2}{A_2} = \frac{\nu_2}{\nu_1} \cdot \mathbf{V}_1 = \frac{0.084}{0.073}\,\mathbf{V}_1 = 1.15\,\mathbf{V}_1$$

and $$\frac{\text{đ}W_x}{\text{d}m} = 0$$

$$h_1 + \frac{\mathbf{V}_1^2}{2} + \frac{\text{đ}Q}{\text{d}m} = h_2 + \frac{\mathbf{V}_2^2}{2}$$

$$\therefore \frac{\left(\mathbf{V}_2^2 - \mathbf{V}_1^2\right)\times 10^{-3}}{2} = h_1 - h_2 + \frac{\text{đ}Q}{\text{d}m} = 3213.6 - 3202.6 + (-8.5) = 2.5 \text{ kJ/kg}$$

$$\mathbf{V}_1^2(1.15^2 - 1^2) = 5 \times 10^3$$

$$\mathbf{V}_1^2 = 15{,}650 \text{ m}^2/\text{s}^2$$

$$\therefore \quad \mathbf{V}_1 = 125.1 \text{ m/s}$$

$\therefore$ Mass flow rate $$w = \frac{A_1\mathbf{V}_1}{\nu_1} = \frac{\frac{\pi}{4}\times(0.2)^2 \text{ m}^2 \times 125.1 \text{ m/s}}{0.073 \text{ m}^3/\text{kg}}$$

$$= 53.8 \text{ kg/s}$$ *Ans.*

Example 5.4

A certain water heater operates under steady flow conditions receiving 4.2 *kg/s of water at* 75°C *temperature, enthalpy* 313.93 *kJ/kg. The water is heated by mixing with steam which is supplied to the heater at temperature* 100.2°C *and enthalpy* 2676 *kJ/kg. The mixture leaves the heater as liquid water at temperature* 100°C *and enthalpy* 419 *kJ/kg. How much steam must be supplied to the heater per hour?*

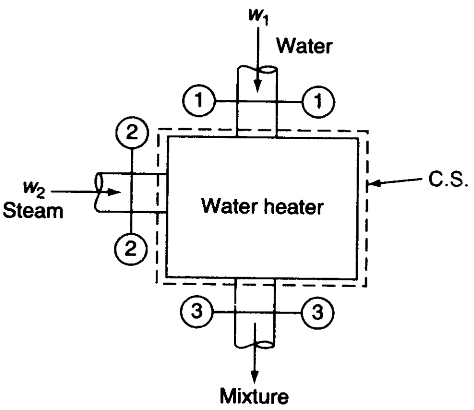
Solution By mass balance across the control surface (Fig. Ex. 5.4)

$$w_1 + w_2 = w_3$$

By energy balance

$$w_1\left(h_1+\frac{\mathbf{V}_1^2}{2}+Z_1g\right)+\frac{đQ}{d\tau}+w_2\left(h_2+\frac{\mathbf{V}_2^2}{2}+Z_2g\right)=w_3\left(h_3+\frac{\mathbf{V}_3^2}{2}+Z_3g\right)+\frac{đW_x}{d\tau}$$

By the nature of the process, there is no shaft work. Potential and kinetic energy terms are assumed to balance zero. The heater is assumed to be insulated. So the steady flow energy equation reduces to



[illegible]

$$w_1h_1 + w_2h_2 = w_3h_3$$

$$4.2 \times 313.93 + w_2 \times 2676 = (4.2 + w_2)\,419$$

$$\therefore \quad w_2 = 0.196 \text{ kg/s}$$

$$= 705 \text{ kg/h}$$

Ans.

Example 5.5

Air at a temperature of 15°C *passes through a heat exchanger at a velocity of* 30 *m/s where its temperature is raised to* 800°C. *It then enters a turbine with the same velocity of* 30 *m/s and expands until the temperature falls to* 650°C. *On leaving the turbine, the air is taken at a velocity of* 60 *m/s to a nozzle where it expands until the temperature has fallen to* 500°C. *If the air flow rate is* 2 *kg/s, calculate* (*a*) *the rate of heat transfer to the air in the heat exchanger,* (*b*) *the power output from the turbine assuming no heat loss, and* (*c*) *the velocity at exit from the nozzle, assuming no heat loss. Take the enthalpy of air as* $h = c_pt$, *where* c_p *is the specific heat equal to* 1.005 *kJ/kg K and t is the temperature.*

Solution As shown in Fig. Ex. 5.5, writing the S.F.E.E. for the heat exchanger and eliminating the terms not relevant,

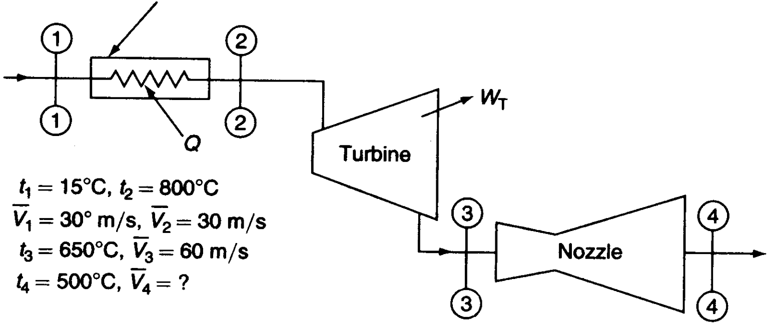


Fig. Ex. 5.5

$$w\left(h_1 + \frac{V_1^2}{2} + Z_1 g\right) + Q_{1-2} = w\left(h_2 + \frac{V_2^2}{2} + Z_2 g\right) + W_{1-2}$$

$$\therefore \quad wh_1 + Q_{1-2} = wh_2$$

$$\therefore \quad Q_{1-2} = w(h_2 - h_1) = wc_p(t_2 - t_1) = 2 \times 1.005\,(800 - 15) = 2.01 \times 785$$

$$= 1580 \text{ kJ/s} \qquad \textit{Ans. } (a)$$

Energy equation for the turbine gives

$$w\left(\frac{V_2^2}{2} + h_2\right) = wh_3 + w\,\frac{V_3^2}{2} + W_T$$

$$\frac{V_2^2 - V_3^2}{2} + (h_2 - h_3) = W_T/w$$

$$\frac{(30^2 - 60^2) \times 10^{-3}}{2} + 1.005\,(800 - 650) = W_T/w$$

$$\therefore \quad \frac{W_T}{w} = 1.35 + 150.75 = 149.4 \text{ kJ/kg}$$

$$\therefore \quad W_T = 149.4 \times 2 \text{ kJ/s}$$

$$= 298.8 \text{ kW} \qquad \textit{Ans. } (b)$$

Writing the energy equation for the nozzle

$$\frac{V_3^3}{2} + h_3 = \frac{V_4^2}{2} + h_4$$

$$\frac{V_4^2 - V_3^2}{2} = c_p\,(t_3 - t_4)$$

$$V_4^2 - V_3^2 = 1.005\,(650 - 500) \times 2 \times 10^3 = 301.50 \times 10^3 \text{ m}^2/\text{s}^2$$

$$V_4^2 = 30.15 \times 10^4 + 0.36 \times 10^4 = 30.51 \times 10^4 \text{ m}^2/\text{s}^2$$

∴ Velocity at exit from the nozzle

$$V_4 = 554 \text{ m/s} \qquad \textit{Ans. } (c)$$

Example 5.6

The air speed of a turbojet engine in flight is 270 *m/s. Ambient air temperature is* – 15°C. *Gas temperature at outlet of nozzle is* 600°C. *Corresponding enthalpy values for air and gas are respectively* 260 *and* 912 *kJ/kg. Fuel-air ratio is* 0.0190. *Chemical energy of the fuel is* 44.5 *MJ/kg. Owing to incomplete combustion,* 5% *of the chemical energy is not released in the reaction. Heat loss from the engine is* 21 *kJ/kg of air. Calculate the velocity of the exhaust jet.*

Solution Energy equation for the turbojet engine (Fig. Ex. 5.6.) gives

$$w_a\left(h_a + \frac{V_a^2}{2}\right) + w_f E_f + Q = w_g\left(h_g + \frac{V_g^2}{2} + E_g\right)$$

$$\left(260 + \frac{270^2 \times 10^{-3}}{2}\right) + 0.0190 \times 44500 - 21$$

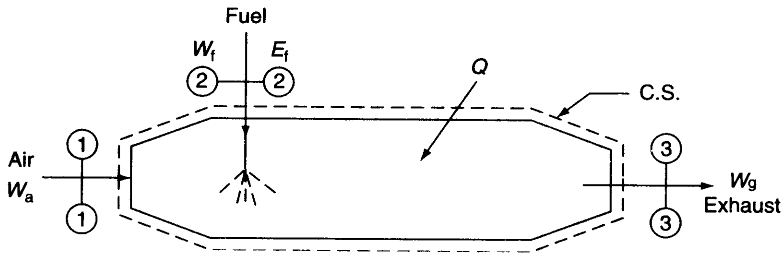


Fig. Ex. 5.6

$$= 1.0190 \left(912 + \frac{\mathbf{V}_g^2 \times 10^{-3}}{2} + 0.05\frac{0.019}{1.019} \times 44500\right)$$

$$260 + 36.5 + 845 - 21 = 1.019\left(912 + \frac{\mathbf{V}_g^2 \times 10^{-3}}{2} + 42\right)$$

$$\therefore \qquad \frac{\mathbf{V}_g^2}{2} = 156 \times 10^3 \text{ m}^2/\text{s}^2$$

$$\mathbf{V}_g = \sqrt{3.12} \times 100 \text{ m/s}$$

Velocity of exhaust gas, $\mathbf{V}_g = 560$ m/s *Ans.*

Example 5.7

In a reciprocating engine, the mass of gas occupying the clearance volume is m_c kg at state p_1, u_1, v_1 and h_1. By opening the inlet valve, m_f kg of gas is taken into the cylinder, and at the conclusion of the intake process the state of the gas is given by p_2, u_2, v_2, h_2. The state of the gas in the supply pipe is constant and is given by p_p, u_p, v_p, h_p, $\mathbf{V}_p$. How much heat is transferred between the gas and the cylinder walls during the intake process?

Solution Let us consider the control volume as shown in Fig. Ex. 5.7. Writing the energy balance on a time rate basis

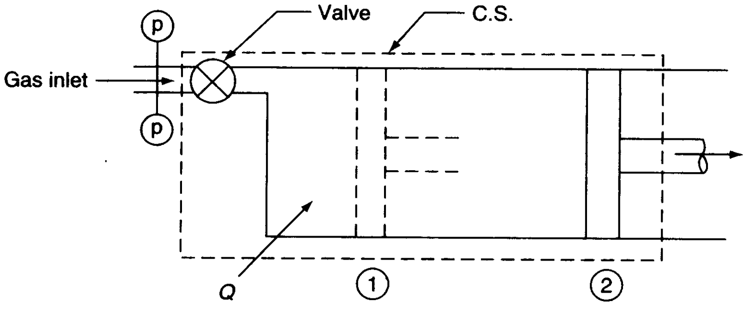


Fig. Ex. 5.7

$$\frac{\mathrm{d}E_V}{\mathrm{d}\tau} = \frac{\text{đ}Q}{\mathrm{d}\tau} - \frac{\text{đ}W}{\mathrm{d}\tau} + \left(h_p + \frac{\mathbf{V}_p^2}{2}\right)\frac{\mathrm{d}m}{\mathrm{d}\tau}$$

With h_p and V_p being constant, the above equation can be integrated to give for the total process

$$\Delta E_v = Q - W + \left(h_p + \frac{V_p^2}{2}\right) m_f$$

Now $$\Delta E_v = U_2 - U_1 = (m_e + m_f)\, u_2 - m_e u_1$$

$$\therefore \quad Q = (m_c + m_f)u_2 - m_c u_1 - m_f \left(h_p + \frac{V_p^2}{2}\right) + W \qquad \textit{Ans.}$$

Example 5.8

The internal energy of air is given by

$$u = u_0 + 0.718\, t$$

where u is in kJ/kg, u_0 is any arbitrary value of u at 0°C, kJ/kg, and t is the temperature in °C. Also for air, $p_v = 0.287\ (t + 273)$, where p is in kPa and v is in m³/kg.

A mass of air is stirred by a paddle wheel in an insulated constant volume tank. The velocities due to stirring make a negligible contribution to the internal energy of the air. Air flows out through a small valve in the tank at a rate controlled to keep the temperature in the tank constant. At a certain instant the conditions are as follows: tank volume 0.12 m³, pressure 1 MPa, temperature 150°C, and power to paddle wheel 0.1 kW. Find the rate of flow of air out of the tank at this instant.

Solution Writing the energy balance for the control volume as shown in Fig. Ex, 5.8

$$\frac{dE_V}{d\tau} = \frac{\text{đ}W}{d\tau} - (h_p)\frac{dm}{d\tau}$$

Since there is no change in internal energy of air in the tank,

$$h_p \cdot \frac{dm}{d\tau} = \frac{\text{đ}W}{d\tau}$$

where $h_p = u + pv.$

Let $u = 0$ at $t = 0\,K = -273°\text{C}$

$$u = u_0 + 0.718\, t$$

$$0 = u_0 + 0.718\,(-273)$$

$$u_0 = 0.718 \times 273 \text{ kJ/kg}$$

At t°C

$$u = 0.718 \times 273 + 0.718\, t$$

$$= 0.718\,(t + 273) \text{ kJ/kg}$$

$$h_p = 0.718\,(t + 273) + 0.287\,(t + 273)$$

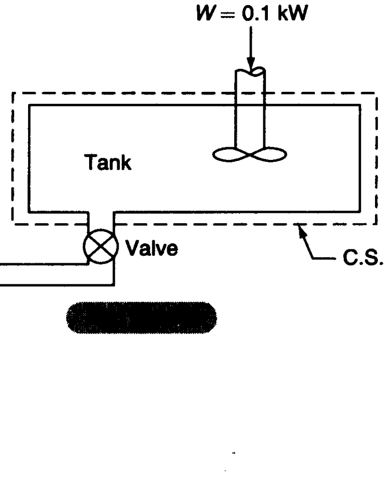
or $$h_p = 1.005\,(t + 273)$$

At 150°C

$$h_p = 1.005 \times 423 = 425 \text{ kJ/kg}$$

$$\therefore \quad \frac{dm}{d\tau} = \frac{1}{h_p}\frac{\text{đ}W}{d\tau}$$

$$= \frac{0.1 \text{ kJ/s}}{425 \text{ kJ/kg}} = 0.236 \times 10^{-3} \text{ kg/s} = 0.845 \text{ kg/h}$$



This is the rate at which air flows out of the tank.

Example 5.9

A well-insulated vessel of volume V contains a gas at pressure p_0 and temperature t_0. The gas from a main at a uniform temperature t_1 is pumped into the vessel and the inflow rate decreases exponentially with time according to $\dot{m} = \dot{m}_0 e^{-a\tau}$, where a is a constant. Determine the pressure and temperature of the gas in the vessel as a function of time. Neglect the K.E. of the gas entering the vessel and assume that the gas follows the relation

$$pv = RT, \quad \text{where } T = t + 273$$

and its specific heats are constant.

(*i*) *If the vessel was initially evacuated, show that the temperature inside the vessel is independent of time.*

(*ii*) *Determine the charging time when the pressure inside the vessel reaches that of the main.*

Solution Since the vessel is well-insulated, $\dot{Q} = 0$ and there is no external work transfer, $W = C$. Therefore,

$$\frac{dE_V}{d\tau} = h_1 \frac{dm}{d\tau} = h_1 \dot{m}_0 e^{-a\tau}$$

where h_1 is the enthalpy of the gas in the main.

On integration,

$$E = E_0 + \frac{h_1 \dot{m}_0}{a} (1 - e^{-a\tau})$$

where E_0 is the initial energy of the vessel at the beginning of the charging process, i.e. $E = E_0$ at $\tau = 0$. Neglecting K.E. and P.E. changes, by energy balance

$$Mu = M_0 u_0 + \frac{\dot{m}_0}{a} (1 - e^{-a\tau}) (u_1 + p_1 v_1) \tag{1}$$

Again,

$$\frac{dm}{d\tau} = \dot{m}_0 e^{-a\tau}$$

On integration,

$$M = M_0 + \frac{\dot{m}_0 \left(1 - e^{-a\tau}\right)}{a} \tag{2}$$

where M_0 is the initial mass of the gas. Eliminating M from Eqs (1) and (2),

$$\left\{M_0 + \frac{\dot{m}_0}{a}\left(1 - e^{-a\tau}\right)\right\} u - M_0 u_0$$

$$= \frac{\dot{m}_0}{a} (1 - e^{-a\tau}) (u_1 + RT_1)$$

$$M_0 c_v (T - T_0) = \frac{\dot{m}_0}{a} (1 - a^{-a\tau}) \{c_v (T_1 - T) + RT_1\}$$

$$\therefore \qquad T = \frac{M_0\, c_v T_0 + \dfrac{\dot{m}_0}{a}\left(1 - e^{-a\tau}\right) c_p T_1}{\left\{M_0 + \dfrac{\dot{m}_0}{a}\left(1 - e^{-a\tau}\right)\right\} c_v}$$

$$p = \frac{MRT}{V} = \frac{R}{Vc_v}\left\{M_0 c_v T_0 + \frac{\dot{m}_0}{a}\left(1 - e^{-a\tau}\right)c_p T_1\right\}$$

$$= p_0 + \frac{\dot{m}_0 R}{aV}\ (1 - e^{-a\tau})\ \gamma T_1$$

The above two equations show the temperature and pressure of the gas in the vessel as functions of time.

(i) If $M_0 = 0$, $T = \gamma T_1$, i.e. the temperature inside the vessel becomes independent of time and is equal to γT_1 throughout the charging process.

(ii) The charging process will stop when pressure inside the vessel reaches that of the main. The charging time can be found by setting $p = p_1$ in the pressure relation

$$p_1 - p_0 = \frac{\dot{m}_0 R\gamma T_1}{aV} - \frac{\dot{m}_0 R}{aV} e^{-a\tau} g\, T_1$$

By rearrangement,

$$e^{a\tau} = \frac{\dot{m}_0 R\gamma T_1/(aV)}{\left(\frac{m_0 R\gamma T_1}{aV}\right) - (p_1 - p_0)}$$

$$\therefore \qquad \tau = -\frac{1}{a}\ln\left[1 - (p_1 - p_0)\frac{aV}{m_0 R\gamma T_1}\right]$$

Review Questions

5.1 Explain the system approach and the control volume approach in the analysis of a flow process.

5.2 What is a steady flow process? What is steady state?

5.3 Write the steady flow energy equation for a single stream entering and a single stream leaving a control volume and explain the various terms in it.

5.4 Give the differential form of the S.F.E.E.

5.5 Under what conditions does the S.F.E.E. reduce to Euler's equation?

5.6 How does Bernoulli's equation compare with S.F.E.E.?

5.7 What will be the velocity of a fluid leaving a nozzle, if the velocity of approach is very small?

5.8 Show that the enthalpy of a fluid before throttling is equal to that after throttling.

5.9 Write the general energy equation for a variable flow process.

5.10 What is the system technique in a bottle-filling process?

5.11 Explain the control volume technique in a variable flow process.

Problems

5.1 A blower handles 1 kg/s of air at 20°C and consumes a power of 15 kW. The inlet and outlet velocities of air are 100 m/s and 150 m/s respectively. Find the exit air temperature, assuming adiabatic conditions. Take c_p of air as 1.005 kJ/kg-K. *Ans.* 28.38°C

5.2 A turbine operates under steady flow conditions, receiving steam at the following state: pressure 1.2 MPa, temperature 188°C, enthalpy 2785 kJ/kg, velocity 33.3 m/s and elevation 3 m. The steam leaves the turbine at the following state: pressure 20 kPa, enthalpy 2512 kJ/kg, velocity 100 m/s, and elevation 0 m. Heat is lost to the surroundings at the rate of 0.29 kJ/s. If the rate of steam flow through the turbine is 0.42 kg/s, what is the power output of the turbine in kW? *Ans.* 112.51 kW

5.3 A nozzle is a device for increasing the velocity of a steadily flowing stream. At the inlet to a certain nozzle, the enthalpy of the fluid passing is 3000 kJ/kg and the velocity is 60 m/s. At the discharge end, the enthalpy is 2762 kJ/kg. The nozzle is horizontal and there is negligible heat loss from it. (a) Find the velocity at exist from the nozzle. (b) If the inlet area is 0.1 m^2 and the specific volume at inlet is 0.187 m^3/kg, find the mass flow rate. (c) If the specific volume at the nozzle exit is 0.498 m^3/kg, find the exit area of the nozzle.

Ans. (a) 692.5 m/s, (b) 32.08 kg/s (c) 0.023 m^2

5.4 In an oil cooler, oil flows steadily through a bundle of metal tubes submerged in a steady stream of cooling water. Under steady flow conditions, the oil enters at 90°C and leaves at 30°C, while the water enters at 25°C and leaves at 70°C. The enthalpy of oil at t°C is given by

$$h = 1.68\,t + 10.5 \times 10^{-4}\,t^2 \text{ kJ/kg}$$

What is the cooling water flow required for cooling 2.78 kg/s of oil? *Ans.* 1.473 kg/s

5.5 A thermoelectric generator consists of a series of semiconductor elements (Fig. P. 5.5), heated on one side and cooled on the other. Electric current flow is produced as a result of energy transfer as heat. In a particular experiment the current was measured to be 0.5 amp and the electrostatic potential at (1) was 0.8 volt above that at (2). Energy transfer as heat to the hot side of the generator was taking place at a rate of 5.5 watts. Determine the rate of energy transfer as heat from the cold side and the energy conversion efficiency.

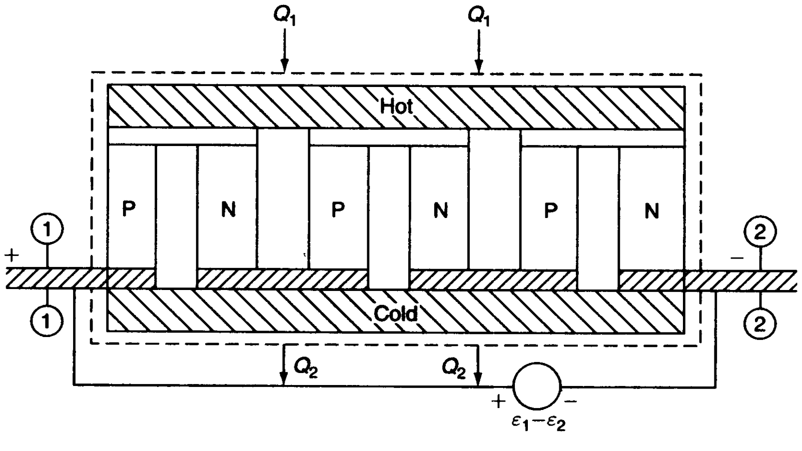
Ans. $Q_2 = 5.1$ watts, $\eta = 0.073$

5.6 A turbocompressor delivers 2.33 m^3/s of air at 0.276 MPa, 43°C which is heated at this pressure to 430°C and finally expanded in a turbine which delivers 1860 kW. During the expansion, there is a heat transfer of 0.09 MJ/s to the surroundings. Calculate the turbine exhaust temperature if changes in kinetic and potential energy are negligible. Take $c_p = 1.005$ kJ/kgK *Ans.* 157°C

5.7 A reciprocating air compressor takes in 2 m^3/min at 0.11 MPa, 20°C which it delivers at 1.5 MPa, 111°C to an aftercooler where the air is cooled at constant pressure to 25°C. The power absorbed by the compressor is 4.15 kW. Determine the heat transfer in (a) the compressor, and (b) the cooler. State your assumptions.

Ans. – 0.17 kJ/s, – 3.76 kJ/s.

5.8 In a water cooling tower air enters at a height of 1 m above the ground level and leaves at a height of 7 m. The inlet and outlet velocities are 20 m/s and 30 m/s respectively. Water enters at a height of 8 m and leaves at a height of 0.8 m. The velocity of water at entry and exit are 3 m/s and 1 m/s respectively. Water temperatures are 80°C and 50°C at the entry and exit respectively. Air



temperatures are 30°C and 70°C at the entry and exit respectively. The cooling tower is well insulated and a fan of 2.25 kW drives the air through the cooler. Find the amount of air per second required for 1 kg/s of water flow. The values of c_p of air and water are 1.005 and 4.187 kJ/kg K respectively.

Ans. 3.16 kg

5.9 Air at 101.325 kPa, 20°C is taken into a gas turbine power plant at a velocity of 140 m/s through an opening of 0.15 m^2 cross-sectional area. The air is compressed heated, expanded through a turbine, and exhausted at 0.18 MPa, 150°C through an opening of 0.10 m^2 cross-sectional area. The power output is 375 kW. Calculate the net amount of heat added to the air in kJ/kg. Assume that air obeys the law $pv = 0.287\ (t + 273)$, where p is the pressure in kPa, v is the specific volume in m^3/kg, and t is the temperature in °C. Take $c_p = 1.005$ kJ/kg K.

Ans. 150.23 kJ/kg

5.10 A gas flows steadily through a rotary compressor. The gas enters the compressor at a temperature of 16°C, a pressure of 100 kPa, and an enthalpy of 391.2 kJ/kg. The gas leaves the compressor at a temperature of 245°C, a pressure of 0.6 MPa, and an enthalpy of 534.5 kJ/kg. There is no heat transfer to or from the gas as it flows through the compressor. (a) Evaluate the external work done per unit mass of gas assuming the gas velocities at entry and exit to be negligible. (b) Evaluate the external work done per unit mass of gas when the gas velocity at entry is 80 m/s and that at exit is 160 m/s. *Ans.* 143.3 kJ/kg, 152.9 kJ/kg

5.11 The steam supply to an engine comprises two streams which mix before entering the engine. One stream is supplied at the rate of 0.01 kg/s with an enthalpy of 2952 kJ/kg and a velocity of 20 m/s. The other stream is supplied at the rate of 0.1 kg/s with an enthalpy of 2569 kJ/kg and a velocity of 120 m/s. At the exit from the engine the fluid leaves as two streams, one of water at the rate of 0.001 kg/s with an enthalpy of 420 kJ/kg and the other of steam; the fluid velocities at the exit are negligible. The engine develops a shaft power of 25 kW. The heat transfer is negligible. Evaluate the enthalpy of the second exit stream.

Ans. 2402 kJ/kg

5.12 The stream of air and gasoline vapour, in the ratio of 14:1 by mass, enters a gasoline engine at a temperature of 30°C and leaves as combustion products at a temperature of 790°C. The engine has a specific fuel consumption of 0.3 kg/kWh. The net heat transfer rate from the fuel-air stream to the jacket cooling water and to the surroundings is 35 kW. The shaft power delivered by the engine is 26 kW. Compute the increase in the specific enthalpy of the fuel-air stream, assuming the changes in kinetic energy and in elevation to be negligible. *Ans.* – 1877 kJ/kg mixture

5.13 An air turbine forms part of an aircraft refrigerating plant. Air at a pressure of 295 kPa and a temperature of 58°C flows steadily into the turbine with a velocity of 45 m/s. The air leaves the turbine at a pressure of 115 kPa, a temperature of 2°C, and a velocity of 150 m/s. The shaft work delivered by the turbine is 54 kJ/kg of air. Neglecting changes in elevation, determine the magnitude and sign of the heat transfer per unit mass of air flowing. For air, take $c_p = 1.005$ kJ/kg K and the enthalpy $h = c_p\, t$.

Ans. + 7.96 kJ/kg

5.14 In a turbomachine handling an incompressible fluid with a density of 1000 kg/m^3 the conditions of the fluid at the rotor entry and exit are as given below

	Inlet	Exit
Pressure	1.15 MPa	0.05 MPa
Velocity	30 m/s	15.5 m/s
Height above datum	10 m	2 m

If the volume flow rate of the fluid is 40 m^3/s, estimate the net energy transfer from the fluid as work. *Ans.* 60.3 MW

5.15 A room for four persons has two fans, each consuming 0.18 kW power, and three 100 W lamps. Ventilation air at the rate of 80 kg/h enters with an enthalpy of 84 kJ/kg and leaves with an enthalpy of 59 kJ/kg. If each person puts out heat at the rate of 630 kJ/h determine the rate at which heat is to be removed by a room cooler, so that a steady state is maintained in the room.

Ans. 1.92 kW

5.16 Air flows steadily at the rate of 0.4 kg/s through an air compressor, entering at 6 m/s with a pressure of 1 bar and a specific volume of 0.85 m^3/kg, and leaving at 4.5 m/s with a pressure of 6.9 bar and a specific volume of 0.16 m^3/kg. The internal energy of the air leaving is 88 kJ/kg greater than that of the air entering. Cooling water in a jacket, surrounding the cylinder absorbs heat from the air at the rate of 59 W. Calculate the power required to drive the compressor and the inlet and outlet cross-sectional areas.

Ans. 45.4 kW, 0.057 m^2, 0.0142 m^2

5.17 Steam flowing in a pipeline is at a steady state represented by p_p, t_p, u_p, v_p, h_p and V_p. A small amount of the total flow is led through a small tube to an evacuated chamber which is allowed to fill slowly until the pressure is equal to the pipeline pressure. If there is no heat transfer, derive an expression for the final specific internal energy in the chamber, in terms of the properties in the pipeline.

5.18 The internal energy of air is given, at ordinary temperatures, by

$u = u_0 + 0.718\,t$

where u is in kJ/kg, u_0 is any arbitrary value of u at 0°C, kJ/kg, and t is temperature in °C.

Also for air,

$pv = 0.287\,(t + 273)$

where p is in kPa and v is in m^3/kg.

(a) An evacuated bottle is fitted with a valve through which air from the atmosphere, at 760 mm Hg and 25°C, is allowed to flow slowly to fill the bottle. If no heat is transferred to or from the air in the bottle, what will its temperature be when the pressure in the bottle reaches 760 mm Hg?

Ans. 144.2°C

(b) If the bottle initially contains 0.03 m^3 of air at 400 mm Hg and 25°C, what will the temperature be when the pressure in the bottle reaches 760 mm Hg?

Ans. 71.6°C

5.19 A pressure cylinder of volume V contains air at pressure p_0 and temperature T_0. It is to be filled from a compressed air line maintained at constant pressure p_1 and temperature T_1. Show that the temperature of the air in the cylinder after it has been charged to the pressure of the line is given by

$$T = \frac{\gamma T_1}{1 + \dfrac{p_0}{p_1}\left(\gamma \dfrac{T_1}{T_0} - 1\right)}$$

5.20 A small reciprocating vacuum pump having the rate of volume displacement V_d is used to evacuate a large vessel of volume V. The air in the vessel is maintained at a constant temperature T by energy transfer as heat. If the initial and final pressures are p_1 and p_2 respectively, find the time taken for the pressure drop and the necessary energy transfer as heat during evacuation. Assume that for air, $pV = mRT$, where m is the mass and R is a constant, and u is a function of T only.

$$\left[\textit{Ans. } t = \frac{V}{V_d} \ln \frac{p_1}{p_2}; \quad Q = (p_1 - p_2)V \right]$$

[Hint: $\mathrm{d}m = -p(V_d \cdot \mathrm{d}t)/(RT) = V\,\mathrm{d}p/(RT)$].

5.21 A tank containing 45 kg of water initially at 45°C has one inlet and one exit with equal mass flow rates. Liquid water enters at 45°C and a mass flow rate of 270 kg/h. A cooling coil immersed in the water removes energy at a rate of 7.6 kW. The water is well mixed by a paddle wheel with a power input of 0.6 kW. The pressures at inlet and exit are equal. Ignoring changes in KE and PE, find the variation of water temperature with time.

Ans. $T = 318 - 22\,[1 - \exp(-6t)]$

5.22 A rigid tank of volume 0.5 m^3 is initially evacuated. A tiny hole develops in the wall, and air from the surroundings at 1 bar, 21°C leaks in. Eventually, the pressure in the tank reaches 1 bar. The process occurs slowly enough that heat transfer between the tank and the surroundings keeps the temperature of the air inside the tank constant at 21°C. Determine the amount of heat transfer.

Ans. – 50 kJ

CHAPTER

6

Second Law of Thermodynamics

6.1 QUALITATIVE DIFFERENCE BETWEEN HEAT AND WORK

The first law of thermodynamics states that a certain energy balance will hold when a system undergoes a change of state or a thermodynamic process. But it does not give any information on whether that change of state or the process is at all feasible or not. The first law cannot indicate whether a metallic bar of uniform temperature can spontaneously become warmer at one end and cooler at the other. All that the law can state is that if this process did occur, the energy gained by one end would be exactly equal to that lost by the other. *It is the second law of thermodynamics which provides the criterion as to the probability of various processes.*

Spontaneous processes in nature occur only in one direction. Heat always flows from a body at a higher temperature to a body at a lower temperature, water always flows downward, time always flows in the forward direction. The reverse of these never happens spontaneously. The spontaneity of the process is due to a finite driving potential, sometimes called the 'force' or the 'cause', and what happens is called the 'flux', the 'current' or the 'effect'. The typical forces like temperature gradient, concentration gradient, and electric potential gradient, have their respective conjugate fluxes of heat transfer, mass transfer, and flow of electric current. These transfer processes can never spontaneously occur from a lower to a higher potential. This directional law puts a limitation on energy transformation other than that imposed by the first law.

Joule's experiments (Article 4.1) amply demonstrate that energy, when supplied to a system in the form of work, can be completely converted into heat (work transfer → internal energy increase → heat transfer). But the complete conversion of heat into work in a cycle is not possible. *So heat and work are not completely interchangeable forms of energy.*

When work is converted into heat, we always have

$$W \underset{\rightarrow}{\equiv} Q$$

but when heat is converted into work in a complete closed cycle process

$$Q \underset{\rightarrow}{\geq} W$$

The arrow indicates the direction of energy transformation. This is illustrated in Fig. 6.1. As shown in Fig. 6.1(a), a system is taken from state 1 to state 2 by work transfer W_{1-2}, and then by heat transfer Q_{2-1} the system is brought back from state 2 to state 1 to complete a cycle. It is always found that $W_{1-2} = Q_{2-1}$. But if the system is taken from state 1 to state 2 by heat transfer Q_{1-2}, as shown in Fig. 6.1(b), then the system cannot be brought back from state 2 to state 1 by work transfer W_{2-1}. Hence, heat cannot be converted completely and continuously into work in a cycle. Some heat has to be rejected. In Fig. 6.1(c), W_{2-3} is the work done and Q_{3-1} is the heat rejected to complete the cycle. This underlies the work of Sadi Carnot, a French military engineer, who

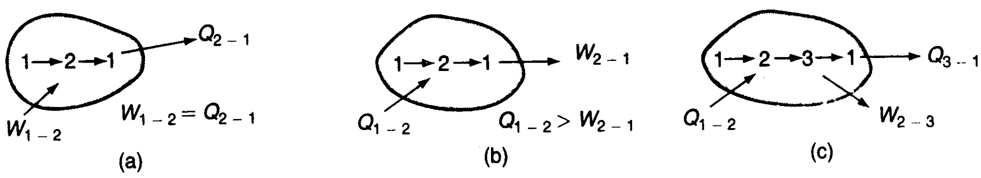


Fig. 6.1 Qualitative distinction between heat and work

first studied this aspect of energy transformation (1824). Work is said to be a *high grade energy* and heat a *low grade energy. The complete conversion of low grade energy into high grade energy in a cycle is impossible.*

6.2 CYCLIC HEAT ENGINE

For engineering purposes, the second law is best expressed in terms of the conditions which govern the production of work by a thermodynamic system operating in a cycle.

A heat engine cycle is a thermodynamic cycle in which there is a net heat transfer *to* the system and a net work transfer *from* the system. The system which executes a heat engine cycle is called a *heat engine.*

A heat engine may be in the form of mass of gas confined in a cylinder and piston machine (Fig. 6.2a) or a mass of water moving in a steady flow through a steam power plant (Fig. 6.2b).

In the cyclic heat engine, as represented in Fig. 6.2(a), heat Q_1 is transferred to the system, work W_E is done by the system, work W_c is done upon the system, and then heat Q_2 is rejected from the system. The system is brought back to the initial state through all these four successive processes which constitute a heat engine cycle. In Fig. 6.2(b) heat Q_1 is transferred from the furnace to the water in the boiler to form steam which then works on the turbine rotor to produce work W_T, then the steam is condensed to water in the condenser in which an amount Q_2 is rejected from the system, and finally work W_p is done on the system (water) to pump it to the boiler. The system repeats the cycle.

The net heat transfer in a cycle to either of the heat engines $Q_{\text{net}} = Q_1 - Q_2$ (6.1)

and the net work transfer in a cycle $W_{\text{net}} = W_T - W_p$ (6.2)

$$(\text{or } W_{\text{net}} = W_E - W_C)$$

By the first law of thermodynamics, we have

$$\sum_{\text{cycle}} Q = \sum_{\text{cycle}} W$$

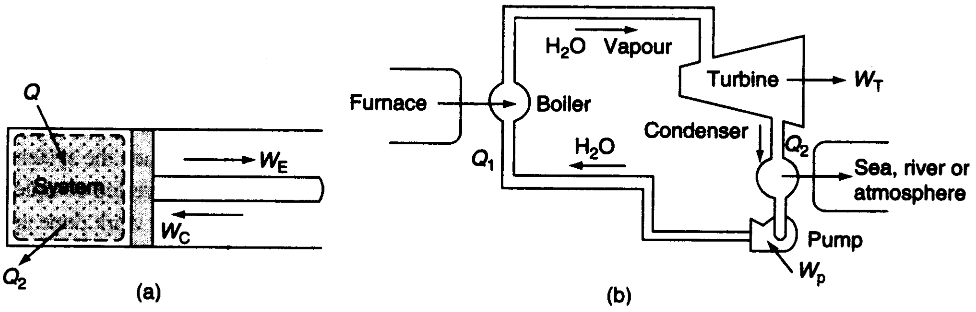
$$\therefore \quad Q_{\text{net}} = W_{\text{net}}$$

or

$$Q_1 - Q_2 = W_T - W_P \tag{6.3}$$

Figure 6.3 represents a cyclic heat engine in the form of a block diagram indicating the various energy interactions during a cycle. Boiler (*B*), turbine (*T*), condenser (*C*), and pump (*P*), all four together constitute a heat engine. A heat engine is here a certain quantity of water undergoing the energy interactions, as shown, in cyclic operations to produce net work from a certain heat input.

The function of a heat engine cycle is to produce work continuously at the expense of heat input to the system. So the net work W_{net} and heat input Q_1 referred to the cycle are of primary interest. The efficiency of a heat engine or a heat engine cycle is defined as



Cyclic heat engine: (a) Heat engine cycle performed by a closed system undergoing four successive energy interactions with the surroundings, (b) Heat engine cycle performed by a steady flow system interacting with the surroundings as shown

$$\eta = \frac{\text{Net work output of the cycle}}{\text{Total heat input to the cycle}} = \frac{W_{\text{net}}}{Q_1} \quad (6.4)$$

From Eqs (6.1), (6.2), (6.3) and (6.4),

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{W_T - W_P}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\eta = 1 - \frac{Q_2}{Q_1} \quad (6.5)$$

This is also known as the *thermal efficiency* of a heat engine cycle. A heat engine is very often called upon to extract as much work (net) as possible from a certain heat input, i.e., to maximize the cycle efficiency.

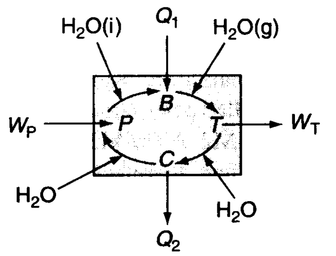


Fig. 6.3 *Cyclic heat engine with energy interactions represented in a block diagram*

6.3 ENERGY RESERVOIRS

A thermal energy reservoir (TER) is defined as a large body of infinite heat capacity, which is capable of absorbing or rejecting an unlimited quantity of heat without suffering appreciable changes in its thermodynamic coordinates. The changes that do take place in the large body as heat enters or leaves are so very slow and so very minute that all processes within it are quasi-static.

The thermal energy reservoir TER_H from which heat Q_1 is transferred to the system operating in a heat engine cycle is called the *source*. The thermal energy reservoir TER_L to which heat Q_2 is rejected from the system during a cycle is the *sink*. A typical source is a constant temperature furnace where fuel is continuously burnt, and a typical sink is a river or sea or the atmosphere itself.

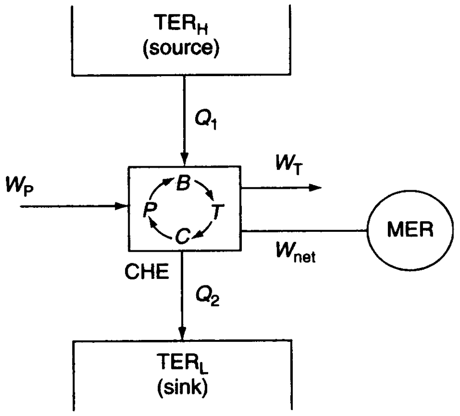


Fig. 6.4 *Cyclic heat engine (CHE) with source and sink*

A mechanical energy reservoir (MER) is a large body enclosed by an adiabatic impermeable wall capable of storing work as potential energy (such as a raised weight or wound spring) or kinetic energy (such as a rotating flywheel). All processes of interest within an MER are essentially quasi-static. An MER receives and delivers mechanical energy quasi-statically.

Figure 6.4 shows a cyclic heat engine exchanging heat with a source and a sink and delivering W_{net} in a cycle to an MER.

6.4 KELVIN-PLANCK STATEMENT OF SECOND LAW

The efficiency of a heat engine is given by

$$\eta = \frac{W_{\text{net}}}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Experience shows that $W_{\text{net}} < Q_1$, since heat Q_1 transferred to a system cannot be completely converted to work in a cycle (Article 6.1). Therefore, η is less than unity. A heat engine can never be 100% efficient. Therefore, $Q_2 > 0$, i.e., there has always to be a heat rejection. To produce net work in a thermodynamic cycle, a heat engine has thus to exchange heat with two reservoirs, the source and the sink.

The *Kelvin-Planck statement* of the second law states: *It is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single fixed temperature.*

If $Q_2 = 0$ (i.e., $W_{net} = Q_1$, or $\eta = 1.00$), the heat engine will produce net work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement (Fig. 6.5). Such a heat engine is called a *perpetual motion machine of the second kind*, abbreviated to PMM2. A PMM2 is impossible.

A heat engine has, therefore, to exchange heat with two thermal energy reservoirs at two different temperatures to produce net work in a complete cycle (Fig. 6.6). So long as there is a difference in temperature, motive power (i.e. work) can be produced. If the bodies with which the heat engine exchanges heat are of finite heat capacities, work will be produced by the heat engine till the temperatures of the two bodies are equalized.

If the second law were not true, it would be possible to drive a ship across the ocean by extracting heat from the ocean or to run a power plant by extracting heat from the surrounding air. Neither of these impollibilities violates the first law of thermodynamics. Both the ocean and the surrounding air contain an enormous store of internal energy, which, in principle, may be extracted in the from of a flow of heat. There is nothing in the first law to preclude the possibility of converting this heat completely into work. The second law is, therefore, a separate law of nature, and not a deduction of the first law. The first law denies the possibility of creating or destroying energy; the second denies the possibility of utilizing energy in a particular way. The continual operation of a machine that creates its own energy and thus violates the first law is called the PMM1. The operation of a machine that utilizes the internal energy of only one TER, thus violating the second law, is called PMM2.

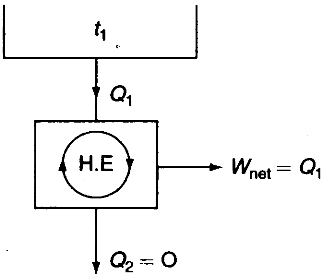


Fig. 6.5 *A PMM2*

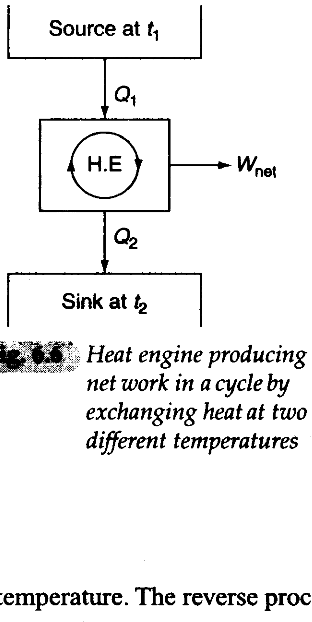


Fig. 6.6 *Heat engine producing net work in a cycle by exchanging heat at two different temperatures*

6.5 CLAUSIUS' STATEMENT OF THE SECOND LAW

Heat always flows from a body at a higher temperature to a body at a lower temperature. The reverse process never occurs spontaneously.

Clausius' statement of the second law gives: *It is impossible to construct a device which, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body.*

Heat cannot flow of itself from a body at a lower temperature to a body at a higher temperature. Some work must be expended to achieve this.

6.6 REFRIGERATOR AND HEAT PUMP

A *refrigerator* is a device which, operating in a cycle, maintains a body at a temperature lower than the temperature of the surroundings. Let the body A (Fig. 6.7) be maintained at t_2, which is lower than the ambient temperature t_1. Even though A is insulated, there will always be heat leakage Q_2 into the body from the surroundings by virtue of the temperature difference. In order to maintain, body A at the constant temperature t_2, heat has to be removed from the body at the same rate at which heat is leaking into the body. This heat (Q_2) is absorbed by a working fluid, called the refrigerant, which evaporates in the evaporator E_1 at a temperature lower than t_2 absorbing the latent heat of vaporization from the body A which is cooled or refrigerated (Process 4–1). The vapour is first compressed

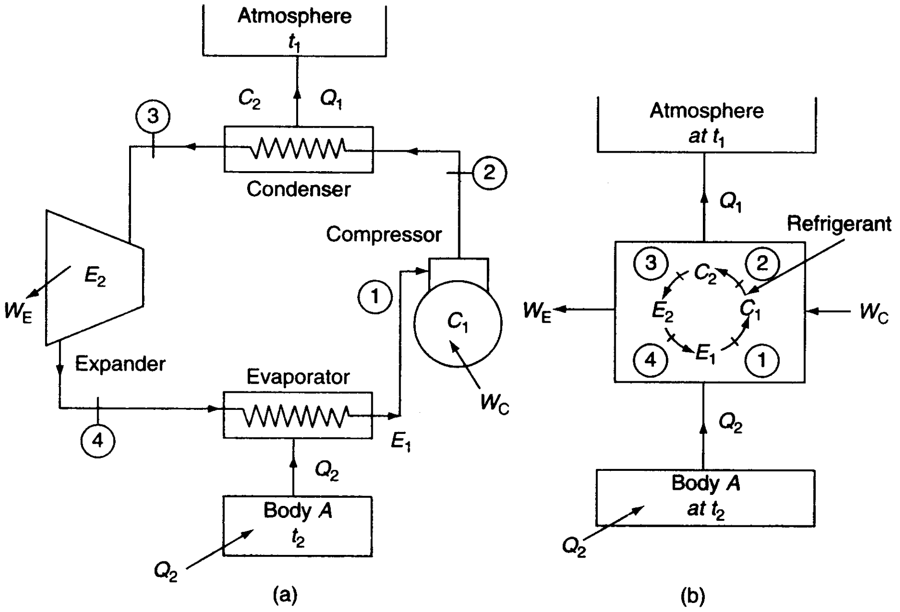


Fig. 6.7 A cyclic refrigeration plant

in the compressor C_1 driven by a motor which absorbs work W_C (Process 1–2), and is then condensed in the condenser C_2 rejecting the latent heat of condensation Q_1 at a temperature higher than that of the atmosphere (at t_1) for heat transfer to take place (Process 2–3). The condensate then expands adiabatically through an expander (an engine or turbine) producing work W_E, when the temperature drops to a value lower than t_2 such that heat Q_2 flows from the body A to make the refrigerant evaporate (Process 3–4). Such a cyclic device of flow through E_1–C_1–C_2–E_2 is called a *refrigerator*. In a refrigerator cycle, attention is concentrated on the body A. Q_2 and W are of primary interest. Just like efficiency in a heat engine cycle, there is a performance parameter in a refrigerator cycle, called the *coefficient of performance*, abbreviated to COP, which is defined as

$$\text{COP} = \frac{\text{Desired effect}}{\text{Work input}} = \frac{Q_2}{W}$$

$$\therefore \qquad [\text{COP}]_{\text{ref}} = \frac{Q_2}{Q_1 - Q_2} \qquad (6.6)$$

A *heat pump* is a device which, operating in a cycle, maintains a body, say B (Fig. 6.8), at a temperature higher than the temperature of the surroundings. By virtue of the temperature difference, there will be heat leakage Q_1 from the body to the surroundings. The body will be maintained at the constant temperature t_1, if heat is discharged into the body at the same rate at which heat leaks out of the body. The heat is extracted from the low temperature reservoir, which is nothing but the atmosphere, and discharged into the high temperature body B, with the expenditure of work W in a cyclic device called a heat pump. The working fluid operates in a cycle flowing through the evaporator E_1,

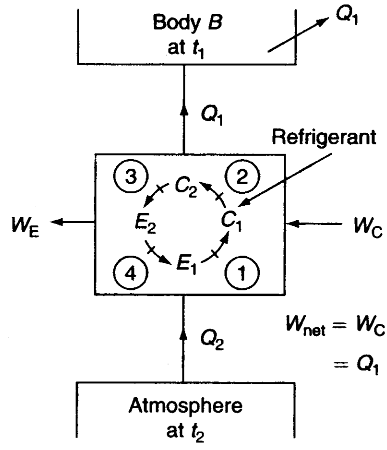


Fig. 6.8 A cycle heat pump

compressor C_1, condenser C_2 and expander E_2, similar to a refrigerator, but the attention is here focussed on the high temperature body B. Here Q_1 and W are of primary interest, and the COP is defined as

$$\text{COP} = \frac{Q_1}{W}$$

$$\therefore \qquad [\text{COP}]_{\text{H.P.}} = \frac{Q_1}{Q_1 - Q_2} \tag{6.7}$$

From Eqs (6.6) and (6.7), it is found that

$$[\text{COP}]_{\text{H.P.}} = [\text{COP}]_{\text{ref}} + 1 \tag{6.8}$$

The COP of a heat pump is greater than the COP of a refrigerator by unity. Equation (6.8) expresses a very interesting feature of a heat pump.

Since

$$Q_1 = [\text{COP}]_{\text{H.P.}}\, W$$

$$= [\text{COP}_{\text{ref}} + 1]\, W \tag{6.9}$$

Q_1 is always greater than W.

For an electrical resistance heater, if W is the electrical energy consumption, then the heat transferred to the space at steady state is W only, i.e., $Q_1 = W$.

A 1 kW electric heater can give 1 kW of heat at steady state and nothing more. In other words, 1 kW of work (high grade energy) dissipates to give 1 kW of heat (low grade energy), which is thermodynamically inefficient.

However, if this electrical energy W is used to drive the compressor of a heat pump, the heat supplied Q_1 will always be more than W, or $Q_1 > W$. Thus, a heat pump provides a thermodynamic advantage over direct heating.

For heat to flow from a cooler to a hotter body, W cannot be zero, and hence, the COP (both for refrigerator and heat pump) cannot be infinity. Therefore, $W > 0$, and COP $< \infty$.

6.7 EQUIVALENCE OF KELVIN-PLANCK AND CLAUSIUS STATEMENTS

At first sight, Kelvin-Planck's and Clausius' statements may appear to be unconnected, but it can easily be shown that they are virtually two parallel statements of the second law and are equivalent in all respects.

The equivalence of the two statements will be proved if it can be shown that the violation of one statement implies the violation of the second, and vice versa. (a) Let us first consider a cyclic heat pump P which transfers heat from a low temperature reservoir (t_2) to a high temperature reservoir (t_1) with no other effect, i.e., with no expenditure of work, violating Clausius statement (Fig. 6.9).

Let us assume a cyclic heat engine E operating between the same thermal energy reservoirs, producing W_{net} in one cycle. The rate of working of the heat engine is such that it draws an amount of heat Q_1 from the hot reservoir equal to that discharged by the heat pump. Then the hot reservoir may be eliminated and the heat Q_1 discharged by the heat pump is fed to the heat engine. So we see that the heat pump P and the heat engine E acting together constitute a heat engine operating in cycles and producing net work while exchanging heat only with one body at a single fixed temperature. This violates the Kelvin-Planck statement.

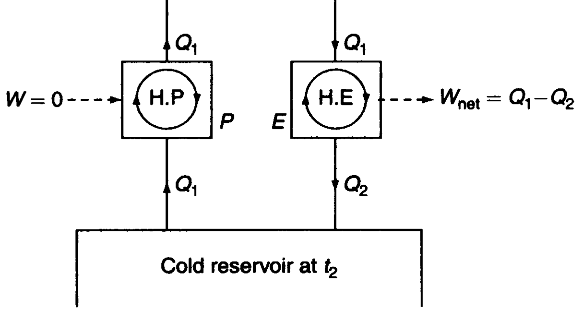


Fig. 6.9 Violation of the Clausius statement

(b) Let us now consider a perpetual motion machine of the second kind (E) which produces net work in a cycle by exchanging heat with only one thermal energy reservoir (at t_1) and thus violates the Kelvin-Planck statement (Fig. 6.10).

Let us assume a cyclic heat pump (P) extracting heat Q_2 from a low temperature reservoir at t_2 and discharging heat to the high temperature reservoir at t_1 with the expenditure of work W equal to what the PMM2 delivers in a complete cycle. So E and P together constitute a heat pump working in cycles and producing the sole effect of transferring heat from a lower to a higher temperature body, thus violating the Clausius statement.

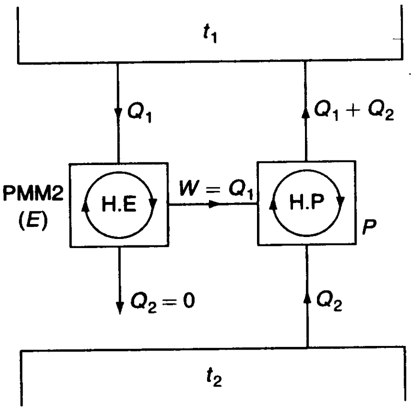


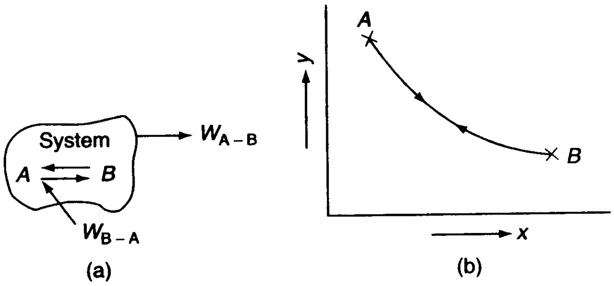
Fig. 6.10 *Violation of the Kelvin-Planck statement*

6.8 REVERSIBILITY AND IRREVERSIBILITY

The second law of thermodynamics enables us to divide all processes into two classes:

(a) Reversible or ideal process.
(b) Irreversible or natural process.

A *reversible* process is one which is performed in such a way that at the conclusion of the process, both the system and the surroundings may be restored to their initial states, without producing any changes in the rest of the universe. Let the state of a system be represented by A (Fig. 6.11), and let the system be taken to state B by following the path $A-B$. If the system and also the surroundings are restored to their initial states and no change in the universe is produced, then the process $A-B$ will be a reversible process. In the reverse process, the system has to be taken from state B to A by following the same path $B-A$. A reversible process should not leave any trace or relic to show that the process had ever occurred.



(a) (b)

Fig. 6.11 *Reversible process*

A reversible process is carried out infinitely slowly with an infinitesimal gradient, so that every state passed through by the system is an equilibrium state. So a reversible process coincides with a quasi-static process.

Any natural process carried out with a finite gradient is an irreversible process. A reversible process, which consists of a *succession of equilibrium states*, is an idealized hypothetical process, approached only as a limit. It is said to be an *asymptote to reality*. All spontaneous processes are irreversible.

6.9 CAUSES OF IRREVERSIBILITY

Broken eggs, split milk, burnt boats, the wasted years of indolence that the locusts have eaten are merly proverbial metaphors for irreversibility.

The irreversibility of a process may be due to either one or both of the following:

(a) Lack of equilibrium during the process.
(b) Involvement of dissipative effects.

6.9.1 Irreversibility due to Lack of Equilibrium

The lack of equilibrium (mechanical, thermal or chemical) between the system and its surroundings, or between two systems, or two parts of the same system, causes a spontaneous change which is irreversible. The following are specific examples in this regard:

(a) Heat Transfer through a Finite Temperature Difference A heat transfer process approaches reversibility as the temperature difference between two bodies approaches zero. We define a reversible heat transfer process as one in which heat is transferred through an infinitesimal temperature difference. So to transfer a finite amount of heat through an infinitesimal temperature difference would require an infinite amount of time, or infinite area. All actual heat transfer processes are through a finite temperature difference and are, therefore, irreversible, and greater the temperature difference, the greater is the irreversibility.

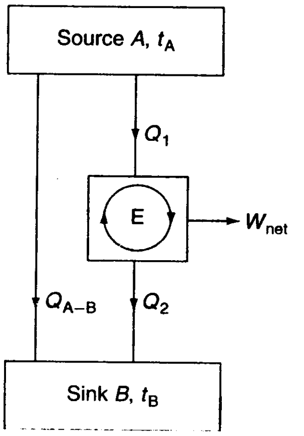


Fig. 6.12 *Heat transfer a finite temperature difference*

We can demonstrate by the second law that heat transfer through a finite temperature difference is irreversible. Let us assume that a source at t_A and a sink at t_B ($t_A > t_B$) are available, and let Q_{A-B} be the amount of heat flowing from A to B (Fig. 6.12). Let us assume an engine operating between A and B, taking heat Q_1 from A and discharging heat Q_2 to B. Let the heat transfer process be reversed, and Q_{B-A} be the heat flowing from B to A, and let the rate of working of the engine be such that $Q_2 = Q_{B-A}$.

(Fig. 6.13). Then the sink B may be eliminated. The net result is that E produces net work W in a cycle by exchanging heat only with A, thus violating the Kelvin-Planck statement. So the heat transfer process Q_{A-B} is irreversible, and Q_{B-A} is not possible.

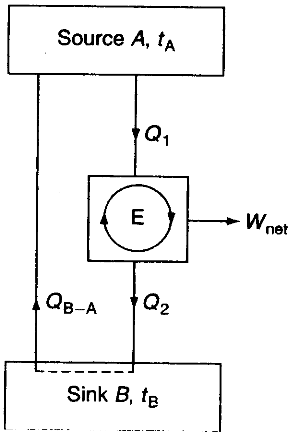


Fig. 6.13 *Heat transfer through a finite temperature difference is irreversible*

(b) Lack of Pressure Equilibrium within the Interior of the System or between the System and the Surroundings When there exists a difference in pressure between the system and the surroundings, or within the system itself, then both the system and its surroundings or the system alone, will undergo a change of state which will cease only when mechanical equilibrium is established. The reverse of this process is not possible spontaneously without producing any other effect. That the reverse process will violate the second law becomes obvious from the following illustration.

(c) Free Expansion Let us consider an insulated container (Fig. 6.14) which is divided into two compartments A and B by a thin diaphragm. Compartment A contains a mass of gas, while compartment B is completely evacuated. If the diaphragm is punctured, the gas in A will expand into B until the pressures in A and B become equal. This is known as free or unrestrained expansion. We can demonstrate by the second law, that the process of free expansion is irreversible.

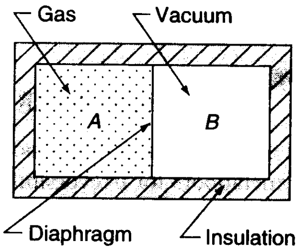


Fig. 6.14 *Free expansion*

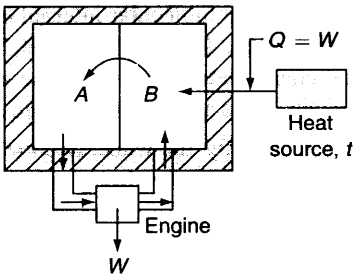


Fig. 6.15 *Second law demonstrates that free expansion is irreversible*

To prove this, let us assume that free expansion is reversible, and that the gas in *B* returns into *A* with an increase in pressure, and *B* becomes evacuated as before (Fig. 6.15). There is no other effect. Let us install an engine (a machine, not a cyclic heat engine) between *A* and *B*, and permit the gas to expand through the engine from *A* to *B*. The engine develops a work output *W* at the expense of the internal energy of the gas. The internal energy of the gas (system) in *B* can be restored to its initial value by heat transfer Q $(= W)$ from a source. Now, by the use of the reversed free expansion, the system can be restored to the initial state of high pressure in *A* and vacuum in *B*. The net result is a cycle, in which we observe that net work output *W* is accomplished by exchanging heat with a single reservoir. This violates the Kelvin-Planck statement. Hence, free expansion is irreversible.

The same argument will hold if the compartment *B* is not in vacuum but at a pressure lower than that in compartment *A* (case b).

6.9.2 Irreversibility due to Dissipative Effects

The irreversibility of a process may be due to the *dissipative effects* in which work is done without producing an equivalent increase in the kinetic or potential energy of any system. The transformation of work into molecular internal energy either of the system or of the reservoir takes place through the agency of such phenomena as friction, viscosity, inelasticity, electrical resistance, and magnetic hysteresis. These effects are known as dissipative effects, and work is said to be dissipated. Dissipation of energy means the transition of ordered macroscopic motion into chaotic molecular motion, the reverse of which is not possible without violating second law.

(a) Friction Friction is always present in moving devices. Friction may be reduced by suitable lubrication, but it can never be completely eliminated. If this were possible, a movable device could be kept in continual motion without violating either of the two laws of thermodynamics. The continual motion of a movable device in the complete absence of friction is known as *perpetual motion of the third kind.*

That friction makes a process irreversible can be demonstrated by the second law. Let us consider a system consisting of a flywheel and a brake block (Fig. 6.16). The flywheel was rotating with a certain rpm, and it was brought to rest by applying the friction brake. The distance moved by the brake block is very small, so work transfer is very nearly equal to zero. If the braking process occurs very rapidly, there is little heat transfer. Using suffix 2 after braking and suffix 1 before braking, and applying the first law, we have

$$Q_{1-2} = E_2 - E_1 + W_{1-2} \qquad 0 = E_2 - E_1 + 0$$

$$\therefore \qquad E_2 = E_1 \qquad (6.10)$$

The energy of the system (isolated) remains constant. Since the energy may exist in the forms of kinetic, potential, and molecular internal energy, we have

$$U_2 + \frac{mV_2^2}{2} + mZ_2g = U_1 + \frac{mV_1^2}{2} + mZ_1g$$

Since the wheel is brought to rest, $V_2 = 0$, and there is no change in P.E.

$$U_2 = U_1 + \frac{mV_1^2}{2} \qquad (6.11)$$

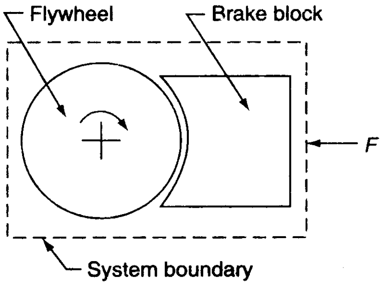


Fig. 6.16 *Irreversibility due to dissipative effect like friction*

Therefore, the molecular internal energy of the system (i.e., of the brake and the wheel) increases by the absorption of the K.E. of the wheel. The reverse process, i.e., the conversion of this increase in molecular internal energy into K.E. within the system to cause the wheel to rotate is not possible. To prove it by the second law, let us assume that it is possible, and imagine the following cycle with three processes:

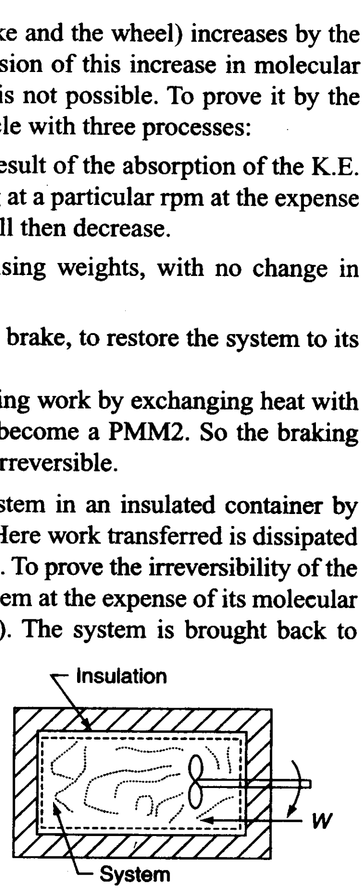
Process A: Initially, the wheel and the brake are at high temperature as a result of the absorption of the K.E. of the wheel, and the flywheel is at rest. Let the flywheel now start rotating at a particular rpm at the expense of the internal energy of the wheel and brake, the temperature of which will then decrease.

Process B: Let the flywheel be brought to rest by using its K.E. in raising weights, with no change in temperature.

Process C: Now let heat be supplied from a source to the flywheel and the brake, to restore the system to its initial state.

Therefore, the processes *A*, *B*, and *C* together constitute a cycle producing work by exchanging heat with a single reservoir. This violates the Kelvin-Planck statement, and it will become a PMM2. So the braking process, i.e., the transformation of K.E. into molecular internal energy, is irreversible.

(b) Paddle-Wheel Work Transfer Work may be transferred into a system in an insulated container by means of a paddle wheel (Fig. 6.17) which is also known as stirring work. Here work transferred is dissipated adiabatically into an increase in the molecular internal energy of the system. To prove the irreversibility of the process, let us assume that the same amount of work is delivered by the system at the expense of its molecular internal energy, and the temperature of the system goes down (Fig. 6.18). The system is brought back to its initial state by heat transfer from a source. These two processes together constitute a cycle in which there is work output and the system exchanges heat with a single reservoir. It becomes a PMM2, and hence the dissipation of stirring work to internal energy is irreversible.



Adiabatic work transfer

(c) Transfer of Electricity through a Resistor The flow of electric current through a wire represents work transfer, because the current can drive a motor which can raise a weight. Taking the wire or the resistor as the system (Fig. 6.19) and writing the first law

$$Q_{1-2} = U_2 - U_1 + W_{1-2}$$

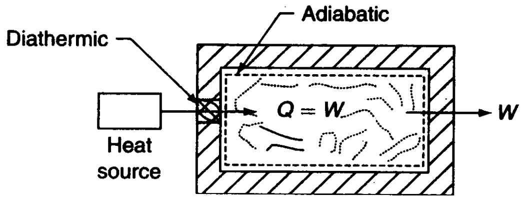
Here both W_{1-2} and Q_{1-2} are negative.

$$\therefore \qquad W_{1-2} = U_2 - U_1 + Q_{1-2} \qquad (6.12)$$

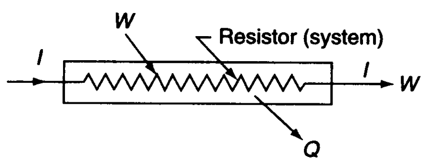
A part of the work transfer is stored as an increase in the internal energy of the wire (to give an increase in its temperature), and the remainder leaves the system as heat. At steady state, the internal energy and hence the temperature of the resistor become constant with respect to time and

$$W_{1-2} = Q_{1-2} \qquad (6.13)$$

The reverse process, i.e., the conversion of heat Q_{1-2} into electrical work W_{1-2} of the same magnitude is not possible. Let us assume that this is possible. Then heat Q_{1-2} will be absorbed and equal work W_{1-2} will be delivered. But this will become a PMM2. So the dissipation of electrical work into internal energy or heat is irreversible.



Irreversibility due to dissipation of stirring work into internal energy



Irreversibility due to dissipation of electrical work into internal energy

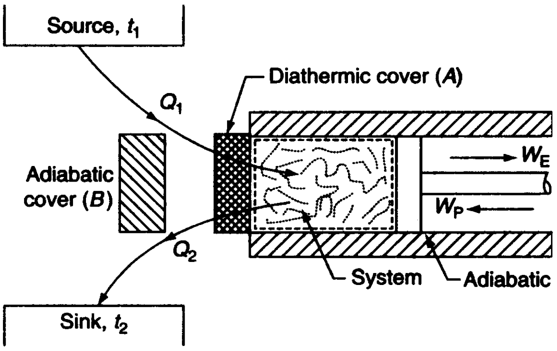
6.10 CONDITIONS FOR REVERSIBILITY

A natural process is irreversible because the conditions for mechanical, thermal and chemical equilibrium are not satisfied, and the dissipative effects, in which work is transformed into an increase in internal energy, are present. For a process to be reversible, it must not possess these features. If a process is performed quasi-statically, the system passes through states of thermodynamic equilibrium, which may be traversed as well in one direction as in the opposite direction. *If there are no dissipative effects, all the work done by the system during the performance of a process in one direction can be returned to the system during the reverse process.*

A process will be reversible when it is performed in such a way *that the system is at all times infinitesimally near a state of thermodynamic equilibrium and in the absence of dissipative effect of any form.* Reversible processes are, therefore, purely ideal, limiting cases of actual processes.

6.11 CARNOT CYCLE

A reversible cycle is an ideal hypothetical cycle in which all the processes constituting the cycle are reversible. Carnot cycle is a reversible cycle. For a stationary system, as in a piston and cylinder machine, the cycle consists of the following four successive processes (Fig. 6.20):



Carnot heat engine-stationary system

(a) *A reversible isothermal process* in which heat Q_1 enters the system at t_1 reversibly from a constant temperature source at t_1 when the cylinder cover is in contact with the diathermic cover A. The internal energy of the system increases.

From First law, $Q_1 = U_2 - U_1 + W_{1-2}$ (6.14)
(for an ideal gas only, $U_1 = U_2$)

(b) *A reversible adiabatic process* in which the diathermic cover A is replaced by the adiabatic cover B, and work W_E is done by the system adiabatically and reversibly at the expense of its internal energy, and the temperature of the system decreases from t_1 to t_2.

Using the first law, $0 = U_3 - U_2 + W_{2-3}$ (6.15)

(c) *A reversible isothermal process* in which B is replaced by A and heat Q_2 leaves the system at t_2 to a constant temperature sink at t_2 reversibly, and the internal energy of the system further decreases.

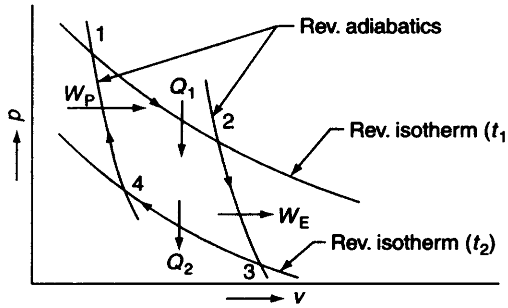
From the first law, $-Q_2 = U_4 - U_3 - W_{3-4}$ (6.16)
only for an ideal gas, $U_3 = U_4$

(d) *A reversible adiabatic process* in which B again replaces A, and work W_p is done upon the system reversibly and adiabatically, and the internal energy of the system increases and the temperature rises from t_2 to t_1.

Applying the first law,

$$0 = U_1 - U_4 - W_{4-1} \quad (6.17)$$

Two reversible isotherms and two reversible adiabatics constitute a Carnot cycle, which is represented in p–v coordinates in Fig. 6.21.



Carnot cycle

Summing up Eqs (6.14) to (6.17),

$$Q_1 - Q_2 = (W_{1-2} + W_{2-3}) - (W_{3-4} + W_{4-1})$$

or

$$\sum_{\text{cycle}} Q_{\text{net}} = \sum_{\text{cycle}} W_{\text{net}}$$

A cyclic heat engine operating on the Carnot cycle is called a Carnot heat engine.

For a steady flow system, the Carnot cycle is represented as shown in Fig. 6.22. Here heat Q_1 is transferred to the system reversibly and isothermally at t_1 in the heat exchanger A, work W_T is done by the system reversibly and adiabatically in the turbine (B), then heat Q_2 is transferred from the system reversibly and isothermally at t_2 in the heat exchanger (C), and then work W_P is done upon the system reversibly and adiabatically by the pump (D). To satisfy the conditions for the Carnot cycle, there must not be any friction or heat transfer in the pipelines through which the working fluid flows.

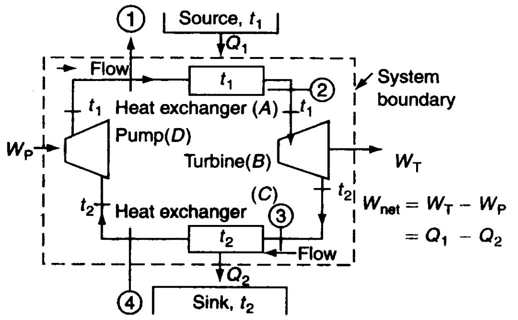


Fig. 6.22 *Carnot heat engine–steady flow system*

6.12 REVERSED HEAT ENGINE

Since all the processes of the Carnot cycle are reversible, it is possible to imagine that the processes are individually reversed and carried out in reverse order. When a reversible process is reversed, all the energy transfers associated with the process are reversed in direction, but remain the same in magnitude. The reversed Carnot cycle for a steady flow system is shown in Fig. 6.23. The reversible heat engine and the reversed Carnot heat engine are represented in block diagrams in Fig. 6.24. If E is a reversible heat engine (Fig. 6.24a), and if it is reversed (Fig. 6.24b), the quantities Q_1, Q_2 and W remain the same in magnitude, and only their directions are reversed. The reversed heat engine Ǝ takes heat from a low temperature body, discharges heat to a high temperature body, and receives an inward flow of network.

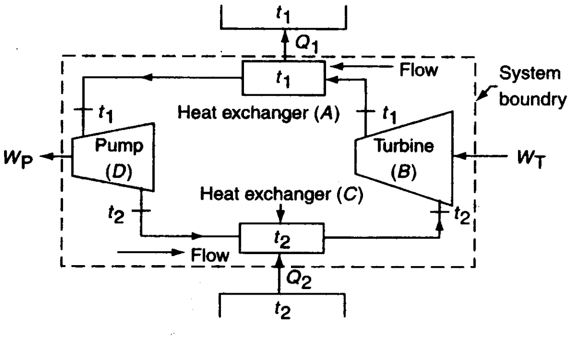
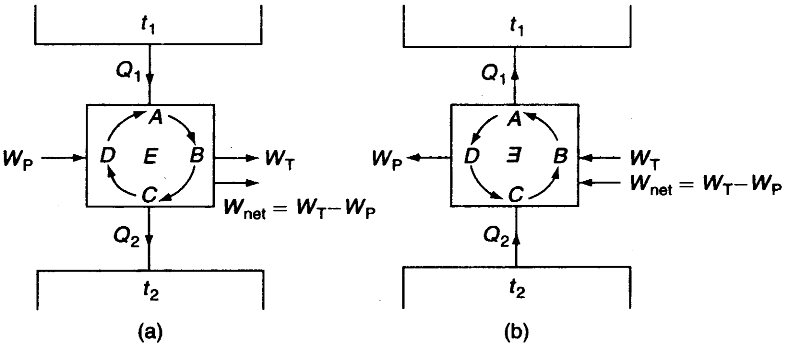


Fig. 6.23 *Reversed carnot heat engine-steady flow process*



(a) (b)

Fig. 6.24 *Carnot heat engine and reversed Carnot heat engine shown in block diagrams*

The names *heat pump* and *refrigerator* are applied to the reversed heat engine, which have already been discussed in Sec. 6.6, where the working fluid flows through the compressor (*B*), condenser (*A*), expander (*D*), and evaporator (*C*) to complete the cycle.

6.13 CARNOT'S THEOREM

It states that of all heat engines operating between a given constant temperature source and a given constant temperature sink, none has a higher efficiency than a reversible engine.

Let two heat engines E_A and E_B operate between the given source at temperature t_1 and the given sink at temperature t_2 as shown in Fig. 6.25.

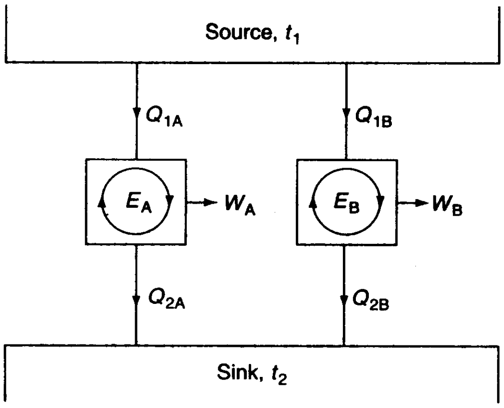


Fig. 6.25 *Two cyclic heat engines E_A and E_B operating between the same source and sink, of which E_B is reversible*

Let E_A be any heat engine and E_B be *any reversible* heat engine. We have to prove that the efficiency of E_B is more than that of E_A. Let us assume that this is not true and $\eta_A > \eta_B$. Let the rates of working of the engines be such that

$$Q_{1A} = Q_{1B} = Q_1$$

Since $\eta_A > \eta_B$

$$\frac{W_A}{Q_{1A}} > \frac{W_B}{Q_{1B}}$$

$$\therefore \qquad W_A > W_B$$

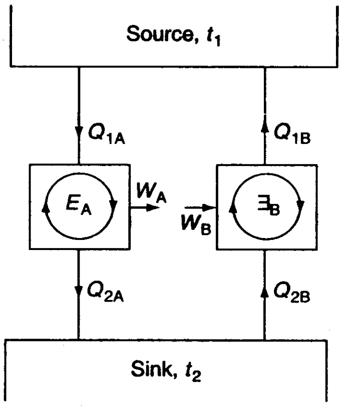


Fig. 6.26 *E_B is reversed*

Now, let E_B be reversed. Since E_B is a reversible heat engine, the magnitudes of heat and work transfer quantities will remain the same, but their directions will be reversed, as shown in Fig. 6.26. Since $W_A > W_B$, some part of W_A (equal to W_B) may be fed to drive the reversed heat engine $\exists_B$.

Since $Q_{1A} = Q_{1B} = Q_1$, the heat discharged by $\exists_B$ may be supplied to E_A. The source may, therefore, be eliminated (Fig. 6.27). The net result is that E_A and $\exists_B$ together constitute a heat engine which, operating in a cycle, produces net work $W_A - W_B$, while exchanging heat with a single reservoir at t_2. This violates the Kelvin-Planck statement of the second law. Hence the assumption that $\eta_A > \eta_B$ is wrong.

Therefore $$\eta_B \geq \eta_A$$

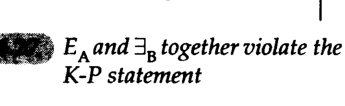


Fig. 6.27 *E_A and $\exists_B$ together violate the K-P statement*

6.14 COROLLARY OF CARNOT'S THEOREM

The efficiency of all reversible heat engines operating between the same temperature levels is the same.

Let both the heat engines E_A and E_B (Fig. 6.25) be reversible. Let us assume $\eta_A > \eta_B$. Similar to the procedure outlined in the preceding article, if E_B is reversed to run, say, as a heat pump using some part of the work output (W_A) of engine E_A, we see that the combined system of heat pump E_B and engine E_A, becomes a PMM2. So η_A cannot be greater than η_B. Similarly, if we assume $\eta_B > \eta_A$ and reverse the engine E_A, we observe that η_B cannot be greater than η_A.

Therefore
$$\eta_A = \eta_B$$

Since the efficiencies of all reversible heat engines operating between the same heat reservoirs are the same, *the efficiency of a reversible engine is independent of the nature or amount of the working substance undergoing the cycle.*

6.15 ABSOLUTE THERMODYNAMIC TEMPERATURE SCALE

The efficiency of any heat engine cycle receiving heat Q_1 and rejecting heat Q_2 is given by

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \tag{6.18}$$

By the second law, it is necessary to have a temperature difference $(t_1 - t_2)$ to obtain work of any cycle. We know that the efficiency of all heat engines operating between the same temperature levels is the same, and it is independent of the working substance. Therefore, for a reversible cycle (Carnot cycle), the efficiency will depend solely upon the temperatures t_1 and t_2, at which heat is transferred, or

$$\eta_{\text{rev}} = f(t_1, t_2) \tag{6.19}$$

where f signifies some function of the temperatures. From Eqs (6.18) and (6.19)

$$1 - \frac{Q_2}{Q_1} = f(t_1, t_2)$$

In terms of a new function F

$$\frac{Q_1}{Q_2} = F(t_1, t_2) \tag{6.20}$$

If some functional relationship is assigned between t_1, t_2 and Q_1/Q_2, the equation becomes the definition of a temperature scale.

Let us consider two reversible heat engines, E_1 receiving heat from the source at t_1, and rejecting heat at t_2 to E_2 which, in turn, rejects heat to the sink at t_3 (Fig. 6.28).

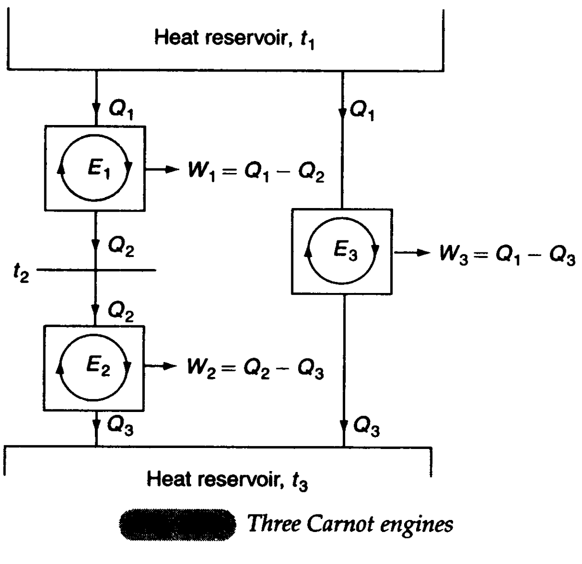
Now $$\frac{Q_1}{Q_2} = F(t_1, t_2); \quad \frac{Q_2}{Q_3} = F(t_2, t_3)$$

E_1 and E_2 together constitute another heat engine E_3 operating between t_1 and t_3.

$$\therefore \quad \frac{Q_1}{Q_3} = F(t_1, t_3)$$

Now $$\frac{Q_1}{Q_2} = \frac{Q_1/Q_3}{Q_2/Q_3}$$

or $$\frac{Q_1}{Q_2} = F(t_1, t_2) = \frac{F(t_1, t_3)}{F(t_2, t_3)} \tag{6.21}$$



Three Carnot engines

The temperatures t_1, t_2 and t_3 are arbitrarily chosen. The ratio Q_1/Q_2 depends only on t_1 and t_2, and is independent of t_3. So t_3 will drop out from the ratio on the right in Eq. (6.21). After it has been cancelled, the numerator can be written as $\phi(t_1)$, and the denominator as $\phi(t_2)$, where ϕ is another unknown function. Thus

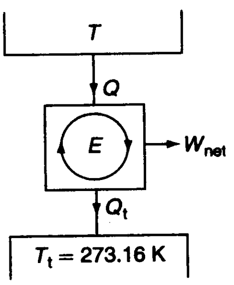
$$\frac{Q_1}{Q_2} = F(t_1, t_2) = \frac{\phi(t_1)}{\phi(t_2)}$$

Since $\phi(t)$ is an arbitrary function, the simplest possible way to define the ***absolute thermodynamic temperature*** T is to let $\phi(t) = T$, as proposed by Kelvin. Then, by definition

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{6.22}$$

The absolute thermodynamic temperature scale is also known as the ***Kelvin scale***. Two temperatures on the Kelvin scale bear the same relationship to each other as do the heats absorbed and rejected respectively by a Carnot engine operating between two reservoirs at these temperatures. The Kelvin temperature scale is, therefore, independent of the peculiar characteristics of any particular substance.

The heat absorbed Q_1 and the heat rejected Q_2 during the two reversible isothermal processes bounded by two reversible adiabatics in a Carnot engine can be measured. In defining the Kelvin temperature scale also, the triple point of water is taken as the standard reference point. For a Carnot engine operating between reservoirs at temperatures T and T_t, T_t being the triple point of water (Fig. 6.29), arbitrarily assigned the value 273.16 K,



Carnot heat engine with sink at triple point of water

$$\frac{Q}{Q_t} = \frac{T}{T_t}$$

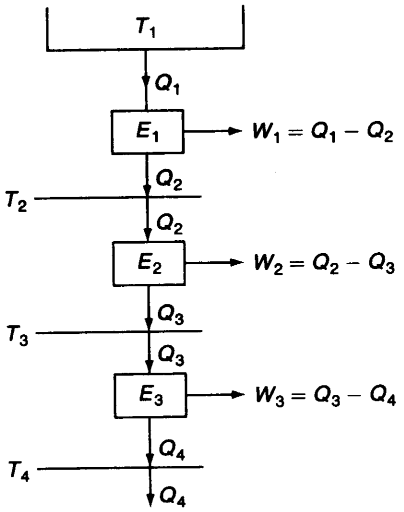
$$\therefore \quad T = 273.16\,\frac{Q}{Q_t} \tag{6.23}$$

If this equation is compared with the equations given in Article 2.3, it is seen that *in the Kelvin scale, Q plays the role of thermometric property*. The amount of heat supply Q changes with change in temperature, just like the thermal emf in a thermocouple.

It follows from the Eq. (6.23), $T = 273.16\,\dfrac{Q}{Q_t}$

that the heat transferred isothermally between the given adiabatics decreases as the temperature decreases. Conversely, the smaller the value of Q, the lower the corresponding T. The smallest possible value of Q is zero, and the corresponding T is absolute zero. Thus, if a system undergoes a reversible isothermal process without transfer of heat, the temperature at which this process takes place is called the *absolute zero*. Thus, *at absolute zero, an isotherm and an adiabatic are identical.*

That the absolute thermodynamic temperature scale has a definite zero point can be shown by imagining a series of reversible engines, extending from a source at T_1 to lower temperatures (Fig. 6.30).



Heat engines operating in series

Since $$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

$\therefore$ $$\frac{T_1 - T_2}{T_2} = \frac{Q_1 - Q_2}{Q_2}$$

or $$T_1 - T_2 = (Q_1 - Q_2)\frac{T_2}{Q_2}$$

Similarly

$$T_2 - T_3 = (Q_2 - Q_3)\frac{T_3}{Q_3}$$

$$= (Q_2 - Q_3)\frac{T_2}{Q_2}$$

$$T_3 - T_4 = (Q_3 - Q_4)\frac{T_2}{Q_2} \quad \text{and so on.}$$

If $T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \ldots$, assuming equal temperature intervals

$$Q_1 - Q_2 = Q_2 - Q_3 = Q_3 - Q_4 = \ldots$$

or $$W_1 = W_2 = W_3 = \ldots$$

Conversely, by making the work quantities performed by the engines in series equal ($W_1 = W_2 = W_3 = \ldots$), we will get $$T_1 - T_2 = T_2 - T_3 = T_3 - T_4 = \ldots$$
at equal temperature intervals. A scale having one hundred equal intervals between the steam point and the ice point could be realized by a series of one hundred Carnot engines operating as in Fig. 6.30. Such a scale would be independent of the working substance.

If enough engines are placed in series to make the total work output equal to Q_1, then by the first law the heat rejected from the last engine will be zero. By the second law, however, the operation of a cyclic heat engine with zero heat rejection cannot be achieved, although it may be approached as a limit. When the heat rejected approaches zero, the temperature of heat rejection also approaches zero as a limit. *Thus it appears that a definite zero point exists on the absolute temperature scale but this point cannot be reached without a violation of the second law.*

Thus any attainable value of absolute temperature is always greater than zero. This is also known as the *Third Law of Thermodynamics* which may be stated as follows: *It is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations.*

This is what is called the Fowler-Guggenheim statement of the third law. The third law itself is an independent law of nature, and not an extension of the second law. The concept of heat engine is not necessary to prove the non-attainability of absolute zero of temperature by any system in a finite number of operations.

6.16 EFFICIENCY OF THE REVERSIBLE HEAT ENGINE

The efficiency of a reversible heat engine in which heat is received solely at T_1 is found to be

$$\eta_{\text{rev}} = \eta_{\max} = 1 - \left(\frac{Q_2}{Q_1}\right)_{\text{rev}} = 1 - \frac{T_2}{T_1}$$

or $$\eta_{\text{rev}} = \frac{T_1 - T_2}{T_1}$$

It is observed here that as T_2 decreases, and T_1 increases, the efficiency of the reversible cycle increases. Since η is always less than unity, T_2 is always greater than zero and positive.

The COP of a refrigerator is given by

$$(\mathrm{COP})_{\mathrm{refr}} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}\ .$$

For a reversible refrigerator, using

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$[\mathrm{COP}_{\mathrm{refr}}]_{\mathrm{rev}} = \frac{T_2}{T_1 - T_2} \tag{6.24}$$

Similarly, for a reversible heat pump

$$[\mathrm{COP}_{\mathrm{H.P}}]_{\mathrm{rev}} = \frac{T_1}{T_1 - T_2} \tag{6.25}$$

6.17 EQUALITY OF IDEAL GAS TEMPERATURE AND KELVIN TEMPERATURE

Let us consider a Carnot cycle executed by an ideal gas, as shown in Fig. 6.31.

The two isothermal processes $a-b$ and $c-d$ are represented by equilateral hyperbolas whose equations are respectively

$$pV = nR\,\theta_1$$

and

$$pV = nR\,\theta_2$$

For any infinitesimal reversible process of an ideal gas, the first law may be written as

$$đQ = C_v\, d\theta + pdV$$

Applying this equation to the isothermal process $a-b$, the heat absorbed is found to be

$$Q_1 = \int_{V_a}^{V_b} p\mathrm{d}V = \int_{V_a}^{V_b} \frac{nR\theta_1}{V}\, dV = nR\theta_1 \ln \frac{V_b}{V_a}$$

Similarly, for the isothermal process $c-d$, the heat rejected is

$$Q_2 = nR\theta_2 \ln \frac{V_c}{V_d}$$

$$\therefore \qquad \frac{Q_1}{Q_2} = \frac{\theta_1 \ln \frac{V_b}{V_a}}{\theta_2 \ln \frac{V_c}{V_d}} \tag{6.26}$$

Since the process $b-c$ is adiabatic, the first law gives

$$-C_v\, d\theta = pdV = \frac{nR\theta}{V}\, dV \qquad \frac{1}{nR}\int_{\theta_2}^{\theta_1} C_v \frac{\mathrm{d}\theta}{\theta} = \ln \frac{V_c}{V_b}$$

Similarly, for the adiabatic process $d-a$

$$\frac{1}{nR}\int_{\theta_2}^{\theta_1} C_v \frac{\mathrm{d}\theta}{\theta} = \ln \frac{V_d}{V_a}$$

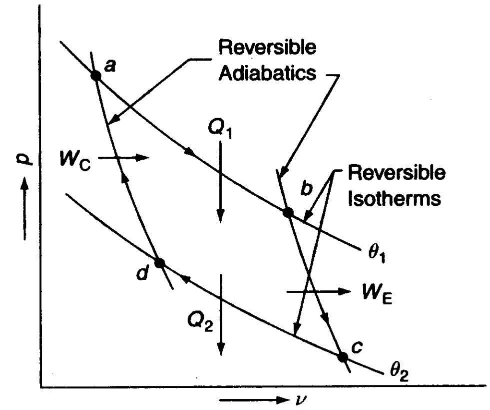


Fig. 6.31 Carnot cycle of an ideal gas

∴ $$\ln \frac{V_c}{V_b} = \ln \frac{V_d}{V_a}$$

or $$\frac{V_c}{V_b} = \frac{V_d}{V_a}$$

or $$\frac{V_b}{V_a} = \frac{V_c}{V_d} \tag{6.27}$$

Equation (6.26) thus reduces to

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2} \tag{6.28}$$

Kelvin temperature was defined by Eq. (6.22)

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

If θ and T refer to any temperature, and θ_t and T_t refer to the triple point of water,

$$\frac{\theta}{\theta_t} = \frac{T}{T_t}$$

Since $\theta_t = T_t = 273.16$ K, it follows that

$$\theta = T \tag{6.29}$$

The Kelvin temperature is, therefore, numerically equal to the ideal gas temperature and may be measured by means of a gas thermometer.

6.18 TYPES OF IRREVERSIBILITY

It has been discussed in Sec. 6.9 that a process becomes irreversible if it occurs due to a finite potential gradient like the gradient in temperature or pressure, or if there is dissipative effect like friction, in which work is transformed into internal energy increase of the system. Two types of irreversibility can be distinguished:

(a) Internal irreversibility
(b) External irreversibility

The *internal irreversibility* is caused by the internal dissipative effects like friction, turbulence, electrical resistance, magnetic hysteresis, etc. within the system. The *external irreversibility* refers to the irreversibility occurring at the system boundary like heat interaction with the surroundings due to a finite temperature gradient.

Sometimes, it is useful to make other distinctions. If the irreversibility of a process is due to the dissipation of work into the increase in internal energy of a system, or due to a finite pressure gradient, it is called *mechanical irreversibility*. If the process occurs on account of a finite temperature gradient, it is *thermal irreversibility*, and if it is due to a finite concentration gradient or a chemical reaction, it is called *chemical irreversibility*.

A heat engine cycle in which there is a temperature difference (i) between the source and the working fluid during heat supply, and (ii) between the working fluid and the sink during heat rejection, exhibits external thermal irreversibility. If the real source and sink are not considered and hypothetical reversible processes for heat supply and heat rejection are assumed, the cycle can be reversible. With the inclusion of the actual source and sink, however, the cycle becomes externally irreversible.

Solved Examples

Example 6.1

A cyclic heat engine operates between a source temperature of 800°C *and a sink temperature of* 30°C. *What is the least rate of heat rejection per kW net output of the engine?*

Solution For a reversible engine, the rate of heat rejection will be minimum (Fig. Ex. 6.1).

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

$$= 1 - \frac{30 + 273}{800 + 273}$$

$$= 1 - 0.282 = 0.718$$

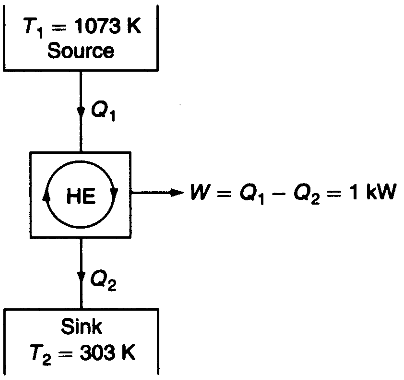
Now $$\frac{W_{\text{net}}}{Q_1} = \eta_{\max} = 0.718$$

∴ $$Q_1 = \frac{1}{0.718} = 1.392 \text{ kW}$$

Now $$Q_2 = Q_1 - W_{\text{net}} = 1.392 - 1$$

$$= 0.392 \text{ kW}$$

This is the least rate of heat rejection.



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Example 6.2

A domestic food freezer maintains a temperature of −15°C. *The ambient air temperature is* 30°C. *If heat leaks into the freezer at the continuous rate of* 1.75 *kJ/s what is the least power necessary to pump this heat out continuously?*

Solution Freezer temperature,

$$T_2 = -15 + 273 = 258 \text{ K}$$

Ambient air temperature,

$$T_1 = 30 + 273 = 303 \text{ K}$$

The refrigerator cycle removes heat from the freezer at the same rate at which heat leaks into it (Fig. Ex. 6.2).

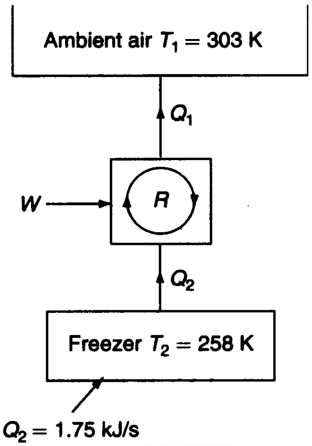
For minimum power requirement

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$$

∴ $$Q_1 = \frac{1.75}{2.8} \times 303 = 2.06 \text{ kJ/s}$$

∴ $$W = Q_1 - Q_2$$

$$= 2.06 - 1.75 = 0.31 \text{ kJ/s} = 0.31 \text{ kW}$$



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Example 6.3

A reversible heat engine operates between two reservoirs at temperatures of 600°C *and* 40°C. *The engine drives a reversible refrigerator which operates between reservoirs at temperatures of* 40°C *and* –20°C. *The heat transfer to the heat engine is* 2000 *kJ and the net work output of the combined engine refrigerator plant is* 360 *kJ.*

(*a*) *Evaluate the heat transfer to the refrigerant and the net heat transfer to the reservoir at* 40°C.
(*b*) *Reconsider* (*a*) *given that the efficiency of the heat engine and the COP of the refrigerator are each 40% of their maximum possible values.*

Solution (a) Maximum efficiency of the heat engine cycle (Fig. Ex. 6.3) is given by

$$\eta_{\max} = 1 - \frac{T_2}{T_1} = 1 - \frac{313}{873}$$

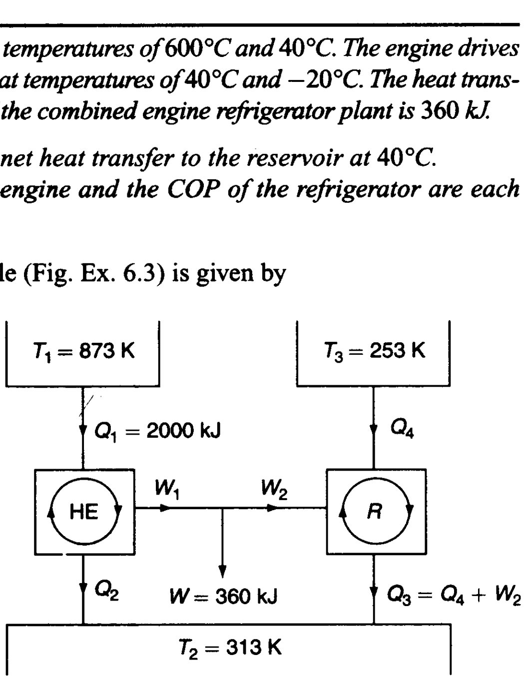
$$= 1 - 0.358 = 0.642$$

Again $\frac{W_1}{Q_1} = 0.642$

$\therefore \quad W_1 = 0.642 \times 2000 = 1284$ kJ

Maximum COP of the refrigerator cycle

$$(\text{COP})_{\max} = \frac{T_3}{T_2 - T_3} = \frac{253}{313 - 253} = 4.22$$



[illegible]

Also $\text{COP} = \frac{Q_4}{W_2} = 4.22$

Since $\quad W_1 - W_2 = W = 360$ kJ

$\therefore \quad W_2 = W_1 - W = 1284 - 360 = 924$ kJ

$\therefore \quad Q_4 = 4.22 \times 924 = 3899$ kJ

$\therefore \quad Q_3 = Q_4 + W_2 = 924 + 3899 = 4823$ kJ

$Q_2 = Q_1 - W_1 = 2000 - 1284 = 716$ kJ

Heat rejection to the 40°C reservoir

$$= Q_2 + Q_3 = 716 + 4823 = 5539 \text{ kJ}$$

Ans. (a)

(b) Efficiency of the actual heat engine cycle

$$\eta = 0.4\, \eta_{\max} = 0.4 \times 0.642$$

$\therefore \quad W_1 = 0.4 \times 0.642 \times 2000 = 513.6$ kJ

$\therefore \quad W_2 = 513.6 - 360 = 153.6$ kJ

COP of the actual refrigerator cycle

$$\text{COP} = \frac{Q_4}{W_2} = 0.4 \times 4.22 = 1.69$$

Therefore

$$Q_4 = 153.6 \times 1.69 = 259.6 \text{ kJ}$$

$$Q_3 = 259.6 + 153.6 = 413.2 \text{ kJ}$$ *Ans.* (b)

$$Q_2 = Q_1 - W_1 = 2000 - 513.6 = 1486.4 \text{ kJ}$$

Heat rejected to the 40°C reservoir

$$= Q_2 + Q_3 = 413.2 + 1486.4 = 1899.6 \text{ kJ}$$ *Ans.* (b)

Example 6.4

Which is the more effective way to increase the efficiency of a Carnot engine: to increase T_1, keeping T_2 constant; or to decrease T_2, keeping T_1 constant?

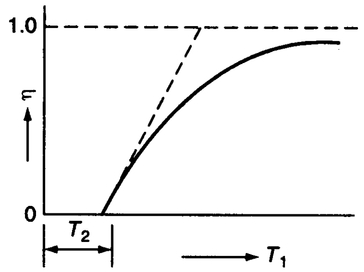
Solution The efficiency of a Carnot engine is given by

$$\eta = 1 - \frac{T_2}{T_1}$$

If T_2 is constant

$$\left(\frac{\partial \eta}{\partial T_1}\right)_{T_2} = \frac{T_2}{T_1^2}$$

As T_1 increases, η increases, and the slope $\left(\frac{\partial \eta}{\partial T_1}\right)_{T_2}$ decreases (Fig. Ex. 6.4.1).

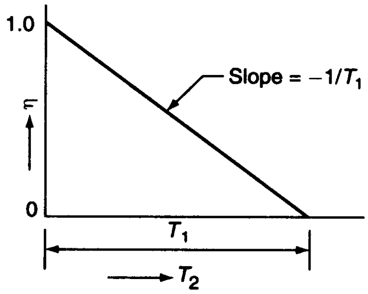


[redacted]

If T_1 is constant,

$$\left(\frac{\partial \eta}{\partial T_2}\right)_{T_1} = -\frac{1}{T_1}$$

As T_2 decreases, η increases, but the slope $\left(\frac{\partial \eta}{\partial T_2}\right)_{T_1}$ remains constant (Fig. Ex. 6.4.2).



[redacted]

Also $$\left(\frac{\partial \eta}{\partial T_1}\right)_{T_1} = \frac{T_2}{T_1^2} \text{ and } \left(\frac{\partial \eta}{\partial T_2}\right)_{T_1} = -\frac{T_1}{T_1^2}$$

Since $$T_1 > T_2, \left(\frac{\partial \eta}{\partial T_2}\right)_{T_1} > \left(\frac{\partial \eta}{\partial T_1}\right)_{T_2}$$

So, the more effective way to increase the efficiency is to decrease T_2. Alternatively, let T_2 be decreased by ΔT with T_1 remaining the same

$$\eta_1 = 1 - \frac{T_2 - \Delta T}{T_1}$$

If T_1 is increased by the same ΔT, T_2 remaining the same

$$\eta_2 = 1 - \frac{T_2}{T_1 + \Delta T}$$

Then

$$\eta_1 - \eta_2 = \frac{T_2}{T_1 + \Delta T} - \frac{T_2 - \Delta T}{T_1} = \frac{(T_1 - T_2)\Delta T + (\Delta T)^2}{T_1(T_1 + \Delta T)}$$

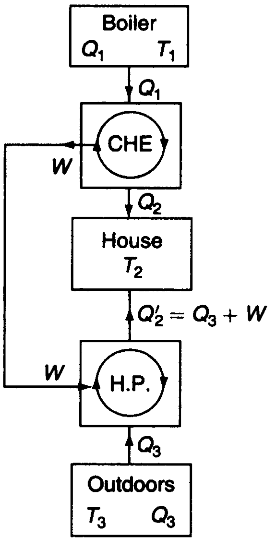
Since $$T_1 > T_2, (\eta_1 - \eta_2) > 0$$

The more effective way to increase the cycle efficiency is to decrease T_2.

Example 6.5

Kelvin was the first to point out the thermodynamic wastefulness of burning fuel for the direct heating of a house. It is much more economical to use the high temperature heat produced by combustion in a heat engine and then to use the work so developed to pump heat from outdoors up to the temperature desired in the house. In Fig. Ex. 6.5 a boiler furnishes heat Q_1 at the high temperature T_1. This heat is absorbed by a heat engine, which extracts work W and rejects the waste heat Q_2 into the house at T_2. Work W is in turn used to operate a mechanical refrigerator or heat pump, which extracts Q_3 from outdoors at temperature T_3 and reject Q'_2 (where $Q'_2 = Q_3 + W$) into the house. As a result of this cycle of operations, a total quantity of heat equal to $Q_2 + Q'_2$ is liberated in the house, against Q_1 which would be provided directly by the ordinary combustion of the fuel. Thus the ratio $(Q_2 + Q'_2)/Q_1$ represents the heat multiplication factor of this method. Determine this multiplication factor if $T_1 = 473$ K, $T_2 = 293$ K, and $T_3 = 273$ K.

Solution For the reversible heat engine (Fig. Ex. 6.5)



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$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$\therefore \quad Q_2 = Q_1\left(\frac{T_2}{T_1}\right)$$

Also

$$\eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

or

$$W = \frac{T_1 - T_2}{T_1} \cdot Q_1$$

For the reversible heat pump

$$\text{COP} = \frac{Q'_2}{W} = \frac{T_2}{T_2 - T_3}$$

$$\therefore \quad Q'_2 = \frac{T_2}{T_2 - T_3} \cdot \frac{T_1 - T_2}{T_1} \cdot Q_1$$

$\therefore$ Multiplication factor (M.F.)

$$= \frac{Q_2 + Q'_2}{Q_1} = \frac{Q_1 \dfrac{T_2}{T_1} + Q_1 \cdot \dfrac{T_2}{T_2 - T_3} \cdot \dfrac{T_1 - T_2}{T_1}}{Q_1}$$

or

$$\text{M.F.} = \frac{T_2^2 - T_2T_3 + T_2T_1 - T_2^2}{T_1(T_2 - T_3)}$$

or

$$\text{M.F.} = \frac{T_2(T_1 - T_3)}{T_1(T_2 - T_3)}$$

Here $T_1 = 473$ K, $T_2 = 293$ K and $T_3 = 273$ K

$$\therefore \quad \text{M.F.} = \frac{293(473 - 273)}{473(293 - 273)} = \frac{2930}{473} = 6.3 \qquad \textit{Ans.}$$

which means that every kg of coal burned would deliver the heat equivalent to over 6 kg. Of course, in an actual case, the efficiencies would be less than Carnot efficiencies, but even with a reduction of 50%, the possible savings would be quite significant.

Example 6.6

It is proposed that solar energy be used to warm a large collector plate. This energy would, in turn, be transferred as heat to a fluid within a heat engine, and the engine would reject energy as heat to the atmosphere. Experiments indicate that about 1880 kJ/m² h of energy can be collected when the plate is operating at 90°C. Estimate the minimum collector area that would be required for a plant producing 1 kW of useful shaft power. The atmospheric temperature may be assumed to be 20°C.

Solution The maximum efficiency for the heat engine operating between the collector plate temperature and the atmospheric temperature is

$$\eta_{\max} = 1 - \frac{T_2}{T_1} = 1 - \frac{293}{363} = 0.192$$

The efficiency of any actual heat engine operating between these temperatures would be less than this efficiency.

$$\therefore \qquad Q_{\min} = \frac{W}{\eta_{\max}} = \frac{1\ \text{kJ/s}}{0.192} = 5.21\ \text{kJ/s}$$

$$= 18{,}800\ \text{kJ/h}$$

∴ Minimum area required for the collector plate

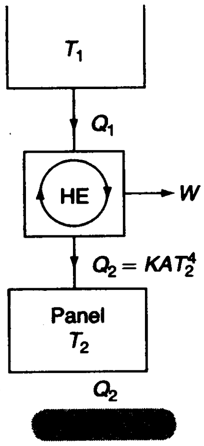
$$= \frac{18{,}800}{1880} = 10\ \text{m}^2 \qquad \textit{Ans.}$$

Example 6.7

A reversible heat engine in a satellite operates between a hot reservoir at T_1 and a radiating panel at T_2. Radiation from the panel is proportional to its area and to T_2^4. For a given work output and value of T_1 show that the area of the panel will be minimum when $\frac{T_2}{T_1} = 0.75$.

Determine the minimum area of the panel for an output of 1 kW if the constant of proportionality is 5.67×10^{-8} W/m² K⁴ and T_1 is 1000 K.

Solution For the heat engine (Fig. Ex. 6.7), the heat rejected Q_2 to the panel (at T_2) is equal to the energy emitted from the panel to the surroundings by radiation. If A is the area of the panel, $Q_2 \propto AT_2^4$, or $Q_2 = KAT_2^4$, where K is a constant.



Now
$$\eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

or
$$\frac{W}{T_1 - T_2} = \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{KAT_2^4}{T_2}$$

$$= KAT_2^3$$

$$\therefore \qquad A = \frac{W}{KT_2^3(T_1 - T_2)} = \frac{W}{K(T_1T_2^3 - T_2^4)}$$

For a given W and T_1, A will be minimum when

$$\frac{dA}{dT_2} = -\frac{W}{K}(3T_1T_2^2 - 4T_2^3)\,.\,(T_1T_2^3 - T_2^4)^{-2} = 0$$

Since $(T_1T_2^3 - T_2^4)^{-2} \neq 0,\ 3T_1T_2^2 = 4T_2^3$

$\therefore$ $\frac{T_2}{T_1} = 0.75$ Proved.

$\because$

$$A_{\min} = \frac{W}{K(0.75)^3T_1^3(T_1 - 0.75T_1)}$$

$$= \frac{W}{K\frac{27}{256}T_1^4} = \frac{256W}{27KT_1^4}$$

Here $W = 1$ kW, $K = 5.67 \times 10^{-8}$ W/m^2 K^4, and $T_1 = 1000$ K

$\therefore$

$$A_{\min} = \frac{256 \times 1\text{kW} \times \text{m}^2\text{K}^4}{27 \times 5.67 \times 10^{-8}\text{W} \times (1000)^4\text{K}^4}$$

$$= \frac{256 \times 10^3}{27 \times 5.67 \times 10^{-8} \times 10^{12}}\ \text{m}^2 = 0.1672\ \text{m}^2$$ *Ans.*

Review Questions

6.1 What is the qualitative difference between heat and work? Why are heat and work not completely interchangeable forms of energy?

6.2 What is a cyclic heat engine?

6.3 Explain a heat engine cycle performed by a closed system.

6.4 Explain a heat engine cycle performed by a steady flow system.

6.5 Define the thermal efficiency of a heat engine cycle. Can this be 100%?

6.6 Draw a block diagram showing the four energy interactions of a cyclic heat engine.

6.7 What is a thermal energy reservoir? Explain the terms 'source' and 'sink'

6.8 What is a mechanical energy reservoir?

6.9 Why can all processes in a TER or an MER be assumed to be quasi-static?

6.10 Give the Kelvin-Planck statement of the second law.

6.11 To produce net work in a thermodynamic cycle, a heat engine has to exchange heat with two thermal reservoirs. Explain.

6.12 What is a PMM2? Why is it impossible?

6.13 Give the Clausius' statement of the second law.

6.14 Explain the operation of a cyclic refrigerator plant with a block diagram.

6.15 Define the COP of a refrigerator.

6.16 What is a heat pump? How does it differ from a refrigerator?

6.17 Can you use the same plant as a heat pump in winter and as a refrigerator in summer? Explain.

6.18 Show that the COP of a heat pump is greater than the COP of a refrigerator by unity.

6.19 Why is direct heating thermodynamically wasteful?

6.20 How can a heat pump upgrade low grade waste heat?

6.21 Establish the equivalence of Kelvin-Planck and Clausius statements.

6.22 What is a reversible process? A reversible process should not leave any evidence to show that the process had ever occurred. Explain.

6.23 How is a reversible process only a limiting process, never to be attained in practice?

6.24 All spontaneous processes are irreversible. Explain.

6.25 What are the causes of irreversibility of a process?

6.26 Show that heat transfer through a finite temperature difference is irreversible.

6.27 Demonstrate, using the second law, that free expansion is irreversible.

6.28 What do you understand by dissipative effects? When is work said to be dissipated?

6.29 Explain perpetual motion of the third kind.

6.30 Demonstrate using the second law how friction makes a process irreversible.

6.31 When a rotating wheel is brought to rest by applying a brake, show that the molecular internal energy of the system (of the brake and the wheel) increases.

6.32 Show that the dissipation of stirring work to internal energy is irreversible.

6.33 Show by second law that the dissipation of electrical work into internal energy or heat is irreversible.

6.34 What is a Carnot cycle? What are the four processes which constitute the cycle?

6.35 Explain the Carnot heat engine cycle executed by: (a) a stationary system, and (b) a steady flow system.

6.36 What is a reversed heat engine?

6.37 Show that the efficiency of a reversible engine operating between two given constant temperatures is the maximum.

6.38 Show that the efficiency of all reversible heat engines operating between the same temperature levels is the same.

6.39 Show that the efficiency of a reversible engine is independent of the nature or amount of the working substance going through the cycle.

6.40 How does the efficiency of a reversible cycle depend only on the two temperatures at which heat is transferred?

6.41 What is the absolute thermodynamic temperature scale? Why is it called absolute?

6.42 How is the absolute scale independent of the working substance?

6.43 How does Q play the role of thermometric property in the Kelvin Scale?

6.44 Show that a definite zero point exists on the absolute temperature scale but that this point cannot be reached without a violation of the second law.

6.45 Give the Fowler-Guggenheim statement of the third law.

6.46 Is the third law an extension of the second law? Is it an independent law of nature? Explain.

6.47 How does the efficiency of a reversible engine vary as the source and sink temperatures are varied? When does the efficiency become 100%?

6.48 For a given T_2, show that the COP of a refrigerator increases as T_1 decreases.

6.49 Explain how the Kelvin temperature can be measured with a gas thermometer.

6.50 Establish the equality of ideal gas temperature and Kelvin temperature.

6.51 What do you understand by internal irreversibility and external irreversibility?

6.52 Explain mechanical, thermal and chemical irreversibilities.

6.53 A Carnot engine with a fuel burning device as source and a heat sink cannot be treated as a reversible plant. Explain.

Problems

6.1 An inventor claims to have developed an engine that takes in 105 MKJ at a temperature of 400 K, rejects 42 MJ at a temperature of 200 K, and delivers 15 kWh of mechanical work. Would you advise investing money to put this engine in the market?

6.2 If a refrigerator is used for heating purposes in winter so that the atmosphere becomes the cold body and the room to be heated becomes the hot body, how much heat would be available for heating for each kW input to the driving motor? The COP of the refrigerator is 5, and the electromechanical efficiency of the motor is 90%. How does this compare with resistance heating?

Ans. 5.4 kW, 1 kW

6.3 Using an engine of 30% thermal efficiency to drive a refrigerator having a COP of 5, what is the heat input into the engine for each MJ removed from the cold body by the refrigerator?

Ans. 666.67 kJ

If this system is used as a heat pump, how many MJ of heat would be available for heating for each MJ of heat input to the engine? *Ans.* 1.8 MJ

6.4 An electric storage battery which can exchange heat only with a constant temperature atmosphere goes through a complete cycle of two processes. In process 1–2, 2.8 kWh of electrical work flow into the battery while 732 kJ of heat flow out to the atmosphere. During process 2–1, 2.4 kWh of work flow out of the battery. (a) Find the heat transfer in process 2–1. (b) If the process 1–2 has occurred as above, does the first law or the second law limit the maximum possible work of process 2–1? What is the maximum possible work? (c) If the maximum possible work were obtained in process 2–1, what will be the heat transfer in the process?

Ans. (a) –708 kJ (b) Second law, $W_{2-1} = 9348$ kJ (c) $Q_{2-1} = 0$

6.5 A household refrigerator is maintained at a temperature of 2°C. Every time the door is opened, warm material is placed inside, introducing an average of 420 kJ, but making only a small change in the temperature of the refrigerator. The door is opened 20 times a day, and the refrigerator operates at 15% of the ideal COP. The cost of work is 32 paise per kWh. What is the monthly bill for this refrigerator? The atmosphere is at 30°C. *Ans.* Rs. 15.20

6.6 A heat pump working on the Carnot cycle takes in heat from a reservoir at 5°C and delivers heat to a reservoir at 60°C. The heat pump is driven by a reversible heat engine which takes in heat from a reservoir at 840°C and rejects heat to a reservoir at 60°C. The reversible heat engine also drives a machine that absorbs 30 kW. If the heat pump extracts 17 kJ/s from the 5°C reservoir, determine (a) the rate of heat supply from the 840°C source, and (b) the rate of heat rejection to the 60°C sink.

Ans. (a) 47.61 kW; (b) 34.61 kW

6.7 A refrigeration plant for a food store operates with a COP which is 40% of the ideal COP of a Carnot refrigarator. The store is to be maintained at a temperature of – 5°C and the heat transfer from the store to the cycle is at the rate of 5 kW. If heat is transferred from the cycle to the atmosphere at a temperature of 25°C, calculate the power required to drive the plant and the heat discharged to the atmosphere. *Ans.* 4.4 kW, 6.4 kW

6.8 A heat engine is used to drive a heat pump. The heat transfers from the heat engine and from the heat pump are used to heat the water circulating through the radiators of a building. The efficiency of the heat engine is 27% and the COP of the heat pump is 4. Evaluate the ratio of the heat transfer to the circulating water to the heat transfer to the heat engine. *Ans.* 1.81

6.9 If 20 kJ are added to a Carnot cycle at a temperature of 100°C and 14.6 kJ are rejected at 0°C, determine the location of absolute zero on the Celsius scale. *Ans.* –270.37°C

6.10 Two reversible heat engines *A* and *B* are arranged in series, A rejecting heat directly to *B*. Engine *A* receives 200 kJ at a temperature of 421°C from a hot source, while engine *B* is in communication with a cold sink at a temperature of 4.4°C. If the work output of *A* is twice that of *B*, find (a) the intermediate temperature between *A* and *B*, (b) the efficiency of each engine, and (c) the heat rejected to the cold sink.

Ans. 143.4°C, 40% & 33.5%, 80 kJ

6.11 A heat engine operates between the maximum and minimum temperatures of 671°C and 60°C respectively, with an efficiency of 50% of the appropriate Carnot efficiency. It drives a heat pump which uses river water at 4.4°C to heat a block of flats in which the temperature is to be maintained at 21.1°C. Assuming that a temperature difference of 11.1°C exists between the working fluid and the river water, on the one hand, and the required room temperature on the other, and assuming the heat pump to operate on the reversed Carnot cycle, but with a COP of 50% of the ideal COP, find the heat input to the engine per unit heat output from the heat pump. Why is direct heating thermodynamically more wasteful?

Ans. 0.79 kJ/kJ heat input

6.12 An ice-making plant produces ice at atmospheric pressure and at 0°C from water at 0°C. The mean temperature of the cooling water circulating through the condenser of the refrigerating machine is 18°C. Evaluate the minimum electrical work in kWh required to produce 1 tonne of ice. (The enthalpy of fusion of ice at atmospheric pressure is 333.5 kJ/kg). *Ans.* 6.11 kWh

6.13 A reversible engine works between three thermal reservoirs, *A*, *B* and *C*. The engine absorbs an equal amount of heat from the thermal reservoirs *A* and *B* kept at temperatures T_A and T_B respectively, and rejects heat to the thermal reservoir *C* kept at temperature T_C. The efficiency of the engine is α times the efficiency of the reversible engine, which works between the two reservoirs *A* and *C*. Prove that

$$\frac{T_A}{T_B} = (2\alpha - 1) + 2(1 - \alpha)\frac{T_A}{T_C}$$

6.14 A reversible engine operates between temperatures T_1 and T ($T_1 > T$). The energy rejected from this engine is received by a second reversible engine at the same temperature *T*. The second engine rejects energy at temperature T_2 ($T_2 < T$). Show that (a) temperature *T* is the arithmetic mean of temperatures T_1 and T_2 if the engines produce the same amount of work output, and (b) temperature *T* is the geometric mean of temperatures T_1 and T_2 if the engines have the same cycle efficiencies.

6.15 Two Carnot engines *A* and *B* are connected in series between two thermal reservoirs maintained at 1000 K and 100 K respectively. Engine *A* receives 1680 kJ of heat from the high-temperature reservoir and rejects heat to the Carnot engine *B*. Engine *B* takes in heat rejected by engine *A* and rejects heat to the low-temperature reservoir. If engines *A* and *B* have equal thermal efficiencies, determine (a) the heat rejected by engine *B*, (b) the temperature at which heat is rejected by engine *A*, and (c) the work done during the process by engines *A* and *B* respectively. If engines *A* and *B* deliver equal work, determine (d) the amount of heat taken in by engine *B*, and (e) the efficiencies of engines *A* and *B*. *Ans.* (a) 168 kJ, b) 316.2 K, (c) 1148.7, 363.3 kJ, (d) 924 kJ, (e) 45%, 81.8%.

6.16 A heat pump is to be used to heat a house in winter and then reversed to cool the house in summer. The interior temperature is to be maintained at 20°C. Heat transfer through the walls and roof is estimated to be 0.525 kJ/s per degree temperature difference between the inside and outside. (a) If the outside temperature in winter is 5°C, what is the minimum power required to drive the heat pump? (b) If the power output is the same as in part (a), what is the maximum outer temperature for which the inside can be maintained at 20°C? *Ans.* (a) 403 W, (b) 35°C.

6.17 Consider an engine in outer space which operates on the Carnot cycle. The only way in which heat can be transferred from the engine is by radiation. The rate at which heat is radiated is proportional to the fourth power of the absolute temperature T_2 and to the area of the radiating surface. Show that for a given power output and a given T_1, the area of the radiator will be a minimum when

$$\frac{T_2}{T_1} = \frac{3}{4}$$

6.18 It takes 10 kW to keep the interior of a certain house at 20°C when the outside temperature is 0°C. This heat flow is usually obtained directly by burning gas or oil. Calculate the power required if the 10 kW heat flow were supplied by operating a reversible heat pump with the house as the upper reservoir and the outside surroundings as the lower reservoir. *Ans.* 0.6826 kW

6.19 Prove that the COP of a reversible refrigerator operating between two given temperatures is the maximum.

6.20 A house is to be maintained at a temperature of 20°C by means of a heat pump pumping heat from the atmosphere. Heat losses through the walls of the house are estimated at 0.65 kW per unit of temperature difference between the inside of the house and the atmosphere. (a) If the atmospheric temperature is − 10°C, what is the minimum power required to drive the pump? (b) It is proposed to use the same heat pump to cool the house in summer. For the same room temperature, the same heat loss rate, and the same power input to the pump, what is the maximum permissible atmospheric temperature? *Ans.* 2 kW, 50°C.

6.21 A solar-powered heat pump receives heat from a solar collector at T_h, rejects heat to the atmosphere at T_a, and pumps heat from a cold space at T_c. The three heat transfer rates are Q_h, Q_a, and Q_c respectively. Derive an expression for the minimum ratio Q_h/Q_c, in terms of the three temperatures.

If $T_h = 400$ K, $T_a = 300$ K, $T_c = 200$ K, $Q_c = 12$ kW, what is the minimum Q_h? If the collector captures 0.2 kW/m^2, what is the minimum collector area required? *Ans.* 24 kW, 120 m^2

6.22 A heat engine operating between two reservoirs at 1000 K and 300 K is used to drive a heat pump which extracts heat from the reservoir at 300 K at a rate twice that at which the engine rejects heat to it. If the efficiency of the engine is 40% of the maximum possible and the COP of the heat pump is 50% of the maximum possible, what is the temperature of the reservoir to which the heat pump rejects heat? What is the rate of heat rejection from the heat pump if the rate of heat supply to the engine is 50 kW? *Ans.* 326.5 K, 86 kW

6.23 A reversible power cycle is used to drive a reversible heat pump cycle. The power cycle takes in Q_1 heat units at T_1 and rejects Q_2 at T_2. The heat pump abstracts Q_4 from the sink at T_4 and discharges Q_3 at T_3. Develop an expression for the ratio Q_4/Q_1 in terms of the four temperatures.

Ans. $\dfrac{Q_4}{Q_1} = \dfrac{T_4(T_1 - T_2)}{T_1(T_3 - T_4)}$

6.24 Prove that the following propositions are logically equivalent: (a) A PMM2 is impossible, (b) A weight sliding at constant velocity down a frictional inclined plane executes an irreversible process.

6.25 A heat engine receives half of its heat supply at 1000 K and half at 500 K while rejecting heat to a sink at 300 K. What is the maximum possible thermal efficiency of this heat engine?

Ans. 0.55%

6.26 A heat pump provides 3 × 10^4 kJ/h to maintain a dwelling at 23°C on a day when the outside temperature is 0°C. The power input to the heat pump is 4 kW. Determine the COP of the heat pump and compare it with the COP of a reversible heat pump operating between the reservoirs at the same two temperatures. *Ans.* 2.08, 12.87

6.27 A reversible power cycle receives energy Q_1 from a reservoir at temperature T_1 and rejects Q_2 to a reservoir at temperature T_2. The work developed by the power cycle is used to drive a reversible heat pump that removes energy Q'_2 from a reservoir at temperature T'_2 and rejects energy Q'_1 to a reservoir at temperature T'_1. (a) Determine an expression for the ratio Q'_1/Q_1 in terms of the four temperatures. (b) What must be the relationship of the temperatures T_1, T_2, T'_1 and T'_2, for Q'_1/Q_1 to exceed a value of unity?

Ans. (a) $\dfrac{Q'_1}{Q_1} = \dfrac{T'_1(T_1 - T_2)}{T_1(T'_1 - T'_2)}$, (b) $\dfrac{T_2}{T'_2} < \dfrac{T_1}{T'_1}$

6.28 When the outside temperature is − 10°C, a residential heat pump must provide 3.5 × 10^6 kJ per day to a dwelling to maintain its temperature at 20°C. If electricity costs Rs. 2.10 per kWh, find the minimum theoretical operating cost for each day of operation. *Ans.* Rs. 208.83

CHAPTER

7

Entropy

7.1 INTRODUCTION

The first law of thermodynamics was stated in terms of cycles first and it was shown that the cyclic integral of heat is equal to the cyclic integral of work. When the first law was applied for thermodynamic processes, the existence of a property, the internal energy, was found. Similarly, the second law was also first stated in terms of cycles executed by systems. When applied to processes, the second law also leads to the definition of a new property, known as entropy. If the first law is said to be the law of internal energy, then second law may be stated to be the law of entropy. In fact, *thermodynamics is the study of three E's, namely, energy, equilibrium and entropy.*

7.2 TWO REVERSIBLE ADIABATIC PATHS CANNOT INTERSECT EACH OTHER

Let it be assumed that two reversible adiabatics AC and BC intersect each other at point C (Fig. 7.1). Let a reversible isotherm AB be drawn in such a way that it intersects the reversible adiabatics at A and B. The three reversible processes AB, BC, and CA together constitute a reversible cycle, and the area included represents the net work output in a cycle. But such a cycle is impossible, since net work is being produced in a cycle by a heat engine by exchanging heat with a single reservoir in the process AB, which violates the Kelvin-Planck statement of the second law. Therefore, the assumption of the intersection of the reversible adiabatics is wrong. *Through one point, there can pass only one reversible adiabatic.*

Since two constant property lines can never intersect each other, it is inferred that a reversible adiabatic path must represent some property, which is yet to be identified.

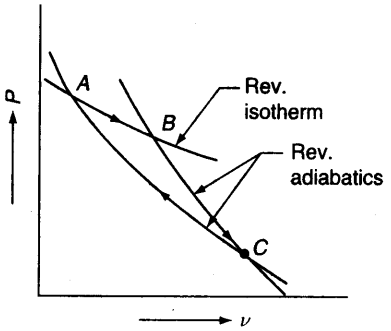


Fig. 7.1 *Assumption of two reversible adiabatics intersecting each other*

7.3 CLAUSIUS' THEOREM

Let a system be taken from an equilibrium state i to another equilibrium state f by following the

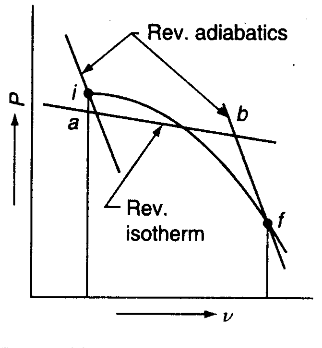


Fig. 7.2 *Reversible path substituted by two reversible adiabatics and a reversible isotherm*

reversible path *i–f* (Fig. 7.2). Let a reversible adiabatic *i–a* be drawn through *i* and another reversible adiabatic *b–f* be drawn through *f*. Then a reversible isotherm *a–b* is drawn in such a way that the area under *i–a–b–f* is equal to the area under *i–f*. Applying the first law for

Process *i–f*

$$Q_{i-f} = U_f - U_i + W_{if} \tag{7.1}$$

Process *i–a–b–f*

$$Q_{iabf} = U_f - U_i + W_{iabf} \tag{7.2}$$

Since

$$W_{if} = W_{iabf}$$

∴ From Eqs (7.1) and (7.2)

$$Q_{if} = Q_{iabf} = Q_{ia} + Q_{ab} + Q_{bf}$$

Since

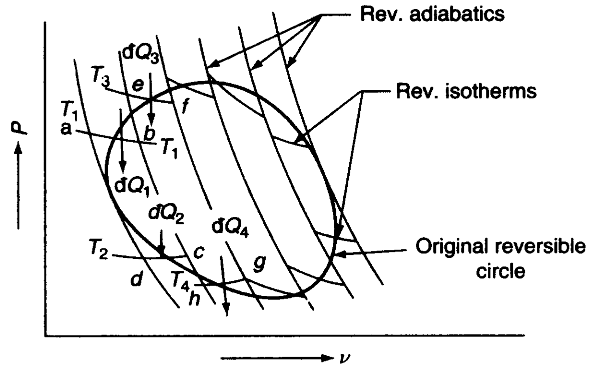
$$Q_{ia} = 0 \text{ and } Q_{bf} = 0$$

$$Q_{if} = Q_{ab}$$

Heat transferred in the process *i–f* is equal to the heat transferred in the isothermal process *a–b*.

Thus any reversible path may be substituted by a reversible zigzag path, between the same end states, consisting of a reversible adiabatic followed by a reversible isotherm and then by a reversible adiabatic, such that the heat transferred during the isothermal process is the same as that transferred during the original process.

Let a smooth closed curve representing a reversible cycle (Fig. 7.3) be considered. Let the closed cycle be divided into a large number of strips by means of reversible adiabatics. Each strip may be closed at the top and bottom by reversible isotherms. The original closed cycle is thus replaced by a zigzag closed path consisting of alternate adiabatic and isothermal processes, such that the heat transferred during all the isothermal processes is equal to the heat transferred in the original cycle. Thus the original cycle is replaced by a large number of Carnot cycles. If the adiabatics are close to one another and the number of Carnot cycles is large, the saw-toothed zigzag line will coincide with the original cycle.



A reversible cycle split into a large number of carnot cycles

For the elemental cycle *abcd* $\text{đ}Q_1$ heat is absorbed reversibly at T_1, and $\text{đ}Q_2$ heat is rejected reversibly at T_2

$$\frac{\text{đ}Q_1}{T_1} = \frac{\text{đ}Q_2}{T_2}$$

If heat supplied is taken as positive and heat rejected as negative

$$\frac{\text{đ}Q_1}{T_1} + \frac{\text{đ}Q_2}{T_2} = 0$$

Similarly, for the elemental cycle *efgh*

$$\frac{\bar{d}Q_3}{T_3}+\frac{\bar{d}Q_4}{T_4}=0$$

If similar equations are written for all the elemental Carnot cycles, then for the whole original cycle

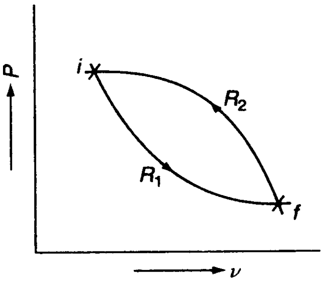
$$\frac{\bar{d}Q_1}{T_1}+\frac{\bar{d}Q_2}{T_2}+\frac{\bar{d}Q_3}{T_3}+\frac{\bar{d}Q_4}{T_4}+\ldots=0$$

or

$$\underset{R}{\oint}\frac{\bar{d}Q}{T}=0 \tag{7.3}$$

The cyclic integral of $\bar{d}Q/T$ for a reversible cycle is equal to zero. This is known as *Clausius' theorem*. The letter R emphasizes the fact that the equation is valid only for a reversible cycle.

7.4 THE PROPERTY OF ENTROPY



Two reversible paths R_1 and R_2 between two equilibrium states i and f

Let a system be taken from an initial equilibrium state i to a final equilibrium state f by following the reversible path R_1 (Fig. 7.4). The system is brought back from f to i by following another reversible path R_2. Then the two paths R_1 and R_2 together constitute a reversible cycle. From Clausius' theorem

$$\underset{R_1R_2}{\oint}\frac{\bar{d}Q}{T}=0$$

The above integral may be replaced as the sum of two integrals, one for path R_1 and the other for path R_2

$$\underset{R_1}{\int_i^f}\frac{\bar{d}Q}{T}+\underset{R_2}{\int_f^i}\frac{\bar{d}Q}{T}=0$$

or

$$\underset{R_1}{\int_i^f}\frac{\bar{d}Q}{T}=-\underset{R_2}{\int_f^i}\frac{\bar{d}Q}{T}$$

Since R_2 is a reversible path

$$\underset{R_1}{\int_i^f}\frac{\bar{d}Q}{T}=\underset{R_2}{\int_i^f}\frac{\bar{d}Q}{T}$$

Since R_1 and R_2 represent any two reversible paths, $\underset{R}{\int_i^f}\frac{\bar{d}Q}{T}$ is independent of the reversible path connecting i and f. Therefore, there exists a property of a system whose value at the final state f minus its value at the initial state i is equal to $\int_{\substack{i\\R}}^{f} \frac{\text{đ}Q}{T}$. This property is called *entropy*, and is denoted by S. If S_i is the entropy at the initial state i, and S_f is the entropy at the final state f, then

$$\int_{\substack{i\\R}}^{f} \frac{\text{đ}Q}{T} = S_f - S_i \tag{7.4}$$

When the two equilibrium states are infinitesimally near

$$\frac{\text{đ}Q_R}{T} = \mathrm{d}S \tag{7.5}$$

where $\mathrm{d}S$ is an *exact differential* because S is a point function and a property. The subscript R in $\text{đ}Q$ indicates that heat $\text{đ}Q$ is transferred *reversibly*.

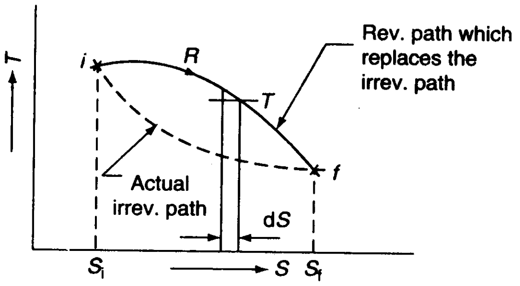
The word 'entropy' was first used by Clausius, taken from the Greek word 'tropee' meaning 'transformation'. It is an extensive property, and has the unit J/K. The specific entropy

$$s = \frac{S}{m} \text{ J/kg K}$$

If the system is taken from an initial equilibrium state i to a final equilibrium state f by an *irreversible path*, since entropy is a point or state function, and the entropy change is independent of the path followed, the non-reversible path is to be replaced by a reversible path to integrate for the evaluation of entropy change in the irreversible process (Fig. 7.5).

$$S_f - S_i = \int_{i}^{f} \frac{\text{đ}Q_{\text{rev}}}{T} = (\Delta S)_{\text{irrev path}} \tag{7.6}$$

Integration can be performed only on a reversible path.



Integration can be done only on a reversible path

7.4.1 Temperature-Entropy Plot

The infinitesimal change in entropy $\mathrm{d}S$ due to reversible heat transfer $\text{đ}Q$ at temperature T is

$$\mathrm{d}S = \frac{\text{đ}Q_{\text{rev}}}{T}$$

If $\text{đ}Q_{\text{rev}} = 0$, i.e., the process is reversible and adiabatic

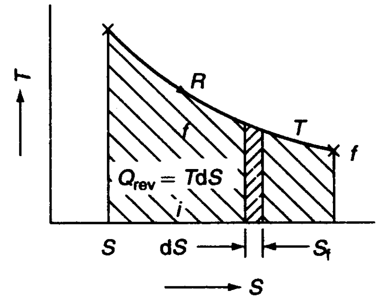
$$\mathrm{d}S = 0$$

and $$S = \text{constant}$$

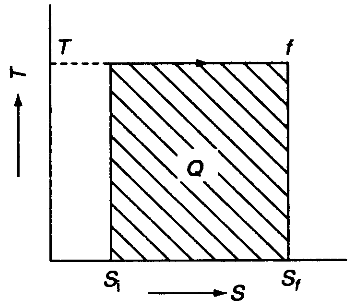
A reversible adiabatic process is, therefore, an isentropic process.

Now $$\text{đ}Q_{\text{rev}} = T\mathrm{d}S$$

or $$Q_{\text{rev}} = \int_{i}^{f} T\mathrm{d}S$$



Area under a reversible path on the T-s plot represents heat transfer



Reversible isothermal heat transfer

The system is taken from i to f reversibly (Fig. 7.6). The area under the curve $\int_i^f TdS$ is equal to the heat transferred in the process.

For reversible isothermal heat transfer (Fig. 7.7), T = constant.

$$\therefore \qquad Q_{rev} = T\int_i^f dS = T(S_f - S_i)$$

For a reversible adiabatic process, $dS = 0$, $S = C$ (Fig. 7.8).

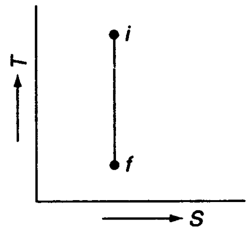
The *Carnot cycle* comprising two reversible isotherms and two reversible adiabatics forms a rectangle in the T–S plane (Fig. 7.9). Process 4–1 represents reversible isothermal heat addition Q_1 to the system at T_1 from an external source, process 1–2 is the reversible adiabatic expansion of the system producing W_E amount of work, process 2–3 is the reversible isothermal heat rejection from the system to an external sink at T_2, and process 3–4 represents reversible adiabatic compression of the system consuming W_c amount of work. Area 1 2 3 4 represents the net work output per cycle and the area under 4–1 indicates the quantity of heat added to the system Q_1.

$$\therefore \qquad \eta_{Carnot} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1(S_1 - S_4) - T_2(S_2 - S_3)}{T_1(S_1 - S_4)}$$

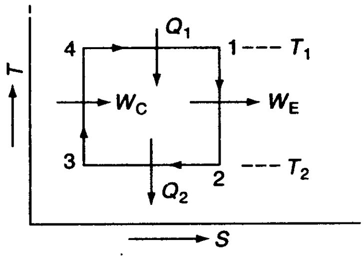
$$= \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

and

$$W_{net} = Q_1 - Q_2 = (T_1 - T_2)(S_1 - S_4)$$



Reversible adiabatic is isentropic



Carnot cycle

7.5 THE INEQUALITY OF CLAUSIUS

Let us consider a cycle *ABCD* (Fig. 7.10). Let *AB* be a general process, either reversible or irreversible, while the other processes in the cycle are reversible. Let the cycle be divided into a number of elementary cycles, as shown. For one of these elementary cycles

$$\eta = 1 - \frac{\text{đ}Q_2}{\text{đ}Q}$$

where $\text{đ}Q$ is the heat supplied at T, and $\text{đ}Q_2$ the heat rejected at T_2.

Now, the efficiency of a general cycle will be equal to or less than the efficiency of a reversible cycle.

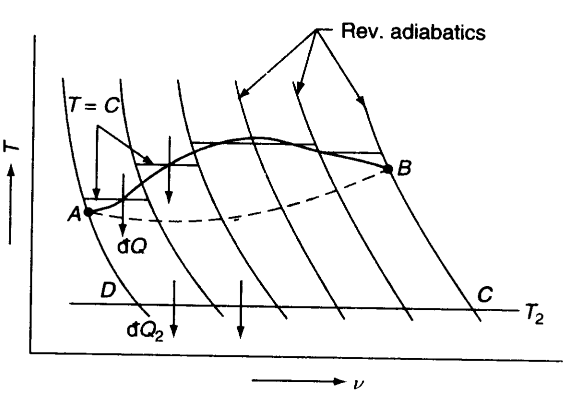


Fig. 7.10 Inequality of clausius

∴
$$1 - \frac{\text{đ}Q_2}{\text{đ}Q} \le \left(1 - \frac{\text{đ}Q_2}{\text{đ}Q}\right)_{\text{rev}}$$

or
$$\frac{\text{đ}Q_2}{\text{đ}Q} \ge \left(\frac{\text{đ}Q_2}{\text{đ}Q}\right)_{\text{rev}}$$

or
$$\frac{\text{đ}Q}{\text{đ}Q_2} \le \left(\frac{\text{đ}Q}{\text{đ}Q_2}\right)_{\text{rev}}$$

Since
$$\left(\frac{\text{đ}Q}{\text{đ}Q_2}\right)_{\text{rev}} = \frac{T}{T_2}$$

∴
$$\frac{\text{đ}Q}{\text{đ}Q_2} \le \frac{T}{T_2}$$

or $\dfrac{\text{đ}Q}{T} \le \dfrac{\text{đ}Q_2}{T_2}$, for any process *AB*, reversible or irreversible.

For a reversible process

$$\text{d}s = \frac{\text{đ}Q_{\text{rev}}}{T} = \frac{\text{đ}Q_2}{T_2} \tag{7.7}$$

Hence, for any process *AB*

$$\frac{\text{đ}Q}{T} \le \text{d}s \tag{7.8}$$

Then for any cycle

$$\oint \frac{\text{đ}Q}{T} \le \oint \text{d}s$$

Since entropy is a property and the cyclic integral of any property is zero

$$\oint \frac{\text{đ}Q}{T} \le 0 \tag{7.9}$$

This equation is known as the *inequality of Clausius*. It *provides the criterion of the reversibility of a cycle.*

If $\oint \frac{\text{đ}Q}{T} = 0$, the cycle is reversible,

$\oint \frac{\text{đ}Q}{T} < 0$, the cycle is irreversible and possible

$\oint \frac{\text{đ}Q}{T} > 0$, the cycle is impossible, since it violates the second law.

7.6 ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

For any process undergone by a system, we have from Eq. (7.8)

$$\frac{\text{đ}Q}{T} \le \mathrm{d}s$$

or

$$\mathrm{d}s \ge \frac{\text{đ}Q}{T} \tag{7.10}$$

This is further clarified if we consider the cycles as shown in Fig. 7.11, where *A* and *B* are reversible processes and *C* is an irreversible process. For the reversible cycle consisting of *A* and *B*

$$\int_{R} \frac{\text{đ}Q}{T} = \int_{\substack{1\\ A}}^{2} \frac{\text{đ}Q}{T} + \int_{\substack{2\\ B}}^{1} \frac{\text{đ}Q}{T} = 0$$

or

$$\int_{\substack{1\\ A}}^{2} \frac{\text{đ}Q}{T} = -\int_{\substack{2\\ B}}^{1} \frac{\text{đ}Q}{T} \tag{7.11}$$

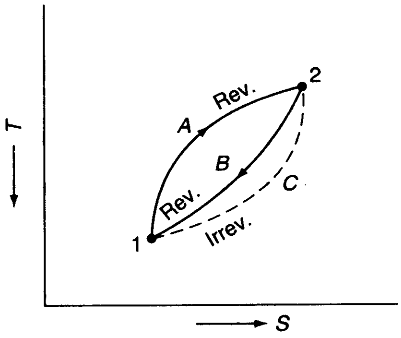


Fig. 7.11 *Entropy change in an irreversible process*

For the irreversible cycle consisting of *A* and *C*, by the inequality of Clausius,

$$\oint \frac{\text{đ}Q}{T} = \int_{\substack{1\\ A}}^{2} \frac{\text{đ}Q}{T} + \int_{\substack{2\\ C}}^{1} \frac{\text{đ}Q}{T} < 0 \tag{7.12}$$

From Eqs (7.11) and (7.12),

$$-\int_{\substack{2\\ B}}^{1} \frac{\text{đ}Q}{T} + \int_{\substack{2\\ C}}^{1} \frac{\text{đ}Q}{T} < 0$$

$$\therefore \quad \int_{\substack{2\\ B}}^{1} \frac{\text{đ}Q}{T} > \int_{\substack{2\\ C}}^{1} \frac{\text{đ}Q}{T} \tag{7.13}$$

Since the path *B* is reversible,

$$\int_{\substack{2\\ B}}^{1} \frac{\text{đ}Q}{T} = \int_{\substack{2\\ B}}^{1} \mathrm{d}S \tag{7.14}$$

Since entropy is a property, entropy changes for the paths B and C would be the same. Therefore,

$$\underset{\mathrm{B}}{\int_{2}^{1}} \mathrm{d}S = \underset{\mathrm{C}}{\int_{2}^{1}} \mathrm{d}S \tag{7.15}$$

From Eqs (7.13) to (7.15),

$$\underset{\mathrm{C}}{\int_{2}^{1}} \mathrm{d}S > \underset{\mathrm{C}}{\int_{2}^{1}} \frac{\text{đ}Q}{T}$$

Thus, for any irreversible process,

$$\mathrm{d}S > \frac{\text{đ}Q}{T}$$

whereas for a reversible process

$$\mathrm{d}S = \frac{\text{đ}Q_{\mathrm{rev}}}{T}$$

Therefore, for the general case, we can write

$$\mathrm{d}S \geq \frac{\text{đ}Q}{T}$$

or

$$S_2 - S_1 \geq \int_{1}^{2} \frac{\text{đ}Q}{T} \tag{7.16}$$

The equality sign holds good for a reversible process and the inequality sign for an irreversible process.

7.7 ENTROPY PRINCIPLE

For any infinitesimal process undergone by a system, we have from Eq. (7.10) for the total mass

$$\mathrm{d}S \geq \frac{\text{đ}Q}{T}$$

For an isolated system which does not undergo any energy interaction with the surroundings, $\text{đ}Q = 0$. Therefore, for an isolated system

$$\mathrm{d}S_{\mathrm{iso}} \geq 0 \tag{7.17}$$

For a reversible process,

$$\mathrm{d}S_{\mathrm{iso}} = 0$$

or

$$S = \text{constant}$$

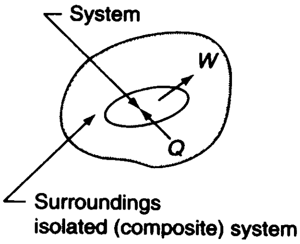
For an irreversible process

$$\mathrm{d}S_{\mathrm{iso}} > 0$$

It is thus proved that *the entropy of an isolated system can never decrease*. It always increases and remains constant only when the process is reversible. This is known as the *principle of increase of entropy*, or simply the *entropy principle*. It is the quantitative general statement of second law from the macroscopic viewpoint.

An isolated system can always be formed by including any system and its surroundings within a single boundary (Fig. 7.12). Sometimes the original system which is then only a part of the isolated system is called a 'subsystem'.

The system and the surroundings together (the universe or the isolated system) include everything which is affected by the process. For all possible processes that a system in the given surroundings can undergo



[illegible] *Isolated system*

$$dS_{\text{univ}} \geq 0$$

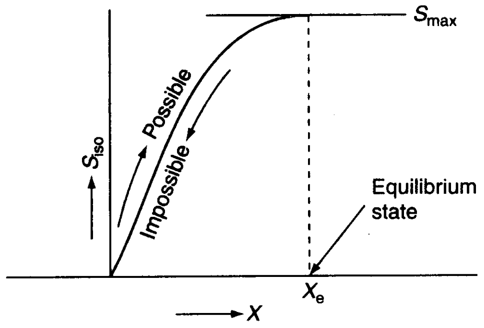
or $$dS_{\text{sys}} + dS_{\text{surr}} \geq 0 \tag{7.18}$$

Entropy may decrease locally at some region within the isolated system, but it must be compensated by a greater increase of entropy somewhere within the system so that the net effect of an irreversible process is an entropy increase of the whole system. The entropy increase of an isolated system is a measure of the extent of irreversibility of the process undergone by the system.

Rudolf Clausius summarized the first and second laws of thermodynamics in the following words:

(a) Die Energie der Welt ist Costant.
(b) Die Entropie der Welt strebt einem Maximum zu.
[(a) The energy of the world (universe) is constant.
(b) The entropy of the world tends towards a maximum.]

The entropy of an isolated system always increases and becomes a maximum at the state of equilibrium. If the entropy of an isolated system varies with some parameter x, then there is a certain value of x_e which maximizes the entropy $\left(\text{when } \frac{dS}{dx} = 0\right)$ and represents the equilibrium state (Fig. 7.13). The system is then said to exist at the peak of the entropy hill, and $dS = 0$.



Equilibrium state of an isolated system

When the system is at equilibrium, any conceivable change in entropy would be zero.

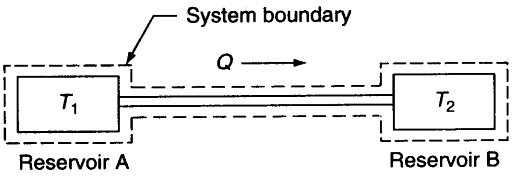
7.8 APPLICATIONS OF ENTROPY PRINCIPLE

The principle of increase of entropy is one of the most important laws of physical science. It is the quantitative statement of the second law of thermodynamics. Every irreversible process is accompanied by entropy increase of the universe, and this entropy increase quantifies the extent of irreversibility of the process. The higher the entropy increase of the universe, the higher will be the irreversibility of the process. A few applications of the entropy principle are illustrated in the following.

7.8.1 Transfer of Heat through a Finite Temperature Difference

Let Q be the rate of heat transfer from reservoir A at T_1 to reservoir B at T_2, $T_1 > T_2$ (Fig. 7.14).

For reservoir A, $\Delta S_A = -Q/T_1$. It is negative because heat Q flows out of the reservoir. For reservoir B, $\Delta S_B = +Q/T_2$. It is positive because heat flows into the reservoir. The rod connecting the reservoirs suffers no entropy change because, once in the steady state, its coordinates do not change.



Heat transfer through a finite temperature difference

Therefore, for the isolated system comprising the reservoirs and the rod, and since entropy is an additive property

$$S = S_A + S_B$$

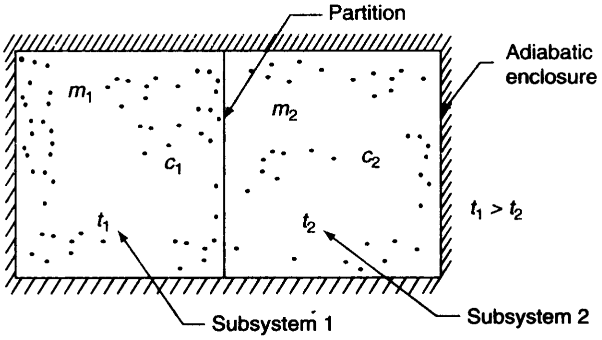
$$\Delta S_{\text{univ}} = \Delta S_A + \Delta S_B$$

or
$$\Delta S_{\text{univ}} = -\frac{Q}{T_1} + \frac{Q}{T_2} = Q \cdot \frac{T_1 - T_2}{T_1 T_2}$$

Since $T_1 > T_2$, ΔS_{univ} is positive, and the process is irreversible and possible. If $T_1 = T_2$, ΔS_{univ} is zero, and the process is reversible. If $T_1 < T_2$, ΔS_{univ} is negative and the process is impossible.

7.8.2 Mixing of Two Fluids

Subsystem 1 having a fluid of mass m_1, specific heat c_1, and temperature t_1, and subsystem 2 consisting of a fluid of mass m_2, specific heat c_2, and temperature t_2, comprise a composite system in an adiabatic enclosure (Fig. 7.15). When the partition is removed, the two fluids mix together, and at equilibrium let t_f be the final temperature, and $t_2 < t_f < t_1$. Since energy interaction is exclusively confined to the two fluids, the system being isolated



Mixing of two fluids

$$m_1 c_1 (t_1 - t_f) = m_2 c_2 (t_f - t_2)$$

$\therefore$
$$t_f = \frac{m_1 c_1 t_1 + m_2 c_2 t_2}{m_1 c_1 + m_2 c_2}$$

Entropy change for the fluid in subsystem 1

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{đQ_{\text{rev}}}{T} = \int_{T_1}^{T_f} \frac{m_1 c_1 dT}{T} = m_1 c_1 \ln \frac{T_f}{T_1}$$
$$= m_1 c_1 \ln \frac{t_f + 273}{t_1 + 273}$$

This will be negative, since $T_1 > T_f$.

Entropy change for the fluid in subsystem 2

$$\Delta S_2 = \int_{T_1}^{T_f} \frac{m_2 c_2 dT}{T} = m_2 c_2 \ln \frac{T_f}{T_2} = m_2 c_2 \ln \frac{t_f + 273}{t_2 + 273}$$

This will be positive, since $T_2 < T_f$

$\therefore$
$$\Delta S_{\text{univ}} = \Delta S_1 + \Delta S_2$$
$$= m_1 c_1 \ln \frac{T_f}{T_1} + m_2 c_2 \ln \frac{T_f}{T_2}$$

ΔS_{univ} will be positive definite, and the mixing process is irreversible.

Although the mixing process is irreversible, to evaluate the entropy change for the subsystems, the irreversible path was replaced by a reversible path on which the integration was performed.

If $m_1 = m_2 = m$ and $c_1 = c_2 = c$.

$$\Delta S_{\text{univ}} = mc \ln \frac{T_f^2}{T_1 \cdot T_2}$$

and
$$T_f = \frac{m_1c_1T_1 + m_2c_2T_2}{m_1c_1 + m_2c_2} = \frac{T_1 + T_2}{2}$$

$$\therefore \quad \Delta S_{\text{univ}} = 2\,mc\ln\frac{(T_1+T_2)/2}{\sqrt{T_1 \cdot T_2}}$$

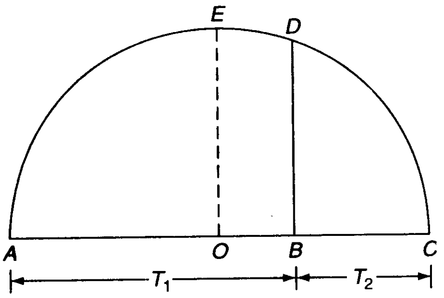
This is always positive, since the arithmetic mean of any two numbers is always greater than their geometric mean. This can also be proved geometrically. Let a semi-circle be drawn with $(T_1 + T_2)$ as diameter (Fig. 7.16).

Here, $AB = T_1$, $BC = T_2$ and $OE = (T_1 + T_2)/2$. It is known that $(DB)^2 = AB \cdot BC = T_1T_2$.

$$\therefore \quad DB = \sqrt{T_1T_2}$$

Now,
$$OE > DB$$

$$\frac{T_1+T_2}{2} = \sqrt{T_1T_2}$$



Geometrical proof to show that g.m. < a.m.

7.8.3 Maximum Work Obtainable from Two Finite Bodies at Temperatures T_1 and T_2

Let us consider two identical finite bodies of constant heat capacity at temperatures T_1 and T_2 respectively, T_1 being higher than T_2. If the two bodies are merely brought together into thermal contact, delivering no work, the final temperature T_f reached would be the maximum

$$T_f = \frac{T_1 + T_2}{2}$$

If a heat engine is operated between the two bodies acting as thermal energy reservoirs (Fig. 7.17), part of the heat withdrawn from body 1 is converted to work W by the heat engine, and the remainder is rejected to body 2. The lowest attainable final temperature T_f corresponds to the delivery of the largest possible amount of work, and is associated with a reversible process.

As work is delivered by the heat engine, the temperature of body 1 will be decreasing and that of body 2 will be increasing. When both the bodies attain the final temperature T_f, the heat engine will stop operating. Let the bodies remain at constant pressure and undergo no change of phase.

Total heat withdrawn from body 1

$$Q_1 = C_p(T_1 - T_f)$$

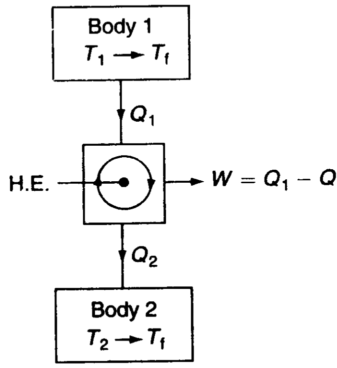
where C_p is the heat capacity of the two bodies at constant pressure.

Total heat rejected to body 2

$$Q_2 = C_p(T_f - T_2)$$

$\therefore$ Amount of total work delivered by the heat engine

$$W = Q_1 - Q_2$$
$$= C_p(T_1 + T_2 - 2T_f) \tag{7.19}$$



Maximum work obtainable from two finite bodies

For given values of C_p, T_1 and T_2, the magnitude of work W depends on T_f. Work obtainable will be maximum when T_f is minimum.

Now, for body 1, entropy change ΔS_1 is given by

$$\Delta S_1 = \int_{T_1}^{T_f} C_p \frac{dT}{T} = C_p \ln \frac{T_f}{T_1}$$

For body 2, entropy change ΔS_2 would be

$$\Delta S_2 = \int_{T_2}^{T_f} C_p \frac{dT}{T} = C_p \ln \frac{T_f}{T_2}$$

Since the working fluid operating in the heat engine cycle does not undergo any entropy change, ΔS of the working fluid in heat engine $= \oint dS = 0$.

Applying the entropy principle

$$\Delta S_{\text{univ}} \geq 0$$

$$\therefore \quad C_p \ln \frac{T_f}{T_1} + C_p \ln \frac{T_f}{T_2} \geq 0$$

$$C_p \ln \frac{T_f^2}{T_1 T_2} \geq 0 \tag{7.20}$$

From Eq. (7.20), for T_f to be a minimum

$$C_p \ln \frac{T_f^2}{T_1 \cdot T_2} = 0$$

Since $C_p \neq 0$,

$$\ln \frac{T_f^2}{T_1 T_2} = 0 = \ln 1$$

$$\therefore \quad T_f = \sqrt{T_1 \cdot T_2} \tag{7.21}$$

For W to be a maximum, T_f will be $\sqrt{T_1 T_2}$. From Eq. (7.19)

$$W_{\max} = C_p (T_1 + T_2 - 2\sqrt{T_1 T_2}) = C_p\left(\sqrt{T_1} - \sqrt{T_2}\right)^2$$

The final temperatures of the two bodies, initially at T_1 and T_2, can range from $(T_1 + T_2)/2$ with no delivery of work to $\sqrt{T_1 T_2}$ with maximum delivery of work.

7.8.4 Maximum Work Obtainable from a Finite Body and a TER

Let one of the bodies considered in the previous section be a thermal energy reservoir. The finite body has a thermal capacity C_p and is at temperature T and the TER is at temperature T_0, such that $T > T_0$. Let a heat engine operate between the two (Fig. 7.18). As heat is withdrawn from the body, its temperature decreases. The temperature of the TER would, however, remain unchanged at T_0. The engine would stop working, when the temperature of the body reaches T_0. During that period, the amount of work delivered is W, and the heat rejected to the TER is $(Q - W)$. Then

$$\Delta S_{\text{Body}} = \int_{T}^{T_0} C_p \frac{dT}{T} = C_p \ln \frac{T_0}{T}$$

$$\Delta S_{HE} = \oint dS = 0$$

$$\Delta S_{TER} = \frac{Q-W}{T_0}$$

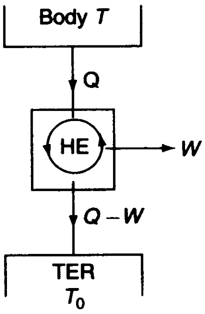
$$\therefore \quad \Delta S_{univ} = C_p \ln\frac{T_0}{T} + \frac{Q-W}{T_0}$$

By the entropy principle,

$$\Delta S_{univ} \geq 0$$

$$C_p \ln\frac{T_0}{T} + \frac{Q-W}{T_0} \geq 0$$

or $$C_p \ln\frac{T_0}{T} \geq \frac{W-Q}{T_0}$$



Maximum work obtainable when one of the bodies is a TER

or $$\frac{W-Q}{T_0} \leq C_p \ln\frac{T_0}{T}$$

or $$W \leq Q + T_0 C_p \ln\frac{T_0}{T}$$

$$\therefore \quad W_{max} = Q + T_0 C_p \ln\frac{T_0}{T}$$

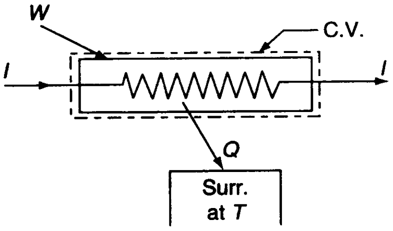
or, $$W_{max} = C_p\left[(T - T_0) - T_0 \ln\frac{T}{T_0}\right] \tag{7.22}$$

7.8.5 Processes Exhibiting External Mechanical Irreversibility

(i) *Isothermal Dissipation of Work* Let us consider the isothermal dissipation of work through a system into the internal energy of a reservoir, as in the flow of an electric current I through a resistor in contact with a reservoir (Fig. 7.19). At steady state, the internal energy of the resistor and hence its temperature is constant. So, by first law

$$W = Q$$

The flow of current represents work transfer. At steady state the work is dissipated isothermally into heat transfer to the surroundings. Since the surroundings absorb Q units of heat at temperature T,



External mechanical irreversibility

$$\Delta S_{surr} = \frac{Q}{T} = \frac{W}{T}$$

At steady state, $$\Delta S_{sys} = 0$$

$$\therefore \quad \Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \frac{W}{T} \tag{7.23}$$

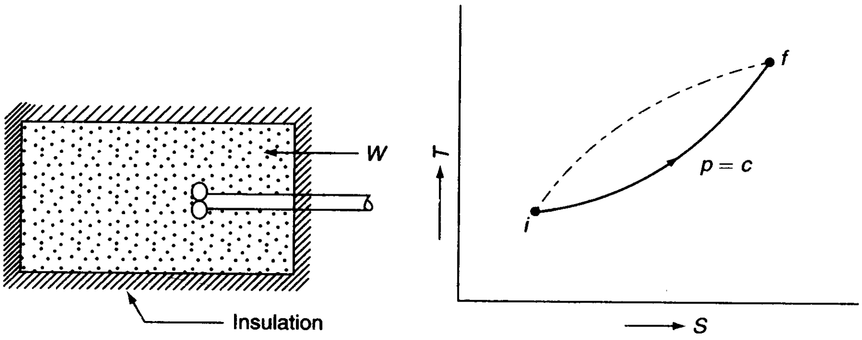
The irreversible process is thus accompanied by an entropy increase of the universe.

(ii) *Adiabatic Dissipation of Work* Let W be the stirring work supplied to a viscous thermally insulated liquid, which is dissipated adibatically into internal energy increase of the liquid, the temperature of which increases from T_i to T_f (Fig. 7.20). Since there is no flow of heat to or from the surroundings,

$$\Delta S_{\text{surr}} = 0$$

To calculate the entropy change of the system, the original irreversible path (dotted line) must be replaced by a reversible one between the same end states, *i* and *f*. Let us replace the irreversible performance of work by a reversible isobaric flow of heat from a series of reservoirs ranging from T_i to T_f to cause the same change in the state of the system. The entropy change of the system will be

$$\Delta S_{\text{sys}} = \int_{\substack{i\\R}}^{f} \frac{\text{đ}Q}{T} = \int_{\substack{i\\R}}^{f} \frac{C_p \mathrm{d}T}{T} = C_p \ln \frac{T_f}{T_i}$$



(a) (b)

Fig. 7.20 Adiabatic dissipation of work

where C_p is the heat capacity of the liquid.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = C_p \ln \frac{T_f}{T_i} \tag{7.24}$$

which is positive.

7.9 ENTROPY TRANSFER MECHANISMS

Entropy can be *transferred* to or from a system in two forms: *heat transfer* and *mass flow*. In contrast, energy is transferred by work also. Entropy transfer is recognized at the system boundary as entropy crosses the boundary, and it represents the entropy gained or lost by a system during a process. The only form of entropy interaction associated with a fixed mass or closed system is heat transfer, and thus the entropy transfer for an adiabatic closed system is zero. It is being explained below in more detail:

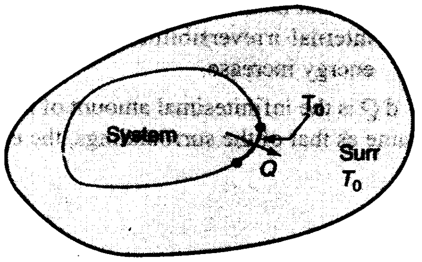
(*a*) *Heat Transfer* Since $\mathrm{d}S = \frac{\text{đ}Q_{\text{rev}}}{T}$, when heat is added to a system, $\text{đ}Q$ is positive, and the entropy of the system increases. When heat is removed from the system, $\text{đ}Q$ is negative, and the entropy of the system decreases.

Heat transferred to the system of fixed mass increases the internal energy of the system, as a result of which the molecules (of a gas) move with higher kinetic energy and collide more frequently, and so the disorder in the system increases. Heat is thus regarded as disorganized or disordered energy transfer which increases molecular chaos (see Sec. 7.16). If heat Q flows reversibly from the system to the surroundings at T_0 (Fig. 7.21), the entropy increase of the surroundings is

$$\Delta S_{\text{surr}} = \frac{Q}{T_0}$$

The entropy of the system is reduced by

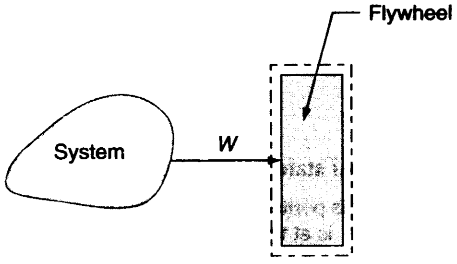
$$\Delta S_{\text{sys}} = -\frac{Q}{T_0}$$



Entropy transfer along with heat flow

The temperature of the boundary where heat transfer occurs is the constant temperature T_0. It may be said that the system has lost entropy to the surroundings. Alternatively, one may state that the surroundings have gained entropy from the system. Therefore, there is *entropy transfer* from the system to the surroundings along with heat flow. In other words, since the heat inflow increases the molecular disorder, there is flow or disorder along with heat. The sign of entropy transfer is the same as the sign of heat transfer: *positive*, if into the system, and *negative*, if out of the system.

On the other hand, ***there is no entropy transfer associated with work.*** In Fig. 7.22, the system delivers work to a flywheel, where energy is stored in a fully recoverable form. The flywheel molecules are simply put into rotation around the axis in a perfectly organized manner, and there is no dissipation and hence no entropy increase of the flywheel. The same can be said about work transfer in the compression of a spring or in the raising of a weight by a certain height. There is thus no entropy transfer along with work. If work is dissipated adiabatically into internal energy increase of the system (Subsection 7.9.5), there is an entropy increase in the system, but there is as such no entropy transfer to it.



No entropy transfer along with work transfer

Work is thus *entropy-free*, and no entropy is transferred with work. Energy is transferred with both heat and work, whereas entropy is transferred only with heat. The first law of thermodynamics makes no distinction between heat transfer and work. It considers them as *equals*. The distinction between heat transfer and work is brought about by the second law: ***an energy interaction which is accompanied by entropy transfer is heat transfer, and an energy interaction which is not accompanied by entropy transfer is work. Thus, only energy is exchanged during work interaction, whereas both energy and entropy are exchanged during heat transfer.***

(b) Mass Flow Mass contains entropy as well as energy, and the entropy and energy of a system are proportional to the mass. When the mass of a system is doubled, so are the entropy and energy of the system. Both entropy and energy are carried into or out of a system by streams of matter, and the rates of entropy and energy transport into or out of a system are proportional to the mass flow rate. Closed systems do not involve any mass flow and thus any entropy transport. When an amount of mass m enters or leaves a system, an entropy of amount ms, s being the specific entropy, accompanies it. Therefore, the entropy of a system increases by ms when the mass of amount m enters it, and decreases by the same amount when it leaves it at the same state.

7.10 ENTROPY GENERATION IN A CLOSED SYSTEM

The entropy of any closed system can increase in two ways:

(a) by heat interaction in which there is entropy transfer

(b) internal irreversibilities or dissipative effects in which work (or K.E.) is dissipated into internal energy increase.

If $\text{đ}Q$ is the infinitesimal amount of heat transferred to the system through its boundary at temperature T, the same as that of the surroundings, the entropy increase dS of the system can be expressed as

$$dS = d_eS + d_iS$$

$$= \frac{\text{đ}Q}{T} + d_iS \qquad (7.25)$$

where d_eS is the entropy increase due to external heat interaction and d_iS is the entropy increase due to internal irreversibility. From Eq. (7.25),

$$dS \geq \frac{\text{đ}Q}{T}$$

$$\therefore \qquad d_iS \geq 0 \qquad (7.26)$$

The entropy increase due to internal irreversibility is also called entropy production or entropy generation, S_{gen}.

In other words, the entropy change of a system during a process is greater than the entropy transfer ($\text{đ}Q/T$) by an amount equal to the entropy generated during the process within the system (d_iS), so that the *entropy balance* gives:

Entropy change = Entropy transfer + Entropy generation

$$\Delta S_{\text{sytem}} = \Delta S_{\text{transfer}} + \Delta S_{\text{gen}}$$

which is a verbal statement of Eq. (7.25) and illustrated in Fig. 7.23.

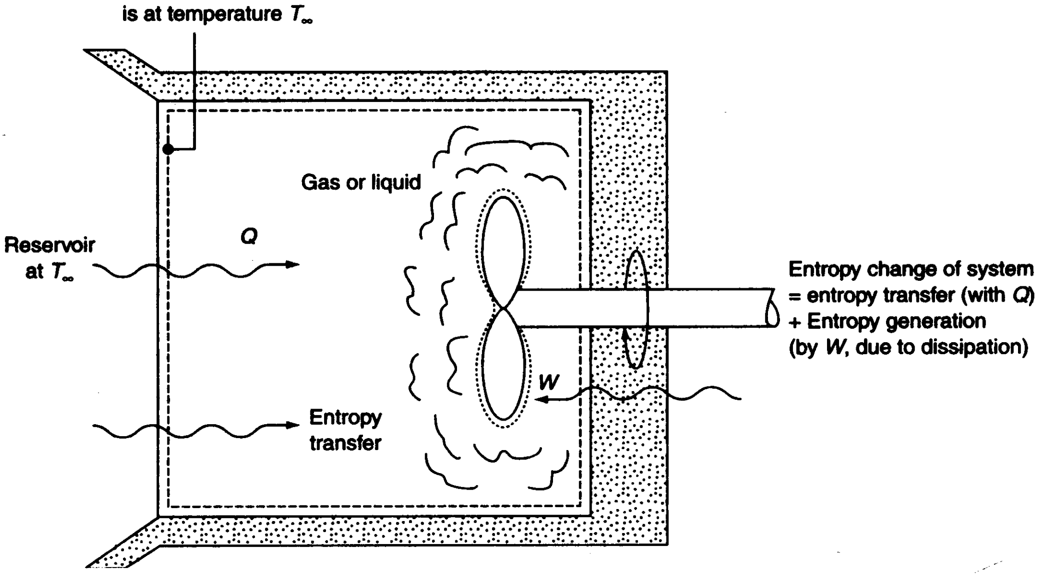


Illustration of the entropy transfer and entropy production concepts

It may so happen that in a process (e.g. the expansion of a hot fluid in a turbine) the entropy decrease of the system due to heat loss to the surroundings $\left(-\int \frac{\text{đ}Q}{T}\right)$ is equal to the entropy increase of the system due to internal irreversibilities such as friction, etc. $\left(\int \mathrm{d_i}S\right)$, in which case the entropy of the system before and after the process will remain the same $\left(\int \mathrm{d}S = 0\right)$. *Therefore, an isentropic process need not be adiabatic or reversible.*

But if the isentropic process is reversible, it must be adiabatic. Also, if the isentropic process is adiabatic, it cannot but be reversible. An adiabatic process need not be isentropic, since entropy can also increase due to friction etc. But if the process is adiabatic and reversible, it must be isentropic.

For an infinitesimal reversible process by a closed system,

$$\text{đ}Q_\mathrm{R} = \mathrm{d}U_\mathrm{R} + p\mathrm{d}V$$

If the process is irreversible,

$$\text{đ}Q_\mathrm{I} = \text{đ}U_\mathrm{I} + \text{đ}W$$

Since U is a property,

$$\mathrm{d}U_\mathrm{R} = \mathrm{d}U_\mathrm{I}$$

$\therefore$

$$\text{đ}Q_\mathrm{R} - p\mathrm{d}V = \text{đ}Q_\mathrm{I} - \text{đ}W$$

or

$$\left(\frac{\text{đ}Q}{T}\right)_\mathrm{R} = \left(\frac{\mathrm{d}Q}{T}\right)_\mathrm{I} + \frac{p\mathrm{d}V - \text{đ}W}{T} \tag{7.27}$$

The difference $(p\mathrm{d}V - \mathrm{d}W)$ indicates the work that is lost due to irreversibility, and is called the *lost work* $\text{đ}(LW)$, which approaches zero as the process approaches reversibility as a limit. Equation (7.27) can be expressed in the form

$$\mathrm{d}S = \mathrm{d_e}S + \mathrm{d_i}S$$

Thus the entropy of a closed system increases due to heat addition ($\mathrm{d_e}S$) and internal dissipation ($\mathrm{d_i}S$).

In any process executed by a system, energy is always conserved, but entropy is produced internally. For any process between equilibrium states 1 and 2 (Fig. 7.24), the first law can be written as

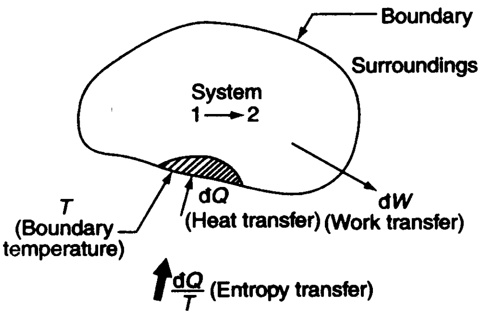
$$\underbrace{\int_1^2 \text{đ}Q - \int_1^2 \text{đ}W}_{\text{Energy transfer}} = \underbrace{E_2 - E_1}_{\text{Energy change}}$$

or

$$Q_{1\text{-}2} = E_2 - E_1 + W_{1\text{-}2}$$

By the second law,

$$S_2 - S_1 \geq \int_1^2 \frac{\text{đ}Q}{T}$$

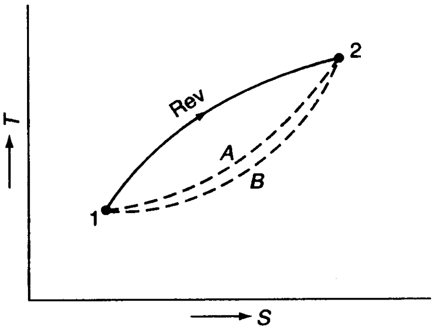


Schematic of a closed system interacting with its surroundings

It is only the transfer of energy as heat which is accompanied by entropy transfer, both of which occur at the boundary where the temperature is T. Work interaction is not accompanied by any entropy transfer. The entropy change of the system $(S_2 - S_1)$ exceeds the entropy transfer $\int_1^2 \frac{\text{đ}Q}{T}$. The difference is produced internally due to irreversibility. The amount of entropy generation S_gen is given by

$$\underbrace{S_2 - S_1}_{\text{Entropy change}} - \underbrace{\int_1^2 \frac{đQ}{T}}_{\text{Entropy transfer}} = \underbrace{S_{\text{gen}}}_{\text{Entropy production}} \tag{7.28}$$

$$\therefore \qquad S_{\text{gen}} \geq 0$$



Entropy generation depends on the path

The second law states that, in general, *any thermodynamic process is accompanied by entropy generation.*

Process 1–2, which does not generate any entropy ($S_{\text{gen}} = 0$), is a reversible process (Fig. 7.25). Paths for which $S_{\text{gen}} > 0$ are considered irreversible. Like heat transfer and work transfer during the process 1–2, *the entropy generation also depends on the path the system follows.* S_{gen} is, therefore, not a thermodynamic property and $đS_{\text{gen}}$ is an inexact differential, although $(S_2 - S_1)$ depends only on the end states. In the differential form, Eq. (7.28) can be written as

$$\text{d}S_{\text{gen}} = \text{d}S - \frac{đQ}{T} \tag{7.29}$$

The amount of entropy generation quantities the intrinsic irreversibility of the process. If the path A causes more entropy generation than path B (Fig. 7.25), i.e.

$$(S_{\text{gen}})_A > (S_{\text{gen}})_B$$

the path A is more irreversible than path B and involves more 'lost work'.

If heat transfer occurs at several locations on the boundary of a system, the entropy transfer term can be expressed as a sum, so Eq. (7.28) takes the form

$$S_2 - S_1 = \sum_j \frac{Q_j}{T_j} + S_{\text{gen}} \tag{7.30}$$

where Q_j/T_j is the amount of entropy transferred through the portion of the boundary at temperature T_j.

On a time rate basis, the entropy balance can be written as

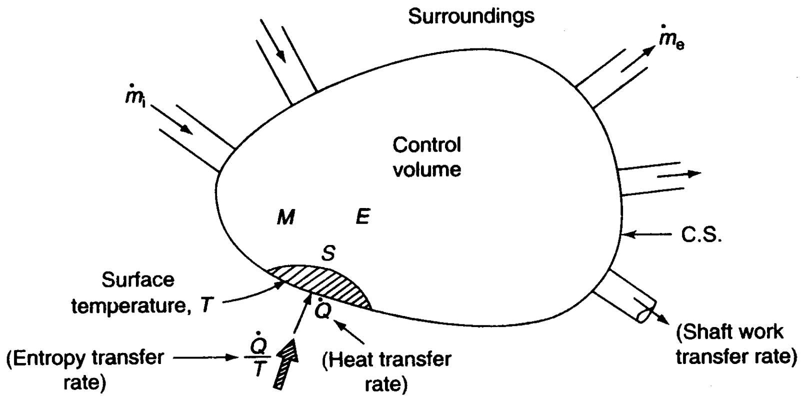
$$\frac{\text{d}S}{\text{d}\tau} = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{S}_{\text{gen}} \tag{7.31}$$

where $\text{d}S/\text{d}\tau$ is the rate of change of entropy of the system, $\dot{Q}_j/T_j$ is the rate of entropy transfer through the portion of the boundary whose instantaneous temperature is T_j, and $\dot{S}_{\text{gen}}$ is the rate of entropy generation due to irreversibilites within the system.

7.11 ENTROPY GENERATION IN AN OPEN SYSTEM

In an open system, there is transfer of three quantities: mass, energy and entropy. The control surface can have one or more openings for mass transfer (Fig. 7.26). It is rigid, and there is shaft work transfer across it.

The *continuity equation* gives



Schematic of an open system and its interaction with surroundings

$$\underbrace{\sum_i \dot{m}_i - \sum_e \dot{m}_e}_{\text{net mass transfer rate}} = \underbrace{\frac{\partial M}{\partial \tau}}_{\text{rate of mass accumulation in the CV}} \tag{7.32}$$

The *energy equation* gives

$$\underbrace{\sum_i \dot{m}_i \left(h + \frac{\mathbf{V}^2}{2} + gZ\right)_i - \sum_e \dot{m}_e \left(h + \frac{\mathbf{V}^2}{2} + gZ\right)_e}_{\text{net rate of energy transfer}} + \dot{Q} - \dot{W}_{sh} = \underbrace{\frac{\partial E}{\partial \tau}}_{\text{rate of energy accumulation in the CV}} \tag{7.33}$$

The *second law inequality* or the entropy principle gives

$$\underbrace{\sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \frac{\dot{Q}}{T}}_{\text{net rate of entropy transfer}} \le \underbrace{\frac{\partial S}{\partial \tau}}_{\text{rate of increase of entropy of the CV}} \tag{7.34}$$

Here $\dot{Q}$ represents the rate of heat transfer at the location of the boundary where the instantaneous temperature is T. The ratio $\dot{Q}/T$ accounts for the entropy transfer along with heat. The terms $\dot{m}_i s_i$ and $\dot{m}_e s_e$ account, respectively, for rates of entropy transfer into and out of the CV accompanying mass flow. The rate of entropy increase of the control volume exceeds, or is equal to, the net rate of entropy transfer into it. The difference is the entropy generated within the control volume due to irreversibility. Hence, the rate of entropy generation is given by

$$\dot{S}_{gen} = \frac{\partial S}{\partial \tau} - \sum_i \dot{m}_i s_i + \sum_e \dot{m}_e s_e - \frac{\dot{Q}}{T} \tag{7.35}$$

By the second law,

$$\dot{S}_{gen} \ge 0$$

If the process is reversible, $\dot{S}_{gen} = 0$. For an irreversible process, $\dot{S}_{gen} > 0$.

The magnitude of $\dot{S}_{gen}$ quantifies the irreversibility of the process. If systems A and B operate so that $(\dot{S}_{gen})_A > (\dot{S}_{gen})_B$ it can be said that the system A operates more irreversibly than system B. The unit of $\dot{S}_{gen}$ is W/K.

At *steady state*, the continuity equation gives

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \tag{7.36}$$

the energy equation becomes

$$0 = \dot{Q} - \dot{W}_{sh} + \sum_i \dot{m}_i \left(h + \frac{\mathbf{V}^2}{2} + gZ \right)_i - \sum_e \dot{m}_e \left(h + \frac{\mathbf{V}^2}{2} + gZ \right)_e \tag{7.37}$$

and the entropy equation reduces to

$$0 = \frac{\dot{Q}}{T} + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_{gen} \tag{7.38}$$

These equations often must be solved simultaneously, together with appropriate property relations.

Mass and energy are conserved quantities, but entropy is not generally conserved. The rate at which entropy is transferred out must exceed the rate at which entropy enters the CV, the difference being the rate of entropy generated within the CV owing to irreversibilities.

For one-inlet and one-exit control volumes, the entropy equation becomes

$$0 = \frac{\dot{Q}}{T} + \dot{m}(s_1 - s_2) + \dot{S}_{gen}$$

$$\therefore \quad s_2 - s_1 = \frac{1}{\dot{m}}\left(\frac{\dot{Q}}{T} \right) + \frac{\dot{S}_{gen}}{\dot{m}} \tag{7.39}$$

7.12 FIRST AND SECOND LAWS COMBINED

By the second law

$$đQ_{rev} = TdS$$

and by the first law, for a closed non-flow system,

$$đQ = dU + pdV$$

$$TdS = dU + pdV \tag{7.40}$$

Again, the enthalpy

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$= TdS + Vdp$$

$$TdS = dH - Vdp \tag{7.41}$$

Equations (7.40) and (7.41) are the thermodynamic equations relating the properties of the system.

Let us now examine the following equations as obtained from the first and second laws:

(a) $đQ = dE + đW$—This equation holds good for any process, reversible or irreversible, and for any system.

(b) $đQ = dU + đW$—This equation holds good for any process undergone by a closed stationary system.

(c) $đQ = dU + pdV$—This equation holds good for a closed system when only pdV-work is present. This is true only for a reversible (quasi-static) process.

(d) $đQ = TdS$—This equation is true only for a reversible process.

(e) $TdS = dU + pdV$—This equation holds good for any process reversible or irreversible, undergone by a closed system, since it is a relation among properties which are independent of the path.

(f) $TdS = dH - Vdp$—This equation also relates only the properties of system. There is no path function term in the equation. Hence the equation holds good for any process.

The use of the term 'irreversible process' is doubtful, since no irreversible path or process can be plotted on thermodynamic coordinates. It is more logical to state that 'the change of state is irreversible' rather than say 'it is an irreversible process'. A natural process which is inherently irreversible is indicated by a dotted line connecting the initial and final states, both of which are in equilibrium. The dotted line has no other meaning, since it can be drawn in any way. To determine the entropy change for a real process, a known reversible path is made to connect the two end states, and integration is performed on this path using either equation (e) or equation (f), as given above. Therefore, the entropy change of a system between two identifiable equilibrium states is the same whether the intervening process is reversible or the change of state is irreversible.

7.13 REVERSIBLE ADIABATIC WORK IN A STEADY FLOW SYSTEM

In the differential form, the steady flow energy equation per unit mass is given by Eq. (5.11),

$$đQ = dh + \mathrm{V}d\mathrm{V} + gdZ + đW_x$$

For a reversible process, $đQ = Tds$

$$\therefore \quad Tds = dh + \mathrm{V}d\mathrm{V} + gdZ + đW_x \tag{7.42}$$

Using the property relation, Eq. (7.41), per unit mass,

$$Tds = dh - vdp$$

in Eq. (7.42), we have

$$-vdp = \mathrm{V}d\mathrm{V} + gdZ + đW_x \tag{7.43}$$

On integration

$$-\int_1^2 vdp = \Delta\frac{\mathrm{V}^2}{2} + W_x \tag{7.44}$$

If the changes in K.E. and P.E. are neglected, Eq. (7.44) reduces to

$$W_x = -\int_1^2 vdp \tag{7.45}$$

If $đQ = 0$, implying $ds = 0$, the property relation gives

$$dh = vdp$$

or

$$h_2 - h_1 = \int_1^2 vdp \tag{7.46}$$

From Eqs (7.45) and (7.46),

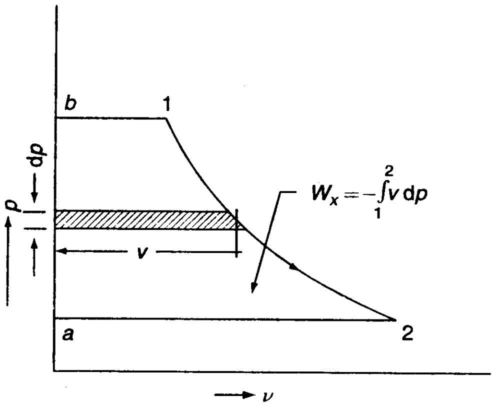
$$W_x = h_1 - h_2 = -\int_1^2 vdp \tag{7.47}$$

The integral $-\int_1^2 v\mathrm{d}p$ represents an area on the p–v plane (Fig. 7.27). To make the integration, one must have a relation between p and v such as pv^n = constant.

$$\therefore \qquad W_{1-2} = h_1 - h_2 = -\int_1^2 v\mathrm{d}p$$

$$= \text{area } 12\,ab\,1$$

Equation (7.47) holds good for a steady flow work-producing machine like an engine or turbine as well as for a work-absorbing machine like a pump or a compressor, when the fluid undergoes reversible adiabatic expansion or compression.



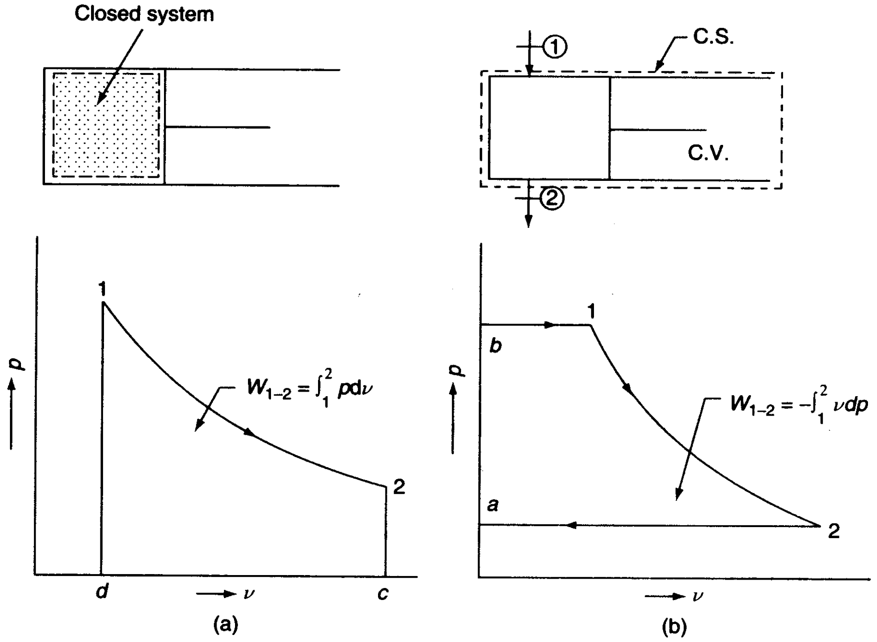
Reversible steady flow work interaction

It may be noted that for a closed stationary system like a gas confined in a piston-cylinder machine (Fig. 7.28a), the reversible work done would be

$$W_{1-2} = \int_1^2 p\mathrm{d}V = \text{Area } 12\ cd\ 1$$

The reversible work done by a steady flow system (Fig. 7.28b) would be

$$W_{1-2} = -\int_1^2 v\mathrm{d}p = \text{Area } 12\ ab\ 1$$



Reversible work transfer in (a) A closed system and (b) A steady flow system

7.14 ENTROPY AND DIRECTION: THE SECOND LAW—A DIRECTIONAL LAW OF NATURE

Since the entropy of an isolated system can never decrease, it follows that only those processes are possible in nature which would give an entropy increase for the system and the surroundings together (the universe). All spontaneous processes in nature occur only in one direction from a higher to a lower potential, and these are accompanied by an entropy increase of the universe. When the potential gradient is infinitesimal (or zero in the limit), the entropy change of the universe is zero, and the process is reversible. The second law indicates the direction in which a process takes place. *A process always occurs in such a direction as to cause an increase in the entropy of the universe.* The macroscopic change ceases only when the potential gradient disappears and the equilibrium is reached when the entropy of the universe assumes a maximum value. To determine the equilibrium state of an isolated system it is necessary to express the entropy as a function of certain properties of the system and then render the function a maximum. At equilibrium, the system (isolated) exists at the peak of the entropy-hill, and $dS = 0$ (Fig. 7.13).

The natural direction of events in which entropy increases indicates the '*arrow of time*' which results from the universe not being in thermodynamic equilibrium. It undergoes a natural evolution, and inexorably approaches the state of quilibrium.

7.15 ENTROPY AND DISORDER

Work is a macroscopic concept. Work involves order or the orderly motion of molecules, as in the expansion or compression of a gas. The kinetic energy and potential energy of a system represent orderly forms of energy. The kinetic energy of a gas is due to the coordinated motion of all the molecules with the same average velocity in the same direction. The potential energy is due to the vantage position taken by the molecules or displacements of molecules from their normal positions. Heat or thermal energy is due to the random thermal motion of molecules in a completely disorderly fashion and the average velocity is zero. Orderly energy can be readily converted into disorderly energy, e.g. mechanical and electrical energies into internal energy (and then heat) by friction and Joule effect. Orderly energy can also be converted into one another. *But there are natural limitations on the conversion of disorderly energy into orderly energy, as delineated by the second law.* When work is dissipated into internal energy, the disorderly motion of molecules is increased. Two gases, when mixed, represent a higher degree of disorder than when they are separated. An irreversible process always tends to take the system (isolated) to a state of greater disorder. It is a tendency on the part of nature to proceed to a state of greater disorder. An isolated system always tends to a state of greater entropy. So there is a close link between entropy and disorder. It may be stated roughly that *the entropy of a system is a measure of the degree of molecular disorder existing in the system.* When heat is imparted to a system, the disorderly motion of molecules increases, and so the entropy of the system increases. The reverse occurs when heat is removed from the system.

Ludwig Boltzmann (1877) introduced statistical concepts to define disorder by attaching to each state a *thermodynamic probability*, expressed by the quantity W, which is greater the more disordered the state is. The increase of entropy implies that the system proceeds by itself from one state to another with a higher thermodynamic probability (or disorder number). An irreversible process goes on until the *most probable state* (equilibrium state when W is maximum) corresponding to the maximum value of entropy is reached. Boltzmann assumed a functional relation between S and W. While entropy is additive, probability is multiplicative. If the two parts A and B of a system in equilibrium are considered, the entropy is the sum

$$S = S_A + S_B$$

and the thermodynamic probability is the product

$$W = W_A \cdot W_B$$

Again, $S = S(W),\ S_A = S(W_A)$, and $S_B = S(W_B)$

$$\therefore \quad S(W) = S(W_A W_B) = S(W_A) + S(W_B)$$

which is a well-known functional equation for the logarithm. Thus the famous relation is reached

$$S = K \ln W \tag{7.48}$$

where K is a constant, known as Boltzmann constant. This is engraved upon Boltzmann's tombstone in Vienna.

When $W = 1$, which represents the greatest order, $S = 0$. This occurs only at $T = 0$ K. This state cannot be reached in a finite number of operations. This is the Nernst-Simon statement of third law of thermodynamics. In the case of a gas, W increases due to an increase in volume V or temperature T. In the reversible adiabatic expansion of a gas the increase in disorder due to an increase in volume is just compensated by the decrease in disorder due to a decrease in temperature, so that the disorder number or entropy remains constant.

7.16 ABSOLUTE ENTROPY

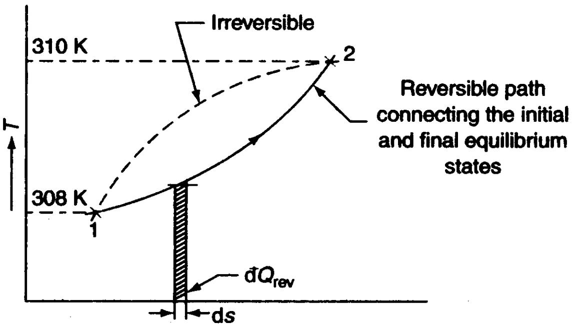
It is important to note that one is interested only in the amount by which the entropy of the system changes in going from an initial to final state, and not in the value of absolute entropy. In cases where it is necessary, a zero value of entropy of the system at an arbitrarily chosen standard state is assigned, and the entropy changes are calculated with reference to this standard state.

Solved Examples

Example 7.1

Water flows through a turbine in which friction causes the water temperature to rise from 35°C to 37°C. If there is no heat transfer, how much does the entropy of the water change in passing through the turbine? (Water is incompressible and the process can be taken to be at constant volume.)

Solution The presence of friction makes the process irreversible and causes an entropy increase for the system. The flow process is indicated by the dotted line joining the equilibrium states 1 and 2 (Fig. Ex. 7.1). Since entropy is a state property and the entropy change depends only on the two end states and is independent of the path the system follows, to find the entropy change, the irreversible path has to be replaced by a reversible path, as shown in the figure, because no integration can be made on a path other than a reversible path.



$$T_2 = 37 + 273 = 310 \text{ K}$$

$$T_1 = 35 + 273 = 308 \text{ K}$$

We have $đQ_{rev} = TdS$

$$dS = \frac{mc_v dT}{T}$$

$$S_2 - S_1 = mc_v \ln \frac{T_2}{T_1} = 1 \times 4.187 \ln \frac{310}{308} = 0.0243 \text{ kJ/K}$$ *Ans.*

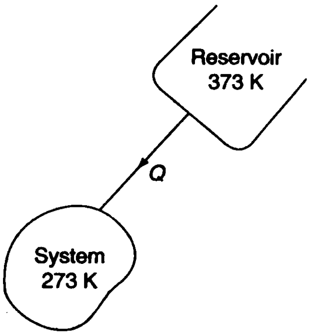
Example 7.2

(*a*) *One kg of water at* 273 *K is brought into contact with a heat reservoir at* 373 *K. When the water has reached* 373 *K, find the entropy change of the water, of the heat reservoir, and of the universe.*

(*b*) *If water is heated from* 273 *K to* 373 *K by first bringing it in contact with a reservoir at* 323 *K and then with a reservoir at* 373 *K, what will the entropy change of the universe be?*

(*c*) *Explain how water might be heated from* 273 *to* 373 *K with almost no change in the entropy of the universe.*

Solution (a) Water is being heated through a finite temperature difference (Fig. Ex. 7.2). The entropy of water would increase and that of the reservoir would decrease so that the net entropy change of the water (system) and the reservoir together would be positive definite. Water is being heated irreversibly, and to find the entropy change of water, we have to assume a reversible path between the end states which are at equilibrium.



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$$(\Delta S)_{\text{water}} = \int \frac{\text{đ}Q}{T} = \int_{T_1}^{T_2} \frac{mc\,dT}{T} = mc \ln \frac{T_2}{T_1}$$

$$= 1 \times 4.187 \ln \frac{373}{273} = 1.305 \text{ kJ/K}$$

The reservoir temperature remains constant irrespective of the amount of heat withdrawn from it.

Amount of heat absorbed by the system from the reservoir,

$$Q = 1 \times 4.187 \times (373 - 273) = 418.7 \text{ kJ}$$

∴ Entropy change of the reservoir

$$(\Delta S)_{\text{res}} = -\frac{Q}{T} = -\frac{418.7}{373} = -1.122 \text{ kJ/K}$$

∴ Entropy change of the universe

$$(\Delta S)_{\text{univ}} = (dS)_{\text{system}} + (\Delta S)_{\text{res}}$$

$$= 1.305 - 1.122 = 0.183 \text{ kJ/K}$$ *Ans.* (a)

(b) Water is being heated in two stages, first from 273 K to 323 K by bringing it in contact with a reservoir at 323 K, and then from 323 K to 373 K by bringing it in contact of a second reservoir at 373 K.

$$(\Delta S)_{\text{water}} = \int_{273\text{K}}^{323\text{K}} mc\frac{dT}{T} + \int_{323\text{K}}^{373\text{K}} mc\frac{dT}{T}$$

$$= 4.187 \left(\ln \frac{323}{273} + \ln \frac{373}{323} \right) \approx (0.1673 + 0.1441)\, 4.187$$

$$= 1.305 \text{ kJ/K}$$

$$(\Delta S)_{\text{res I}} = -\frac{1 \times 4.187 \times (323 - 273)}{323} = -0.647 \text{ kJ/K}$$

$$(\Delta S)_{\text{res II}} = \frac{1 \times 4.187 \times (373 - 323)}{373} = -0.56 \text{ kJ/K}$$

$$\therefore \quad (\Delta S)_{\text{uni V}} = (\Delta S)_{\text{water}} + (\Delta S)_{\text{res I}} + (\Delta S)_{\text{res II}}$$

$$= 1.305 - 0.647 - 0.56$$

$$= 0.098 \text{ kJ/K} \qquad \textit{Ans.}$$

(c) The entropy change of the universe would be less and less if the water is heated in more and more stages, by bringing the water in contact successively with more and more heat reservoirs, each succeeding reservoir being at a higher temperature than the preceding one.

When water is heated in infinite steps, by bringing it in contact with an infinite number of reservoirs in succession, so that at any instant the temperature difference between the water and the reservoir in contact is infinitesimally small, then the net entropy change of the universe would be zero, and the water would be *reversibly* heated.

Example 7.3

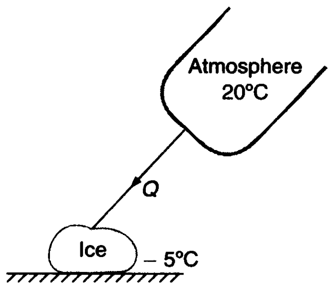
One kg of ice at – 5°C is exposed to the atmosphere which is at 20°C. The ice melts and comes into thermal equilibrium with the atmosphere. (a) *Determine the entropy increase of the universe.* (b) *What is the minimum amount of work necessary to convert the water back into ice at – 5°C?* c_p *of ice is* 2.093 *kJ/kg K and the latent heat of fusion of ice is* 333.3 *kJ/kg.*

Solution Heat absorbed by ice Q from the atmosphere (Fig. Ex. 7.3.1)

= Heat absorbed in solid phase + Latent heat
+ Heat absorbed in liquid phase

$$= 1 \times 2.093 \times [0 - (-5)] + 1 \times 333.3 + 1 \times 4.187 \times (20 - 0)$$

$$= 427.5 \text{ kJ}$$



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Entropy change of the atmosphere.

$$(\Delta S)_{\text{atm}} = -\frac{Q}{T} = -\frac{427.5}{293} = -1.46 \text{ kJ/K}$$

Entropy change of the system (ice) as it gets heated from –5°C to 0°C

$$(\Delta S_{\text{I}})_{\text{system}} = \int_{268}^{293} mc_p \frac{dT}{T} = 1 \times 2.093 \ln \frac{273}{268} = 2.093 \times 0.0186$$

$$= 0.0389 \text{ kJ/K}$$

Entropy change of the system as ice melts at 0°C to become water at 0°C

$$(\Delta S_{II})_{system} = \frac{333.3}{273} = 1.22 \text{ kJ/K}$$

Entropy change of water as it gets heated from 0°C to 20°C

$$(\Delta S_{III})_{system} = \int_{273}^{293} mc_p \frac{dT}{T} = 1 \times 4.187 \ln \frac{293}{273} = 0.296 \text{ kJ/K}$$

Total entropy change of ice as it melts into water

$$(\Delta S)_{total} = \Delta S_I + \Delta S_{II} + \Delta S_{III}$$

$$= 0.0389 + 1.22 + 0.296 = 1.5549 \text{ kJ/K}$$

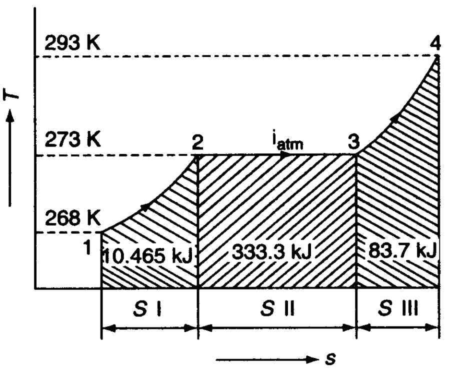
The entropy-temperature diagram for the system as ice at – 5°C converts to water at 20°C is shown in Fig. Ex. 7.3.2.

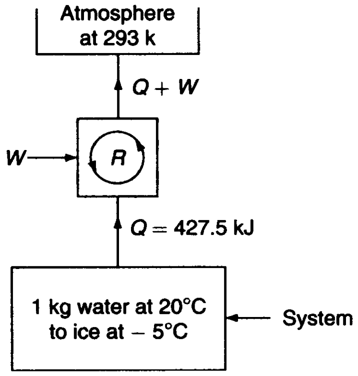
∴ Entropy increase of the universe

$$(\Delta S)_{univ} = (\Delta S)_{system} + (\Delta S)_{atm}$$

$$= 1.5549 - 1.46 = 0.0949 \text{ kJ/K}$$ *Ans.* (a)

(b) To convert 1 kg of water at 20°C to ice at – 5°C, 427.5 kJ of heat have to be removed from it, and the system has to be brought from state 4 to state 1 (Fig. 7.3.2). A refrigerator cycle, as shown in Fig. 7.3.3, is assumed to accomplish this.





The entropy change of the system would be the same, i.e. $S_4 - S_1$, with the only difference that its sign will be negative, because heat is removed from the system (Fig. Ex. 7.3.2).

$$(\Delta S)_{system} = S_1 - S_4$$
(negative)

The entropy change of the working fluid in the refrigerator would be zero, since it is operating in a cycle, i.e.,

$$(\Delta S)_{ref} = 0$$

The entropy change of the atmosphere (positive)

$$(\Delta S)_{\text{atm}} = \frac{Q+W}{T}$$

∴ Entropy change of the universe

$$(\Delta S)_{\text{univ}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{ref}} + (\Delta S)_{\text{atm}}$$

$$= (S_1 - S_4) + \frac{Q+W}{T}$$

By the principle of increase of entropy

$$(\Delta S)_{\text{univ or isolated system}} \geq 0$$

$$\therefore \quad \left[(S_1 - S_4) + \frac{Q+W}{T}\right] \geq 0$$

$$\therefore \quad \frac{Q+W}{T} \geq (S_4 - S_1)$$

$$W \geq T(S_4 - S_1) - Q$$

$$\therefore \quad W_{(\min)} = T(S_4 - S_1) - Q$$

Here $Q = 427.5$ kJ

$$T = 293 \text{ K}$$

$$S_4 - S_1 = 1.5549 \text{ kJ/K}$$

$$\therefore \quad W_{(\min)} = 293 \times 1.5549 - 427.5$$

$$= 28.5 \text{ kJ}$$

Ans. (b)

Example 7.4

Two identical bodies of constant heat capacity are at the same initial temperature T_i. A refrigerator operates between these two bodies until one body is cooled to temperature T_2. If the bodies remain at constant pressure and undergo no change of phase, show that the minimum amount of work needed to do this is

$$W_{(\min)} = C_p\left(\frac{T_i^2}{T_2} + T_2 - 2T_i\right)$$

Solution Both the finite bodies A and B are initially at the same temperature T_i. Body A is to be cooled to temperature T_2 by operating the refrigerator cycle, as shown in Fig. Ex. 7.4. Let T_2' be the final temperature of body B.

Heat removed from body A to cool it from T_i to T_2

$$Q = C_p(T_i - T_2)$$

where C_p is the constant pressure heat capacity of the identical bodies A and B.

Heat discharged to body B

$$= Q + W = C_p(T_2' - T_i)$$

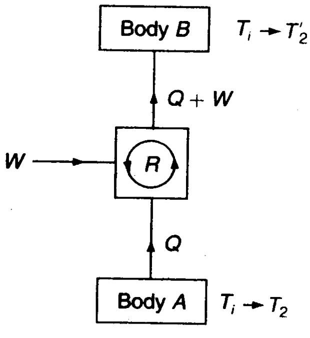


Fig. Ex. 7.4