

# Unit - IV

## Properties of Pure Substances

A pure substance is a substance of constant chemical composition throughout its mass. It is a one-component system. It may exist in one or more phases.

### 9.1 $p-v$ Diagram for a Pure Substance

Assume a unit mass of ice (solid water) at  $-10^{\circ}\text{C}$  and 1 atm contained in a cylinder and piston machine (Fig. 9.1). Let the ice be heated slowly so that its temperature is always uniform. The changes which occur in the mass of water would be traced as the temperature is increased while the pressure is held constant. Let the state changes of water be plotted on  $p-v$  coordinates. The distinct regimes of heating, as shown in Fig. 9.2, are:

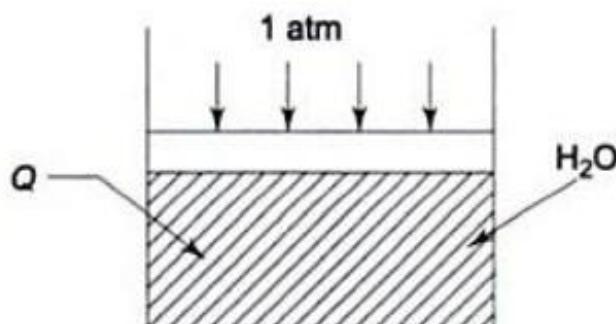


Fig. 9.1 Heating of H<sub>2</sub>O at a constant pressure of 1 atm

1-2 The temperature of ice increases from  $-10^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ . The volume of ice would increase, as would be the case for any solid upon heating. At state 2, i.e.  $0^{\circ}\text{C}$ , the ice would start melting.

2-3 Ice melts into water at a constant temperature of  $0^{\circ}\text{C}$ . At state 3, the melting process ends. *There is a decrease in volume, which is a peculiarity of water.*

3-4 The temperature of water increases, upon heating, from 0°C to 100°C. The volume of water increases because of thermal expansion.

4-5 The water starts boiling at state 4 and boiling ends at state 5. This phase change from liquid to vapour occurs at a constant temperature of 100°C (the pressure being constant at 1 atm). There is a large increase in volume.

5-6 The vapour is heated to, say, 250°C (state 6). The volume of vapour increases from  $v_5$  to  $v_6$ .

Water existed in the solid phase between 1 and 2, in the liquid phase between 3 and 4, and in the gas phase beyond 5. Between 2 and 3, the solid changed into the liquid phase by absorbing the latent heat of fusion and between 4 and 5, the liquid changed into the vapour phase by absorbing the latent heat of vaporization, both at constant temperature and pressure.

The states 2, 3, 4 and 5 are known as *saturation states*. A saturation state is a state from which a change of phase may occur without a change of pressure or temperature. State 2 is a *saturated solid state* because a solid can change into liquid at constant pressure and temperature from state 2. States 3 and 4 are both saturated liquid states. In state 3, the liquid is saturated with respect to solidification, whereas in state 4, the liquid is saturated with respect to vaporization. State 5 is a *saturated vapour state*, because from state 5, the vapour can condense into liquid without a change of pressure or temperature.

If the heating of ice at -10°C to steam at 250°C were done at a constant pressure of 2 atm, similar regimes of heating would have been obtained with similar saturation states 2, 3, 4 and 5, as shown in Fig. 9.2. All the state changes of the system can similarly be plotted on the  $p$ - $v$  coordinates, when it is heated at different constant pressures. All the saturated solid states 2 at various pressures are joined by a line, as shown in Fig. 9.3.

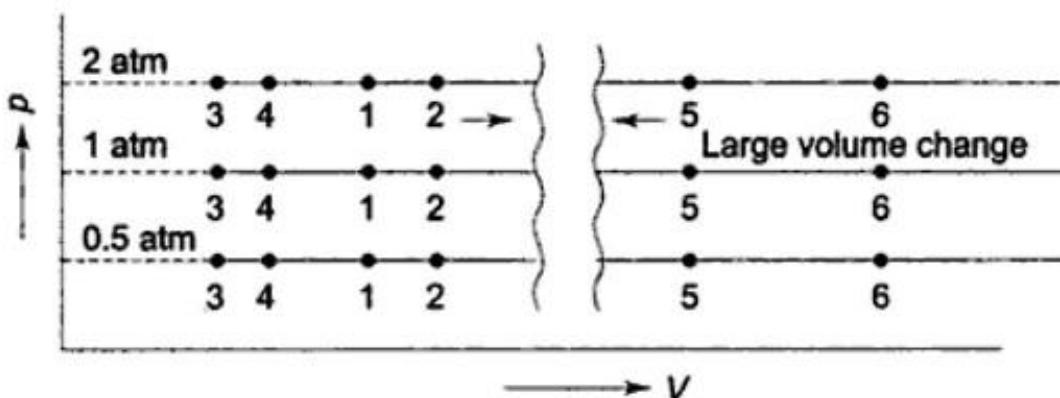


Fig. 9.2 Changes in the volume of water during heating at constant pressure

Similarly, all the saturated liquid states 3 with respect to solidification, all the saturated liquid states 4 with respect to vaporization, and all the saturated vapour states 5, are joined together.

Figure 9.4 shows state changes of a pure substance other than water whose volume increases on melting.

The line passing through all the saturated solid states 2 (Figs 9.3 and 9.4) is called the *saturated solid line*. The lines passing through all the saturated liquid states 3 and 4 with respect to solidification and vaporization respectively are

known as the *saturated liquid lines*, and the line passing through all the saturated vapour states 5, is the *saturated vapour line*. The saturated liquid line with respect to vaporization and the saturated vapour line incline towards each other and form what is known as the *saturation or vapour dome*. The two lines meet at the *critical state*.

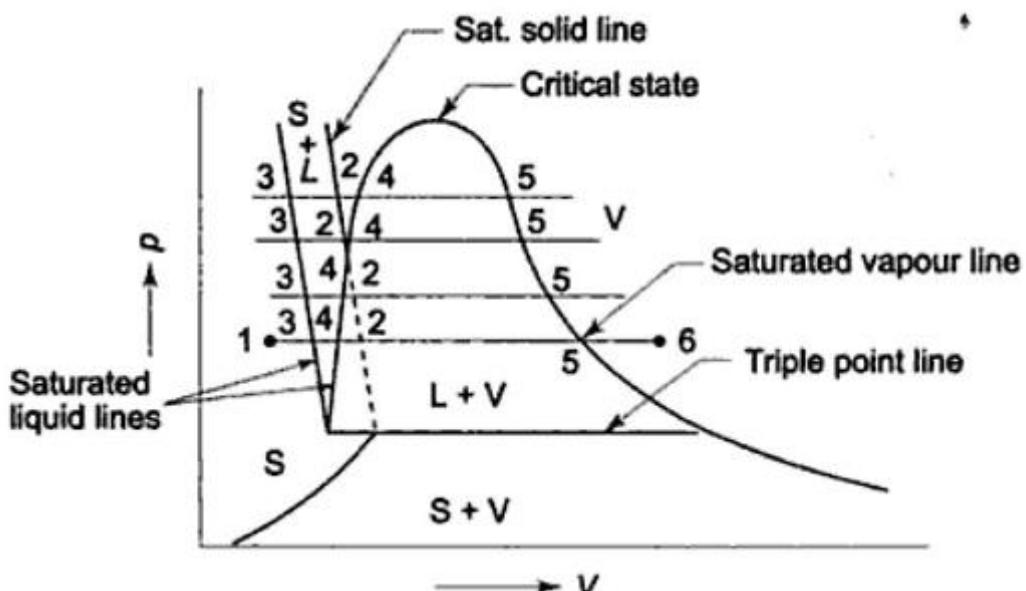


Fig. 9.3 *p-v diagram of water, whose volume decreases on melting*

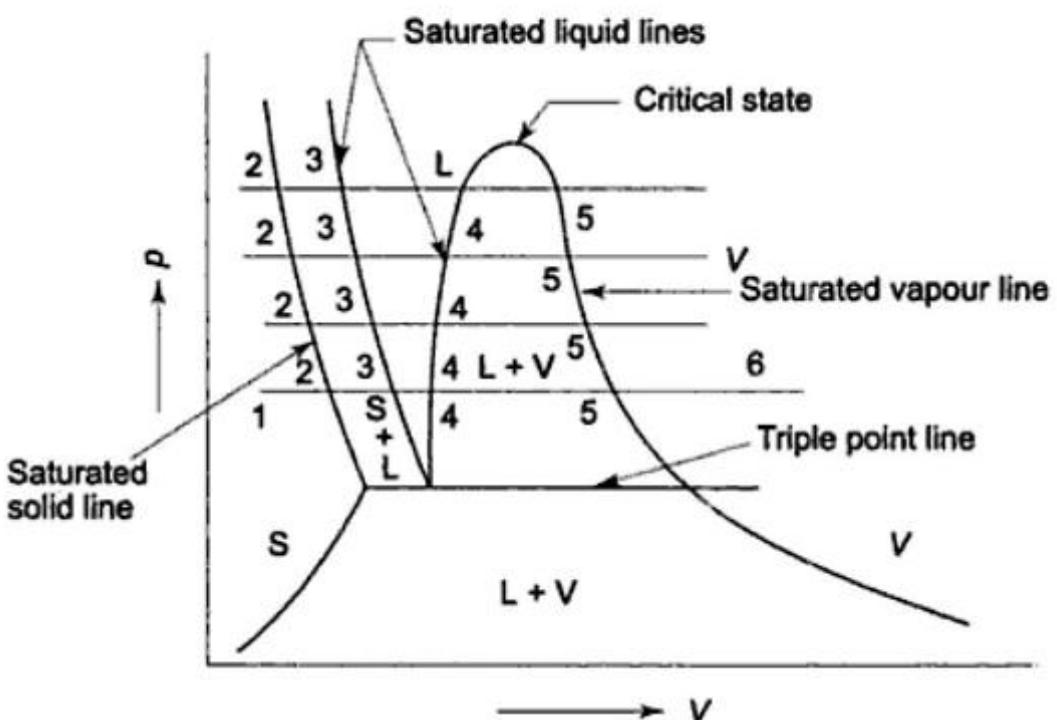


Fig. 9.4 *p-v diagram of a pure substance other than water, whose volume increases on melting*

To the left of the saturated solid line is the solid (*S*) region (Fig. 9.4). Between the saturated solid line and saturated liquid line with respect to solidification there exists the *solid-liquid mixture* (*S + L*) region. Between the two saturated liquid lines is the *compressed liquid region*. The *liquid-vapour mixture region* (*L + V*) exists within the vapour dome between the saturated liquid and saturated vapour lines. To the right of the saturated vapour line is the *vapour region*. The *triple point* is a line on the *p-v* diagram, where all the three phases, solid, liquid

and gas, exit in equilibrium. At a pressure below the triple point line, the substance cannot exist in the liquid phase, and the substance, when heated, transforms from solid to vapour (known as sublimation) by absorbing the latent heat of sublimation from the surroundings. The region below the triple point line is, therefore, the *solid-vapour (S + V) mixture region*. Table 9.1 gives the triple point data for a number of substances.

**Table 9.1 Triple-Point Data**

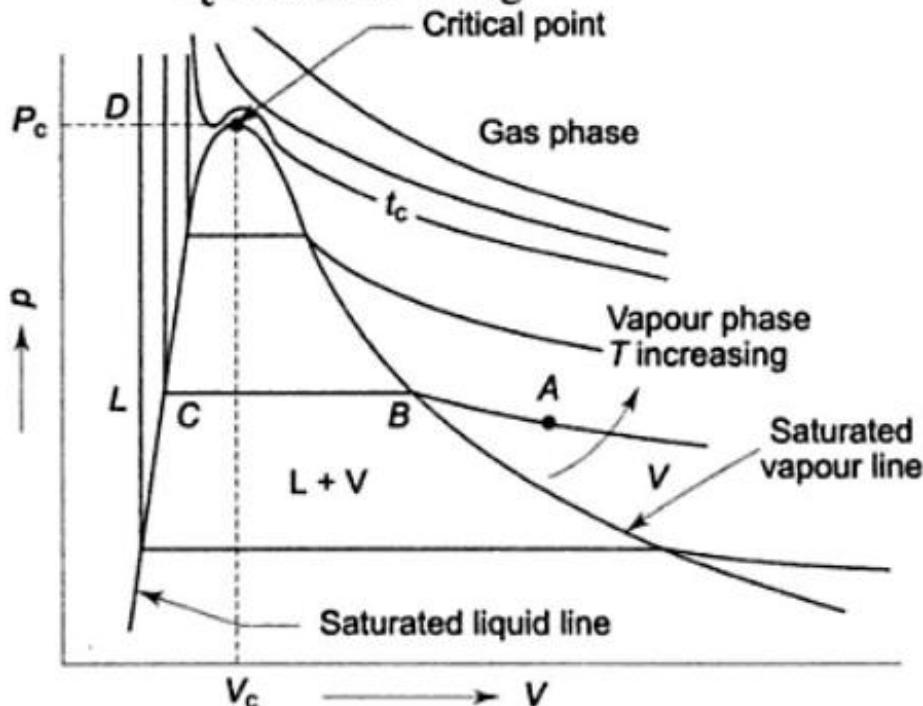
Substance	Temperature, K	Pressure, mm Hg
Acetylene, $C_2H_2$	192.4	962
Ammonia, $NH_3$	195.42	45.58
Argon, A	83.78	515.7
Carbon dioxide, $CO_2$	216.55	3885.1
Carbon monoxide, CO	68.14	115.14
Methane, $C_2H_6$	89.88	0.006
Ethylene, $C_2H_4$	104.00	0.9
Hydrogen, $H_2$	13.84	52.8
Methane, $CH_4$	90.67	87.7
Nitrogen, $N_2$	63.15	94.01
Oxygen, $O_2$	54.35	1.14
Water, $H_2O$	273.16	4.587

Liquid is, most often, the working fluid in power cycles, etc. and interest is often confined to the liquid-vapour regions only. So to locate the state points, the solid regions from Figs 9.3 and 9.4 can be omitted. The  $p-v$  diagram then becomes as shown in Fig. 9.5. If the vapour at state *A* is compressed slowly and isothermally, the pressure will rise until there is saturated vapour at point *B*. If the compression is continued, condensation takes place, the pressure remaining constant so long as the temperature remains constant. At any point between *B* and *C*, the liquid and vapour are in equilibrium. Since a very large increase in pressure is needed to compress the liquid, line *CD* is almost vertical. *ABCD* is a typical *isotherm* of a pure substance on a  $p-v$  diagram. Some isotherms are shown in Fig. 9.5. As the temperature increases, the liquid-vapour transition, as represented by *BC*, decreases, and becomes zero at the critical point. Below the critical point only, there is a liquid-vapour transition zone, where a saturated liquid, on heating, absorbs the latent heat of vaporization, and becomes saturated vapour at a constant pressure and temperature. Similarly, a saturated vapour, on cooling, releases the latent heat of condensation at constant pressure and temperature to become saturated liquid. Above the critical point, however, a liquid, upon heating, suddenly *flashes* into vapour, or a vapour, upon cooling, suddenly condenses into liquid. There is no distinct transition zone from liquid to vapour and vice versa. The isotherm passing through the critical point is called the *critical isotherm*, and the corresponding temperature is known as the *critical temperature* ( $t_c$ ). The pressure and volume at the critical point are known as the *critical pressure* ( $p_c$ ) and the *critical volume* ( $v_c$ ) respectively. For water

$$p_c = 221.2 \text{ bar}$$

$$t_c = 374.15^\circ\text{C}$$

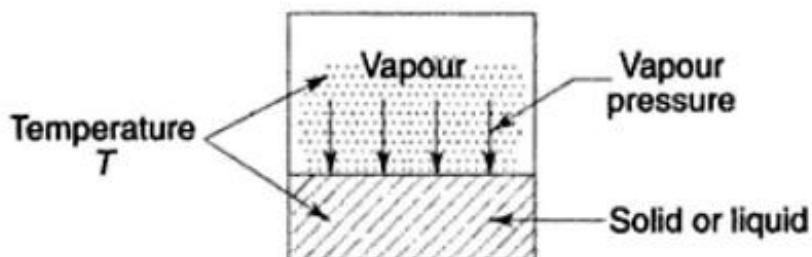
$$v_c = 0.00317 \text{ m}^3/\text{kg}$$



**Fig. 9.5 Saturation curve on  $p$ - $v$  diagram**

The critical point data of certain substances are given in Appendix F. Above the critical point, the isotherms are continuous curves that at large volumes and low pressures approach equilateral hyperbolas.

When a liquid or solid is in equilibrium with its vapour at a given temperature, the vapour exerts a pressure that depends only on the temperature (Fig. 9.6). In general, the greater the temperature, the higher is the *vapour pressure*. The temperature at which the vapour pressure is equal to 760 mm Hg is called the *normal boiling point*.



**Fig. 9.6 Vapour pressure**

Phase change occurs at constant pressure and temperature. A pure liquid at a given pressure will transform into vapour only at a particular temperature, known as *saturation temperature*, which is a function of pressure. Similarly, if the temperature is fixed, the liquid will boil (or condense) only at a particular pressure, called the *saturation pressure*, which is a function of temperature. In Fig. 9.7, if  $p_1$  is the pressure, the corresponding saturation temperature is  $(t_{\text{sat}})_1$ , or if  $t_2$  is the given temperature, the saturation pressure is  $(p_{\text{sat}})_2$ . As the pressure increases, the saturation temperature increases. Saturation states exist up to the critical point. At point A, the liquid starts boiling, and at point B, the boiling gets completed. At A, it is all liquid (saturated) and there is no vapour, while at B, it is all vapour (saturated) and there is no liquid. Vapour content progressively increases as the liquid changes its state from A towards B.

If  $u_v$  is the specific volume of the saturated liquid at a given pressure, and  $v_g$  the specific volume of the saturated vapour, then  $(v_g - v_f)$  or  $v_{fg}$  is the change in specific volume during phase transition (boiling or condensation) at that pressure. As pressure increases,  $v_{fg}$  decreases, and at the critical point  $v_{fg}$  becomes zero.

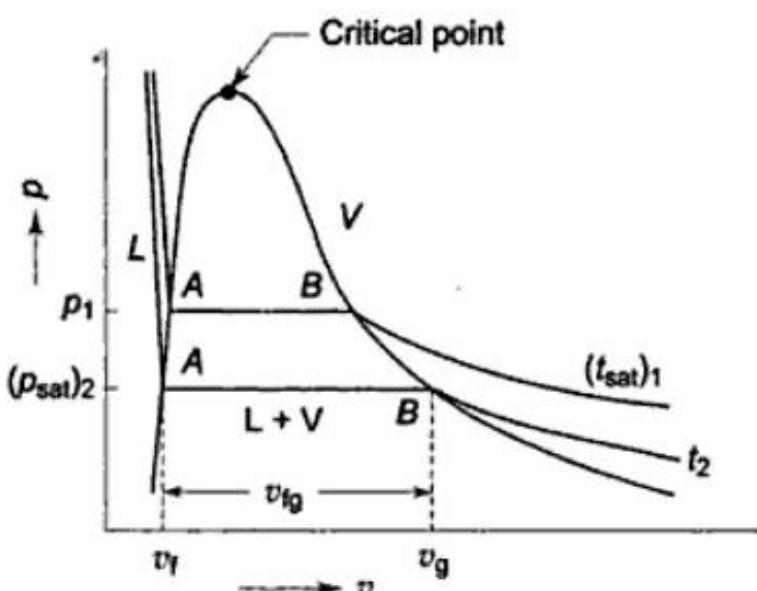


Fig. 9.7 Saturation pressure and temperature

## 9.2 $p$ -T Diagram for a Pure Substance

The state changes of a pure substance, upon slow heating at different constant pressures, are shown on the  $p$ -v plane, in Figs 9.2, 9.3, and 9.4. If these state changes are plotted on  $p$ -T coordinates, the diagram, as shown in Fig. 9.8, will be obtained. If the heating of ice at  $-10^\circ\text{C}$  to steam at  $250^\circ\text{C}$  at the constant pressure of 1 atm is considered, 1-2 is the solid (ice) heating, 2-3 is the melting of ice at  $0^\circ\text{C}$ , 3-4 is the liquid heating, 4-5 is the vaporization of water at  $100^\circ\text{C}$ , and 5-6 is the heating in the vapour phase. The process will be reversed from state 6 to state 1 upon cooling. The curve passing through the 2, 3 points is called the *fusion curve*, and the curve passing through the 4, 5 points (which indicate the vaporization or condensation at different temperatures and pressures) is called

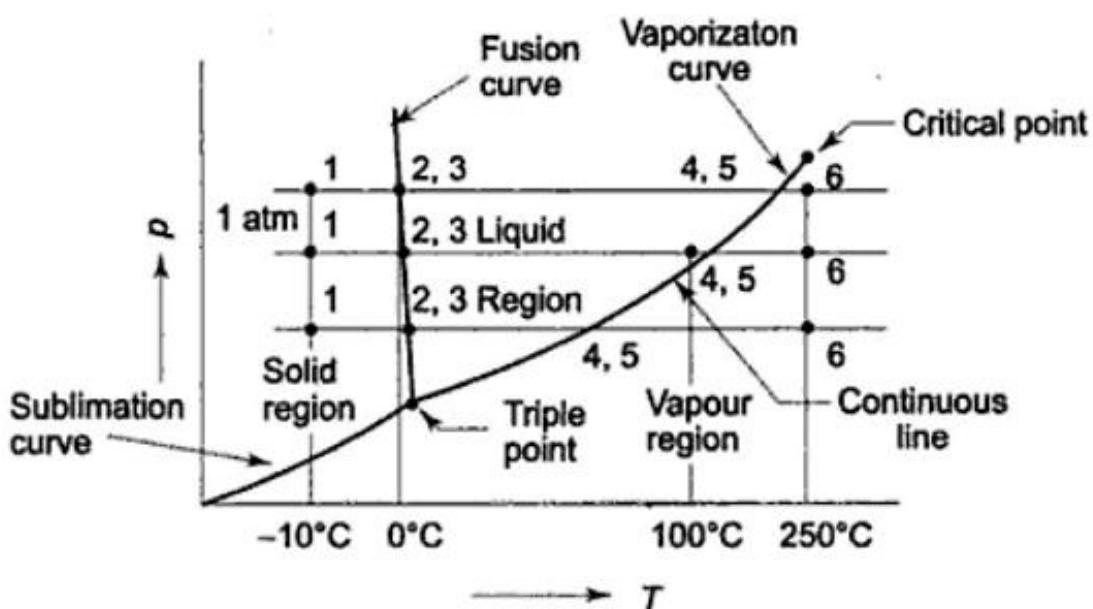


Fig. 9.8 Phase equilibrium diagram on  $p$ -T coordinates

the *vaporization curve*. If the vapour pressure of a solid is measured at different temperatures, and these are plotted, the *sublimation curve* will be obtained. The fusion curve, the vaporization curve, and the sublimation curve meet at triple point.

The slopes of the sublimation and vaporization curves for all substances are positive. The slope of the fusion curve for most substances is positive, but for water, it is negative. The temperature at which a liquid boils is very sensitive to pressure, as indicated by the vaporization curve which gives the saturation temperatures at different pressures, but the temperature at which a solid melts is not such a strong function of pressure, as indicated by the small slope of the fusion curve.

The triple point of water is at 4.58 mm Hg and 273.16 K, whereas that of CO<sub>2</sub> is at 3885 mm Hg (about 5 atm) and 216.55 K. So when solid CO<sub>2</sub> ('dry ice') is exposed to 1 atm pressure, it gets transformed into vapour directly, absorbing the latent heat of sublimation from the surroundings, which gets cooled or 'refrigerated'.

### 9.3 *p-v-T* Surface

The relationships between pressure, specific volume, and temperature can be clearly understood with the aid of a three-dimensional *p-v-T* surface. Figure 9.9 illustrates a substance like water that expands upon freezing and Fig. 9.10 illustrates substances other than water which contract upon freezing. The projections on the *p-T* and *p-v* planes are also shown in these figures. Any point on the *p-v-T* surface represents an equilibrium state of the substance. The triple point line when projected to the *p-T* plane becomes a point. The critical isotherm has a point of inflection at the critical point.

### 9.4 *T-s* Diagram for a Pure Substance

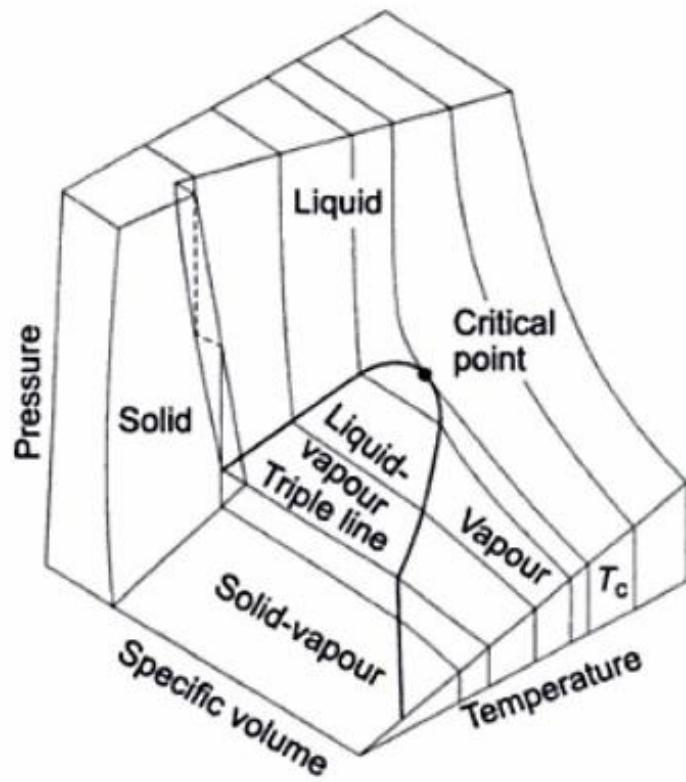
The heating of the system of 1 kg of ice at -5°C to steam at 250°C is again considered, the pressure being maintained constant at 1 atm. The entropy increases of the system in different regimes of heating are given below.

1. The entropy increase of ice as it is heated from -5°C to 0°C at 1 atm. ( $c_{p_{\text{ice}}} = 2.093 \text{ kJ/kg K}$ ).

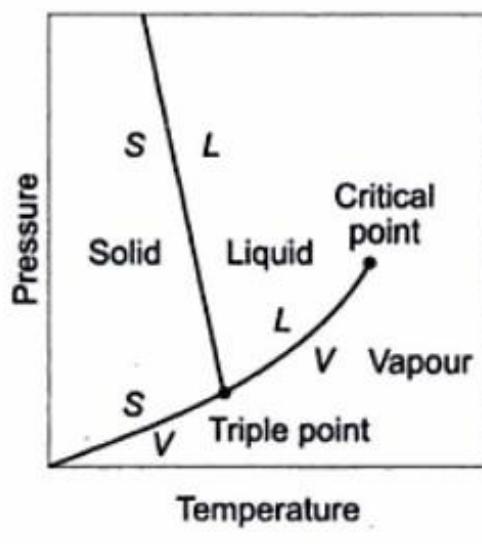
$$\begin{aligned}\Delta s_1 &= s_2 - s_1 = \int \frac{dQ}{T} = \int_{T_1=268}^{T_2=273} \frac{mc_p dT}{T} = c_p \ln \frac{273}{268} \\ &= 2.093 \ln \frac{273}{268} = 0.0398 \text{ kJ/kg K.}\end{aligned}$$

2. The entropy increase of ice as it melts into water at 0°C (latent heat of fusion of ice = 334.96 kJ/kg)

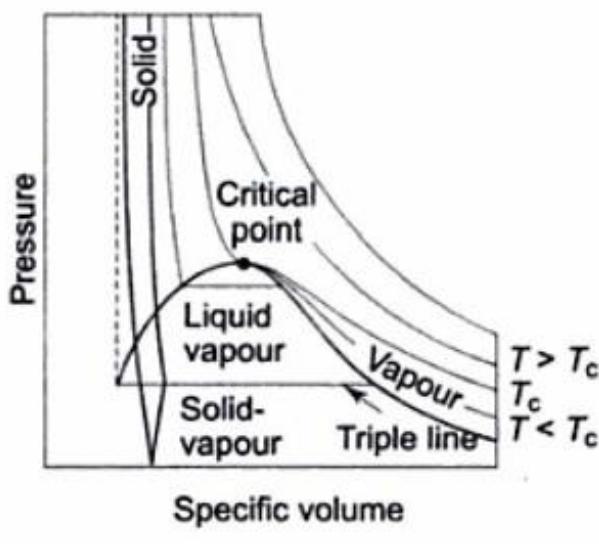
$$\Delta s_2 = s_3 - s_2 = \frac{334.96}{273} = 1.23 \text{ kJ/kg K}$$



(a)



(b)



(c)

**Fig. 9.9**  $p$ - $v$ - $T$  surface and projections for a substance that expands on freezing  
 (a) Three-dimensional view (b) Phase diagram (c)  $p$ - $v$  diagram

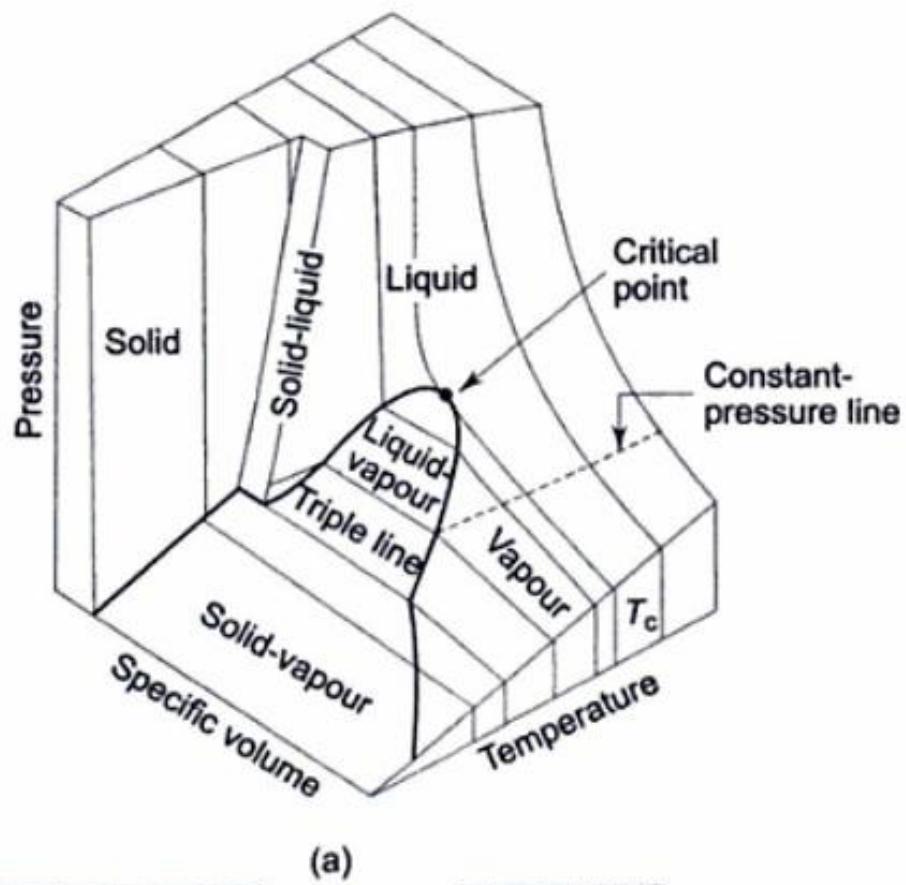
3. The entropy increase of water as it is heated from  $0^\circ\text{C}$  to  $100^\circ\text{C}$   
 $(c_p \text{ water} = 4.187 \text{ kJ/kg K})$

$$\begin{aligned}\Delta s_3 &= s_4 - s_3 = c_p \ln \frac{T_3}{T_2} = 4.187 \ln \frac{373}{273} \\ &= 1.305 \text{ kJ/kg K}\end{aligned}$$

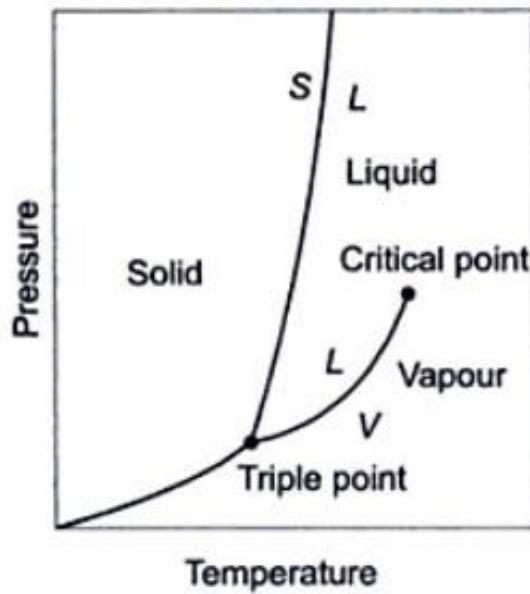
4. The entropy increase of water as it is vaporized at  $100^\circ\text{C}$ , absorbing the latent heat of vaporization ( $2257 \text{ kJ/kg}$ )

$$\Delta s_4 = s_5 - s_4 = \frac{2257}{273} = 6.05 \text{ kJ/kg K}$$

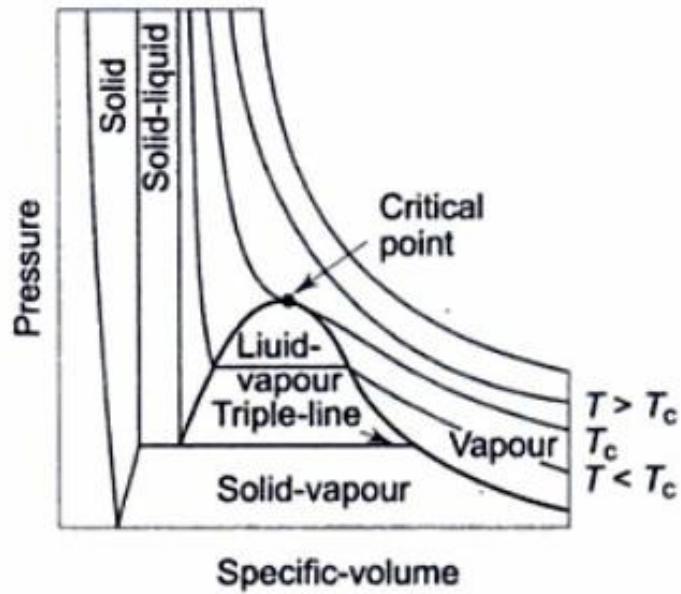
5. The entropy increase of vapour as it is heated from  $100^\circ\text{C}$  to  $250^\circ\text{C}$  at 1 atm



(a)



(a)



(c)

**Fig. 9.10** *p-v-T* surface and projections for a substance that contracts on freezing  
 (a) Three-dimensional view (b) Phase diagram (c) *p-v* diagram

$$\Delta s_5 = s_6 - s_5 = \int_{373}^{523} c_p \frac{dT}{T} = 2.093 \ln \frac{523}{373}$$

$$= 0.706 \text{ kJ/kg K}$$

assuming the average specific heat of steam in the temperature range of 100°C to 250°C as 2.093 kJ/kg K.

These entropy changes are shown in Fig. 9.11. The curve 1-2-3-4-5-6 is the isobar of 1 atm. If, during the heating process, the pressure had been maintained constant at 2 atm, a similar curve would be obtained. The states 2, 3, 4, and 5 are saturation states. If these states for different pressures are joined, as in Figs 9.3 and 9.4, the phase equilibrium diagram of a pure substance on the *T-s* coordinates, as shown in Fig. 9.12, would be obtained.

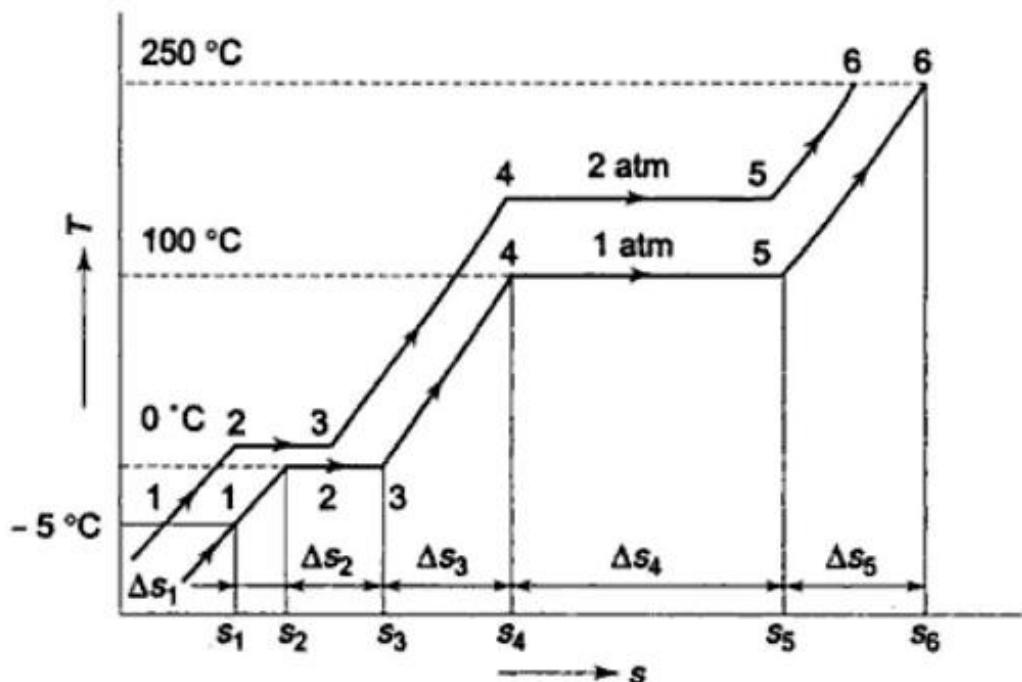


Fig. 9.11 Isobars on *T-s* plot

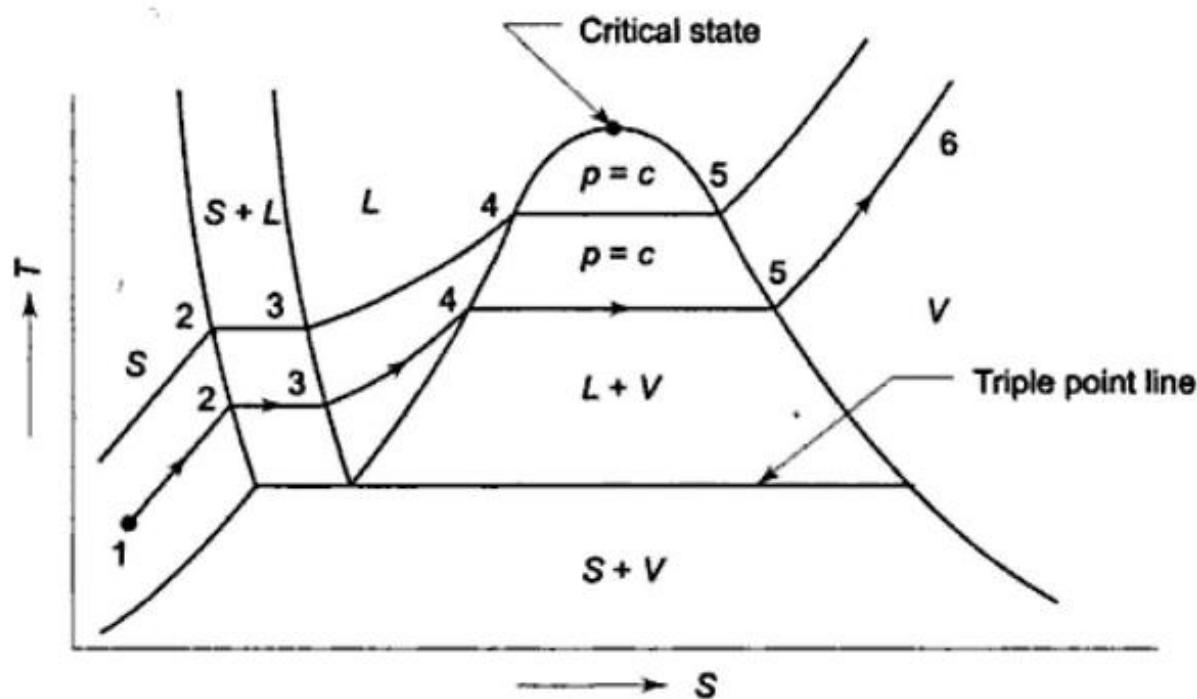


Fig. 9.12 Phase equilibrium diagram on *T-s* coordinates

Most often, liquid-vapour transformations only are of interest, and Fig. 9.13 shows the liquid, the vapour, and the transition zones only. At a particular pressure,  $s_f$  is the specific entropy of saturated water, and  $s_g$  is that of saturated vapour. The entropy change of the system during the phase change from liquid to vapour at that pressure is  $s_{fg}$  ( $= s_g - s_f$ ). The value of  $s_{fg}$  decreases as the pressure increases, and becomes zero at the critical point.

## 9.5 *h-s* Diagram or Mollier Diagram for a Pure Substance

From the first and second laws of thermodynamics, the following property relation was obtained.

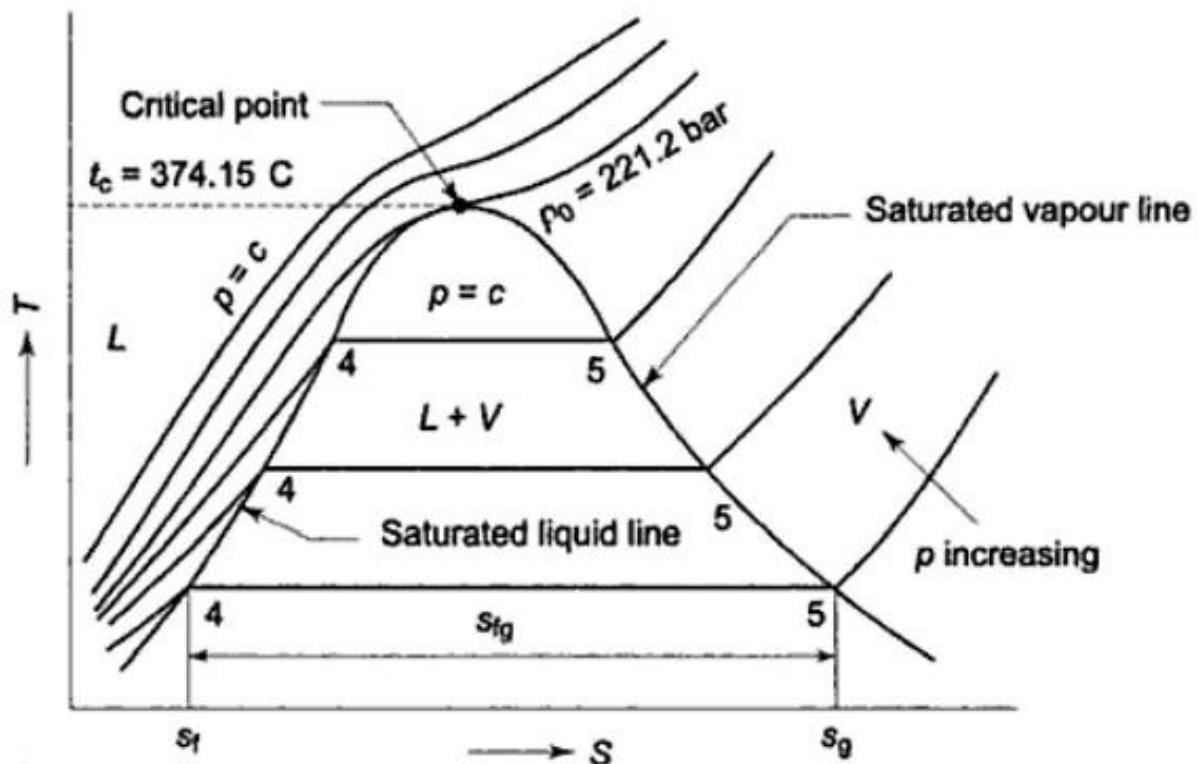


Fig. 9.13 Saturation (or vapour) dome for water

$$Tds = dh - vdp$$

$$\text{or } \left( \frac{\partial h}{\partial s} \right)_p = T \quad (9.1)$$

This equation forms the basis of the *h-s* diagram of a pure substance, also called the Mollier diagram. The slope of an isobar on the *h-s* coordinates is equal to the absolute saturation temperature ( $t_{\text{sat}} + 273$ ) at that pressure. If the temperature remains constant the slope will remain constant. If the temperature increases, the slope of the isobar will increase.

Consider the heating of a system of ice at  $-5^\circ\text{C}$  to steam at  $250^\circ\text{C}$ , the pressure being maintained constant at 1 atm. The slope of the isobar of 1 atm on the *h-s* coordinates (Fig. 9.14) first increases as the temperature of the ice increases from  $-5^\circ\text{C}$  to  $0^\circ\text{C}$  (1-2). Its slope then remains constant as ice melts into water at the

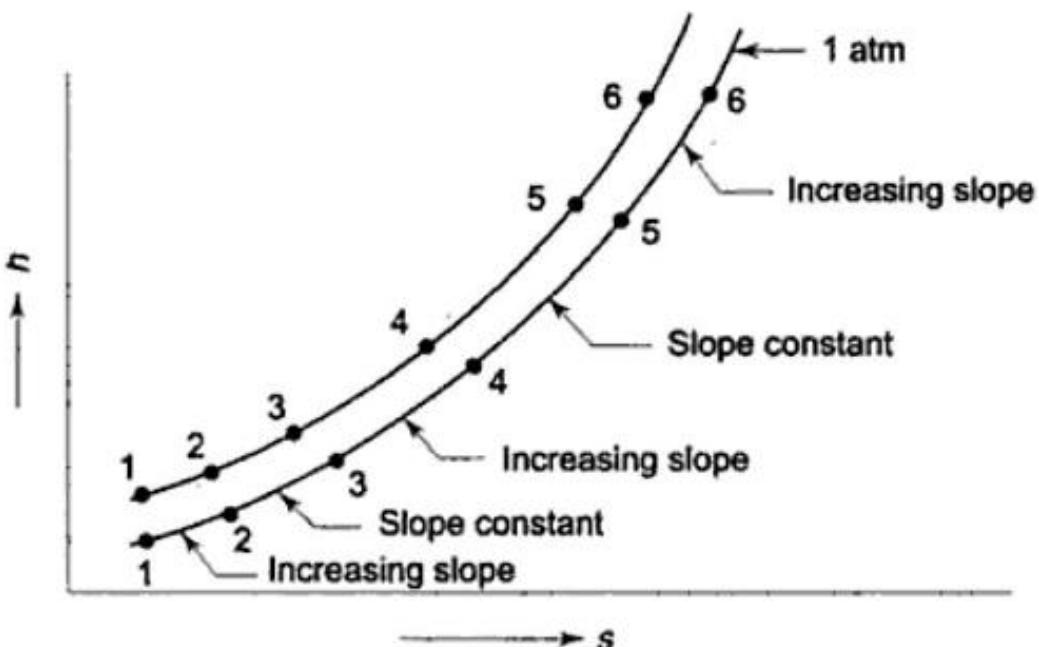


Fig. 9.14 Isobars on *h-s* plot

constant temperature of 0°C (2–3). The slope of the isobar again increases as the temperature of water rises from 0°C to 100°C (3–4). The slope again remains constant as water vaporizes into steam at the constant temperature of 100°C (4–5). Finally, the slope of the isobar continues to increase as the temperature of steam increases to 250°C (5–6) and beyond. Similarly, the isobars of different pressures can be drawn on the *h-s* diagram as shown in Figs 9.14 and 9.15. States 2, 3, 4, and 5 are saturation states. Figure 9.15 shows the phase equilibrium diagram of a pure substance on the *h-s* coordinates, indicating the saturated solid line, saturated liquid lines and saturated vapour line, the various phases, and the transition (mixture) zones.

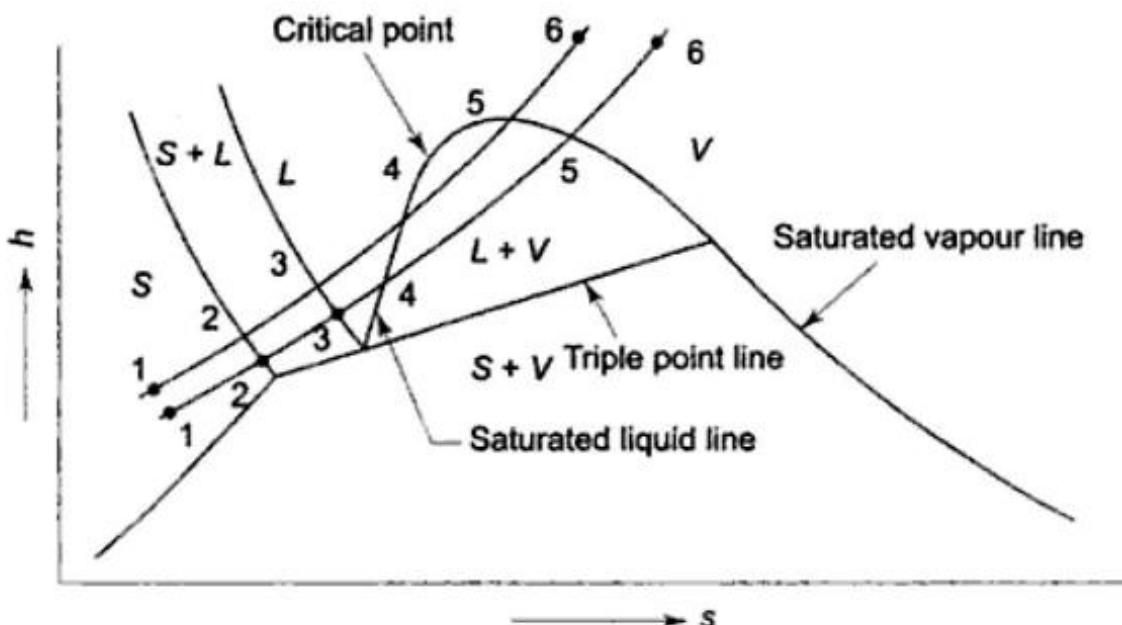


Fig. 9.15 Phase equilibrium diagram on *h-s* coordinates (Mollier diagram)

Figure 9.16 is the *h-s* or the Mollier diagram indicating only the liquid and vapour phases. As the pressure increases, the saturation temperature increases, and so the slope of the isobar also increases. Hence, the *constant pressure lines diverge from one another*, and the critical isobar is a tangent at the critical point, as shown. In the vapour region, the states of equal slopes at various pressures are joined by lines, as shown, which are the *constant temperature lines*. Although the slope of an isobar remains continuous beyond the saturated vapour line, the isotherm bends towards the right and its slope decreases asymptotically to zero, because in the ideal gas region it becomes horizontal and the constant enthalpy

implies constant temperature.  $\left[ \left( \frac{\partial h}{\partial s} \right)_T = T + v \left( \frac{\partial p}{\partial s} \right)_T = T - v \left( \frac{\partial T}{\partial v} \right)_p \right]$ , by

Maxwell's relation, chapter 11. For an ideal gas,  $\left( \frac{\partial h}{\partial s} \right)_T = T - v \frac{T}{v} = 0$ . For  $T = c$ ,

$h = c$ ] At a particular pressure,  $h_f$  is the specific enthalpy of saturated water,  $h_g$  is that of saturated vapour, and  $h_{fg}$  ( $= h_g - h_f$ ) is the latent heat of vaporization at that pressure. As the pressure increases  $h_{fg}$  decreases, and at the critical pressure,  $h_{fg}$  becomes zero.

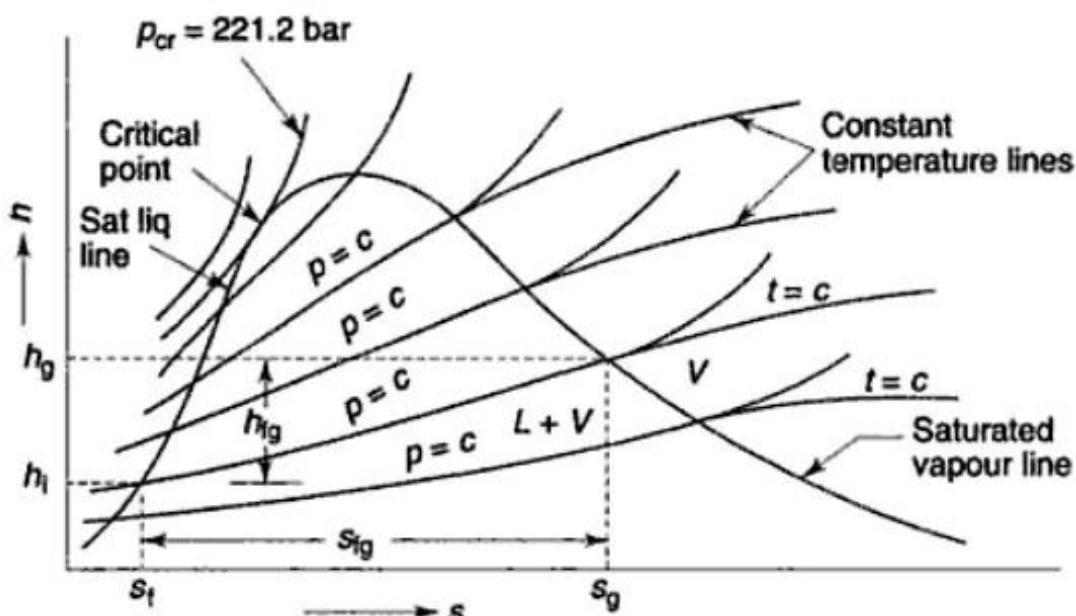


Fig. 9.16 Enthalpy-entropy diagram of water

## 9.6 Quality or Dryness Fraction

If in 1 kg of liquid-vapour mixture,  $x$  kg is the mass of vapour and  $(1-x)$  kg is the mass of liquid, then  $x$  is known as the *quality* or dryness fraction of the liquid-vapour mixture. Therefore, quality indicates the mass fraction of vapour in a liquid vapour mixture, or

$$x = \frac{m_v}{m_v + m_l}$$

where  $m_v$  and  $m_l$  are the masses of vapour and liquid respectively in the mixture. The value of  $x$  varies between 0 and 1. For saturated water, when water just starts boiling,  $x = 0$ , and for saturated vapour, when vaporization is complete,  $x = 1$ , for which the vapour is said to be *dry saturated*.

Points  $m$  in Fig. 9.17 (a), (b), and (c) indicate the saturated liquid states with  $x = 0$ , and points  $n$  indicate the saturated vapour states with  $x = 1$ , the lines  $mn$  indicating the transition from liquid to vapour. Points  $a$ ,  $b$ , and  $c$  at various pressures indicate the situations when the masses of vapour reached 25%, 50%, and 75% of the total mass, i.e. at points  $a$ , the mass of liquid is 75% and the mass of vapour is 25% of the total mass, at point  $b$ , the mixture consists of 50% liquid and 50% vapour by mass, and at points  $c$ , the mixture consists of 75% vapour and 25% liquid by mass. The lines passing through points  $a$ ,  $b$  and  $c$  are the constant quality lines of 0.25, 0.50, and 0.75 respectively. Constant quality lines start from the critical point.

Let  $V$  be the total volume of a liquid vapour mixture of quality  $x$ ,  $V_f$  the volume of the saturated liquid, and  $V_g$  the volume of the saturated vapour, the corresponding masses being  $m$ ,  $m_f$ , and  $m_g$  respectively.

Now

$$m = m_f + m_g$$

and

$$V = V_f + V_g$$

$$mV = m_f V_f + m_g V_g$$

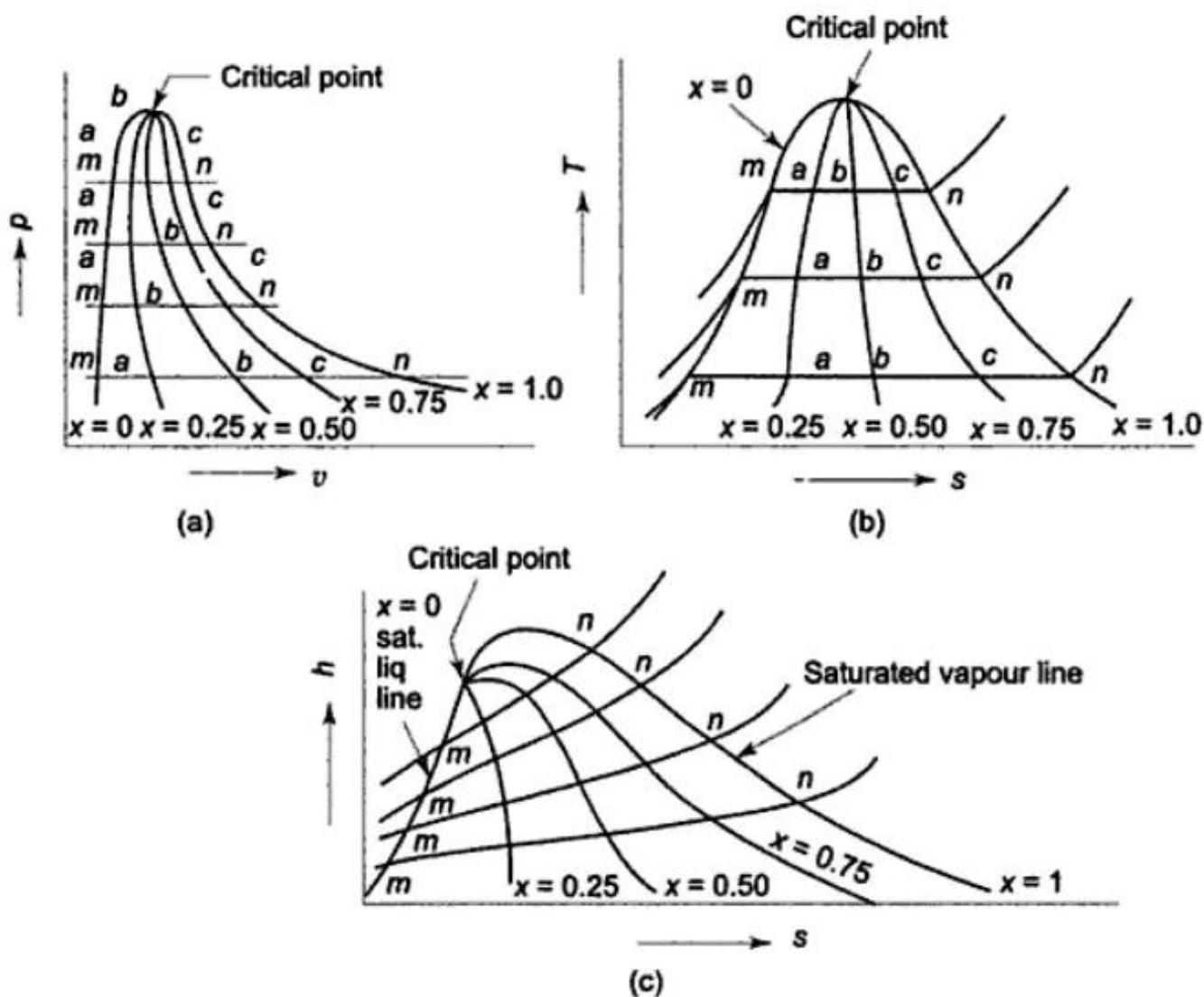


Fig. 9.17 Constant quality lines on  $p$ - $v$ ,  $T$ - $s$  and  $h$ - $s$  diagrams

$$\begin{aligned}
 &= (m - m_g) v_f + m_g v_g \\
 \therefore v &= \left(1 - \frac{m_g}{m}\right) v_f + \frac{m_g}{m} v_g \\
 v &= (1 - x) v_f + x v_g
 \end{aligned} \tag{9.2}$$

where  $x = \frac{m_g}{m}$ ,  $v_f$  = specific volume of saturated liquid,  $v_g$  = specific volume of saturated vapour, and  $v$  = specific volume of the mixture of quality  $x$ .  
Similarly

$$s = (1 - x) s_f + x s_g \tag{9.3}$$

$$h = (1 - x) h_f + x h_g \tag{9.4}$$

$$u = (1 - x) u_f + x u_g \tag{9.5}$$

where  $s$ ,  $h$ , and  $u$  refer to the mixture of quality  $x$ , the suffix  $f$  and suffix  $g$  indicate the conditions of saturated liquid and saturated vapour respectively.

From Eq. (9.2)

$$\begin{aligned}
 v &= (1 - x) v_f + x v_g \\
 &= v_f + x(v_g - v_f) \\
 &= v_f + x, v_{fg}
 \end{aligned}$$

or  $v = v_f + x v_{fg}$  (9.6)

Similarly

$$h = h_f + x h_{fg} \quad (9.7)$$

$$s = s_f + x s_{fg} \quad (9.8)$$

$$u = u_f + x u_{fg} \quad (9.9)$$

However,

$$\rho \neq \rho_f + x \rho_{fg}$$

Volume fraction of vapour or voidage,  $\alpha = v_g/v$

$$m = m_f + m_g$$

$$\rho v = \rho_f v_f + \rho_g v_g = \rho_f(v - v_g) + \rho_g v_g$$

$$\rho = (1 - \alpha)\rho_f + \alpha\rho_g \quad (9.9a)$$

## 9.7 Steam Tables

The properties of water are arranged in the steam tables as functions of pressure and temperature. Separate tables are provided to give the properties of water in the saturation states and in the liquid and vapour phases. The *internal energy of saturated water at the triple point ( $t = 0.01^\circ\text{C}$ ) is arbitrarily chosen to be zero*. Since  $h = u + pv$ , the enthalpy of saturated water at  $0.01^\circ\text{C}$  is slightly positive because of the small value of ( $pv$ ) term. The *entropy of saturated water is also chosen to be zero at the triple point*.

### 9.7.1 Saturation States

When a liquid and its vapour are in equilibrium at a certain pressure and temperature, only the pressure or the temperature is sufficient to identify the saturation state. If the pressure is given, the temperature of the mixture gets fixed, which is known as the saturation temperature, or if the temperature is given, the saturation pressure gets fixed. Saturated liquid or the saturated vapour has only one independent variable, i.e. only one property is required to be known to fix up the state. Tables A.1(a) and A.1(b) in the appendix give the properties of saturated liquid and saturated vapour. In Table A.1(a), the independent variable is temperature. At a particular temperature, the values of saturation pressure  $p$ , and  $v_f$ ,  $v_g$ ,  $h_f$ ,  $h_{fg}$ ,  $h_g$ ,  $s_f$  and  $s_g$  are given, where  $v_f$ ,  $h_f$ , and  $s_f$  refer to the saturated liquid states;  $v_g$ ,  $h_g$  and  $s_g$  refer to the saturated vapour state; and  $v_{fg}$ ,  $h_{fg}$ , and  $s_{fg}$  refer to the changes in the property values during evaporation (or condensation) at that temperature, where  $v_{fg} = v_g - v_f$  and  $s_{fg} = s_g - s_f$ .

In Table A.1(b), the independent variable is pressure. At a particular pressure, the values of saturation temperature  $t$ , and  $v_f$ ,  $v_g$ ,  $h_f$ ,  $h_{fg}$ ,  $h_g$ ,  $s_f$ , and  $s_g$  are given. Depending upon whether the pressure or the temperature is given, either Table A.1(a) or Table A.1(b) can be conveniently used for computing the properties of saturation states.

If data are required for intermediate temperatures or pressures, *linear interpolation is normally accurate*. The reason for the two tables is to reduce the amount of interpolation required.

### 9.7.2 Liquid-vapour mixtures

Let us consider a mixture of saturated liquid water and water vapour in equilibrium at pressure  $p$  and temperature  $t$ . The composition of the mixture by mass will be given by its quality  $x$ , and its state will be within the vapour dome (Fig. 9.18). The properties of the mixture are as given in Article 9.6, i.e.

$$v = v_f + x v_{fg}$$

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

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

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

where  $v_f$ ,  $v_{fg}$ ,  $u_f$ ,  $u_{fg}$ ,  $h_f$ ,  $h_{fg}$ ,  $s_f$  and  $s_{fg}$  are the saturation properties at the given pressure and temperature.

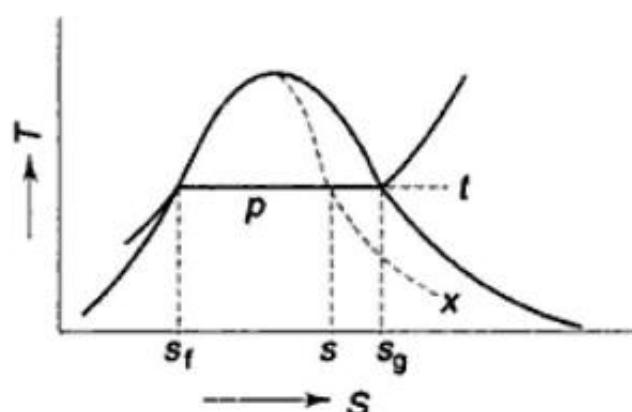


Fig. 9.18 Property in two phase region

If  $p$  or  $t$  and the quality of the mixture are given, the properties of the mixture ( $v$ ,  $u$ ,  $h$ , and  $s$ ) can be evaluated from the above equations. Sometimes, instead of quality, one of the above properties, say, specific volume  $v$ , and pressure or temperature are given. In that case, the quality of the mixture  $x$  has to be calculated from the given  $v$  and  $p$  or  $t$  and then  $x$  being known, other properties are evaluated.

### 9.7.3 Superheated Vapour

When the temperature of the vapour is greater than the saturation temperature corresponding to the given pressure, the vapour is said to be *superheated* (state 1 in Fig. 9.19). The difference between the temperature of the superheated vapour and the saturation temperature at that pressure is called the *superheat* or the *degree of superheat*. As shown in Fig. 9.19, the difference ( $t_1 - t_{\text{sat}}$ ) is the superheat.

In a superheated vapour at a given pressure, the temperature may have different values greater than the saturation temperature. Table A.2 in the appendix gives the values of the properties (volume, enthalpy, and entropy) of superheated vapour for each tabulated pair of values of pressure and temperature, both of which are now independent. Interpolation or extrapolation is to be used for pairs of values of pressure and temperature not given.

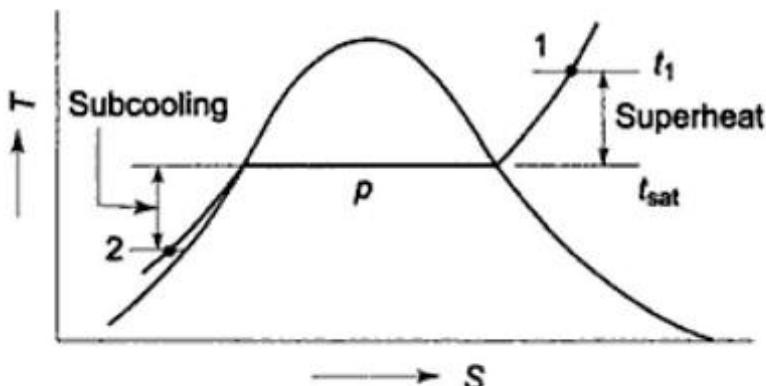


Fig. 9.19 Superheat and subcooling

#### 9.7.4 Compressed Liquid

When the temperature of a liquid is less than the saturation temperature at the given pressure, the liquid is called *compressed liquid* (state 2 in Fig. 9.19). The pressure and temperature of compressed liquid may vary independently, and a table of properties like the superheated vapour table could be arranged to give the properties at any  $p$  and  $t$ . However, the *properties of liquids vary little with pressure*. Hence the properties are taken from the saturation tables at the temperature of the compressed liquid. When a liquid is cooled below its saturation temperature at a certain pressure it is said to be *subcooled*. The difference in saturation temperature and the actual liquid temperature is known as the degree of subcooling, or simply, subcooling (Fig. 9.17).

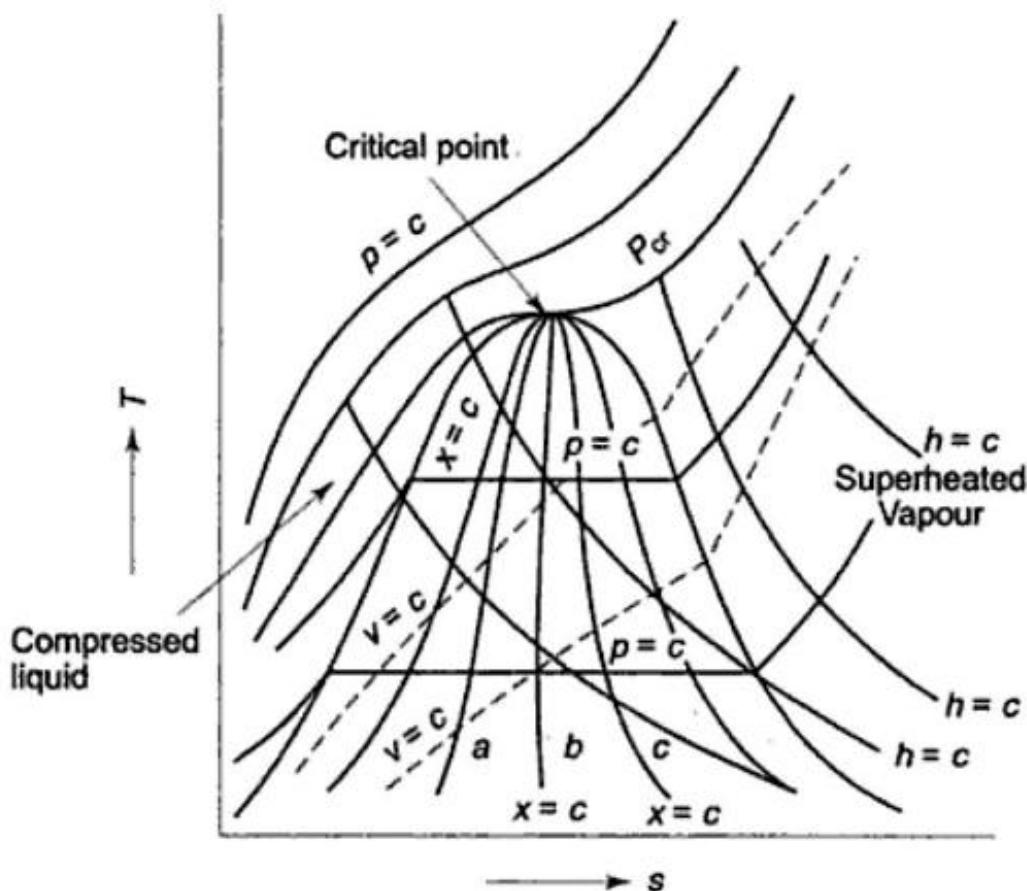
### 9.8 Charts of Thermodynamic Properties

The presentation of properties of substances in the form of a chart has certain obvious advantages. The manner of variation of properties is clearly demonstrated in the chart and there is no problem of interpolation. However, the precision is not as much as in steam tables.

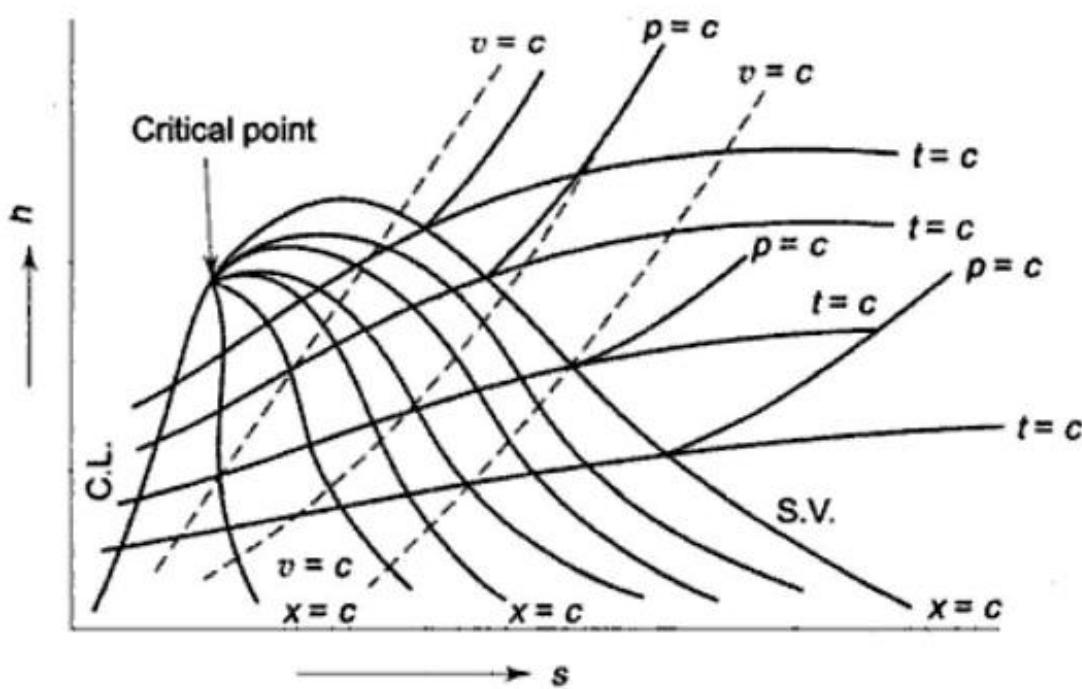
The temperature-entropy plot and enthalpy-entropy plot (Fig. 9.20a) are commonly used. The temperature-entropy plot shows the vapour dome and the lines of constant pressure, constant volume, constant enthalpy, constant quality, and constant superheat. However, its scale is small and limited in use. The enthalpy-entropy plot or Mollier chart, has a larger scale to provide data suitable for many computations. It contains the same data as does the  $T$ - $s$  chart. The Mollier chart for water is given in Appendix F.I. The Mollier diagram for steam with data taken from Keenan et al. Steam Tables (John Wiley, N. Y., 1969 is given in Fig. 9.21.)

### 9.9 Measurement of Steam Quality

The state of a pure substance gets fixed if two independent properties are given. A pure substance is thus said to have two degrees of freedom. Of all thermodynamic properties, it is easiest to measure the pressure and temperature of a substance. Therefore, whenever pressure and temperature are independent properties, it is

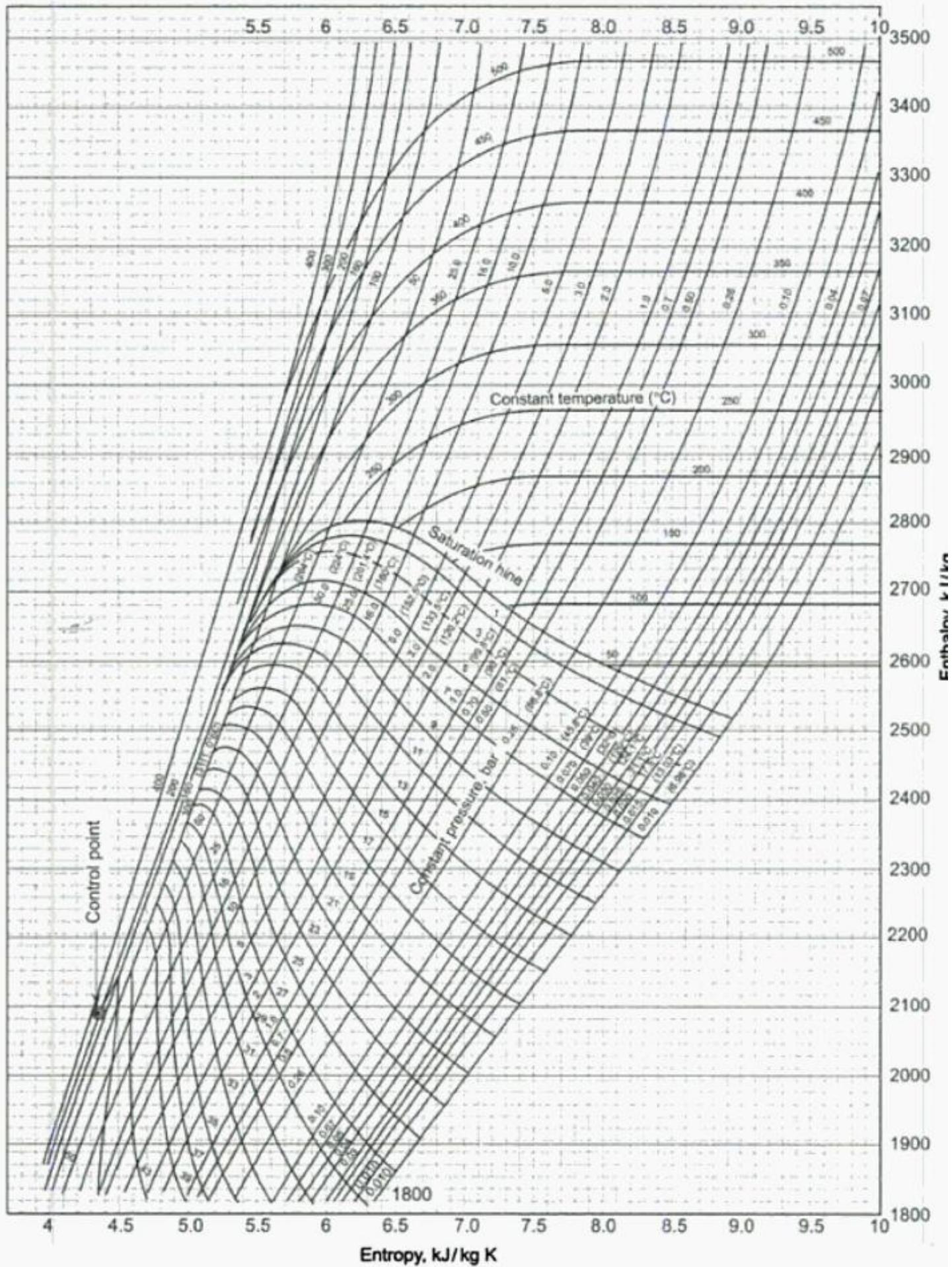


(a) Constant property lines on  $T$ - $s$  plot



(b) Constant property lines on Mollier diagram

the practice to measure them to determine that state of the substance. This is done in the compressed liquid region or the superheated vapour region (Fig. 9.22), where the measured values of pressure and temperature would fix up the state. But when the substance is in the saturation state or two-phase region (Fig. 9.22), the measured values of pressure and temperature could apply equally well to saturated liquid point  $f$ , saturated vapour point  $g$ , or to mixtures of any quality, points  $x_1$ ,  $x_2$  or  $x_3$ . Of the two properties,  $p$  and  $t$ , only one is independent; the other is a dependent property. If pressure is given, the saturation temperature gets



**Fig. 9.21** Mollier diagram for steam (Data taken from Keenan, J.H., F.G. Keyes, P.C. Hill and J.g. Moore, Steam Tables, John Wiley, N.Y., 1969)

automatically fixed for the substance. In order to fix up the state of the mixture, apart from either pressure or temperature, one more property, such as specific

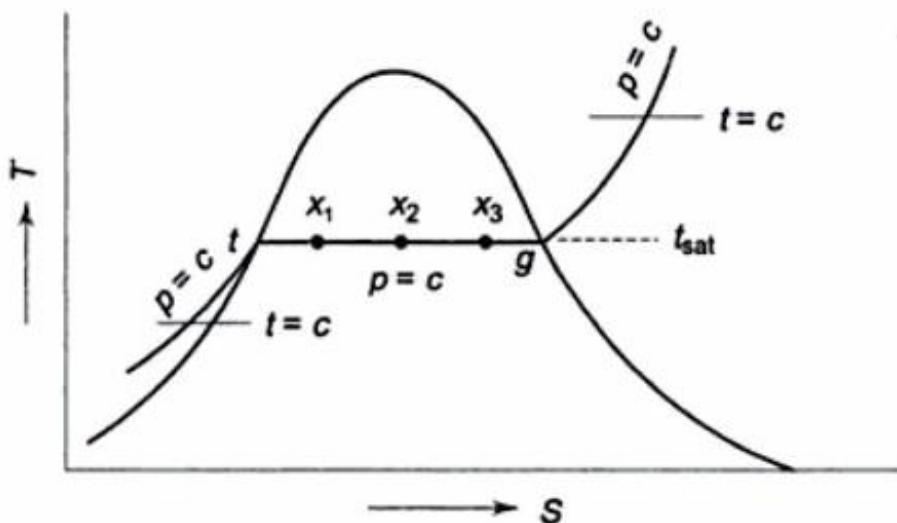


Fig. 9.22 Quality of liquid-vapour mixture

volume, enthalpy or composition of the mixture (quality) is required to be known. Since it is relatively difficult to measure the specific volume of a mixture, devices such as calorimeters are used for determining the quality or the enthalpy of the mixture.

In the measurement of quality, the object is always to bring the state of the substance from the two-phase region to the single-phase or superheated region, where both pressure and temperature are independent, and measured to fix the state, either by adiabatic throttling or electric heating.

In the *throttling calorimeter*, a sample of wet steam of mass  $m$  and at pressure  $p_1$  is taken from the steam main through a perforated sampling tube (Fig. 9.23). Then it is throttled by the partially-opened valve (or orifice) to a pressure  $p_2$ , measured by mercury manometer, and temperature  $t_2$ , so that after throttling the steam is in the superheated region. The process is shown on the  $T$ - $s$  and  $h$ - $s$

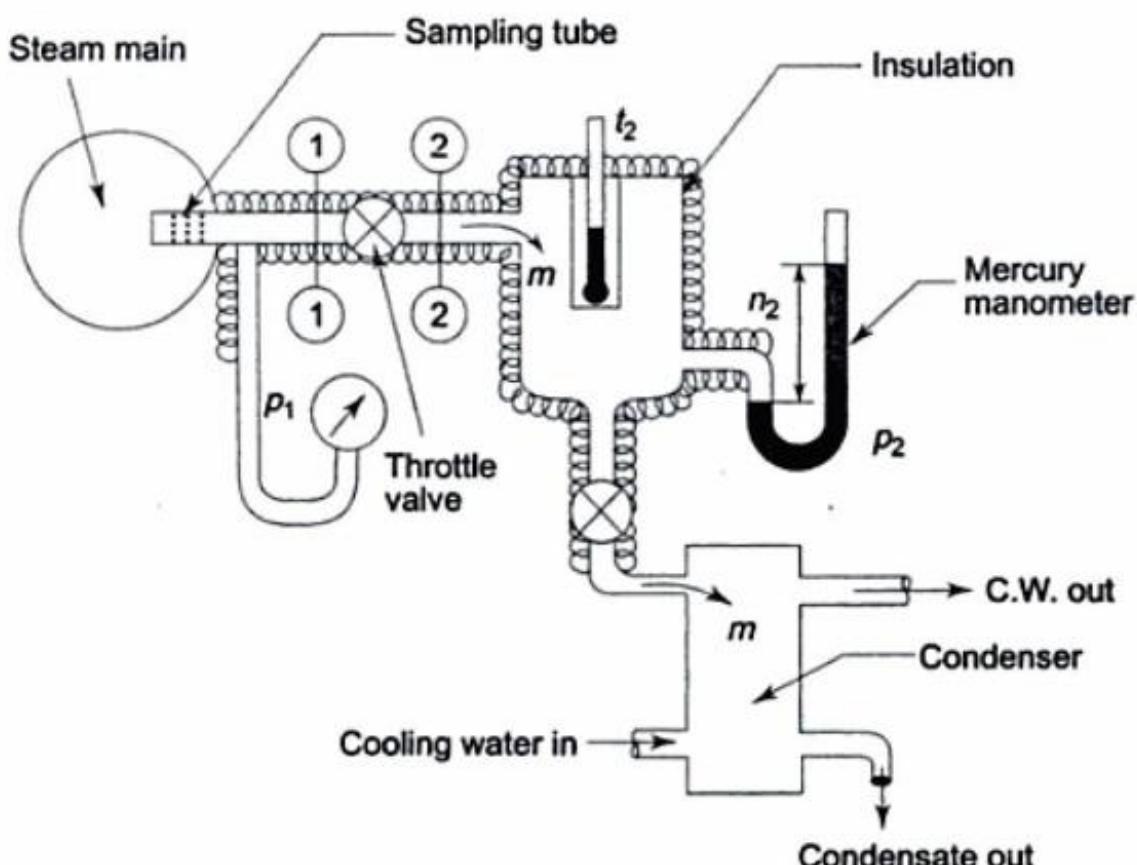


Fig. 9.23 Throttling calorimeter

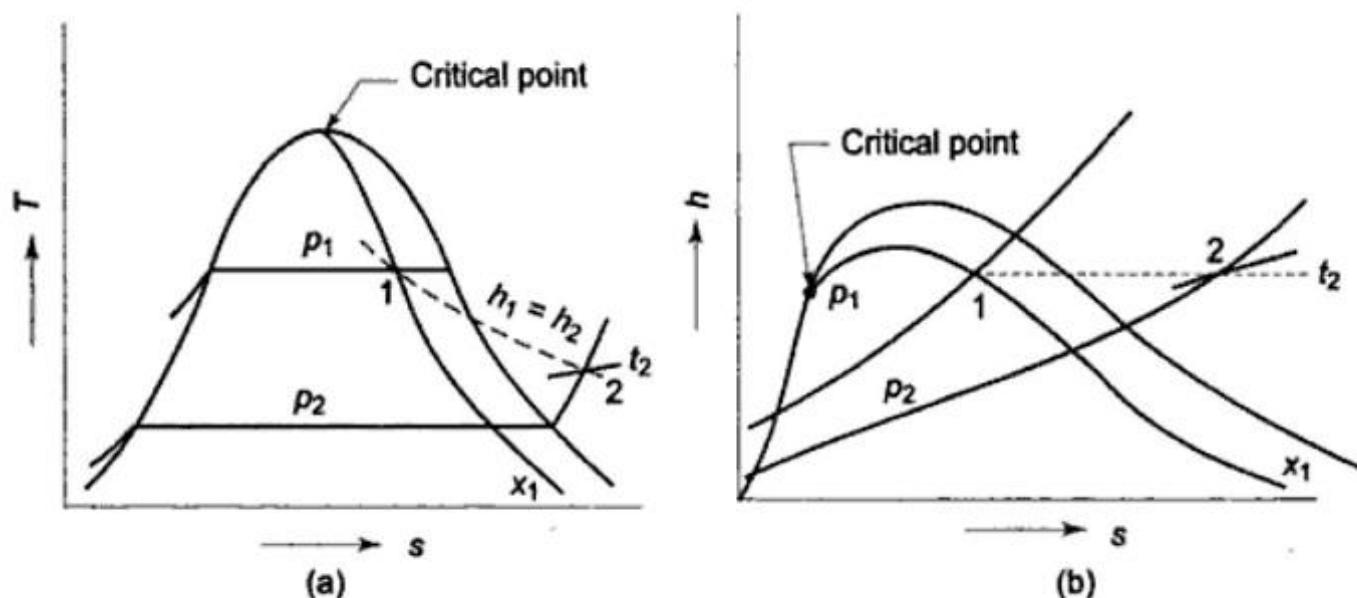


Fig. 9.24 Throttling process on  $T$ - $s$  and  $h$ - $s$  plots

diagrams in Fig. 9.24. The steady flow energy equation gives the enthalpy after throttling as equal to enthalpy before throttling. The initial and final equilibrium states 1 and 2 are joined by a dotted line since throttling is irreversible (adiabatic but not isentropic) and the intermediate states are non-equilibrium states not describable by thermodynamic coordinates. The initial state (wet) is given by  $p_1$  and  $x_1$ , and the final state by  $p_2$  and  $t_2$  (superheated). Now

since

$$h_1 = h_2$$

$$h_{fp1} + x_1 h_{fgp1} = h_2$$

or

$$x_1 = \frac{h_2 - h_{fp1}}{h_{fgp1}}$$

With  $p_2$  and  $t_2$  being known,  $h_2$  can be found out from the superheated steam table. The values of  $h_f$  and  $h_{fg}$  are taken from the saturated steam table corresponding to pressure  $p_1$ . Therefore, the quality of the wet steam  $x_1$  can be calculated.

To be sure that steam after throttling is in the single-phase or superheated region, a minimum of 5°C superheat is desired. So if the pressure after throttling is given and the minimum 5°C superheat is prescribed, then there is the minimum quality of steam (or the maximum moisture content) at the given pressure  $p_1$  which can be measured by the throttling calorimeter. For example, if  $p_2 = 1$  atm., then  $t_2 = 105^\circ\text{C}$  and the state 2 after throttling gets fixed as shown in Fig. 9.25. From state 2, the constant enthalpy line intersects the constant pressure  $p_1$  line at 1. Therefore, the quality  $x_1$  is the minimum quality that can be measured simply by throttling. If the quality is, say,  $x'_1$  less than  $x_1$ , then after throttling to  $p_2 = 1$  atm., the superheat after throttling is less than 5°C. If the quality is  $x''_1$ , then throttling to 1 atm. does not give any superheat at all.

When the steam is very wet and the pressure after throttling is not low enough to take the steam to the superheated region, then a *combined separating and throttling calorimeter* is used for the measurement of quality. Steam from the

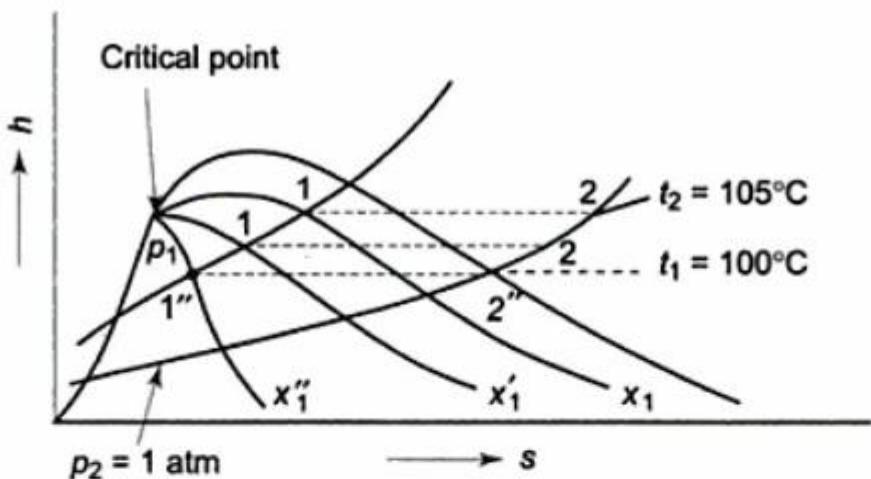


Fig. 9.25 Minimum quality that can be measured only by throttling

main is first passed through a separator (Fig. 9.26), where some part of the moisture separates out due to the sudden change in direction and falls by gravity, and the partially dry vapour is then throttled and taken to the superheated region. In Fig. 9.27, process 1-2 represents the moisture separation from the wet sample of steam at constant pressure  $p_1$  and process 2-3 represents throttling to pressure  $p_2$ . With  $p_2$  and  $t_3$  being measured,  $h_3$  can be found out from the superheated steam table.

Now,

$$h_3 = h_2 = h_{fpl} + x_2 h_{fgpl}$$

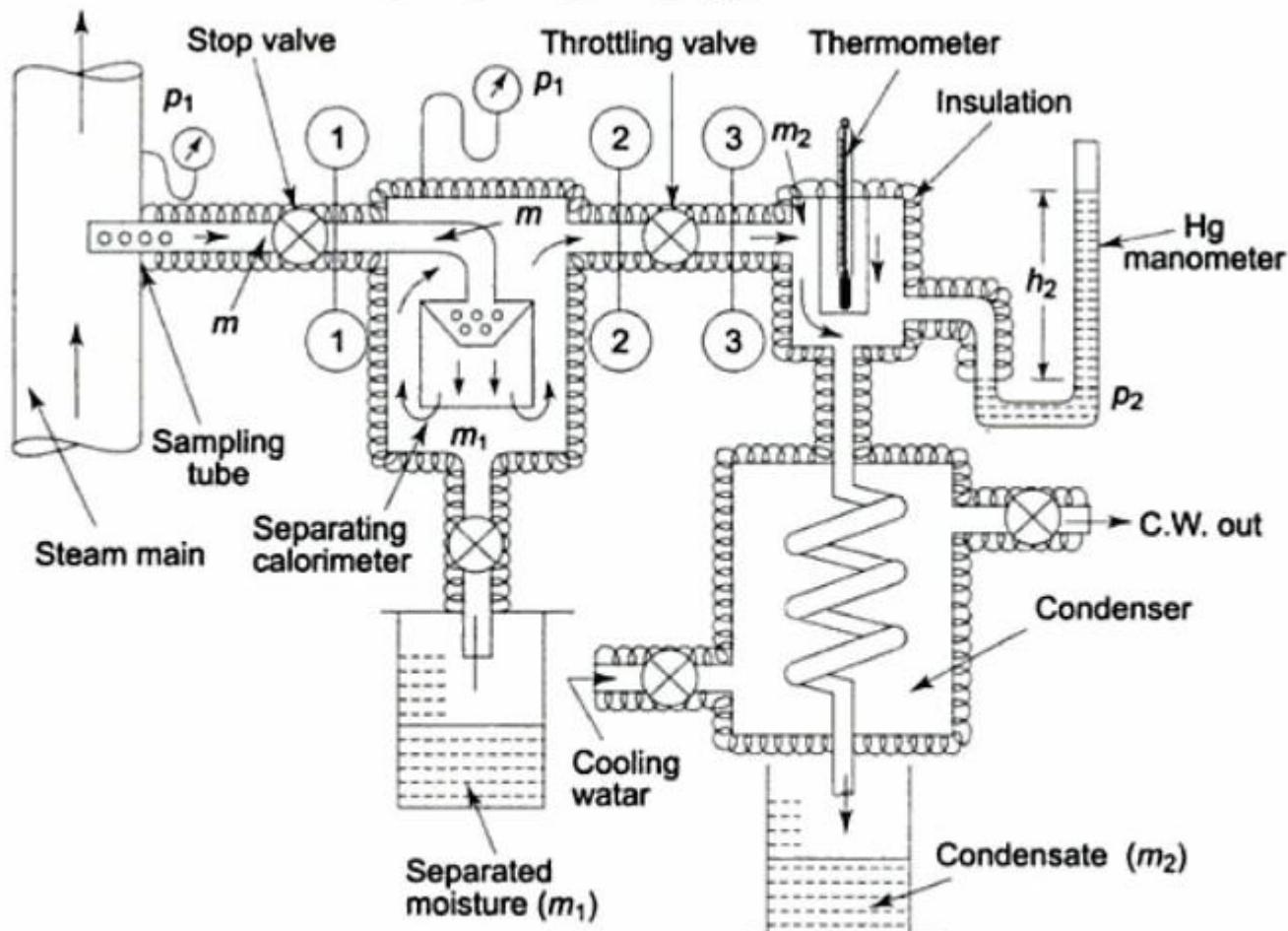
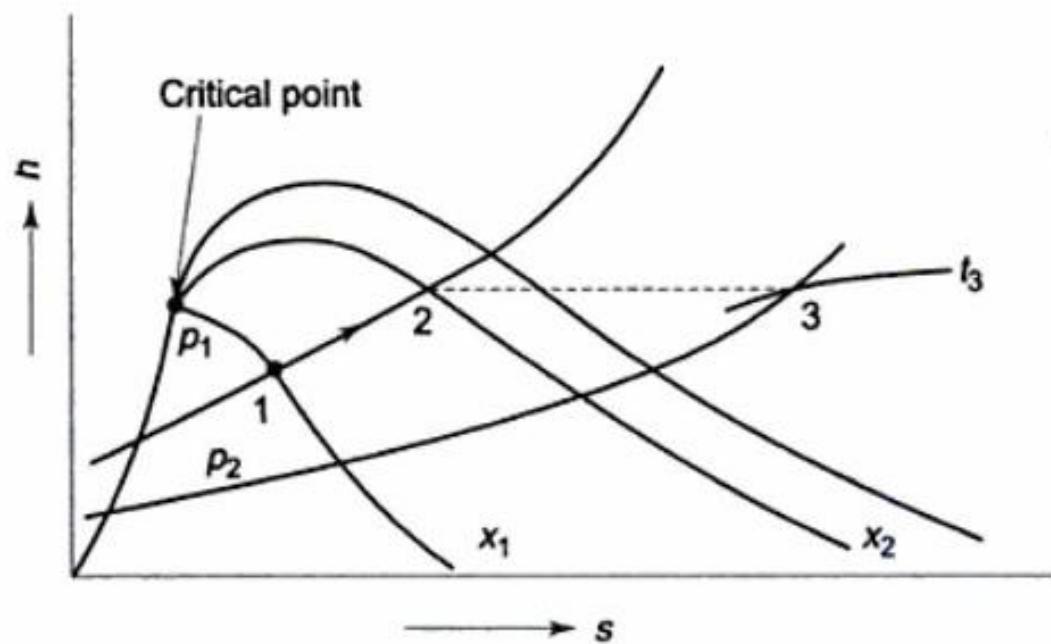


Fig. 9.26 Separating and throttling calorimeter

Therefore,  $x_2$ , the quality of steam after partial moisture separation, can be evaluated. If  $m$  kg of steam is taken through the sampling tube in  $t$  secs,  $m_1$  kg of



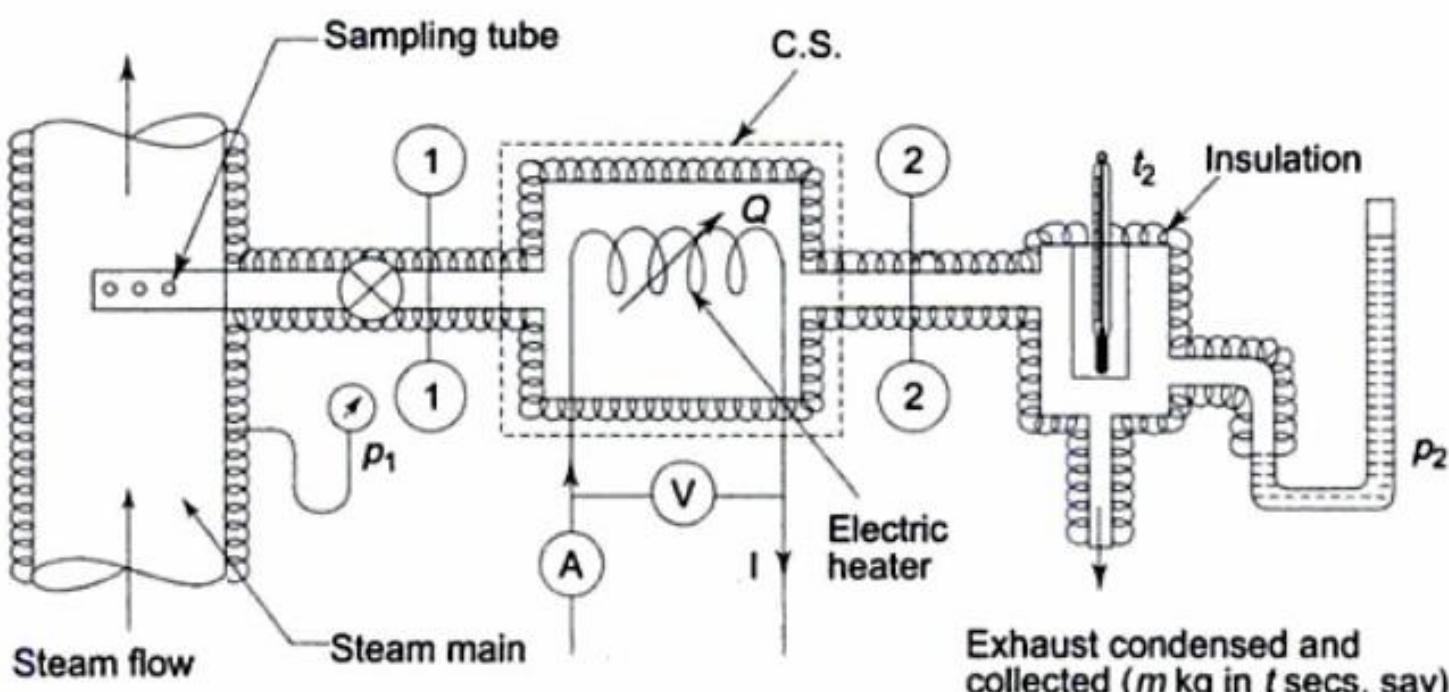
**Fig. 9.27 Separating and throttling processes on h-s plot**

is separated, and  $m_2$  kg is throttled and then condensed to water and collected when  $m = m_1 + m_2$ , and at state 2, the mass of dry vapour will be  $x_2 m_2$ . Therefore the quality of the sample of steam at state 1,  $x_1$  is given by

$$x_1 = \frac{\text{mass of dry vapour at state 1}}{\text{mass of liquid-vapour mixture at state 1}}$$

$$= \frac{x_2 m_2}{m_1 + m_2}$$

The quality of wet steam can also be measured by an *electric calorimeter* (see Fig. 9.28). The sample of steam is passed in steady flow through an electric heater, as shown. The electrical energy input  $Q$  should be sufficient to take the steam to the superheated region where pressure  $p_2$  and temperature  $t_2$  are measured. If  $I$  is the current flowing through the heater in amperes and  $V$  is the voltage across the coil, then at steady state  $Q = VI \times 10^{-3}$  kW. If  $m$  is the mass of steam taken in  $t$  seconds under steady flow condition, then the steady flow energy equation for the heater (as control volume) gives



**Fig. 9.28 Electrical calorimeter**

$$w_1 h_1 + Q = w_1 h_2$$

where  $w_1$  is the steam flow rate in kg/s ( $w_1 = \frac{m}{t}$  kg/s)

$$\therefore h_1 + \frac{Q}{w_1} = h_2$$

With  $h_2$ ,  $Q$  and  $w_1$  being known,  $h_1$  can be computed. Now

$$h_1 = h_{fpl} + x_1 h_{fgpl}$$

Hence  $x_1$  can be evaluated.

## SOLVED EXAMPLES

**Example 9.1** Find the saturation temperature, the changes in specific volume and entropy during evaporation, and the latent heat of vaporization of steam at 1 MPa.

*Solution* At 1 MPa, from Table A.1(b) in the Appendix

$$t_{sat} = 179.91^\circ\text{C}$$

$$v_f = 0.001127 \text{ m}^3/\text{kg}$$

*Ans.*

$$v_g = 0.19444 \text{ m}^3/\text{kg}$$

$$\therefore v_{fg} = v_g - v_f = 0.1933 \text{ m}^3/\text{kg}$$

$$s_f = 2.1387 \text{ kJ/kg K}$$

$$s_g = 6.5865 \text{ kJ/kg K}$$

$$\therefore s_{fg} = s_g - s_f = 4.4478 \text{ kJ/kg K}$$

*Ans.*

$$h_{fg} = h_g - h_f = 2015.3 \text{ kJ/kg}$$

*Ans.*

**Example 9.2** Saturated steam has an entropy of 6.76 kJ/kg K. What are its pressure, temperature, specific volume, and enthalpy?

*Solution* In Table A.1(b), when  $s_g = 6.76 \text{ kJ/kg K}$

$$p = 0.6 \text{ MPa}, \quad t = 158.85^\circ\text{C}$$

$$v_g = 0.3156 \text{ m}^3/\text{kg}, \text{ and } h_g = 2756.8 \text{ kJ/kg}$$

*Ans.*

**Example 9.3** Find the enthalpy and entropy of steam when the pressure is 2 MPa and the specific volume is  $0.09 \text{ m}^3/\text{kg}$ .

*Solution* In Table A.1(b), when  $p = 2 \text{ MPa}$ ,  $v_f = 0.001177 \text{ m}^3/\text{kg}$  and  $v_g = 0.09963 \text{ m}^3/\text{kg}$ . Since the given volume lies between  $v_f$  and  $v_g$ , the substance will be a mixture of liquid and vapour, and the state will be within the vapour dome. When in the two-phase region, the composition of the mixture or its quality has to be evaluated first. Now

$$v = v_f + x v_{fg}$$

$$0.09 = 0.001177 + x (0.09963 - 0.001177)$$

or  $x = 0.904$  or  $90.4\%$

At  $2 \text{ MPa}$ ,  $h_f = 908.79$  and  $h_{fg} = 1890.7 \text{ kJ/kg}$   
 $s_f = 2.4474$  and  $s_{fg} = 3.8935 \text{ kJ/kg K}$   

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

$$= 908.79 + 0.904 \times 1890.7 = 2618.79 \text{ kJ/kg} \quad \text{Ans.}$$

$s = s_f + x s_{fg}$   
 $= 2.4474 + 0.904 \times 3.8935$   
 $= 5.9534 \text{ kJ/kg K} \quad \text{Ans.}$

**Example 9.4** Find the enthalpy, entropy, and volume of steam at  $1.4 \text{ MPa}$ ,  $380^\circ\text{C}$ .

**Solution** At  $p = 1.4 \text{ MPa}$ , in Table A.1(b),  $t_{\text{sat}} = 195.07^\circ\text{C}$ . Therefore, the state of steam must be in the superheated region. In Table A.2, for properties of superheated steam,

at  $1.4 \text{ MPa}$ ,  $350^\circ\text{C}$        $v = 0.2003 \text{ m}^3/\text{kg}$   
 $h = 3149.5 \text{ kJ/kg}$   
 $s = 7.1360 \text{ kJ/kg K}$

and at  $1.4 \text{ MPa}$ ,  $400^\circ\text{C}$        $v = 0.2178 \text{ m}^3/\text{kg}$   
 $h = 3257.5 \text{ kJ/kg}$   
 $s = 7.3026 \text{ kJ/kg K}$

$\therefore$  By interpolation

at  $1.4 \text{ MPa}$ ,  $380^\circ\text{C}$        $v = 0.2108 \text{ m}^3/\text{kg}$   
 $h = 3214.3 \text{ kJ/kg}$   
 $s = 7.2360 \text{ kJ/kg K} \quad \text{Ans.}$

**Example 9.5** A vessel of volume  $0.04 \text{ m}^3$  contains a mixture of saturated water and saturated steam at a temperature of  $250^\circ\text{C}$ . The mass of the liquid present is  $9 \text{ kg}$ . Find the pressure, the mass, the specific volume, the enthalpy, the entropy, and the internal energy.

**Solution** From Table A.1(a), at  $250^\circ\text{C}$        $p_{\text{sat}} = 3.973 \text{ MPa}$

$$v_f = 0.0012512 \text{ m}^3/\text{kg}, \quad v_g = 0.05013 \text{ m}^3/\text{kg}$$

$$h_f = 1085.36 \text{ kJ/kg}, \quad h_{fg} = 1716.2 \text{ kJ/kg}$$

$$s_f = 2.7927 \text{ kJ/kg K}, \quad s_{fg} = 3.2802 \text{ kJ/kg K}$$

Volume of liquid,       $V_f = m_f v_f$   
 $= 9 \times 0.0012512$   
 $= 0.01126 \text{ m}^3$

Volume of vapour,       $V_g = 0.04 - 0.01126$   
 $= 0.02874 \text{ m}^3$

$\therefore$  Mass of vapour

$$m_g = \frac{V_g}{v_g} = \frac{0.02874}{0.05013} = 0.575 \text{ kg}$$

∴ Total mass of mixture,

$$m = m_f + m_g = 9 + 0.575 = 9.575 \text{ kg}$$

Ans.

Quality of mixture,

$$x = \frac{m_g}{m_f + m_g} = \frac{0.575}{9.575} = 0.06$$

$$\begin{aligned}\therefore v &= v_f + xv_{fg} \\ &= 0.0012512 + 0.06 (0.05013 - 0.0012512) \\ &= 0.00418 \text{ m}^3/\text{kg}\end{aligned}$$

Ans.

$$\begin{aligned}h &= h_f + xh_{fg} \\ &= 1085.36 + 0.06 \times 1716.2 \\ &= 1188.32 \text{ kJ/kg}\end{aligned}$$

Ans.

$$\begin{aligned}s &= s_f + xs_{fg} \\ &= 2.7927 + 0.06 \times 3.2802 \\ &= 2.9895 \text{ kJ/kg K}\end{aligned}$$

Ans.

$$\begin{aligned}u &= h - pv \\ &= 1188.32 - 3.973 \times 10^3 \times 0.00418 \\ &= 1171.72 \text{ kJ/kg}\end{aligned}$$

Ans.

Also, at 250°C,

$$u_f = 1080.39 \text{ and } u_{fg} = 1522.0 \text{ kJ/kg}$$

$$\therefore u = u_f + xu_{fg}$$

$$\begin{aligned}&= 1080.39 + 0.06 \times 1522 \\ &= 1071.71 \text{ kJ/kg}\end{aligned}$$

Ans.

**Example 9.6** Steam initially at 0.3 MPa, 250°C is cooled at constant volume.

(a) At what temperature will the steam become saturated vapour? (b) What is the quality at 80°C? What is the heat transferred per kg of steam in cooling from 250°C to 80°C?

**Solution** At 0.3 MPa,  $t_{\text{sat}} = 133.55^\circ\text{C}$

Since  $t > t_{\text{sat}}$ , the state would be in the superheated region (Fig. Ex. 9.6). From Table A.2, for properties of superheated steam, at 0.3 MPa, 250°C

$$v = 0.7964 \text{ m}^3/\text{kg}$$

$$h = 2967.6 \text{ kJ/kg}$$

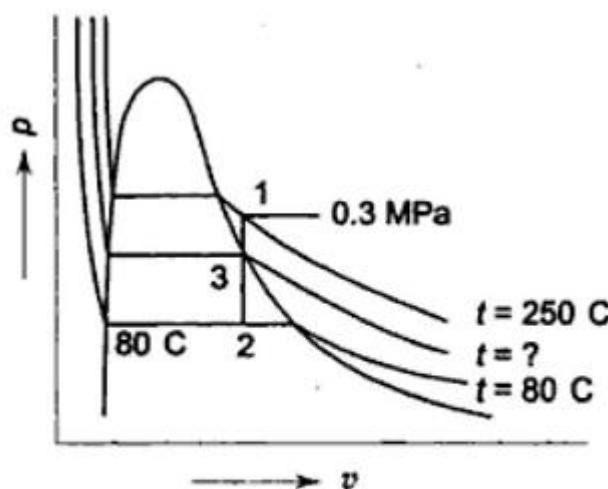


Fig. Ex. 9.6

$$\therefore v_1 = v_3 = v_2 = 0.7964 \text{ m}^3/\text{kg}$$

In Table A.1

when  $v_g = 0.8919, t_{\text{sat}} = 120^\circ\text{C}$

when  $v_g = 0.7706, t_{\text{sat}} = 125^\circ\text{C}$

Therefore, when  $v_g = 0.7964, t_{\text{sat}}$ , by linear interpolation, would be  $123.9^\circ$ .

Steam would become saturated vapour at  $t = 123.9^\circ\text{C}$

*Ans. (a)*

At  $80^\circ\text{C}, v_f = 0.001029 \text{ m}^3/\text{kg}, v_g = 3.407 \text{ m}^3/\text{kg}$ ,

$$h_f = 334.91 \text{ kJ/kg}, h_{fg} = 2308.8 \text{ kJ/kg}, p_{\text{sat}} = 47.39 \text{ kPa}$$

$$v_1 = v_2 = 0.7964 \text{ m}^3/\text{kg} = v_{f80^\circ\text{C}} + x_2 v_{fg80^\circ\text{C}} \\ = 0.001029 + x_2 (3.407 - 0.001029)$$

$$\therefore x_2 = \frac{0.79539}{3.40597} = 0.234 \quad \text{Ans. (b)}$$

$$h_2 = 334.91 + 0.234 \times 2308.8 = 875.9 \text{ kJ/kg}$$

$$h_2 = 2967.6 \text{ kJ/kg}$$

From the first law of thermodynamics

$$dQ = du + pdv$$

$$\therefore (dQ)_v = du$$

$$\text{or } Q_{1.2} = u_2 - u_1 = (h_2 - p_2 v_2) - (h_1 - p_1 v_1)$$

$$= (h_2 - h_1) + v(p_1 - p_2)$$

$$= 875.9 - 2967.6 + 0.7964 (300 - 47.39)$$

$$= 2091.7 + 201.5$$

$$= -1890.2 \text{ kJ/kg}$$

*Ans. (c)*

**Example 9.7** Steam initially at 1.5 MPa,  $300^\circ\text{C}$  expands reversibly and adiabatically in a steam turbine to  $40^\circ\text{C}$ . Determine the ideal work output of the turbine per kg of steam.

**Solution** The steady flow energy equation for the control volume, as shown in Fig. Ex. 9.7.1, gives (other energy terms being neglected)

$$h_1 = h_2 + W$$

$$\therefore W = h_1 - h_2$$

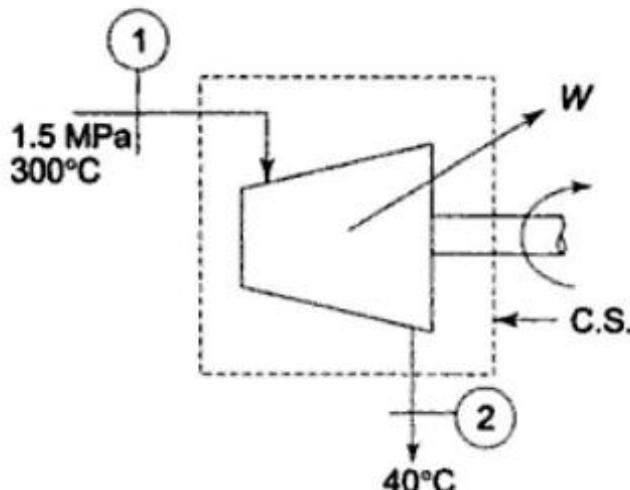


Fig. Ex. 9.7.1

Work is done by steam at the expense of a fall in its enthalpy value. The process is reversible and adiabatic, so it is isentropic. The process is shown on the  $T-s$  and  $h-s$  diagrams in Fig. Ex. 9.7.2.

From Table A.1(a), at 40°C

$$p_{\text{sat}} = 7.384 \text{ kPa}, s_f = 0.5725, \text{ and } s_{fg} = 7.6845 \text{ kJ/kg K}$$

$$h_f = 167.57, \text{ and } h_{fg} = 2406.7 \text{ kJ/kg}$$

At  $p = 1.5 \text{ MPa}$ ,  $t = 300^\circ\text{C}$ , from the tabulated properties of superheated steam (Table A.2)

$$\begin{aligned}s_1 &= 6.9189 \text{ kJ/kg K} \\ h_1 &= 3037.6 \text{ kJ/kg}\end{aligned}$$

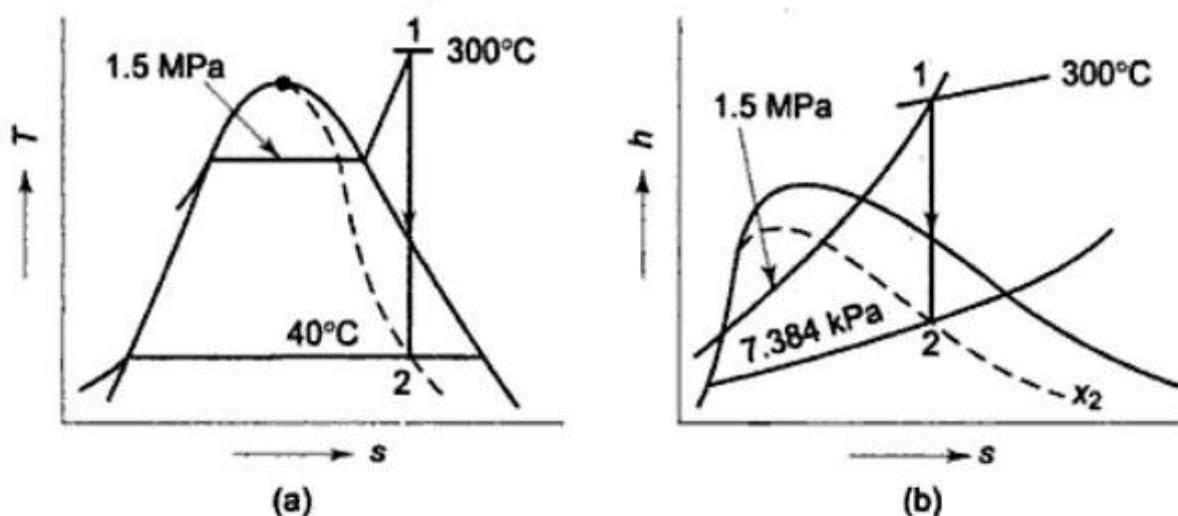


Fig. Ex. 9.7.2

Since

$$s_1 = s_2$$

$$\begin{aligned}6.9189 &= s_f + x_2 s_{fg} \text{ at } 40^\circ\text{C} \\ &= 0.5725 + x_2 \times 7.6845\end{aligned}$$

$$x_2 = \frac{6.3464}{7.6845} = 0.826 \text{ or } 82.6\%$$

$$\begin{aligned}h_2 &= h_{f40^\circ\text{C}} + x_2 h_{fg40^\circ\text{C}} \\ &= 167.57 + 0.826 \times 2406.7 \\ &= 2152.57 \text{ kJ/kg}\end{aligned}$$

$$\begin{aligned}\therefore W &= h_1 - h_2 = 3037.6 - 2152.57 \\ &= 885.03 \text{ kJ/kg}\end{aligned}$$

Ans.

**Example 9.8** Steam at 0.8 MPa, 250°C and flowing at the rate of 1 kg/s passes into a pipe carrying wet steam at 0.8 MPa, 0.95 dry. After adiabatic mixing the flow rate is 2.3 kg/s. Determine the condition of steam after mixing.

The mixture is now expanded in a frictionless nozzle isentropically to a pressure of 0.4 MPa. Determine the velocity of the steam leaving the nozzle. Neglect the velocity of steam in the pipeline.

**Solution** Figure Ex. 9.8.1 gives the flow diagram.

$$w_2 = w_3 - w_1 = 2.3 - 1.0 = 1.3 \text{ kg/s}$$

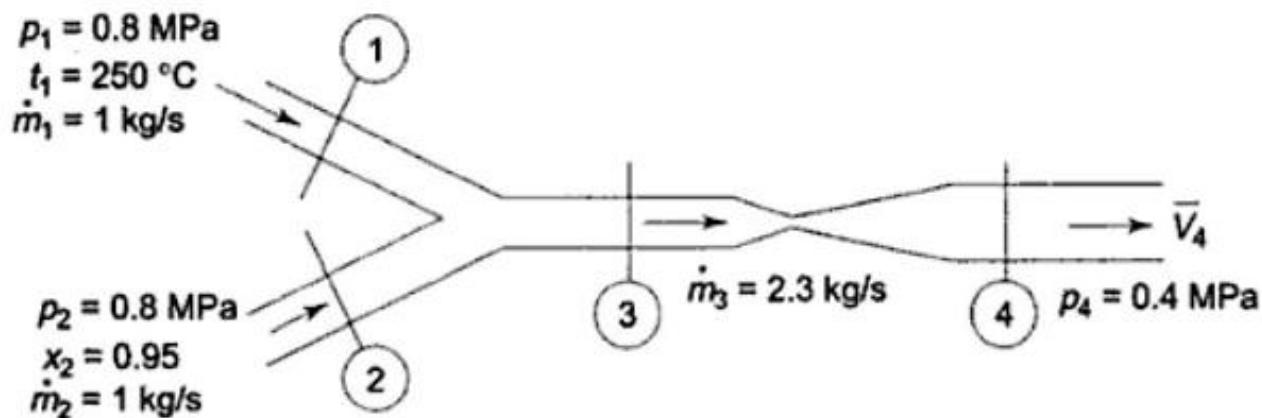


Fig. Ex. 9.8.1

The energy equation for the adiabatic mixing of the two streams gives

$$w_1 h_1 + w_2 h_2 = w_3 h_3 \quad (9.8.1)$$

At 0.8 MPa, 250°C,  $h_1 = 2950.0 \text{ kJ/kg}$

At 0.8 MPa, 0.95 dry

$$\begin{aligned} h_2 &= h_f + 0.95 h_{fg} \\ &= 721.11 + 0.95 \times 2048.0 \\ &= 2666.71 \text{ kJ/kg} \end{aligned}$$

∴ From Eq. (9.8.1)

$$1 \times 2950 + 1.3 \times 2666.71 = 2.3 \times h_3$$

$$\therefore h_3 = 2790 \text{ kJ/kg}$$

Since  $(h_g)_{0.8 \text{ MPa}} = 2769.1 \text{ kJ/kg}$

and  $h_3 > h_g$ , the state must be in the superheated region. From the steam tables, when  $p = 0.8 \text{ MPa}$ ,  $t = 200^\circ\text{C}$

$$h = 2839.3 \text{ kJ/kg}$$

When

$$\begin{aligned} p &= 0.8 \text{ MPa}, t_{\text{sat}} = 170.43^\circ\text{C} \\ h_g &= 2769.1 \text{ kJ/kg} \end{aligned}$$

By linear interpolation

$$t_3 = 179^\circ\text{C}$$

∴ Degree of superheat =  $179 - 170.33 = 8.57^\circ\text{C}$

∴ Condition of steam after mixing = 0.8 MPa, 179°C

*Ans.*

The energy equation for the nozzle gives

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

since  $V_3 = -$  velocity of steam in the pipeline = 0

Steam expands isentropically in the nozzle to 0.4 MPa. By interpolation,

$$s_3 = 6.7087 \text{ kJ/kg K} = s_4$$

$$\therefore 6.7087 = 1.7766 + x_4 \times 5.1193$$

$$x_4 = 0.964$$

$$\therefore h_4 = 604.74 + 0.964 \times 2133.8 = 2660 \text{ kJ/kg}$$

$$V_4^2 \times 10^{-3} = 2(h_3 - h_4) = 2 \times 130 = 260$$

$$V_4 = \sqrt{26} \times 100 = 509.9 \text{ m/s}$$

*Ans.*

The processes are shown on the *h-s* and *T-s* diagrams in Fig. Ex. 9.8.2.

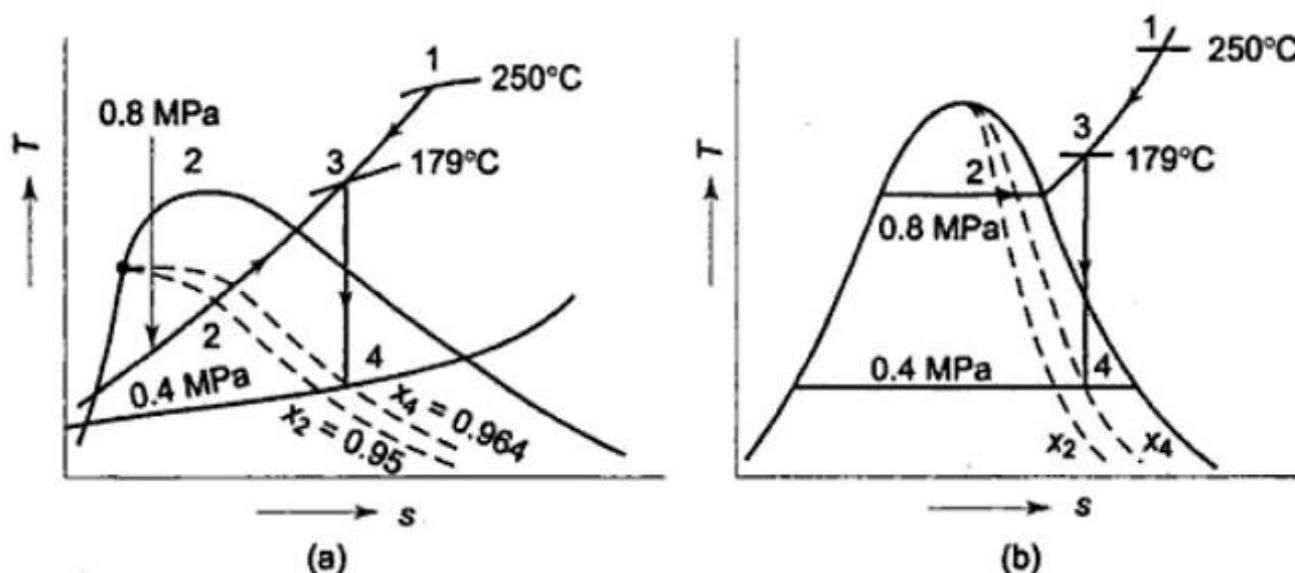


Fig. Ex. 9.8.2

**Example 9.9** Steam flows in a pipeline at 1.5 MPa. After expanding to 0.1 MPa in a throttling calorimeter, the temperature is found to be 120°C. Find the quality of steam in the pipeline. What is the maximum moisture at 1.5 MPa that can be determined with this set-up if at least 5°C of superheat is required after throttling for accurate readings?

**Solution** At state 2 (Fig. Ex. 9.9), when  $p = 0.1 \text{ MPa}$ ,  $t = 120^\circ\text{C}$  by interpolation

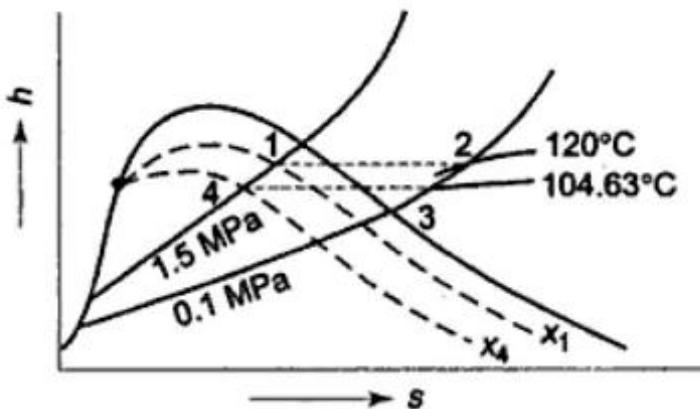


Fig. Ex. 9.9

$h_2 = 2716.2 \text{ kJ/kg}$ , and at  $p = 1.5 \text{ MPa}$

$h_f = 844.89$  and  $h_{fg} = 1947.3 \text{ kJ/kg}$

Now  $h_1 = h_2$

or  $h_{f1.5\text{MPa}} + x_1 h_{fg1.5\text{MPa}} = h_2$

$$844.89 + x_1 \times 1947.3 = 2716.2$$

$$x_1 = \frac{1871.3}{1947.3} = 0.963$$

*Ans.*

When  $p = 0.1 \text{ MPa}$  and  $t = 99.63 + 5 = 104.63^\circ\text{C}$

$$h_3 = 2685.5 \text{ kJ/kg}$$

Since

$$h_3 = h_4$$

$$2685.5 = 844.89 + x_4 \times 1947.3$$

$$\therefore x_4 = \frac{1840.6}{1947.3} = 0.948$$

The maximum moisture that can be determined with this set-up is only 5.2%.

*Ans.*

**Example 9.10** The following data were obtained with a separating and throttling calorimeter:

Pressure in pipeline

1.5 MPa

Condition after throttling

0.1 MPa, 110°C

During 5 min moisture collected in the separator

0.150 litre at 70°C

Steam condensed after throttling during 5 min

3.24 kg

Find the quality of steam in the pipeline

**Solution** As shown in Fig. Ex. 9.10,

at 0.1 MPa, 110°C  $h_3 = 2696.2 \text{ kJ/kg}$

Now  $h_3 = h_2 = h_{f1.5\text{MPa}} + x_2 h_{fg1/5\text{MPa}}$

or  $2696.2 = 844.89 + x_2 \times 1947.3$

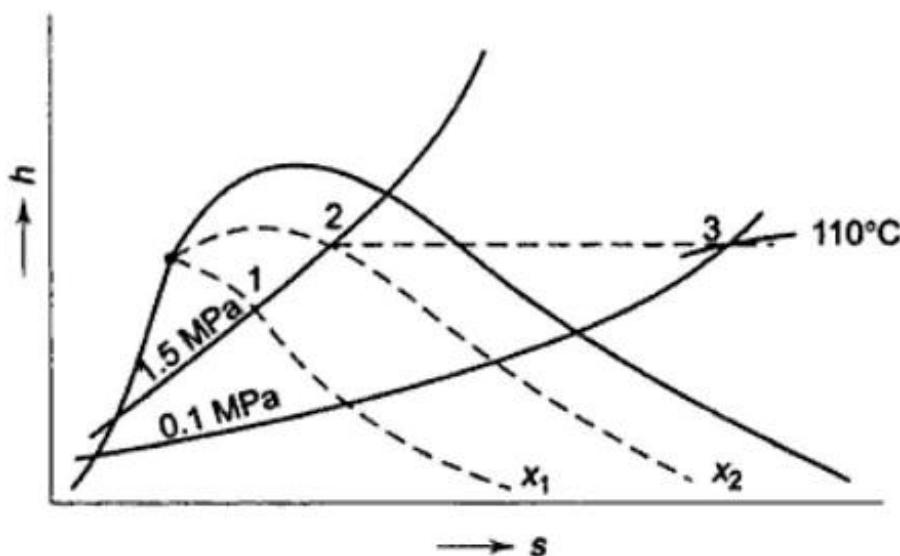


Fig. Ex. 9.10

$$\therefore x_2 = \frac{1851.31}{1947.3} = 0.955$$

If  $m_1$  = mass of moisture collected in separator in 5 min and  $m_2$  = mass of steam condensed after throttling in 5 min.

then

$$x_1 = \frac{x_2 m_2}{m_1 + m_2}$$

At 70°C,

$$v_f = 0.001023 \text{ m}^3/\text{kg}$$

$$m_1 = \frac{150 \times 10^{-6} \text{ m}^3}{1023 \times 10^{-6} \text{ m}^3/\text{kg}}$$

## 11.8 Clausius-Clapeyron Equation

During phase transitions like melting, vaporization and sublimation, the temperature and pressure remain constant, while the entropy and volume change. If  $x$  is the fraction of initial phase  $i$  which has been transformed into final phase  $f$ , then

$$s = (1 - x)s^{(i)} + xs^{(f)}$$
$$v = (1 - x)v^{(i)} + xv^{(f)}$$

where  $s$  and  $v$  are linear functions of  $x$ .

For reversible phase transition, the heat transferred per mole (or per kg) is the latent heat, given by

$$l = T\{s^{(f)} - s^{(i)}\}$$

which indicates the change in entropy.

Now  $dg = -sdT + vdp$

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

and  $v = \left(\frac{\partial g}{\partial p}\right)_T$

A *phase change of the first order* is known as any phase change that satisfies the following requirements:

- There are changes of entropy and volume.
- The first-order derivatives of Gibbs function change discontinuously.

Let us consider the first-order phase transition of one mole of a substance from phase  $i$  to phase  $f$ . Using the first  $TdS$  equation

$$TdS = c_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv$$

for the phase transition which is reversible, isothermal and isobaric, and integrating over the whole change of phase, and since  $\left(\frac{\partial p}{\partial T}\right)_v$  is independent of  $v$

$$T\{s^{(f)} - s^{(i)}\} = T \frac{dp}{dT} \cdot \{v^{(f)} - v^{(i)}\}$$
$$\therefore \frac{dp}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{l}{T[v^{(f)} - v^{(i)}]} \quad (11.18)$$

The above equation is known as the *Clausius-Clapeyron equation*.

The Clausius-Clapeyron equation can also be derived in another way.

For a reversible process at constant  $T$  and  $p$ , the Gibbs function remains constant. Therefore, for the first-order phase change at  $T$  and  $p$

$$g^{(i)} = g^{(f)}$$

and for a phase change at  $T + dT$  and  $p + dp$  (Fig. 11.7)

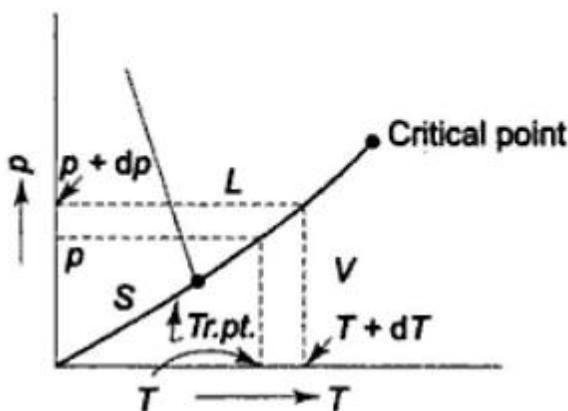


Fig. 11.7 First order phase transition

$$g^{(i)} + dg^{(i)} = g^{(f)} + dg^{(f)}$$

Subtracting

$$dg^{(i)} = dg^{(f)}$$

or

$$\begin{aligned} & -s^{(i)} dT + v^{(i)} dp \\ & = -s^{(f)} dT + v^{(f)} dp \end{aligned}$$

∴

$$\frac{dp}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{l}{T[v^{(f)} - v^{(i)}]}$$

For fusion

$$\frac{dp}{dT} = \frac{l_{fu}}{T(v'' - v')}$$

where  $l_{fu}$  is the latent heat of fusion, the first prime indicates the saturated solid state, and the second prime the saturated liquid state. The slope of the fusion curve is determined by  $(v'' - v')$ , since  $l_{fu}$  and  $T$  are positive. If the substance expands on melting,  $v'' > v'$ , the slope is positive. This is the usual case. Water, however, contracts on melting and has the fusion curve with a negative slope (Fig. 11.8).

For vaporization

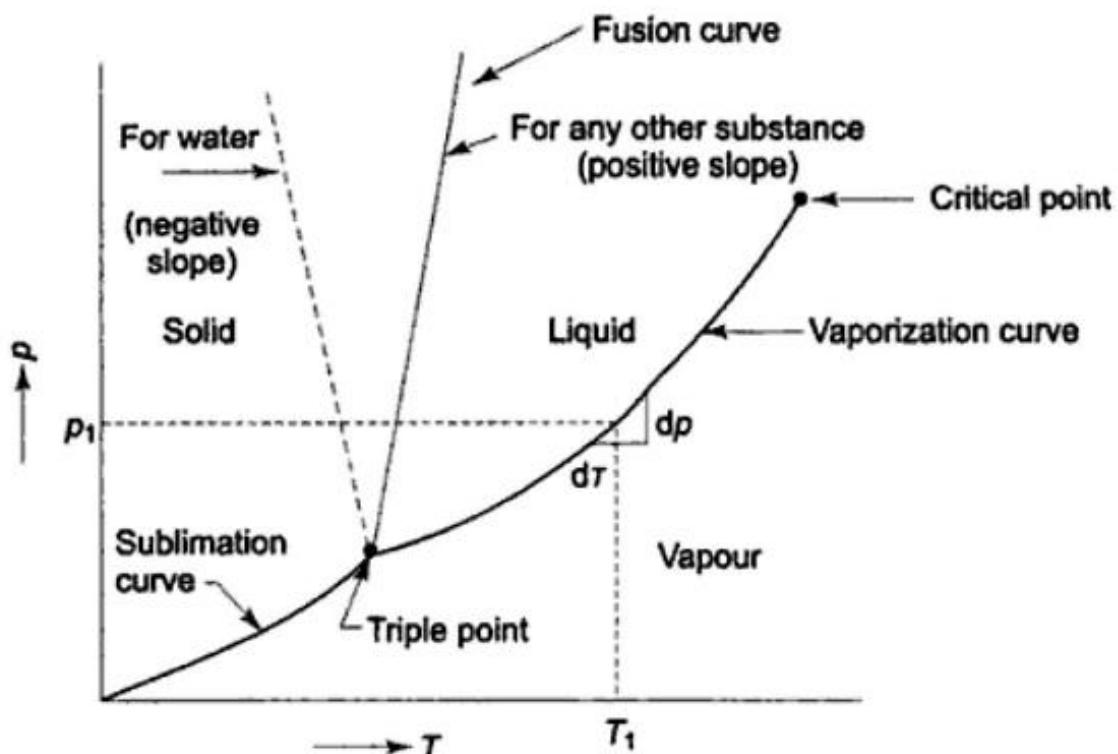
$$\frac{dp}{dT} = \frac{l_{vap}}{T(v''' - v'')}$$

where  $l_{vap}$  is the latent heat of vaporization, and the third prime indicates the saturated vapour state.

$$\therefore l_{vap} = T \frac{dp}{dT} (v''' - v'')$$

At temperatures considerably below the critical temperature,  $v''' \gg v''$  and using the ideal gas equation of state for vapour

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



**Fig. 11.8 Phase diagram for water and any other substance on  $p$ - $T$  coordinates**

$$l_{\text{vap}} \equiv T \cdot \frac{dp}{dT} \frac{RT}{p}$$

$$\text{or } l_{\text{vap}} = \frac{RT^2}{p} \frac{dp}{dT} \quad (11.19)$$

If the slope  $dp/dT$  at any state (e.g. point  $p_1$ ,  $T_1$  in Fig. 11.8) is known, the latent heat of vaporization can be computed from the above equation.

The vapour pressure curve is of the form

$$\ln p = A + \frac{B}{T} + C \ln T + DT$$

where  $A$ ,  $B$ ,  $C$  and  $D$  are constants. By differentiating with respect to  $T$

$$\frac{1}{p} \frac{dp}{dT} = -\frac{B}{T^2} + \frac{C}{T} + D \quad (11.20)$$

Equations (11.19) and (11.20) can be used to estimate the latent heat of vaporization.

Clapeyron's equation can also be used to estimate approximately the vapour pressure of a liquid at any arbitrary temperature in conjunction with a relation for the latent heat of a substance, known as *Trouton's rule*, which states that

$$\frac{\bar{h}_{fg}}{T_B} \equiv 88 \text{ kJ/kgmol K}$$

where  $\bar{h}_{fg}$  is the latent heat of vaporization in  $\text{kJ/kgmol}$  and  $\Delta T_B$  is the boiling point at 1.013 bar. On substituting this into Eq. (11.19)

$$\frac{dp}{dT} = \frac{88 T_B}{R T^2} p$$

or

$$\int_{101.325}^P \frac{dp}{P} = \frac{88T_B}{R} \int_{T_B}^T \frac{dT}{T^2}$$

$$\ln \frac{P}{101.325} = -\frac{88T_B}{R} \left( \frac{1}{T} - \frac{1}{T_B} \right)$$

$$\therefore P = 101.325 \exp \left[ \frac{88}{R} \left( 1 - \frac{T_B}{T} \right) \right] \quad (11.21)$$

This gives the vapour pressure  $P$  in kPa at any temperature  $T$ .

For sublimation

$$\frac{dp}{dT} = \frac{l_{\text{sub}}}{T(v''' - v')}$$

where  $l_{\text{sub}}$  is the latent heat of sublimation.

Since  $v''' \gg v'$ , and vapour pressure is low,  $v''' = \frac{RT}{P}$

$$\frac{dp}{dT} = \frac{l_{\text{sub}}}{T \cdot \frac{RT}{P}} = \frac{l_{\text{sub}}}{T^2}$$

or

$$l_{\text{sub}} = -2.303 R \frac{d(\log p)}{d(1/T)}$$

the slope of  $\log p$  vs.  $1/T$  curve is negative, and if it is known,  $l_{\text{sub}}$  can be estimated.

At the triple point (Fig. 9.12),

$$l_{\text{sub}} = l_{\text{vap}} + l_{\text{fus}} \quad (11.23)$$

$$\left( \frac{dp}{dT} \right)_{\text{vap}} = \frac{p_{\text{tp}} l_{\text{vap}}}{R T_{\text{tp}}^2}$$

$$\left( \frac{dp}{dT} \right)_{\text{sub}} = \frac{p_{\text{tp}} l_{\text{sub}}}{R T_{\text{tp}}^2}$$

Since  $l_{\text{sub}} > l_{\text{vap}}$ , at the triple point

$$\left( \frac{dp}{dT} \right)_{\text{sub}} > \left( \frac{dp}{dT} \right)_{\text{vap}}$$

Therefore, the slope of the sublimation curve at the triple point is greater than that of the vaporization curve (Fig. 11.8).

## 11.9 Evaluation of Thermodynamic Properties from an Equation of State

Apart from calculating pressure, volume, or temperature, an equation of state can also be used to evaluate other thermodynamic properties such as internal energy, enthalpy and entropy. The property relations to be used are: