

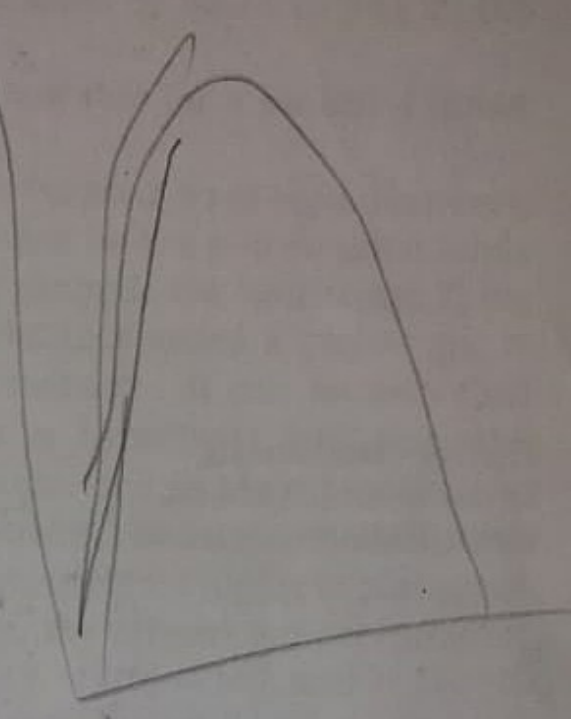
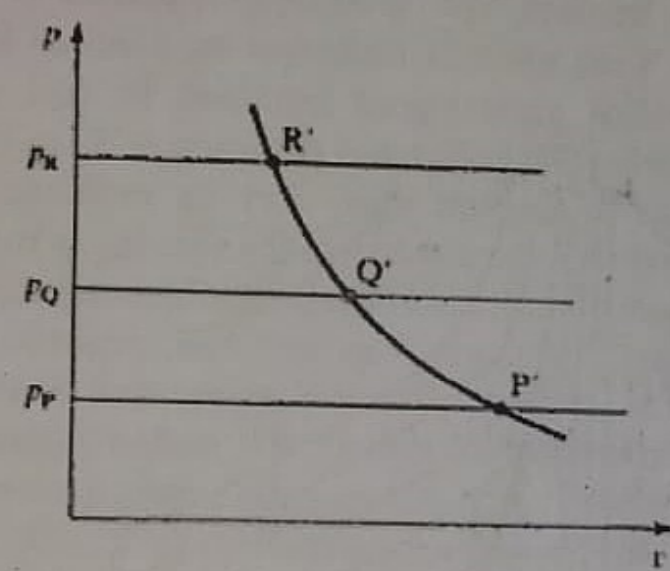
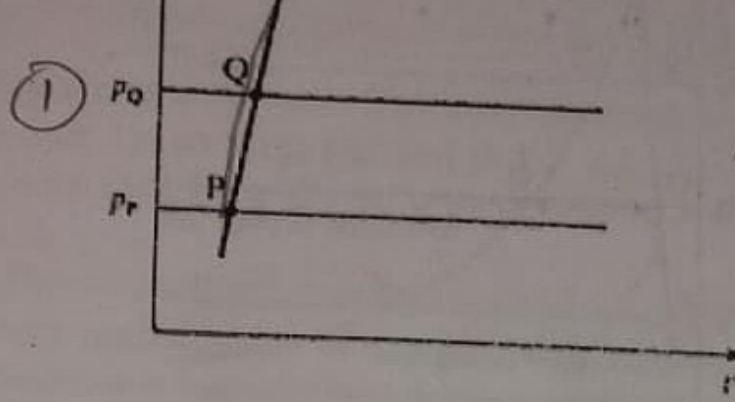
In section 1.3 the matter contained within the boundaries of a system is defined as the working fluid, and it is stated that when two independent properties of the fluid are known then the thermodynamic state of the fluid is defined. In thermodynamic systems the working fluid can be in the liquid, vapour or gaseous phase. All substances can exist in any one of these phases, but we wish to identify all substances with the phase in which they are in equilibrium at atmospheric pressure and temperature. For instance, substances such as oxygen and nitrogen are thought of as gases; H_2O is thought of as liquid or vapour (i.e. water or steam); mercury is thought of as a liquid. All these substances can exist in different phases: oxygen and nitrogen can be liquefied; H_2O can become a gas at very high temperatures; mercury can be vaporized and act as a gas if the temperature is raised high enough.

Fig-
com
plot
p-v

2.1 Liquid, vapour, and gas

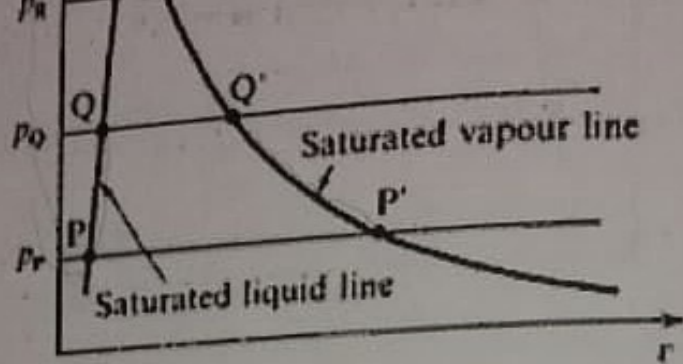
Consider a $p-v$ diagram for any substance. The solid phase is not important in engineering thermodynamics, being more the province of the metallurgist or physicist. When a liquid is heated at any one constant pressure there is a fixed temperature at which bubbles of vapour form in the liquid; this phenomenon is known as boiling. The higher the pressure of the liquid the higher the temperature at which boiling occurs. It is also found that the volume occupied by 1 kg of a boiling liquid at a higher pressure is slightly larger than the volume occupied by 1 kg of the same liquid when it is boiling at a low pressure. A series of boiling-points plotted on a $p-v$ diagram will appear as a sloping line, as shown in Fig. 2.1. The points P, Q, and R represent the boiling-points of a liquid at pressure p_P , p_Q , and p_R respectively.

When a liquid at boiling-point is heated further at constant pressure the additional heat supplied changes the phase of the substance from liquid to vapour; during this change of phase the pressure and temperature remain constant. The heat supplied is called latent heat of vaporization. It is found that

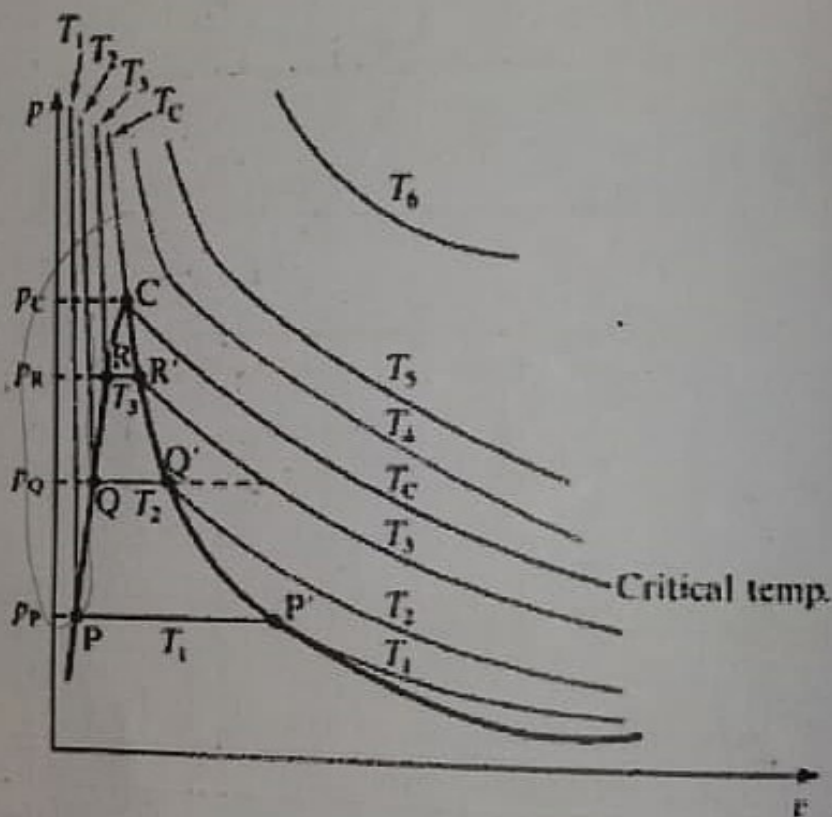


pressure, at the point at which vaporization is complete; hence a series of points such as P' , Q' , R' can be plotted and joined to form a line as shown in Fig. 2.2.

When the two curves already drawn are extended to higher pressures they form a continuous curve, thus forming a loop (see Fig. 2.3). The pressure at which the turning point occurs is called the *critical pressure* and the turning point itself is called the *critical point* (point C on Fig. 2.3). It can be seen that at the critical point the specific enthalpy of vaporization is zero. The substance existing at a state point inside the loop consists of a mixture of liquid and dry vapour and is known as a *wet vapour*. A *saturation state* is defined as a state at which a change of phase may occur without change of pressure or temperature. Hence the boiling-points P , Q , and R are saturation states, and a series of such boiling-points joined up is called the *saturated liquid line*. Similarly the points P' , Q' , and R' , at which the liquid is completely changed into vapour, are saturation states, and a series of such points joined up is called the *saturated vapour line*. The word 'saturation' as used here refers to energy saturation. For example, a slight addition of heat to a boiling liquid changes some of it into a vapour, and it is no longer a liquid but is now a wet vapour. Similarly when a substance just on the saturated vapour line is cooled slightly, droplets of liquid will begin to form, and the saturated vapour becomes a wet vapour. A saturated vapour is usually called dry saturated to emphasize the fact that no



2.4 Isothermals of a vapour plotted on a p-v diagram



the saturated liquid line and the saturated vapour line (e.g. between P and P', Q and Q', R and R'). Thus there is a corresponding *saturation temperature* for each *saturation pressure*. At pressure p_P the saturation temperature is T_1 , at pressure p_Q the saturation temperature is T_2 , and at pressure p_R the saturation temperature is T_3 . The critical temperature line T_C just touches the top of the loop at the critical point C.

When a dry saturated vapour is heated at constant pressure its temperature rises and it becomes *superheated*. The difference between the actual temperature of the superheated vapour and the saturation temperature at the pressure of the vapour is called the *degree of superheat*. For example, the vapour at P (Fig. 2.4) is superheated at p_Q and T_3 , and the degree of superheat is $T_3 - T_2$.

In section 1.5 it is stated that two independent properties are sufficient to define the state of a substance. Now between P and P', Q and Q', R and R', the temperature and specific volume are independent properties.

(Sometimes a wetness fraction is defined as the mass of liquid in 1 kg of the mixture, i.e. wetness fraction = $1 - x$.)

Note that for a dry saturated vapour $x = 1$, and that for a saturated liquid $x = 0$.

The distinction between a gas and a superheated vapour is not rigid. However, at very high degrees of superheat an isothermal line on the $p-v$ diagram tends to become a hyperbola (i.e. $pv = \text{constant}$). For example the isothermal T_6 on Fig. 2.4 is almost a hyperbola. An idealized substance called a *perfect gas* is assumed to have an equation of state $pv/T = \text{constant}$. It can be seen that when a line of constant temperature follows a hyperbolic law then the equation $pv/T = \text{constant}$ is satisfied. All substances tend to obey the equation $pv/T = \text{constant}$ at very high degrees of superheat. Substances which are thought of as gases (e.g. oxygen, nitrogen, hydrogen, etc.) are highly superheated at normal atmospheric conditions. For example, the critical temperatures of oxygen, nitrogen, and hydrogen are approximately -119 , -147 , and -240°C respectively. Substances normally existing as vapours must be raised to high temperatures before they begin to act as a perfect gas. For example, the critical temperatures of ammonia, sulphur dioxide, and water vapour are 130 , 157 , and 374.15°C respectively.

The working fluid in practical engineering problems is either a substance which is approximately a perfect gas, or a substance which exists mainly as liquid and vapour, such as steam and the refrigerant vapours. For the substances which approximate to perfect gases certain laws relating the properties can be assumed. For the substances in the liquid and vapour phases the properties are not related by definite laws, and values of the properties are determined empirically and tabulated in a convenient form.

2.2 The use of vapour tables

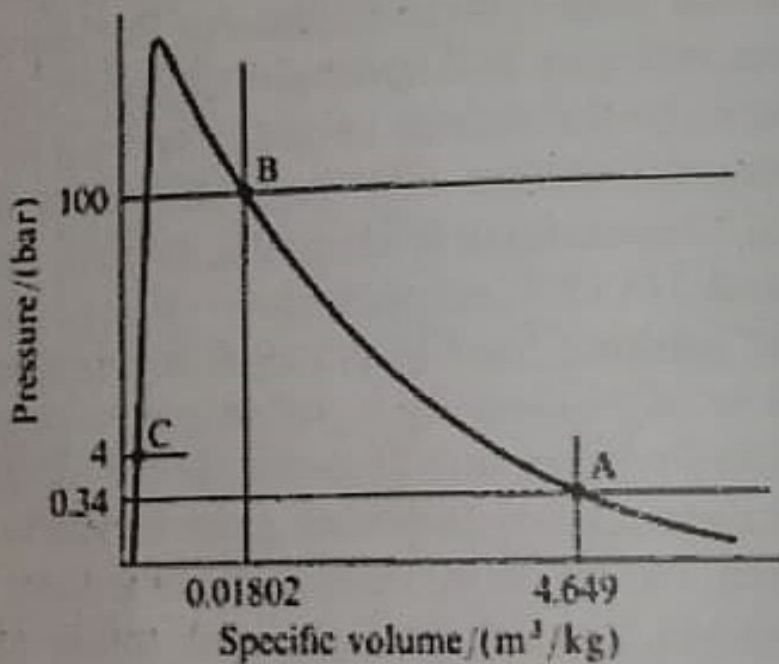
Tables are available for a wide variety of substances which normally exist in the vapour phase. The tables which will be used in this book are those arranged by Rogers and Mayhew (ref. 2.1), which are suitable for student use. For more comprehensive tables for steam, ref. 2.2 should be consulted. The tables of Rogers and Mayhew are mainly concerned with steam, but some properties of refrigerants are also given.

Saturation state properties

The saturation pressures and corresponding saturation temperatures of steam for pressures ranging from

at each pressure and corresponding saturation temperature. The suffix g is used to denote the dry saturated stage. A specimen row from the tables is given in Table 2.1. For example at 0.34 bar the saturation temperature is 311°C, the specific volume of dry saturated vapour, v_g , at this pressure is 4.649 m³/kg, the internal energy of dry saturated vapour, u_g , is 2472 kJ/kg, and the enthalpy of dry saturated vapour, h_g , is 2630 kJ/kg. The steam is in the state represented by point A on Fig. 2.5. At point B dry saturated steam at a pressure of 100 bar has a specific volume, v_g , of 0.01802 m³/kg, an internal energy, u_g , of 2545 kJ/kg and enthalpy, h_g , of 2725 kJ/kg.

Points
marked on a
p-v diagram for steam



The specific internal energy, specific enthalpy, and specific entropy of saturated liquid are also tabulated, the suffix f being used for this state. For example at 4 bar and the corresponding saturation temperature 160°C, saturated water has a specific internal energy, u_f , of 605 kJ/kg, and a specific enthalpy, h_f , of 605 kJ/kg. This state corresponds to point C on Fig. 2.5. The specific volume of saturated water, v_f , is tabulated in a separate table, but is usually negligibly small in comparison with the specific volume of saturated vapour, and its variation with temperature is very small; the liquid line on a $p-v$ diagram is very nearly coincident with the pressure axis in comparison with the width of the wet loop (see Fig. 2.5). As seen from Table 2.1, values of v_f vary from about 0.001 m³/kg at 0.01°C to about 0.001 m³/kg at 160°C; as the pressure approaches the critical value, the increase in v_f becomes more marked.

is represented by the area under the horizontal line on the $p-v$ diagram,

i.e. $W = -(v_g - v_f)p$

therefore

$$Q = (u_g - u_f) + p(v_g - v_f) \\ = (u_g + pv_g) - (u_f + pv_f)$$

From equation (1.9)

$$h = u + pv$$

therefore

$$Q = h_g - h_f = h_{fg}$$

The heat required to change a saturated liquid to a dry saturated vapour is called the specific enthalpy of vaporization, h_{fg} .

In the case of steam tables, the specific internal energy of saturated liquid is taken to be zero at the triple point (i.e. at 0.01°C and 0.006112 bar). Then since, from equation (1.9), $h = u + pv$, we have

$$h \text{ at } 0.01^\circ\text{C and } 0.006112 \text{ bar} = 0 + \frac{0.006112 \times 10^5 \times 0.0010002}{10^3}$$

where v_f at 0.01°C is $0.0010002 \text{ m}^3/\text{kg}$.

i.e. $h = 6.112 \times 10^{-4} \text{ kJ/kg}$

This is negligibly small and hence the zero for enthalpy may be taken at 0.01°C .

Note that at the other end of the pressure range tabulated in the first table the pressure of 221.2 bar is the critical pressure, 374.15°C is the critical temperature, and the specific enthalpy of vaporization, h_{fg} , is zero.

Properties of wet vapour

For a wet vapour the total volume of the mixture is given by the volume of liquid present plus the volume of dry vapour present. Therefore the specific volume is given by

$$v = \frac{\text{volume of liquid} + \text{volume of dry vapour}}{\text{total mass of wet vapour}}$$

Now for 1 kg of wet vapour there are $x\text{ kg}$ of dry vapour and $(1-x)\text{ kg}$ of liquid, where x is the dryness fraction as defined earlier. Hence,

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

The volume of the liquid is usually negligibly small compared to the volume

i.e. $h = h_f + xh_{fg}$
Similarly, the internal energy of a wet vapour is given by the internal energy of the liquid plus the internal energy of the dry vapour,

i.e. $u = (1 - x)u_f + xu_g$

or $u = u_f + x(u_g - u_f)$

Equation (2.4) can be expressed in a form similar to equation (2.3) and (2.4) are more convenient since u_g and u_f are tabulated. The difference, $u_g - u_f$, is not tabulated in ref. 2.1.

Example 2.1

Calculate the specific volume, specific enthalpy, and specific internal energy of wet steam at 18 bar, dryness fraction 0.9.

Solution

From equation (2.1)

$$v = xv_g$$

therefore

$$v = 0.9 \times 0.1104 = 0.0994 \text{ m}^3/\text{kg}$$

From equation (2.2)

$$h = h_f + xh_{fg}$$

therefore

$$h = 885 + (0.9 \times 1912) = 2605.8 \text{ kJ/kg}$$

From equation (2.3)

$$u = (1 - x)u_f + xu_g$$

therefore

$$u = (1 - 0.9)883 + (0.9 \times 2598) = 2426.5 \text{ kJ/kg}$$

(b) The steam is dry saturated

i.e. $u = u_g = 2600 \text{ kJ/kg}$

(c) The steam is wet at 10 bar with $x = 0.937$. Therefore

$$u = (1 - x)u_f + xu_g \quad \text{from equation (2.3)}$$

i.e. $u = (1 - 0.937)762 + (0.937 \times 2584) = 2470 \text{ kJ/kg}$

(d) The steam is superheated at 6 bar, 350°C ,

i.e. $u = 2881 \text{ kJ/kg}$

Example 2.7

Using the properties of ammonia given in ref. 2.1, calculate:

- (i) the enthalpy at 1.902 bar, dryness fraction 0.95;
- (ii) the enthalpy at 8.57 bar, 60°C .

Solution (i) From equation (2.2)

$$h = h_f + xh_{fg}$$

Therefore, at 1.902 bar,

$$\begin{aligned} h &= 89.8 + 0.95(1420.0 - 89.8) \\ &= 1353.5 \text{ kJ/kg} \end{aligned}$$

(ii) At 8.570 bar the saturation temperature is 20°C so the ammonia is superheated by $(60 - 20) = 40 \text{ K}$. It is therefore necessary to find the enthalpy,

i.e.
$$\begin{aligned} h &= 1462.6 + \frac{40}{50} \times (1597.2 - 1462.6) \\ &= 1570.3 \text{ kJ/kg} \end{aligned}$$

2.3 The perfect gas

The characteristic equation of state

imaginary ideal gas which obeys the law is called a *perfect gas*, and the equation, $pv/T = R$, is called the characteristic equation of state of a perfect gas. The constant, R , is called the *specific gas constant*. The units of R are N m/kg K or kJ/kg K . Each perfect gas has a different specific gas constant.

The characteristic equation is usually written

$$pv = RT \quad (2.5)$$

or for a mass, m , occupying a volume, V ,

$$pV = mRT \quad (2.6)$$

Another form of the characteristic equation can be derived using the *amount of substance* (sometimes called the mole). The amount of substance is defined by the 1971 General Conference of Weights and Measures (CGPM) as follows:

The amount of substance of a system is that quantity which contains as many elementary entities as there are atoms in 0.012 kg of carbon-12; the elementary entities must be specified and may be atoms, molecules, ions, electrons, or other particles, or specific groups of such particles.

The normal unit symbol used for the amount of substance is 'mol'. In SI it is convenient to use 'kmol'.

The mass of any substance per amount of substance is known as the *molar mass*, \bar{m} , i.e.

$$\bar{m} = \frac{m}{n} = \frac{32}{1} = 32 \text{ kg/kmol} \quad (2.7)$$

where m is the mass and n is the amount of substance. The normal units used for m and n are kg and kmol, therefore the normal unit for \bar{m} is kg/kmol.

Relative masses of the various elements are commonly used, and physicists and chemists agreed in 1960 to give the value of 12 to the isotope 12 of carbon (this led to the definition of the amount of substance as above). A scale is thus obtained of *relative atomic mass* or *relative molecular mass* (e.g. the relative atomic mass of the element oxygen is approximately 16; the relative molecular mass of oxygen gas, O_2 , is approximately 32).

The relative molecular mass is numerically equal to the molar mass, \bar{m} , but is dimensionless.

Substituting for m from equation (2.7) in equation (2.6) gives

$$pV = n\bar{m}RT \quad \text{or} \quad \bar{m}R = \frac{pV}{nT}$$

Now *Avogadro's hypothesis* states that the volume of 1 mol of any gas is the same as the volume of 1 mol of any other gas, when the gases are at the same temperature and pressure. Therefore V/n is the same for all gases at the same value of p and T . That is, the quantity pV/nT is a constant for all gases. This constant is called the *molar gas constant*, and is given the symbol, R ,

From equation (2.9), if the molar mass is known, e.g. for oxygen of molar mass 32 kg/kmol, the specific gas constant is

$$R = \frac{\bar{R}}{\bar{m}} = \frac{8314.5}{32} = 259.83 \text{ N m/kg K}$$

Example 2.8

A vessel of volume 0.2 m^3 contains nitrogen at 1.013 bar and 15°C . If 0.2 kg of nitrogen is now pumped into the vessel, calculate the new pressure if the vessel has returned to its initial temperature. The molar mass of nitrogen is 28 kg/kmol , and it may be assumed to be a perfect gas.

Solution From equation (2.9)

$$\text{Specific gas constant, } R = \frac{\bar{R}}{\bar{m}} = \frac{8314.5}{28} = 296.95 \text{ N m/kg K}$$

From equation (2.6), for the initial conditions

$$p_1 V_1 = m_1 R T_1$$

therefore

$$m_1 = \frac{p_1 V_1}{R T_1} = \frac{1.013 \times 10^5 \times 0.2}{296.95 \times 288} = 0.237 \text{ kg}$$

where $T_1 = 15 + 273 = 288 \text{ K}$

The mass of nitrogen added is 0.2 kg , hence $m_2 = 0.2 + 0.237 = 0.437 \text{ kg}$. Then from equation (2.6), for the final conditions

$$p_2 V_2 = m_2 R T_2$$

but $V_2 = V_1$ and $T_2 = T_1$, therefore

$$p_2 = \frac{m_2 R T_2}{V_2} = \frac{0.437 \times 296.95 \times 288}{10^5 \times 0.2}$$

i.e. $p_2 = 1.87 \text{ bar}$

therefore

$$R = \frac{p_1 V_1}{m T_1} = \frac{7 \times 10^5 \times 0.003}{0.01 \times 404} = 520 \text{ N m/kg K}$$

where $T_1 = 131 + 273 = 404 \text{ K}$.

Then from equation (2.9)

$$R = \frac{\bar{R}}{\bar{m}}$$

therefore

$$\bar{m} = \frac{\bar{R}}{R} = \frac{8314.5}{520} = 16 \text{ kg/kmol}$$

i.e. Molar mass = 16 kg/kmol

(ii) From equation (2.6)

$$p_2 V_2 = m R T_2$$

therefore

$$T_2 = \frac{p_2 V_2}{m R} = \frac{1 \times 10^5 \times 0.02}{0.01 \times 520} = 384.5 \text{ K}$$

i.e. Final temperature = $384.5 - 273 = 111.5^\circ\text{C}$

Specific heat capacity

The specific heat capacity of a solid or liquid is usually defined as the heat required to raise unit mass through one degree temperature rise. We have $dQ = mc dT$, where m is the mass, dT is the increase in temperature, and c is the specific heat capacity. For a gas there are an infinite number of ways in which heat may be added between two temperatures, and hence a gas could have an infinite number of specific heat capacities. However, only two specific heat capacities for gases are defined; the specific heat capacity at constant volume, c_v , and the specific heat capacity at constant pressure, c_p .

The definition must be restricted to reversible non-flow processes, since irreversibilities can cause temperature changes which are indistinguishable from those due to reversible heat and work quantities. Specific heat capacities can be introduced more rigorously as properties of a fluid. We have in the limit

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v \quad \text{and} \quad c_p = \left(\frac{\partial h}{\partial T} \right)_p$$

and

$$dQ = mc_v dT \text{ for a reversible non-flow process at constant } v$$

For a perfect gas the values of c_p and c_v are constant for any one set of pressures and temperatures. Hence integrating equations (2.10) and (2.11) have for a reversible constant pressure process

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

for a reversible constant volume process

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

For real gases, c_p and c_v vary with temperature, but for most practical purposes a suitable average value may be used.

Joule's law

Joule's law states that the internal energy of a perfect gas is a function of absolute temperature only, i.e. $u = f(T)$. To evaluate this function let unit mass of a perfect gas be heated at constant volume. From the non-flow energy equation, (1.5),

$$dQ + dW = du$$

Since the volume remains constant then no work is done, i.e. $dW = 0$, then

$$dQ = du$$

At constant volume for a perfect gas, from equation (2.11), for unit mass

$$dQ = c_v dT$$

Therefore, $dQ = du = c_v dT$, and integrating

$$u = c_v T + K$$

where K is a constant.

Joule's law states that $u = f(T)$, hence it follows that the internal energy varies linearly with absolute temperature. Internal energy can be made zero at any arbitrary reference temperature. For a perfect gas it can be assumed that $u = 0$ when $T = 0$, hence the constant K is zero,

i.e.

Specific

The gain of internal energy for a perfect gas between two states is always given by equation (2.16), for any process, reversible or irreversible. (2.16)

Relationship between the specific heat capacities

Let a perfect gas be heated at constant pressure from T_1 to T_2 . From the non-flow equation (1.4), $Q + W = (U_2 - U_1)$. Also, for a perfect gas, from equation (2.16), $U_2 - U_1 = mc_v(T_2 - T_1)$. Hence,

$$Q + W = mc_v(T_2 - T_1)$$

In a constant pressure process the work done is given by the pressure times the change in volume, i.e. $W = -p(V_2 - V_1)$. Then using equation (2.6), $pV_2 = mRT_2$ and $pV_1 = mRT_1$, we have

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

Therefore substituting

$$Q - mR(T_2 - T_1) = mc_v(T_2 - T_1)$$

therefore

$$Q = m(c_v + R)(T_2 - T_1)$$

But for a constant pressure process from equation (2.12)

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

Hence by equating the two expressions for the heat flow, Q , we have

$$m(c_v + R)(T_2 - T_1) = mc_p(T_2 - T_1)$$

therefore

$$c_v + R = c_p$$

or $c_p - c_v = R$

(2.17)

Specific enthalpy of a perfect gas

From equation (1.9) specific enthalpy $h = u + pv$

For mass, m , of a perfect gas

$$H = mc_p T$$

(Note that, since it has been assumed that $u = 0$ at $T = 0$, then $h = 0$)

Ratio of specific heat capacities

The ratio of the specific heat capacity at constant pressure to the specific heat capacity at constant volume is given the symbol γ (gamma),

i.e.
$$\gamma = \frac{c_p}{c_v}$$

Note that since $c_p - c_v = R$, from equation (2.17), it is clear that c_p is greater than c_v for any perfect gas. It follows therefore that the ratio, c_p/c_v , is always greater than unity. In general, γ is about 1.4 for diatomic gases

as carbon monoxide (CO), hydrogen (H_2), nitrogen (N_2), and oxygen (O_2). For monoatomic gases such as argon (A), and helium (He), γ is about 1.67. For triatomic gases such as carbon dioxide (CO_2), and sulphur dioxide (SO_2), γ is about 1.3. For some hydrocarbons the value of γ is quite low (e.g. for ethane (C_2H_6), $\gamma = 1.22$, and for isobutane (C_4H_{10}), $\gamma = 1.11$).

Some useful relationships between c_p , c_v , R , and γ can be derived from equation (2.17)

$$c_p - c_v = R$$

Dividing through by c_v

$$\frac{c_p}{c_v} - 1 = \frac{R}{c_v}$$

Therefore using equation (2.17), $\gamma = c_p/c_v$, then,

$$\gamma - 1 = \frac{R}{c_v}$$

therefore

$$c_v = \frac{R}{\gamma - 1}$$

Example 2.10 A perfect gas has specific heat capacities as follows:

$$c_p = 0.846 \text{ kJ/kg K} \quad \text{and} \quad c_v = 0.657 \text{ kJ/kg K}$$

Calculate the gas constant and the molar mass of the gas.

Solution From equation (2.17)

$$c_p - c_v = R$$

i.e. $R = 0.846 - 0.657 = 0.189 \text{ kJ/kg K} = 189 \text{ N m/kg K}$

From equation (2.9)

$$R = \frac{\bar{R}}{\bar{m}}$$

i.e. $\bar{m} = \frac{8314.5}{189} = 44 \text{ kg/kmol}$

Example 2.11

A perfect gas has a molar mass of 26 kg/kmol and a value of $\gamma = 1.26$. Calculate the heat rejected:

- (i) when unit mass of the gas is contained in a rigid vessel at 3 bar and 315°C, and is then cooled until the pressure falls to 1.5 bar;
- (ii) when unit mass flow rate of the gas enters a pipeline at 280°C, and flows steadily to the end of the pipe where the temperature is 20°C. Neglect changes in velocity of the gas in the pipeline.

Solution From equation (2.9)

$$R = \frac{\bar{R}}{\bar{m}} = \frac{8314.5}{26} = 319.8 \text{ N m/kg K}$$

From equation (2.21)

$$c_v = \frac{R}{(\gamma - 1)} = \frac{319.8}{10^3(1.26 - 1)} = 1.229 \text{ kJ/kg K}$$

Also from equation (2.20)

$$\frac{c_p}{c_v} = \gamma$$

therefore

$$c_p = \gamma c_v = 1.26 \times 1.229 = 1.548 \text{ kJ/kg K}$$

(i) The volume remains constant for the mass of gas present, and hence specific volume remains constant. From equation (2.5),

$$p_1 v_1 = RT_1 \quad \text{and} \quad p_2 v_2 = RT_2$$