ENTROPY

An important property which arose as a consequence of the First Law is Internal Energy.

Another important property, Entropy, follows from the Second Law.

Consider a reversible adiabatic process for any system on a P-V diagram. This is represented by line AB on Fig. 4.4

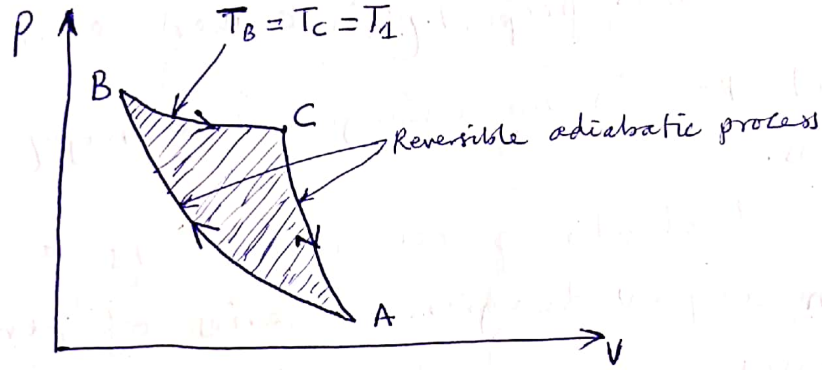


Fig. 4.4 Hypothetical cycle on a P-V diagram

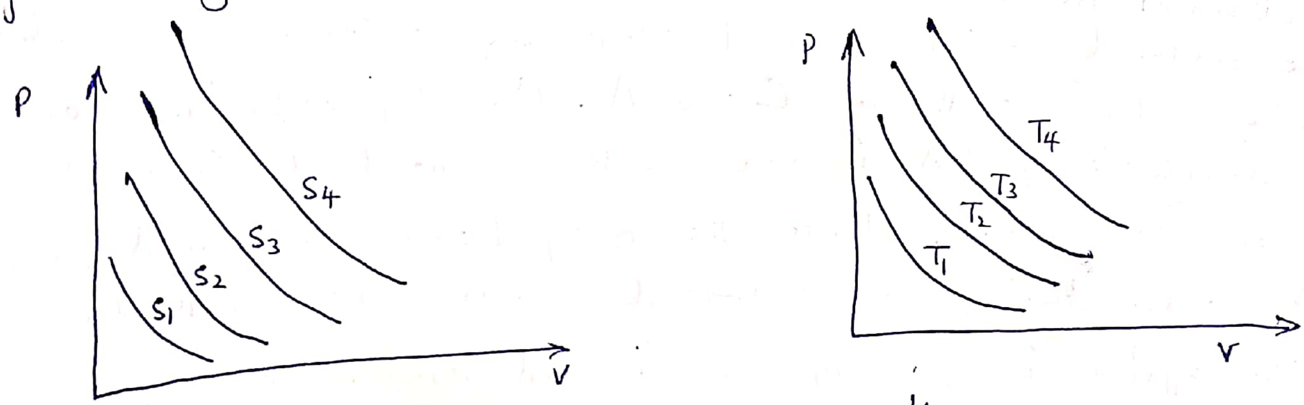
Suppose that it is possible for the system to undergo a reversible isothermal process at temperature T_1 from B to C and then be restored to its original state by a second reversible adiabatic process from C to A. Now by definition an adiabatic process is one in which no heat flows to or from the system. Hence the only heat transferred is from B to C during the isothermal process. The work done by the system is given by the enclosed area. We therefore have a system undergoing a cycle and developing a net work output while drawing heat from a reservoir at one fixed temperature. This is impossible because it violates the Second Law. Therefore the original ~~st~~ supposition is wrong, and it is not possible to have two reversible adiabatic processes passing through the same state A.

Now one of the characteristics of a property of a system is that there is one unique line which represents a value of property on a diagram of properties. (For Example, the line BC on Fig. 4.4 represents the isothermal at T_1)

Hence there must be a property represented by a reversible adiabatic process. This property is called entropy, s

It follows that there is no change of entropy in a reversible adiabatic process.

Each reversible adiabatic process represents a unique value of entropy. On a p-v diagram a series of reversible adiabatic processes appear as shown in Fig. 4.5(a), each line representing one value of entropy. This is similar to Fig. 4.5 (b) in which a series of isothermals is drawn, each representing one value of temperature.



(b)

(a)

Fig 4.5 A series of constant entropy and constant temperature lines on a p-v diagram.

Starting with the non-flow energy equation for a reversible process $dQ = du + pdv$

for a perfect gas $dQ = C_v dT + RT\frac{dv}{v}$

This equation can be integrated after dividing through by T,

i.e $$\frac{dQ}{T} = \frac{C_v dT}{T} + \frac{R dv}{v}$$

Also for an adiabatic process, $dQ = 0$

i.e $$\frac{dQ}{T} = \frac{C_v dT}{T} + \frac{R dv}{v} = 0$$

We can say that $\frac{dQ}{T} = 0$ for a reversible adiabatic process. For any other reversible process $\frac{dQ}{T} \neq 0$.
This result can be shown to apply to all working substances, i.e $ds = \frac{dQ}{T}$ for all working substances where s is entropy.

The change of entropy is more important than its absolute value, and the zero of entropy can be chosen quite arbitrarily.
Integrating the equation gives

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} \qquad (4.8)$$

The units of specific entropy (considering unit mass of fluid) is given by KJ/Kg K

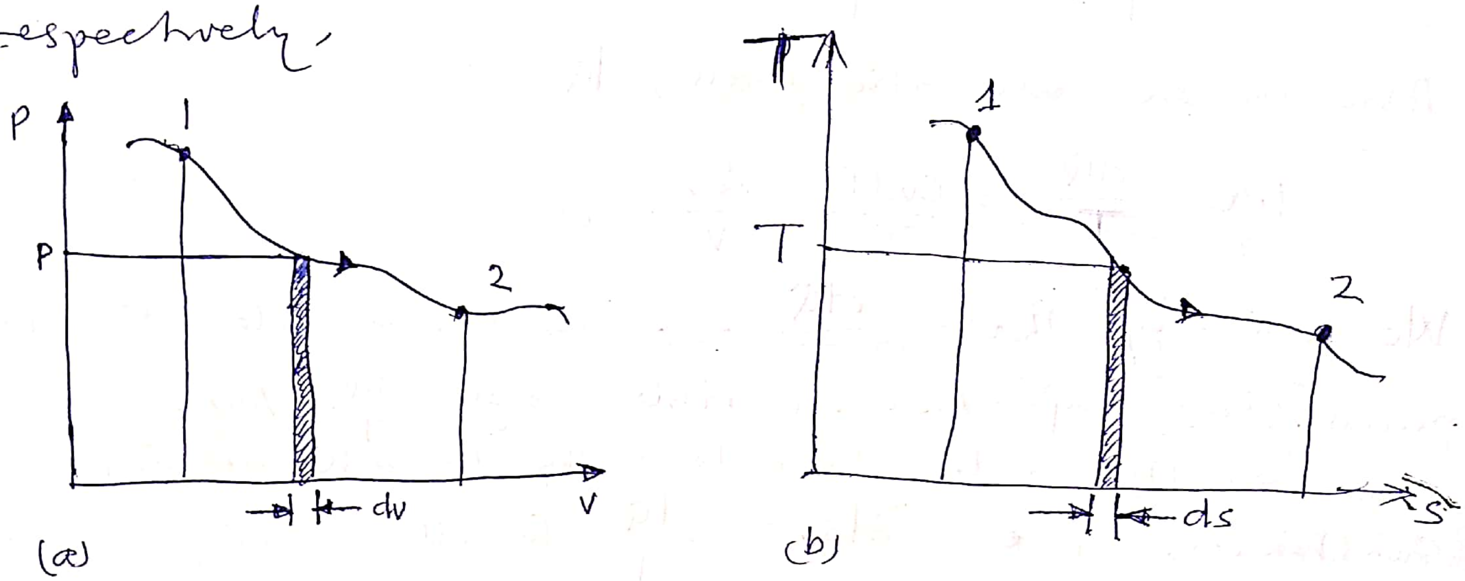
re-writing $ds = \frac{dQ}{T}$ we have
$$dQ = Tds$$

for a reversible process $\dot{Q} = \int_1^2 T\,ds$

A.

This equation is analogous to $W = -\int_1^2 p\,dv$ for any reversible process.

Thus, as there is a diagram on which areas represent work output in a reversible process, there is also a diagram on which areas represent heat supplied in a reversible process. These diagrams are the p-v and the T-s diagrams respectively.



(a) (b)

~~For a~~, Fig. 4.6 Area under a reversible process on a p-v and on a T-s diagram

For a reversible process 1-2 in Fig. 4.6 (a), the shaded area $\int_1^2 p\,dv$ represents work output, $-W$; for a reversible process 1-2 in Fig. 4.6 (b), the shaded area $\int_1^2 T\,ds)$ represents heat supplied, Q. Therefore one great use of the property entropy is that it enables a diagram to be drawn on which areas represent heat flow in a reversible process.

The T–s diagram for a Vapour

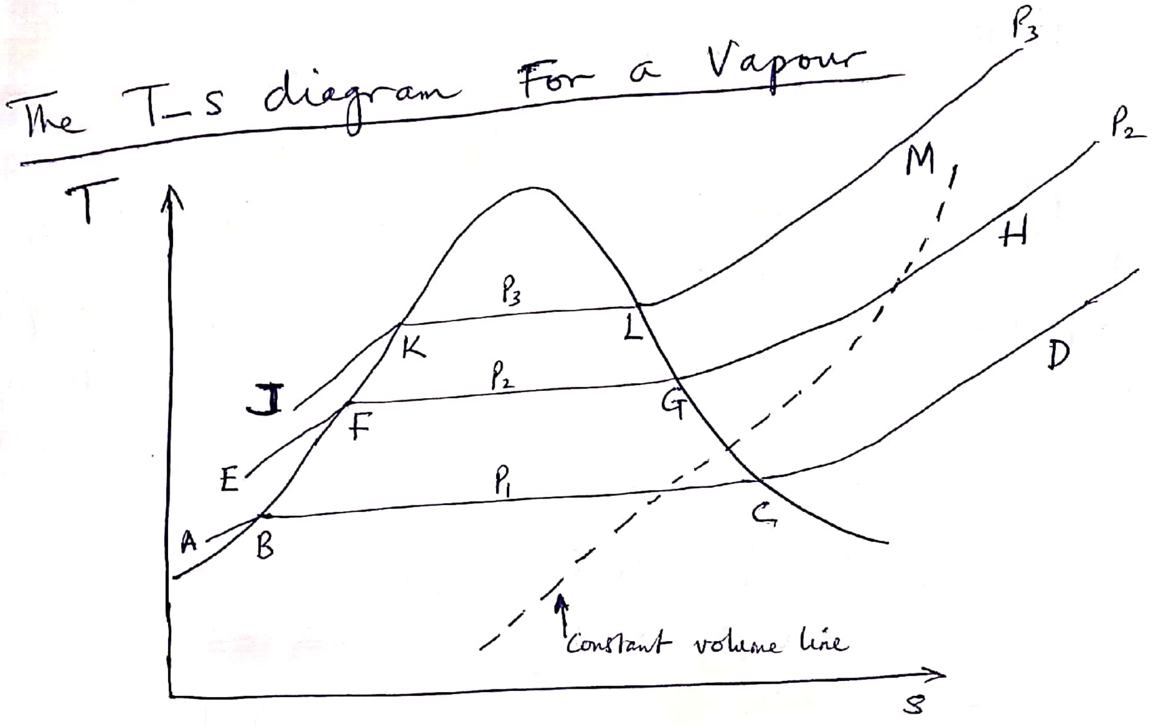


Fig. 4.7 T–s diagram for a vapour

Three lines of constant pressure (P_1, P_2 and P_3) are shown (i.e. lines ABCD, EFGH, and JKLM). The pressure lines in the liquid region are practically coincident with the saturated liquid line (i.e. portions AB, EF, and JK), and the difference is usually neglected. The pressure remains constant with temperature when the latent heat is added, hence the pressure lines are horizontal in the wet region (i.e portions BC, FG, and KL). The pressure lines are horizontal in the wet region (i.e portions BC, FG, and KL). The pressure lines curve upwards in the superheat region as shown (i.e. portions CD, GH and LM.) Thus the temperature rises as heating continues at constant pressure. One constant volume line (shown as a broken line) is drawn in Fig. 4.7. Lines of constant volume are concave down in the wet region and slope up more steeply than pressure lines in the superheat region.

In steam tables the entropy of the saturated liquid an the dry saturated vapour are represented by s_f and s respectively. The difference, $s_g - s_f = s_{fg}$, is also tabulated. The entropy of wet steam is given by the entropy of the water in the mixture plus the entropy of the dry steam in the mixture. For wet steam with dryness fraction, x, we have

$$s = (1-x)s_f + x s_g \qquad \text{———} (4.10)$$

or $\quad s = s_f + x(s_g - s_f) \qquad$ ———~~(4.11)~~

i.e $\quad s = s_f + x s_{fg} \qquad$ ———(4.11)

Then the dryness fraction is given by

$$x = \frac{s - s_f}{s_{fg}} \qquad \text{———} (4.12)$$

It can be seen from equation (4.12) that the dryness fraction is proportional to the distance of the state point from the liquid line on a T–s diagram. For example, for state 1 on Fig. 4.8 the dryness fraction

$$x_1 = \frac{\text{distance F1}}{\text{distance FG}} = \frac{s_1 - s_{f1}}{s_{fg1}}$$

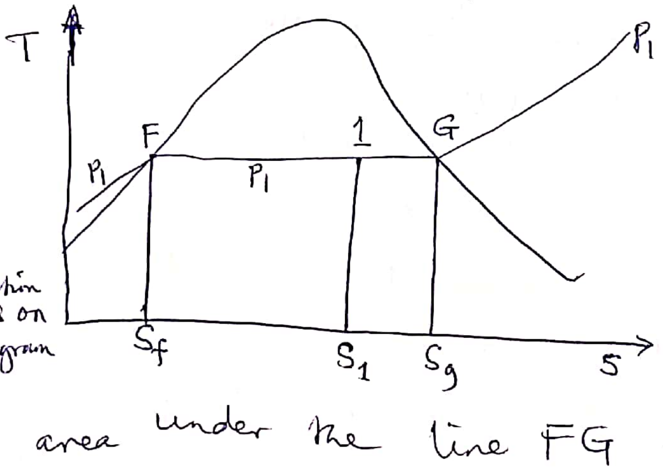


Fig. 4.8 Dryness fraction from areas on a T–s diagram

The area under the line FG on Fig. 4.8 represents the specific enthalpy of vaporization h_{fg}. The area under the line F1 is given by $x_1 h_{fg}$

Example 1 1 kg of steam at 7 bar, entropy 6.5 kJ/kgK, is ~~heated~~ heated reversibly at constant pressure until the temperature is 250 °C. Calculate the heat supplied, and show on a T-s diagram the area which represents the heat flow.

Solution At 7 bar, $S_g = 6.709$ kJ/kgK, hence the steam is wet, since the actual entropy, s is less than S_g.

From equation (4.12)

$$x_1 = \frac{S_1 - S_{f1}}{S_{fg1}} = \frac{6.5 - 1.992}{4.717} = 0.955$$

Then $h_1 = h_{f1} + x_1 h_{fg1} = 697 + (0.955 \times 2067)$

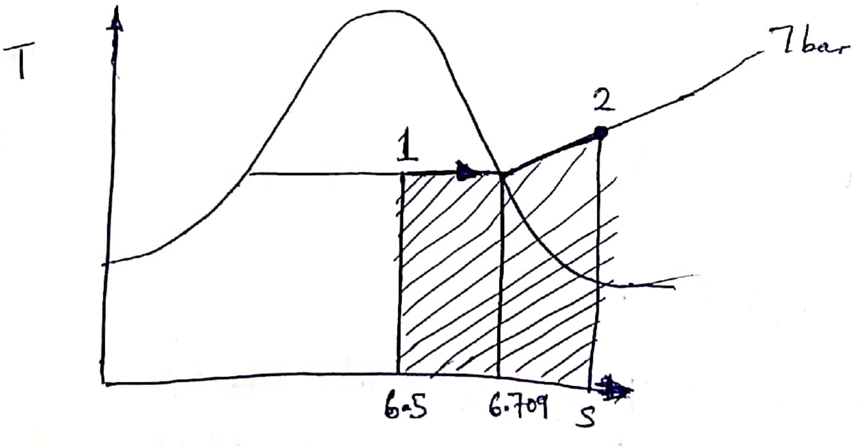
$$h_1 = 697 + 1975 = 2672 \text{ kJ/kg}$$

At state 2 the steam is at 250 °C at 7 bar, and is therefore superheated. From superheat tables, $h_2 = 2955$ kJ/kg.

At constant pressure from equation (3.3)

$$Q = h_2 - h_1 = 2955 - 2672 = 283 \text{ kJ/kg}$$

i.e heat supplied = 283 kJ/kg



Specific entropy/(kJ/kgK)

Example 2 A rigid cylinder of volume $0.025 m^3$ contains steam at 80 bar and 350°C. The cylinder is cooled until the pressure is 50 bar. Calculate the state of the steam after cooling and the amount of heat rejected by the steam. Sketch the process on a T–S diagram indicating the area which represents the heat flow.

Solution : Steam at 80 bar and 350 °C is superheated, and the specific volume from tables is $0.02994 \ m^3/kg$. Hence the mass of steam in the cylinder is given by $m = \frac{0.025}{0.02994} = 0.835 \ kg$

For superheated steam above 80 bar the internal energy is found from the equation $h = u + pv$

$$u_1 = h_1 - P_1 v_1 = 2990 - \frac{80 \times 10^5 \times 0.02994}{10^3}$$

$$= 2990 - 239.5$$

i.e $u_1 = 2750.5 \ KJ/kg$

At state 2, $P_2 = 50$ bar and $v_2 = 0.02994 \ m^3/kg$. Therefore the steam is wet and the dryness fraction is given by $x_2 = \frac{v_2}{v_{g_2}} = \frac{0.02994}{0.03944} = 0.758$

From $u_2 = (1-x_2) u_{f_2} + x_2 u_{g_2}$

$$= (0.242 \times 1149) + (0.758 \times 2597)$$

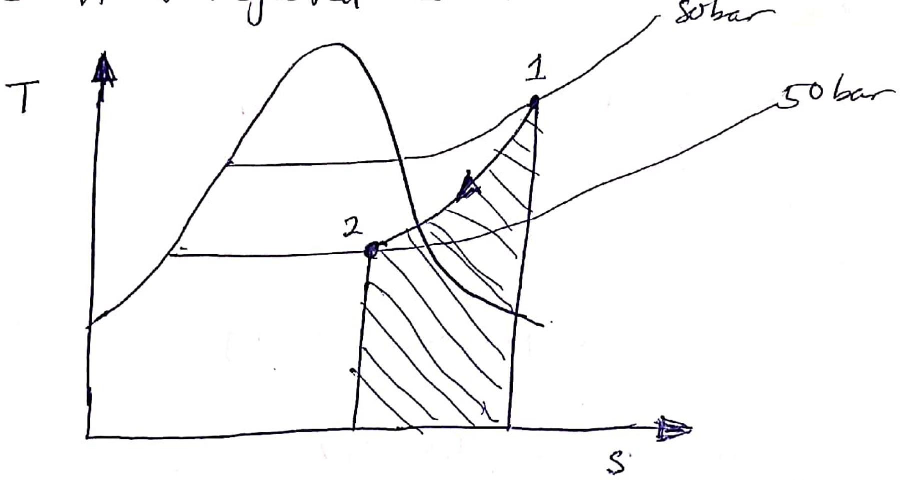
i.e $u_2 = 278 + 1969 = 2247 \ KJ/kg$

At constant volume from equation (3.2)

$$Q = U_2 - U_1 = m(u_2 - u_1) = 0.835(2247 - 2750.5)$$

i.e $Q = -0.835 \times 503.5 = -420\ \text{KJ}$

i.e Heat rejected = 420 KJ



1 bar $= 10^5\ \text{N/m}^2 = 10^5\ \text{Pa}$

Constant volume process

If there is no paddle work, the energy equation for unit mass of any fluid undergoing a constant volume process is $Q = u_2 - u_1$

When the fluid is a perfect gas this becomes
$$Q = C_v(T_2 - T_1)$$

For a perfect gas we also have the following relations between properties which are valid for any two states of the same volume. From the equation of state,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

and from the definition of entropy,

$$S_2 - S_1 = \int_1^2 \left(\frac{dQ}{T}\right)_{rev} = \int_1^2 \frac{C_v}{T}\,dT = C_v \ln\frac{T_2}{T_1}$$

The latter equation can also be obtained for putting $V_2 = V_1$ in the general expression for the entropy change.

$$S_2 - S_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$

Constant Pressure process

For reversible constant pressure process undergone by unit mass of any fluid,

$$W = -p\int_1^1 dV = -p(V_2 - V_1)$$

$$Q = (U_2 - U_1) - W = (U_2 - U_1) + p(V_2 - V_1) = h_2 - h_1$$

$$dh = du + p\,dV$$

When the fluid is a perfect gas,

$$W = -R(T_2 - T_1)$$

$$Q = C_p(T_2 - T_1)$$

For a perfect gas we also have the following relations between properties which are valid for any two states of the same pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$S_2 - S_1 = \int_1^2 \left(\frac{dQ}{T}\right)_{rev} = \int_1^2 \frac{C_p}{T}\,dT = C_p \ln\frac{T_2}{T_1}$$

The latter equation can also be obtained by putting $P_2 = P_1$ in the general expression ~~of~~ for the entropy change.

$u = (1-x)\,u_f + x\,u_g$

$h = (1-x)\,h_f + x\,h_g$

$s = (1-x)\,s_f + x\,s_g$

$v = (1-x)\,v_f + x\,v_g$

$u = u_f + x\,u_{fg}$

$h = h_f + x\,h_{fg}$

$s = s_f + x\,s_{fg}$

$v = x\,v_g$ If we neglect the term containing v_f

Constant volume

Example :

A fluid in a closed vessel of fixed volume $0.14\,m^3$, exerts a pressure of 10 bar ~~at~~ 250 °C. If the vessel is cooled so that the pressure falls to 3.5 bar, determine the final temperature, ~~and~~ heat transfer and change in entropy.

(a) Steam

Step 1 : Find the mass of fluid in the system

$T_1 = 250°C$ since $T_1 >$ the saturation temperature corresponding to P_1, the vapour is initially superheated. Using the superheat table we find $v_1 = 0.2328\ m^3/kg$

Since $V = 0.14\,m^3$,

$$m = \frac{V}{v_1} = \frac{0.14}{0.2328} = 0.6014\ kg$$

The vapour must be wet in its final state because mv_g is $0.6014 \times 0.5241 = 0.3152\,m^3$ which is greater that $0.14\,m^3$. The temperature must therefore be the saturation temperature corresponding to P_2

i.e $T_2 = 138.9\,°C$

The dryness fraction can be found from

$$x_2 = \frac{V}{mV_{g2}} = \frac{0.14}{0.3152} = 0.444$$

or from $x = \frac{V - V_{f_2}}{V_{fg_2}} = 0.443$

From the superheat table:

$$U_1 = 2711 \text{ kJ/kg}$$

From the saturation table:

$$U_2 = U_{f_2} + x_2 U_{fg2} = 584 + 0.444(2549 - 584) = 1457 \text{ kJ/kg}$$

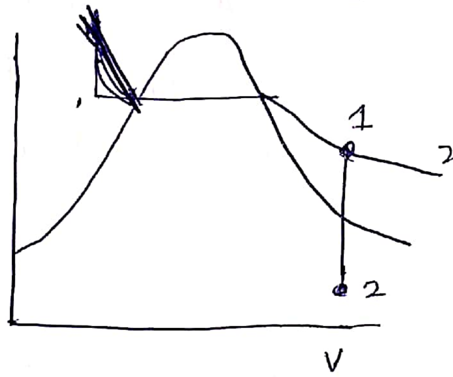


Fig. 9.1(a)

Steam

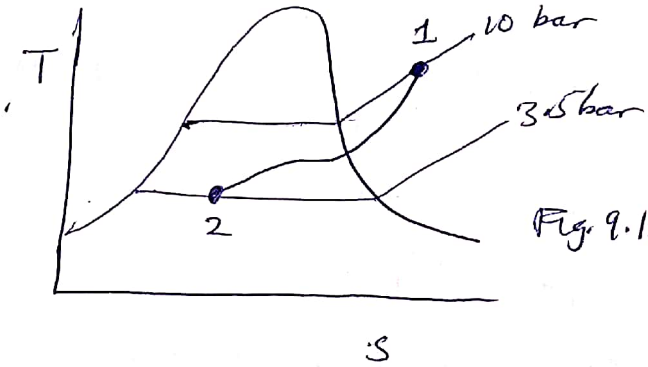


Fig. 9.1a

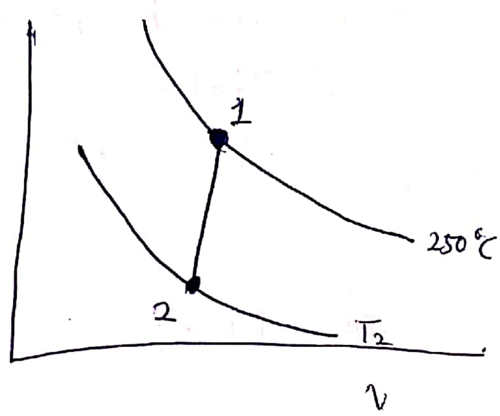


Fig. 9.1(b)

Air

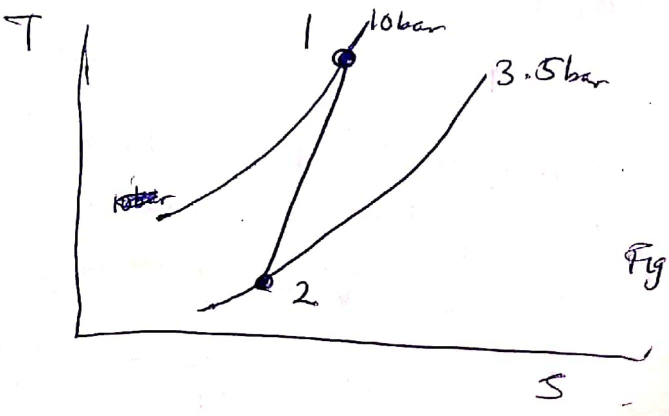


Fig. 9.1b

Heat Transfer:

$$Q = m(U_2 - U_1) = 0.6014(1457 - 2711) = -754 \text{ kJ}$$

From superheat table $S_1 = 6.926$ KJ/kgK, and from the saturation table:

$$S_2 = S_{f2} + x_2 S_{fg2} = 1.727 + (0.444 \times 5.214)$$
$$= 4.042 \text{ KJ/kgK}$$

Change of entropy:

$$S_2 - S_1 = m(s_2 - s_1) = 0.6014(4.042 - 6.926)$$
$$= -1.734 \text{ KJ/K}$$

b) If the fluid is Air (Fig. 9.16)

Mass of gas:

$$m = \frac{P_1 V}{RT_1} = \frac{100 \times 10 \times 0.14}{0.287(250+273)} \quad 0.933 \text{kg}$$

Final temperature:

$$T_2 = \frac{P_2}{P_1} T_1 = \frac{3.5}{10} 523 = 183 \text{K}$$

Heat transfer:

$$Q = mC_v(T_2 - T_1) = 0.933 \times 0.718(183 - 523)$$
$$= -228 \text{ KJ}$$

Change of entropy:

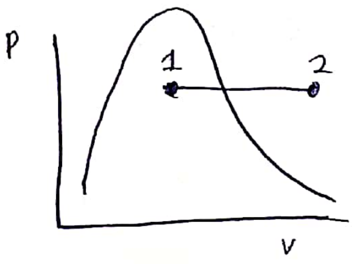
$$S_2 - S_1 = mC_v \ln\frac{T_2}{T_1} = 0.933 \times 0.718 \ln\frac{183}{523}$$
$$= -0.703 \text{ KJ/K}$$

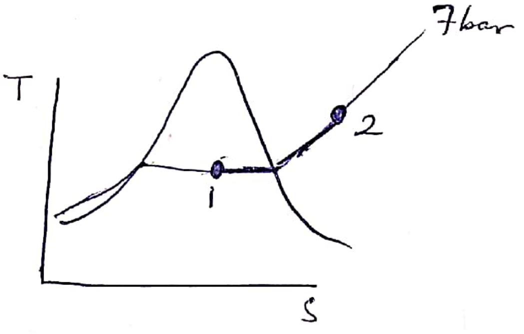
Constant pressure

Example A mass of 0.2kg of fluid, initially at a temperature of 165°C, expands reversibly at a constant pressure of 7 bar until the volume is doubled. Find the final temperature, work and heat transfers in two cases: (a) when the fluid is steam with an initial dryness fraction of 0.7, (b) when the fluid is air

Solution

(a) Steam





Initial specific volume:

$$v_1 = x_1 v_{g1} = 0.7 \times 0.2728 = 0.191 \ m^3/kg$$

Final specific volume:

$$v_2 = 2v_1 = 0.382 \ m^3/kg$$

Since $v_2 > v_{g2}$, the vapour must be superheated in its final state. From the Supeheat table by interpolation, the final temperature is

$$T_2 = 300 + \left(\frac{0.382 - 0.3714}{0.4058 - 0.3714}\right) 50 = 315°C$$

Work transfer:

$$W = -mp(v_2 - v_1) = -0.2 \times 100 \times 7(0.382 - 0.191)$$
$$= -26.7 \ kJ$$

rom the saturation table :

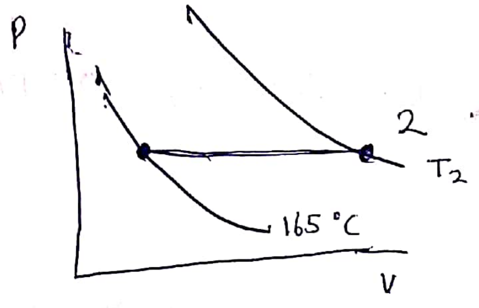
$$h_1 = h_{f_1} + x_1 h_{fg_1} = 697 + (0.7 \times 2067)$$
$$= 2144 \text{ kJ/kg}$$

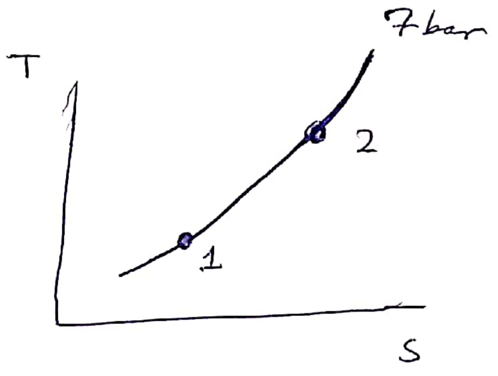
From the superheat table, by interpolation :

$$h_2 = 3060 + \frac{15}{50}(3164 - 3060) = 3091 \text{ kJ/kg}$$

Heat transfer : $Q = m(h_2 - h_1) = 0.2(3091 - 2144)$
$$= 189 \text{ kJ}$$

(b) Air





Initial volume :

$$V_1 = \frac{mRT_1}{P_1} = \frac{0.2 \times 0.287 \times 438}{100 \times 7} = 0.03592 \text{ m}^3$$

Final volume :

$$V_2 = 2V_1 = 0.07184 \text{ m}^3$$

Final temperature :

$$T_2 = \frac{V_2}{V_1} T_1 \doteq 876 \text{ K}$$

Work transfer :

$$W = -P(V_2 - V_1) = -100 \times 7 \times 0.03592$$
$$= -25.1 \text{ kJ}$$

Heat transfer:

$$Q = m C_p (T_2 - T_1) = 0.2 \times 1.005 \times 438 = 88.0 \, KJ$$

Problem Set 1

① 1 Kg of steam at 20 bar, dryness fraction 0.9, is heated reversibly at constant pressure to a temperature of 300°C. Calculate the heat supplied, and the change of entropy, and show the process on a T-s diagram, indicating the area which represents the heat flow. [415 KJ/Kg ; 0.8173 KJ/kgK

② 0.05 Kg of steam at 10 bar, dryness fraction 0.84, is heated reversibly in a rigid vessel until the pressure is 20 bar. Calculate the change of entropy and the heat supplied. Show the area which represents the heat supplied on a T-s diagram.

[0.0704 KJ/kgK; 36.85 KJ]