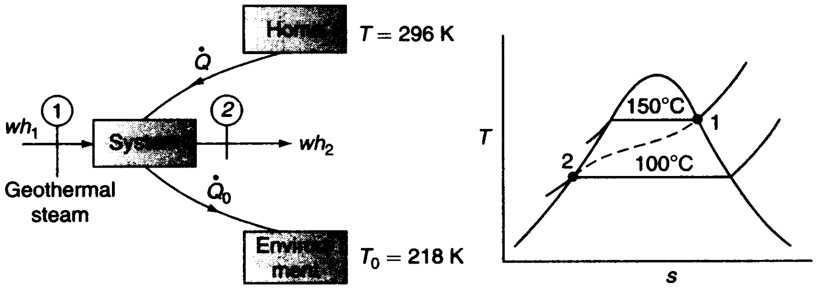
Solution The energy balance of the control volume as shown in Fig. Ex. 9.18 gives:

$$\dot{Q} + wh_1 = \dot{Q}_0 + wh_2$$



(a) (b)

Fig. Ex. 9.18

The entropy balance is:

$$\dot{S}_{\text{gen}} = \left[\frac{\dot{Q}_0}{T_0} + ws_2\right] - \left[\frac{\dot{Q}}{T} + ws_1\right]$$

where T is the temperature maintained in the homes.

Solving for $\dot{Q}$,

$$\dot{Q} = \frac{w\left[(h_1 - T_0 s_1) - (h_2 - T_0 s_2)\right] - T_0 \dot{S}_{\text{gen}}}{(T_0/T) - 1}$$

By second law, $\dot{S}_{\text{gen}} > 0$.

Therefore, for a given discharge state 2, the maximum $\dot{Q}$ would be

$$\dot{Q}_{\max} = \frac{w(b_1 - b_2)}{(T_0/T) - 1}$$

State-1: $T_1 = 150°\text{C} = 423$ K, saturated vapour

$h_1 = 2746.4$ kJ/kg

$s_1 = 6.8387$ kJ/kg K

State-2: $T_2 - 100°\text{C} = 373$ K, saturated liquid

$h_2 = 419.0$ kJ/kg

$s_2 = 1.3071$ kJ/kg K

So, since $T_0 = 318$ K,

$b_1 = h_1 - T_0 s_1 = 2746.4 - 318 \times 6.8387 = 571.7$ kJ/kg

$b_2 = h_2 - T_0 s_2 = 419.0 - 318 \times 1.3071 = 3.3$ kJ/kg

$$\dot{Q}_{\max} = \frac{50 \times (571.7 - 3.3)}{(318/296) - 1} = 3.82 \times 10^5 \text{ kJ/h} = 106 \text{ kW}$$ *Ans.*

Review Questions

9.1 What is a pure substance?

9.2 What are saturation states?

9.3 What do you understand by triple point? Give the pressure and temperature of water at its triple point.

9.4 What is the critical state? Explain the terms critical pressure, critical temperature and critical volume of water?

9.5 What is normal boiling point.

9.6 Draw the phase equilibrium diagram on $p-v$ coordinates for a substance which shrinks in volume on melting and then for a substance which expands in volume on melting. Indicate thereon the relevant constant property lines.

9.7 Draw the phase equilibrium diagram for a purc substance on $p-T$ coordinates. Why does the fusion line for water have negative slope?

9.8 Draw the phase equilibrium diagram for a pure substance on $T-s$ plot with relevant constant property lines.

9.9 Draw the phase equilibrium diagram for a pure substance on $h-s$ plot with relevant constant property lines.

9.10 Why do the isobars on Mollier diagram diverge from one another?

9.11 Why do isotherms on Mollier diagram become horizontal in the superheated region at low pressures?

9.12 What do you understand by the degree of superheat and the degree of subcooling?

9.13 What is quality of steam? What are the different methods of measurement of quality?

9.14 Why cannot a throttling calorimeter measure the quality if the steam is very wet? How is the quality measured then?

9.15 What is the principle of operation of an electrical calorimeter?

Problems

9.1 Complete the following table of properties for 1 kg of water (liquid, vapour or mixture).

	p (bar)	t (°C)	v (m^3/kg)	x (%)	Super-heat (°C)	h (kJ/kg)	s (kJ/kg K)
(a)	—	35	25.22	—	—	—	—
(b)	—	—	0.001044	—	—	419.04	—
(c)	—	212.42	—	90	—	—	—
(d)	1	—	—	—	—	—	6.104
(e)	10	320	—	—	—	—	—
(f)	5	—	0.4646	—	—	—	—
(g)	4	—	0.4400	—	—	—	—
(h)	—	500	—	—	—	3445.3	—
(i)	20	—	—	—	50	—	—
(j)	15	—	—	—	—	—	7.2690

9.2 (a) A rigid vessel of volume 0.86 m^3 contains 1 kg of steam at a pressure of 2 bar. Evaluate the specific volume, temperature, dryness fraction, internal energy, enthalpy, and entropy of steam.

(b) The steam is heated to raise its temperature to 150°C. Show the process on a sketch of the $p-v$ diagram, and evaluate the pressure, increase in enthalpy, increase in internal energy, increase in entropy of steam, and the heat transfer. Evaluate also the pressure at which the steam becomes dry saturated.

Ans. (a) 0.86 m^3/kg, 120.23°C, 0.97, 2468.54 kJ/kg, 2640.54 kJ/kg, 6.9592 kJ/kg K
(b) 2.3 bar, 126 kJ/kg, 106.6 kJ/kg, 0.2598 kJ/kg K, 106.6 kJ/K

9.3 Ten kg of water at 45°C is heated at a contant pressure of 10 bar until it becomes superheated vapour at 300°C. Find the changes in volume, enthalpy, internal energy and entropy.

Ans. 2.569 m^3, 28627.5 kJ, 26047.6 kJ, 64.842 kJ/K

9.4 Water at 40°C is continuously sprayed into a pipeline carrying 5 tonnes of steam at 5 bar, 300°C per hour. At a section downstream where the pressure is 3 bar, the quality is to be 95%. Find the rate of water spray in kg/h. *Ans.* 912.67 kg/h

9.5 A rigid vessel contains 1 kg of a mixture of saturated water and saturated steam at a pressure of 0.15 MPa. When the mixture is heated, the state passes through the critical point. Determine (a) the volume of vessel (b) the mass of liquid and of vapour in the vessel initially, (c) the temperature of the mixture when the pressure has risen to 3 MPa, and (d) the heat transfer required to produce the final state (c).

Ans. (a) 0.003155 m^3, (b) 0.9982 kg, 0.0018 kg, (c) 233.9°C, (d) 581.46 kJ/kg

9.6 A rigid closed tank of volume 3 m^3 contains 5 kg of wet steam at a pressure of 200 kPa. The tank is heated until the steam becomes dry saturated. Determine the final pressure and the heat transfer to the tank. *Ans.* 304 kPa, 3346 kJ

9.7 Steam flows through a small turbine at the rate of 5000 kg/h entering at 15 bar, 300°C and leaving at 0.1 bar with 4% moisture. The steam enters at 80 m/s at a point 3 m above the discharge and leaves at 40 m/s. Compute the shaft power assuming that the device is adiabatic but considering kinetic and potential energy changes. How much error would be made if these terms were neglected? Calculate the diameters of the inlet and discharge tubes.

Ans. 765.6 kW, 0.44%, 6.11 cm, 78.9 cm

9.8 A sample of steam from a boiler drum at 3 MPa is put through a throttling calorimeter in which the pressure and temperature are found to be 0.1 MPa, 120°C. Find the quality of the sample taken from the boiler. *Ans.* 0.951

9.9 It is desired to measure the quality of wet steam at 0.5 MPa. The quality of steam is expected to be not more than 0.9.

(a) Explain why a throttling calorimeter to atmospheric pressure will not serve the purpose.

(b) Will the use of a separating calorimeter, ahead of the throttling calorimeter, serve the purpose, if at best 5°C of superheat is desirable at the end of throttling? What is the minimum dryness fraction required at the exit of the separating calorimeter to satisfy this condition? *Ans.* 0.97

9.10 The following observations were recorded in an experiment with a combined separating and throttling calorimeter:

Pressure in the steam main—15 bar
Mass of water drained from the separator—0.55 kg
Mass of steam condensed after passing through the throttle valve —4.20 kg
Pressure and temperature after throttling—1 bar, 120°C

Evaluate the dryness fraction of the steam in the main, and state with reasons, whether the throttling calorimeter alone could have been used for this test. *Ans.* 0.85

9.11 Steam from an engine exhaust at 1.25 bar flows steadily through an electric calorimeter and comes out at 1 bar, 130°C. The calorimeter has two 1 kW heaters and the flow is measured to be 3.4 kg in 5 min. Find the quality in the engine exhaust. For the same mass flow and pressures, what is the maximum moisture that can be determined if the outlet temperature is at least 105°C?

Ans. 0.944, 0.921

9.12 Steam expands isentropically in a nozzle from 1 MPa, 250°C to 10 kPa. The steam flow rate is 1 kg/s. Find the velocity of steam at the exit from the nozzle, and the exit area of the nozzle. Neglect the velocity of steam at the inlet to the nozzle.

The exhaust steam from the nozzle flows into a condenser and flows out as saturated water. The cooling water enters the condenser at 25°C and leaves at 35°C. Determine the mass flow rate of cooling water.

Ans. 1224 m/s, 0.0101 m^2. 47.81 kg/s

9.13 A reversible polytropic process, begins with steam at $p_1 = 10$ bar, $t_1 = 200$°C, and ends with $p_2 =$ 1 bar. The exponent n has the value 1.15. Find the final specific volume, the final temperature, and the heat transferred per kg of fluid.

9.14 Two streams of steam, one at 2 MPa, 300°C and the other at 2 MPa, 400°C, mix in a steady flow adiabatic process. The rates of flow of the two streams are 3 kg/min and 2 kg/min respectively. Evaluate the final temperature of the emerging stream, if there is no pressure drop due to the mixing process. What would be the rate of increase in the entropy of the universe? This stream with a negligible velocity now expands adiabatically in a nozzle to a pressure of 1 kPa. Determine the exit velocity of the stream and the exit area of the nozzle.

Ans. 340°C, 0.042 kJ/K min, 1530 m/s, 53.77 cm^2

9.15 Boiler steam at 8 bar, 250°C, reaches the engine control valve through a pipeline at 7 bar, 200°C. It is throttled to 5 bar before expanding in the engine to 0.1 bar, 0.9 dry. Determine per kg of steam (a) the heat loss in the pipeline, (b) the temperature drop in passing through the throttle valve, (c) the work output of the engine, (d) the entropy change due to throttling and (e) the entropy change in passing through the engine.

Ans. (a) 105.3 kJ/kg, (b) 5°C, (c) 499.35 kJ/kg, (d) 0.1433 kJ/kg K, (e) 0.3657 kJ/kg K

9.16 Tank A (Fig. P9.16) has a volume of 0.1 m^3 and contains steam at 200°C, 10% liquid and 90% vapour by volume, while tank *B* is evacuated. The valve is then opened, and the tanks eventually come to the same pressure, which is found to be 4 bar. During this process, heat is transferred such that the steam remains at 200°C. What is the volume of tank *B*?

Ans. 4.89 m^3

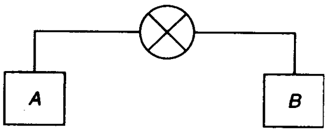


Fig. P9.16

9.17 Calculate the amount of heat which enters or leaves 1 kg of steam initially at 0.5 MPa and 250°C, when it undergoes the following processes:

(a) It is confined by a piston in a cylinder and is compressed to 1 MPa and 300°C as the piston does 200 kJ of work on the steam.

(b) It passes in steady flow through a device and leaves at 1 MPa and 300°C while, per kg of steam flowing through it, a shaft puts in 200 kJ of work. Changes in K.E. and P.E. are negligible.

(c) It flows into an evacuated rigid container from a large source which is maintained at the initial condition of the steam. Then 200 kJ of shaft work is transferred to the steam, so that its final condition is 1 MPa and 300°C.

Ans. (a) – 130 kJ (b) – 109 kJ, and (c) – 367 kJ

9.18 A sample of wet steam from a steam main flows steadily through a partially open valve into a pipeline in which is fitted an electric coil. The valve and the pipeline are well insulated. The steam mass flow rates 0.008 kg/s while the coil takes 3.91 amperes at 230 volts. The main pressure is 4 bar, and the pressure and temperature of the steam downstream of the coil are 2 bar and 160°C respectively. Steam velocities may be assumed to be negligible.

(a) Evaluate the quality of steam in the main.

(b) State, with reasons, whether an insulated throttling calorimeter could be used for this test.

Ans. (a) 0.97, (b) not suitable

9.19 Two insulated tanks, *A* and *B*, are connected by a valve. Tank *A* has a volume of 0.70 m^3 and contains steam at 1.5 bar, 200°C. Tank *B* has a volume of 0.35 m^3 and contains steam at 6 bar with a quality of 90%. The valve is then opened, and the two tanks come to a uniform state. If there is no heat transfer during the process, what is the final pressure? Compute the entropy change of the universe.

Ans. 322.6 KPa, 0.1985 kJ/K

9.20 A spherical aluminium vessel has an inside diameter of 0.3 m and a 0.62 cm thick wall. The vessel contains water at 25°C with a quality of 1%. The vessel is then heated until the water inside is saturated vapour. Considering the vessel and water together as a system, calculate the heat transfer during this process. The density of aluminium is 2.7 g/cm^3 and its specific heat is 0.896 kJ/kg K.

Ans. 2682.82 kJ

9.21 Steam at 10 bar, 250°C flowing with negligible velocity at the rate of 3 kg/min mixes adiabatically with steam at 10 Bar, 0.75 quality, flowing also with negligible velocity at the rate of 5 kg/min. The combined stream of steam is throttled to 5 bar and then expanded isentropically in a nozzle to 2 bar. Determine (a) the state of steam after mixing, (b) the steam after throttling, (c) the increase in entropy due to throttling, (d) the velocity of steam at the exit from the nozzle, and (e) the exit area of the nozzle. Neglect the K.E. of steam at the inlet to the nozzle.

Ans. (a) 10 bar, 0.975 dry, (b) 5 bar, 0.894 dry, (c) 0.2669 kJ/kg K, (d) 540 m/s, (e) 1.864 cm^2

9.22 Steam of 65 bar, 400°C leaves the boiler to enter a steam turbine fitted with a throttle governor. At a reduced load, as the governor takes action, the pressure of steam is reduced to 59 bar by throttling before it is admitted to the turbine. Evaluate the availabilities of steam before and after the throttling process and the irreversibility due to it.

Ans. I = 21 kJ/kg

9.23 A mass of wet steam at temperature 165°C is expanded at constant quality 0.8 to pressure 3 bar. It is then heated at constant pressure to a degree of superheat of 66.5°C. Find the enthalpy and entropy changes during expansion and during heating. Draw the *T–s* and *h–s* diagrams.
Ans. – 59 kJ/kg, 0.163 kJ/kg K during expansion and 676 kJ/kg, 1.588 kJ/kg K during heating

9.24 Steam enters a turbine at a pressure of 100 bar and a temperature of 400°C. At the exit of the turbine the pressure is 1 bar and the entropy is 0.6 J/g K greater than that at inlet. The process is adiabatic and changes in KE and PE may be neglected. Find the work done by the steam in J/g. What is the mass flow rate of steam required to produce a power output of 1 kW? *Ans.* 625 J/g, 1.6 kg/s

9.25 One kg of steam in a closed system undergoes a thermodynamic cycle composed the following reversible processes: (1–2) The steam initially at 10 bar, 40% quality is heated at constant volume until the pressure rises to 35 bar; (2–3). It is then expanded isothermally to 10 bar; (3–1). It is finally cooled at constant pressure back to its initial state. Sketch the cycle on *T–s* coordinates, and calculate the work done, the heat transferred, and the change of entropy for each of the three processes. What is the thermal efficiency of the cycle?
Ans. 0; 1364 kJ; 2.781 kJ/K, 367.5 kJ; 404.6 kJ; 0.639 kJ/K; – 209.1 kJ; – 1611 kJ; – 3.419 kJ/K 8.93%

9.26 Determine the exergy per unit mass for the steady flow of each of the following:
(a) steam at 1.5 MPa, 500°C
(b) air at 1.5 MPa, 500°C
(c) water at 4MPa, 300K
(d) air at 4 MPa, 300 K
(e) air at 1.5 MPa, 300 K
Ans. (a) 1220 kJ/kg, (b) 424 kJ/kg, (c) 3.85 kJ/kg; (d) 316 kJ/kg, (e) 232 kJ/kg

9.27 A liquid (c_p = 6 kJ/kg K) is heated at an approximately constant pressure from 298 K to 90°C by passing it through tubes immersed in a furnace. The mass flow rate is 0.2 kg/s. Determine (a) the heating load in kW. (b) the exergy production rate in kW corresponding to the temperature rise of the fluid.
Ans. (a) 78 kW, (b) 7.44 kW

9.28 A flow of hot water at 80°C is used to heat cold water from 20°C to 45°C in a heat exchanger. The cold water flows at the rate of 2 kg/s. When operated in parallel mode, the exit temperature of hot water stream cannot be less than 55°C, while in the counterflow mode, it can be as low as 30°C. Assuming the surroundings are at 300 K, compare the second law efficiencies for the two modes of operation.

9.29 Water at 90°C is flowing in a pipe. The pressure of the water is 3 bar, the mass flow rate is 10 kg/s, the velocity is 0.5 m/s and the elevation of the pipe is 200 m above the exit plane of the pipeline (ground level). Compute (a) the thermal exergy flux, (b) the pressure exergy flux, (c) the exergy flux from KE, (d) the exergy flux from PE, (e) total exergy flux of the stream.
Ans. (a) 260 kW, (b) 2.07 kW, (c) 1.25×10^{-3} kW, (d) 19.6 kW, (e) 282 kW

9.30 A cylinder fitted with a piston contains 2 kg steam at 500 kPa, 400°C. Find the entropy change and the work done when the steam expands to a final pressure of 200 kPa in each of the following ways: (a) adiabatically and reversibly, (b) adiabatically and irreversibly to an equilibrium temperature of 300°C.
Ans. (a) 0, 386.7 kJ, (b) 0.1976 kJ/K, 309.4 kJ

9.31 Steam expands isentropically in a nozzle from 1 MPa, 250°C to 10 kPa. The steam flow rate is 1 kg/s. Neglecting the KE of steam at inlet to the nozzle, find the velocity of steam at exit from the nozzle and the exit area of the nozzle.
Ans. 1223 m/s, 100 cm^2

9.32 Hot helium gas at 800°C is supplied to a steam generator and is cooled to 450°C while serving as a heat source for the generation of steam. Water enters the steam generator at 200 bar, 250°C and leaves as superheated steam at 200 bar, 500°C. The temperature of the surroundings is 27°C. For 1 kg helium, determine (a) the maximum work that could be produced by the heat removed from helium, (b) the mass of steam generated per kg of helium, (c) the actual work done in the steam cycle per kg of helium, (d) the net change for entropy of the universe, and (e) the irreversibility. Take the average c_p for helium as 5.1926 kJ/kg K and the properties of water at inlet to the steam generator as those of saturated water at 250°C.
Ans. (a) 1202.4 kJ/kg He, (b) 0.844 kg H_2O/kg He (c) 969.9 kJ/kg He, (d) 0.775 kJ/(kg He-K), (e) 232.5 kJ/kg He

CHAPTER 10

Properties of Gases and Gas Mixtures

10.1 AVOGADRO'S LAW

A mole of a substance has a mass numerically equal to the molecular weight of the substance.

One g mol of oxygen has a mass of 32 g, 1 kg mol of oxygen has a mass of 32 kg, 1 kg mol of nitrogen has a mass of 28 kg, and so on.

Avogadro's law states that the volume of a g mol of all gases at the pressure of 760 mm Hg and temperature of 0°C is the same, and is equal to 22.4 litres. Therefore, 1 g mole of a gas has a volume of 22.4×10^3 cm^3 and 1 kg mol of a gas has a volume of 22.4 m^3 at normal temperature and pressure (N.T.P.).

For a certain gas, if m is its mass in kg, and μ its molecular weight, then the number of kg moles of the gas, n, would be given by

$$n = \frac{m \text{ kg}}{\mu \dfrac{\text{kg}}{\text{kg mol}}} = \frac{m}{\mu} \text{ kg moles}$$

The molar volume, v, is given by

$$v = \frac{V}{n} \ m^3/\text{kg mol}$$

where V is the total volume of the gas in m^3.

10.2 EQUATION OF STATE OF A GAS

The functional relationship among the properties, pressure p, molar or specific volume v, and temperature T, is known as an *equation of state,* which may be expressed in the form,

$$f(p, v, T) = 0$$

If two of these properties of a gas are known, the third can be evaluated from the equation of state.

It was discussed in Chapter 2 that gas is the best-behaved thermometric substance because of the fact that the ratio of pressure p of a gas at any temperature to pressure p_t of the same gas at the triple point, as both p and p_t approach zero, approaches a value independent of the nature of the gas. The ideal gas temperature T of the system at whose temperature the gas exerts pressure p (Article 2.5) was defined as

$$T = 273.16 \lim_{p_t \to 0} \frac{p}{p_t} \qquad \text{(Const. } V)$$

$$T = 273.16 \lim_{p_p \to 0} \frac{V}{V_t} \qquad \text{(Const. } p)$$

The relation between pv and p of a gas may be expressed by means of a power series of the form

$$pv = A(1 + B'p + C'p^2 + \dots) \qquad (10.1)$$

where A, B', C', etc., depend on the temperature and nature of the gas.

A fundamental property of gases is that $\lim_{p\to 0}(pv)$ is independent of the nature of the gas and depends only on T. This is shown in Fig. 10.1, where the product pv is plotted against p for four different gases in the bulb (nitrogen, air, hydrogen, and oxygen) at the boiling point of sulphur, at steam point and at the triple point of water. In each case, it is seen that as $p \to 0$, pv approaches the same value for all gases at the same temperature. From Eq. (10.1)

$$\lim_{p\to 0} pv = A$$

Therefore, the constant A is a function of temperature only and independent of the nature of the gas.

$$\lim \frac{p}{p_t}\,(\text{Const. } V) = \lim \frac{pV}{p_tV} = \frac{\lim pv}{(pv)_t} = \frac{A}{A_t}$$

$$\lim \frac{V}{V_t}\,(\text{Const. } p) = \lim \frac{pV}{pV_t} = \frac{\lim pv}{\lim (pv)_t} = \frac{A}{A_t}$$

The ideal gas temperature T, is thus

$$T = 273.16\,\frac{\lim(pv)}{\lim(pv)_t}$$

$$\therefore \quad \lim(pv) = \left[\frac{\lim(pv)_t}{273.16}\right]T$$

The term within bracket is called the *universal gas constant* and is denoted by $\bar{R}$. Thus,

$$\bar{R} = \frac{\lim(pv)_t}{273.16} \qquad (10.2)$$

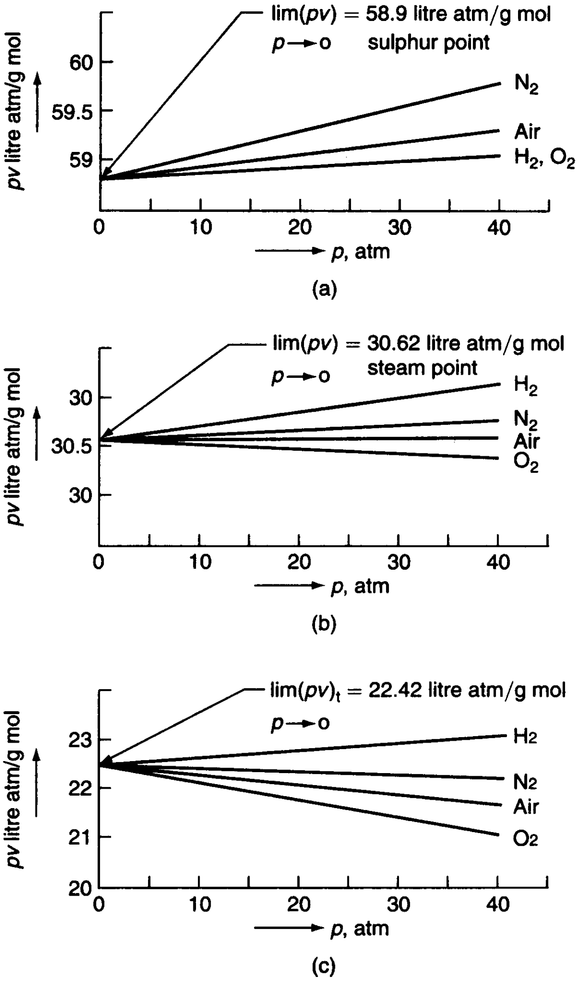


Fig. 10.1 *For any gas* $\lim_{p\to 0}(pv)_T$ *is independent of the nature of the gas and depends only on T*

The value obtained for $\lim_{p\to 0}(pv)_t$ is 22.4 $\dfrac{\text{litre-atm}}{\text{g mol}}$

$$\therefore \quad \bar{R} = \frac{22.4}{273.16} = 0.083\,\frac{\text{litre-atm}}{\text{g mol K}}$$

The equation of state of a gas is thus

$$\lim_{p\to 0} p\bar{v} = \bar{R}T \qquad (10.3)$$

where $\bar{v}$ is the molar volume.

10.3 IDEAL GAS

A hypothetical gas which obeys the law $p\bar{v} = \bar{R}T$ at all pressures and temperatures is called an *ideal gas.*

Real gases do not conform to this equation of state with complete accuracy. As $p \to 0$, or $T \to \infty$, the real gas approaches the ideal gas behaviour. In the equation $p\bar{v} = \bar{R}T$, as $T \to 0$, i.e. $t \to -273.15°\text{C}$, if $\bar{v}$ remains constant, $p \to 0$, or if p remains constant $\bar{v} \to 0$. Since negative volume or negative pressure is inconceivable, the lowest possible temperature is 0 K or – 273.15°C. T is, therefore, known as the absolute temperature.

There is no permanent or perfect gas. At atmospheric condition only, these gases exist in the gaseous state. They are subject to liquefication or solidification, as the temperatures and pressures are sufficiently lowered.

From Avogadro's law, when $p = 760$ mm Hg $= 1.013 \times 10^5$ N/m^2, $T = 273.15$ K, and $\bar{v} = 22.4$ m^3/kg mol

$$\bar{R} = \frac{1.013 \cdot 10^5 \cdot 22.4}{273.15}$$

$$= 8314.3 \text{ Nm/kg mol K}$$

$$= 8.3143 \text{ kJ/kg mol K}$$

Since $\bar{v} = V/n$, where V is the total volume and n the number of moles of the gas, the equation of state for an ideal gas may be written as

$$pV = n\bar{R}T \tag{10.4}$$

Also
$$n = \frac{m}{\mu}$$

where μ is the molecular weight

$\therefore$
$$pV = m \cdot \frac{\bar{R}}{\mu} \cdot T$$

or
$$pV = mRT \tag{10.5}$$

where
$$R = \text{characteristic gas constant} = \frac{\bar{R}}{\mu} \tag{10.6}$$

For oxygen, e.g.,
$$R_{o2} = \frac{8.3143}{32} = 0.2598 \text{ kJ/kg K}$$

For air,
$$R_{\text{air}} = \frac{8.3143}{28.96} = 0.287 \text{ kJ/kg K}$$

There are 6.023×10^{23} molecules in a g mol of a substance.
This is known as Avogadro's number (A).

$\therefore$
$$A = 6.023 \times 10^{26} \text{ molecules/kg mol}$$

In n kg moles of gas, the total number of molecules, N, are

$$N = nA$$

or
$$n = N/A$$

$$pV = N\frac{\bar{R}}{A}T = NKT \tag{10.7}$$

where K = Boltzmann constant
$$= \frac{\bar{R}}{A} = \frac{8314.3}{6.023 \times 10^{26}} = 1.38 \times 10^{-23} \text{ J/molecule K}$$

Therefore, the equation of state of an ideal gas is given by

$$pV = mRT$$

$$= n\bar{R}T$$

$$= NKT$$

10.3.1 Specific Heats, Internal Energy, and Enthalpy of an Ideal Gas

An ideal gas not only satisfies the equation of state $pv = RT$, but its *specific heats are constant* also. For real gases, these vary appreciably with temperature, and little with pressure.

The properties of a substance are related by

$$T\mathrm{d}s = \mathrm{d}u + p\mathrm{d}v$$

or

$$\mathrm{d}s = \frac{du}{T} + \frac{p}{T}\,\mathrm{d}v \tag{10.8}$$

The internal energy u is assumed to be a function of T and v, i.e.

$$u = f(T, v)$$

or

$$\mathrm{d}u = \left(\frac{\partial u}{\partial T}\right)_{\mathrm{v}} \mathrm{d}T + \left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} \mathrm{d}v \tag{10.9}$$

From Eqs (10.8) and (10.9)

$$\mathrm{d}s = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_{\mathrm{v}} \mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} + p\right] \mathrm{d}v \tag{10.10}$$

Again, let

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

$$\mathrm{d}s = \left(\frac{\partial s}{\partial T}\right)_{\mathrm{v}} \mathrm{d}T + \left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}} \mathrm{d}v \tag{10.11}$$

Comparing Eqs (10.10) and (10.11)

$$\left(\frac{\partial s}{\partial T}\right)_{\mathrm{v}} = \frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_{\mathrm{v}} \tag{10.12}$$

$$\left(\frac{\partial s}{\partial v}\right)_{\mathrm{T}} = \frac{1}{T}\left[\left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} + p\right] \tag{10.13}$$

Differentiating Eq. (10.12) with respect to v when T is constant

$$\frac{\partial^2 s}{\partial T \partial v} = \frac{1}{T}\frac{\partial^2 u}{\partial T \partial v} \tag{10.14}$$

Differentiating Eq. (10.13) with respect to T when v is constant

$$\frac{\partial^2 s}{\partial v\, \partial T} = \frac{1}{T}\frac{\partial^2 u}{\partial v \partial T} + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_{\mathrm{v}} - \frac{1}{T^2}\left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} - \frac{p}{T^2} \tag{10.15}$$

From Eqs (10.14) and (10.15)

$$\frac{1}{T}\frac{\partial^2 u}{\partial T \cdot \partial v} = \frac{1}{T}\frac{\partial^2 u}{\partial v \cdot \partial T} + \frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_{\mathrm{v}} - \frac{1}{T^2}\left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} - \frac{p}{T^2}$$

or

$$\left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} + p = T\left(\frac{\partial p}{\partial T}\right)_{\mathrm{v}} \tag{10.16}$$

For an ideal gas

$$pv = RT$$

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

$$\left(\frac{\partial p}{\partial T}\right)_{\mathrm{v}} = \frac{R}{v} = \frac{p}{T} \tag{10.17}$$

From Eqs (10.16) and (10.17)

$$\left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} = 0 \tag{10.18}$$

Therefore, u does not change when v changes at constant temperature.

Similarly, if $u = f(T, p)$, it can be shown that $\left(\frac{\partial u}{\partial p}\right)_{\mathrm{T}} = 0$. Therefore, u does not change with p either, when T remains constant.

u does not change unless T changes.

Then

$$u = f(T) \tag{10.19}$$

only for an ideal gas. This is known as *Joule's law.*

If

$$u = f(T, v)$$

$$\mathrm{d}u = \left(\frac{\partial u}{\partial T}\right)_{\mathrm{v}} \mathrm{d}T + \left(\frac{\partial u}{\partial v}\right)_{\mathrm{T}} \mathrm{d}v$$

Since the last term is zero by Eq. (10.18), and by definition

$$c_{\mathrm{v}} = \left(\frac{\partial u}{\partial T}\right)_{\mathrm{v}}$$

$$\mathrm{d}u = c_{\mathrm{v}}\, \mathrm{d}T \tag{10.20}$$

The equation $\mathrm{d}u = c_{\mathrm{v}}\, \mathrm{d}T$ holds good for an ideal gas for any process, whereas for any other substance it is true for a constant volume process only.

Since c_{v} is constant for an ideal gas,

$$\Delta u = c_{\mathrm{v}}\, \Delta T$$

The enthalpy of any substance is given by

$$h = u + pv$$

For an ideal gas

$$h = u + RT$$

Therefore

$$h = f(T) \tag{10.21}$$

only for an ideal gas

Now

$$\mathrm{d}h = \mathrm{d}u + R\mathrm{d}T$$

Since R is a constant

$$\begin{aligned}\Delta h &= \Delta u + R\Delta T \\ &= c_{\mathrm{v}}\, \Delta T + R\Delta T \\ &= (c_{\mathrm{v}} + R)\, \Delta T\end{aligned} \tag{10.22}$$

Since h is a function of T only, and by definition

$$c_{\mathrm{p}} = \left(\frac{\partial h}{\partial T}\right)_{\mathrm{p}}$$

$$\mathrm{d}h = c_{\mathrm{p}}\, \mathrm{d}T \tag{10.23}$$

or

$$\Delta h = c_{\mathrm{p}}\, \Delta T \tag{10.24}$$

From Eqs (10.22) and (10.23)

$$c_p = c_v + R$$

or

$$c_p - c_v = R \tag{10.25}$$

The Eq. $dh = c_p\, dT$ holds good for an ideal gas, even when pressure changes, but for any other substance, this is true only for a constant pressure change.

The ratio of c_p/c_v is of importance in ideal gas computations, and is designated by the symbol γ, i.e.

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

or

$$c_p = \gamma\, c_v$$

From Eq. (10.25)

$$(\gamma - 1)\, c_v = R$$

and

$$\left.\begin{aligned} c_v &= \frac{R}{\gamma - 1} \\ c_p &= \frac{\gamma R}{\gamma - 1} \end{aligned}\right\} \text{kJ/kg K} \tag{10.26}$$

If $R = \dfrac{\bar{R}}{\mu}$ is substituted in Eq. (10.26)

and

$$\left.\begin{aligned} \bar{c}_v &= \mu c_v = (c_v)_{\text{mol}} = \frac{\bar{R}}{\gamma - 1} \\ \bar{c}_p &= \mu c_p = (c_p)_{\text{mol}} = \frac{\gamma \bar{R}}{\gamma - 1} \end{aligned}\right\} \text{kJ/(kg mol)(K)} \tag{10.27}$$

$\bar{c}_v$ and $\bar{c}_p$ are the *molar or molal specific heats* at constant volume and at constant pressure respectively.

It can be shown by the classical kinetic theory of gases that the values of γ are 5/3 for monatomic gases and 7/5 for diatomic gases. When the gas molecule contains more than two atoms (i.e. for polyatomic gases) the value of γ may be taken approximately as 4/3. The minimum value of γ is thus 1 and the maximum is 1.67.

The value of γ thus depends only on the molecular structure of the gas, i.e. whether the gas is monatomic, diatomic or polyatomic having one, two or more atoms in a molecule. It may be noted that c_p and c_v of an ideal gas depend only on γ and R, i.e. the number of atoms in a molecule and the molecular weight of the gas. They are independent of temperature or pressure of the gas.

10.3.2 Entropy Change of an Ideal Gas

From the general property relations

$$T ds = du + p dv$$

$$T ds = dh - v dp$$

and for an ideal gas, $du = c_v\, dT$, $dh = c_p\, dT$, and $pv = RT$, the entropy change between any two states 1 and 2 may be computed as given below

$$ds = \frac{du}{T} + \frac{p}{T}\, dv$$

$$= c_v \frac{dT}{T} + R \frac{dv}{v}$$

$$\therefore \quad s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \tag{10.28}$$

Also
$$ds = \frac{dh}{T} - \frac{v}{T}\,dp = c_p\,\frac{dT}{T} - R\,\frac{dp}{p}$$

or
$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1} \qquad (10.29)$$

Since $R = c_p - c_v$, Eq. (10.29) may be written as
$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - c_p \ln \frac{p_2}{p_1} + c_v \ln \frac{p_2}{p_1}$$

or
$$s_2 - s_1 = c_p \ln \frac{v_2}{v_1} + c_v \ln \frac{p_2}{p_1} \qquad (10.30)$$

Any one of the three Eqs (10.28), (10.29), and (10.30), may be used for computing the entropy change between any two states of an ideal gas.

10.3.3 Reversible Adiabatic Process

The general property relations for an ideal gas may be written as
$$Tds = du + pdv = c_v\,dT + pdv$$

and
$$Tds = dh - vdp = c_p\,dT - vdp$$

For a reversible adiabatic change, $ds = 0$

$\therefore$
$$c_v\,dT = -pdv \qquad (10.31)$$

and
$$c_p\,dT = vdp \qquad (10.32)$$

By division
$$\frac{c_p}{c_v} = \gamma = -\frac{vdp}{pdv}$$

or
$$\frac{dp}{p} + \gamma\frac{dv}{v} = 0$$

or
$$d(\ln p) + \gamma d(\ln v) = d(\ln c)$$

where c is a constant.

$\therefore$
$$\ln p + \gamma \ln v = \ln c$$
$$pv^\gamma = c \qquad (10.33)$$

Between any two states 1 and 2
$$p_1 v^\gamma{}_1 = p_2 v^\gamma{}_2$$

or
$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^\gamma$$

For an ideal gas
$$pv = RT$$

From Eq. (10.33)
$$p = c \cdot v^{-\gamma}$$

$\therefore$
$$c \cdot v^{-\gamma} \cdot v = RT$$
$$c \cdot v^{1-\gamma} = RT$$
$$Tv^{\gamma-1} = \text{constant} \qquad (10.34)$$

Between any two states 1 and 2, for a reversible adiabatic process in the case of an ideal gas

$$T_1 v_1^{\gamma-1} = T_2 v_2^{\gamma-1}$$

or $$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} \qquad (10.35)$$

Similarly, substituting from Eq. (10.33)

$$v = \left(\frac{c}{p}\right)^{1/\gamma} \text{ in the Eq. } pv = RT$$

$$p \cdot \frac{c'}{p^{1/\gamma}} = RT$$

$$p^{1-(1/\gamma)} \times c' = RT$$

$\therefore$ $$Tp^{(1-\gamma)/\gamma} = \text{constant} \qquad (10.36)$$

Between any two states 1 and 2

$$T_1 p_1^{(1-\gamma)/\gamma} = T_2 p_2^{(1-\gamma)/\gamma}$$

$\therefore$ $$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} \qquad (10.37)$$

Equations (10.33), (10.34), and (10.36) give the relations among p, v, and T in a reversible adiabatic process for an ideal gas.

The *internal energy change* of an ideal gas for a reversible adiabatic process is given by

$$Tds = du + pdv = 0$$

or $$\int_1^2 du = -\int_1^2 pdv = -\int_2^2 \frac{c}{v^\gamma}\, dv$$

where $$pv^\gamma = p_1 v_1^\gamma = p_2 v_2^\gamma = c$$

$\therefore$ $$u_2 - u_1 = c\frac{v_2^{1-\gamma} - v_1^{1-\gamma}}{\gamma - 1} = \frac{p_2 v_2^\gamma \cdot v_2^{1-\gamma} - p_1 v_1^\gamma \cdot v_1^{1-\gamma}}{\gamma - 1}$$

$$= \frac{p_2 v_2 - p_1 v_1}{\gamma - 1}$$

$$= \frac{R(T_2 - T_1)}{\gamma - 1} = \frac{RT_1}{\gamma - 1}\left(\frac{T_2}{T_1} - 1\right)$$

$$= \frac{RT_1}{\gamma - 1}\left[\left(\frac{p_2}{p_1}\right)^{\gamma-1/\gamma} - 1\right] \qquad (10.38)$$

The enthalpy change of an ideal gas for a reversible adiabatic process may be similarly derived.

$$Tds = dh - vdp = 0$$

or $$\int_1^2 dh = \int_1^2 vdp = \int_1^2 \frac{(c)^{1/\gamma}}{p^{1/\gamma}}$$

where $$p_1 v^{\gamma}_1 = p_2 v^{\gamma}_2 = c$$

$$\therefore \quad h_2 - h_1 = \frac{\gamma}{\gamma - 1} c^{1/\gamma} [p_2^{(\gamma-1)/\gamma} - p_1^{(\gamma-1)/\gamma}]$$

$$= \frac{\gamma}{\gamma - 1} (p_1 v_1^{\gamma})^{1/\gamma} \cdot (p_1)^{(\gamma-1)/\gamma} \left[\left(\frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} - 1 \right]$$

$$= \frac{\gamma p_1 v_1}{\gamma - 1} \left[\left(\frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} - 1 \right]$$

$$= \frac{\gamma R T_1}{\gamma - 1} \left[\left(\frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} - 1 \right] \qquad (10.39)$$

The work done by an ideal gas in a reversible adiabatic process is given by

$$đQ = \mathrm{d}U + đW = 0$$

or $$đW = -\,\mathrm{d}U$$

i.e. work is done at the expense of the internal energy.

$$\therefore \quad W_{1-2} = U_1 - U_2 = m(u_1 - u_2)$$

$$= \frac{m(p_1 v_1 - p_2 v_2)}{\gamma - 1} = \frac{mR(T_1 - T_2)}{\gamma - 1} = \frac{mRT_1}{\gamma - 1} \left[1 - \left(\frac{p_2}{p_1} \right)^{(\gamma-1)/\gamma} \right] \qquad (10.40)$$

where m is the mass of gas.

In a steady flow process, where both flow work and external work are involved, we have from S.F.E.E.,

$$W_x + \Delta \frac{V^2}{2} + g\Delta z = h_1 - h_2 = c_p (T_1 - T_2) = \frac{\gamma R(T_1 - T_2)}{\gamma - 1}$$

$$= \frac{\gamma(p_1 v_1 - p_2 v_2)}{\gamma - 1} = \frac{\gamma}{\gamma - 1} p_1 v_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{\gamma-1/\gamma} \right] \qquad (10.41)$$

If K.E. and P.E. changes are neglected,

$$W_x = \frac{\gamma}{\gamma - 1} p_1 v_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{\gamma-1/\gamma} \right] \qquad (10.42)$$

10.3.4 Reversible Isothermal Process

When an ideal gas of mass m undergoes a reversible isothermal process from state 1 to state 2, the work done is given by

$$\int_1^2 đW = \int_{V_1}^{V_2} p\mathrm{d}V$$

or $$W_{1-2} = \int_{V_1}^{V_2} \frac{mRT}{V} \mathrm{d}V = mRT \ln \frac{V_2}{V_1}$$

$$= mRT \ln \frac{p_1}{p_2} \qquad (10.43)$$

The heat transfer involved in the process

$$Q_{1-2} = U_2 - U_1 + W_{1-2}$$
$$= W_{1-2} = mRT \ln V_2/V_1 = T(S_2 - S_1) \qquad (10.44)$$

10.3.5 Polytropic Process

An equation of the form pv^n = constant, where n is a constant can be used approximately to describe many processes which occur in practice. Such a process is called a *polytropic process*. It is not adiabatic, but it can be reversible. It may be noted that γ is a property of the gas, whereas n is not. The value of n depends upon the process. It is possible to find the value of n which more or less fits the experimental results. For two statses on the process,

$$p_1 v^n_1 = p_2 v^n_2 \qquad (10.45)$$

or

$$\left(\frac{v_2}{v_1}\right)^n = \frac{p_1}{p_2}$$

$$n = \frac{\log p_1 - \log p_2}{\log v_2 - \log v_1} \qquad (10.46)$$

For known values of p_1, p_2, v_1 and v_2, n can be estimated from the above relation.

Two other relations of a polytropic process, corresponding to Eqs (10.35) and (10.37), are

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1} \qquad (10.47)$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{n-1/n} \qquad (10.48)$$

(i) *Entropy Change in a Polytropic Process* In a reversible adiabatic process, the entropy remains constant. But in a reversible polytropic process, the entropy changes. Substituting Eqs (10.45), (10.47) and (10.48) in Eqs (10.28), (10.29) and (10.30), we have three expressions for entropy change as given below

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$
$$= \frac{R}{\gamma - 1} \ln \frac{T_2}{T_1} + \frac{R}{n-1} \ln \frac{T_1}{T_2}$$
$$= \frac{n-\gamma}{(\gamma-1)(n-1)} R \ln \frac{T_2}{T_1} \qquad (10.49)$$

Relations in terms of pressure and specific volume can be similarly derived. These are

$$s_2 - s_1 = \frac{n-\gamma}{n(\gamma-1)} R \ln \frac{p_2}{p_1} \qquad (10.50)$$

and

$$s_2 - s_1 = -\frac{n-\gamma}{\gamma-1} R \ln \frac{v_2}{v_1} \qquad (10.51)$$

It can be noted that when $n = \gamma$, the entropy change becomes zero. If $p_2 > p_1$, for $n \leq \gamma$, the entropy of the gas decreases, and for $n > \gamma$, the entropy of the gas increases. The increase of entropy may result from reversible heat transfer to the system from the surroundings. Entropy decrease is also possible if the gas is cooled.

(ii) *Heat and Work in a Polytropic Process* Using the first law to unit mass of an ideal gas,

$$
\begin{aligned}
Q - W &= u_2 - u_1 \\
&= c_v (T_2 - T_1) = \frac{R(T_2 - T_1)}{\gamma - 1} \\
&= \frac{p_2 v_2 - p_1 v_1}{\gamma - 1} \\
&= \frac{p_1 v_1}{\gamma - 1}\left[\left(\frac{p_2}{p_1}\right)^{n-1/n} - 1\right] = \frac{p_1 v_1}{\gamma - 1}\left[\left(\frac{v_1}{v_2}\right)^{n-1} - 1\right] \qquad (10.52)
\end{aligned}
$$

For a steady flow system of unit mass of ideal gas, the S.F.E.E. Eq. (5.10), gives

$$
\begin{aligned}
Q &= W_x - \Delta\left[\frac{\bar{V}^2}{2} + gz\right] = h_2 - h_1 \\
&= c_p (T_2 - T_1) = \frac{\gamma R\,(T_2 - T_1)}{\gamma - 1} \\
&= \frac{\gamma}{\gamma - 1}\,(p_2 v_2 - p_1 v_1) \qquad (10.53)
\end{aligned}
$$

For a polytropic process,

$$
\begin{aligned}
Q - W_x &= \Delta\left[\frac{\bar{V}^2}{2} + gz\right] = \frac{\gamma p_1 v_1}{\gamma - 1}\left[\left(\frac{p_2}{p_1}\right)^{n-1/n} - 1\right] \\
&= \frac{\gamma p_1 v_1}{\gamma - 1}\left[\left(\frac{v_1}{v_2}\right)^{n-1} - 1\right] \qquad (10.54)
\end{aligned}
$$

Equations (10.52) and (10.54) can be used to determine heat and work quantities for a closed and a steady flow system respectively.

(iii) *Integral Property Relations in a Polytropic Process* In a pv^n = constant process,

$$
\begin{aligned}
\int_1^2 p\mathrm{d}v &= \int_1^2 \frac{p_1 v_1^n}{v^n}\,\mathrm{d}v = \frac{p_1 v_1}{n-1}\left[1 - \left(\frac{v_1}{v_2}\right)^{n-1}\right] \\
&= \frac{p_1 v_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{n-1/n}\right] \qquad (10.55)
\end{aligned}
$$

Similarly,

$$
\begin{aligned}
-\int_1^2 v\mathrm{d}p &= \frac{np_1 v_1}{n-1}\left[1 - \left(\frac{v_1}{v_2}\right)^{n-1}\right] \\
&= \frac{np_1 v_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{n-1/n}\right] \qquad (10.56)
\end{aligned}
$$

The integral of $T\mathrm{d}s$ is obtained from the property relation

$$T\mathrm{d}s = \mathrm{d}u + p\mathrm{d}v$$

$$\therefore \quad \int_1^2 Tds = \int_1^2 du + \int_1^2 pdv \quad = u_2 - u_1 + \int_1^2 pdv$$

Substituting from Eqs (10.50) and (10.53)

$$\int_1^2 Tds = \frac{\gamma - n}{(\gamma-1)(n-1)} p_1v_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{n-1/n}\right]$$

$$= \frac{\gamma - n}{(\gamma-1)(n-1)} p_1v_1 \left[1 - \left(\frac{v_1}{v_2}\right)^{n-1}\right]$$

$$= \frac{\gamma - n}{(\gamma-1)(n-1)} R(T_1 - T_2) \qquad (10.57)$$

Since $R/(\gamma - 1) = c_v$, and putting $\Delta T = T_2 - T_1$, the reversible heat transfer

$$Q_R = \int_1^2 Tds = c_v \frac{\gamma - n}{1-n} \Delta T = c_n \Delta T \qquad (10.58)$$

where $c_n = c_v (\gamma - n)/(1 - n)$ is called the polytropic specific heat. For $n > \gamma$ there will be positive heat transfer and gain in entropy. For $n < \gamma$, heat transfer will be negative and entropy of the gas would decrease.

Ordinarily both heat and work are involved in a polytropic process. To evaluate the heat transfer during such a process, it is necessary to first evaluate the work via either $\int p dv$ or $-\int v dp$, depending on whether it is a closed or an open steady flow system. The application of the first law will then yield the heat transfer.

The polytropic processes for various values of n are shown in Fig. 10.2 on the p–v and T–s diagrams.

$$pv^n = C$$

On differentiation,

$$v^n \, dp + pnv^{n-1} \, dv = 0$$

$$\frac{dp}{dv} = -n\frac{p}{v} \qquad (10.59)$$

The slope of the curve increases in the negative direction with increase of n. The values of n for some familiar processes are given below

Isobaric process ($p = c$), $n = 0$
Isothermal process ($T = c$), $n = 1$
Isentropic process ($s = c$), $n = \gamma$
Isometric or isochoric process ($v = c$), $n = \infty$.

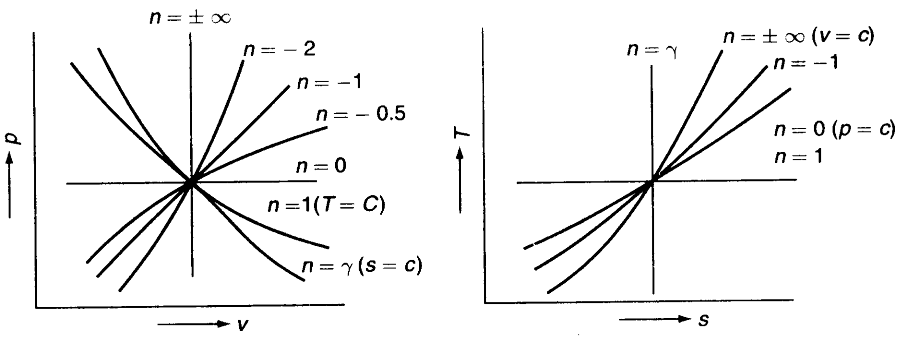


Fig. 10.2 Process in which pv^n = constant

10.4 EQUATIONS OF STATE

The ideal gas equation of state $p\bar{v} = \bar{R}T1$ can be established from the positulates of the kinetic theory of gases developed by Clerk Maxwell, with two important assumptions that there is little or no attraction between the molecules of the gas and that the volume occupied by the molecules themselves is negligibly small compared to the volume of the gas. When pressure is very small or temperature very large, the intermolecular attraction and the volume of the molecules compared to the total volume of the gas are nor of much significance, and the real gas obeys very closely the ideal gas equation. But as pressure increases, the intermolecular forces of attraction and repulsion increase, and also the volume of the molecules becomes appreciable compared to the gas volume. So then the real gases deviate considerably from the ideal gas equation. Van der Waals, by applying the laws of mechanics to individual molecules, introduced two correction terms in the equation of ideal gas, and his equation is given below.

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{10.60}$$

The coefficient a was introduced to account for the existence of mutual attraction between the molecules. The term a/v^2 is called the *force of cohesion*. The coefficient b was introduced to account for the volumes of the molecules, and is known as *co-volume*.

Real gases conform more closely with the van der Waals equation of state than the ideal gas equation of state, particularly at higher pressures. But it is not obeyed by a real gas in all ranges of pressures and temperatures. Many more equations of state were later introduced, and notable among these are the equations developed by Berthelot, Dieterici, Beattie-Bridgeman, Kammerlingh Onnes, Hirshfelder-Bird-Spotz-McGee-Sutton, Wohl, Redlich-Kwong, and Martin-Hou.

Apart from the van der Waals equation, three two-constant equations of state are those of Berthelot, Dieterici, and Redlich-Kwong, as given below:

Berthelot:
$$p = \frac{RT}{v - b} - \frac{a}{Tv^2} \tag{10.61}$$

Dieterici:
$$p = \frac{RT}{v - b} . e^{-\mathrm{a}/\mathrm{RT}_\mathrm{v}} \tag{10.62}$$

Redlich-Kwong:
$$p = \frac{RT}{v - b} - \frac{a}{T^{1/2}v(v + b)} \tag{10.63}$$

The constants, a and b are evaluated from the critical data, as shown for van der Waals equation in Article 10.6. The Berthelot and Dieterici equations of state, like the van der Waals equation, are of limited accuracy. But the Redlich-Kwong equation gives good results at high pressures and is fairly accurate for temperatures above the critical value.

Another two-constant equation which is again of limited accuracy is the Saha-Bose equation of state given as follows.

$$p = -\frac{RT}{2b} e^{-\mathrm{a}/\mathrm{RT}_\mathrm{v}} \mathrm{In}\left(\frac{v - 2b}{v}\right) \tag{10.64}$$

It is, however, quite accurate for densities less than about 0.8 times the critical density.

One more widely used equation of state with good accuracy is the Beattie-Bridgeman equation:

$$p = \frac{RT(1 - e)}{v^2}(v + B) - \frac{A}{v^2} \tag{10.65}$$

where

$$A = A_o\left(1 - \frac{a}{v}\right), B = B_o\left(1 - \frac{b}{v}\right), e = \frac{c}{vT^3}$$

There are five constants, A_0, B_0, a, b, and c, which have to be determined experimentally for each gas. The Beattie-Bridgeman equation does not give satisfactory results in the critical point region.

All these equations mentioned above reduce to the ideal gas equation for large volumes and temperatures and for small pressures.

10.5 VIRIAL EXPANSIONS

The relations between $p\bar{v}$ and p in the form of power series, as given in Eq. (10.1), may be expressed as

$$p\bar{v} = A(1 + B'p + C'p^2 + D'p^3 + \ldots)$$

For any gas, from Eq. (10.3)

$$\lim_{p\to 0} p\bar{v} = A = \bar{R}T$$

$$\therefore \quad \frac{p\bar{v}}{\bar{R}T} = 1 + B'p + C'p^2 + D'p^3 + \ldots \tag{10.66}$$

An alternative expression is

$$\frac{p\bar{v}}{\bar{R}T} = 1+\frac{B}{\bar{v}}+\frac{C}{\bar{v}^2}+\frac{D}{\bar{v}^3}+\cdots \tag{10.67}$$

Both expressions in Eqs (10.66) and (10.67) are known as virial expansions or virial equations of state, first introduced by the Dutch physicist, Kammerlingh Onnes, B', C', B, C, etc. are called *virial coefficients*. B' and B are called second virial coefficients, C' and C are called third virial coefficients, and so on. For a given gas, these coefficients are functions of temperature only.

The ratio $p\bar{v}/\bar{R}T$ is called the compressibility factor, Z. For an ideal gas $Z = 1$. The magnitude of Z for a certain gas at a particular pressure and temperature gives an indication of the extent of deviation of the gas from the ideal gas behaviour. The virial expansions become

$$Z = 1 + B'p + C'p^2 + D'p^3 + \ldots \tag{10.68}$$

and

$$Z = 1+\frac{B}{\bar{v}}+\frac{C}{\bar{v}^2}+\frac{D}{\bar{v}^3}+\cdots \tag{10.69}$$

The relations between B', C' and B, C, ... can be derived as given below

$$\begin{aligned}
\frac{pv}{\bar{R}T} &= 1 + B'p + C'p^2 + D'p^3 + \ldots \\
&= 1 + B'\left[\frac{\bar{R}T}{\bar{v}}\left(1+\frac{B}{\bar{v}}+\frac{C}{\bar{v}^2}+\ldots\right)\right] \\
&\quad +C'\left[\left(\frac{\bar{R}T}{\bar{v}}\right)^2\left(1+\frac{B}{\bar{v}}+\frac{C}{\bar{v}^2}+\ldots+\right)^2\right]+\ldots \\
&= 1+\frac{B'\bar{R}T}{\bar{v}}+\frac{B'B\bar{R}T+C'(\bar{R}T)^2}{\bar{v}^2} \\
&\quad +\frac{B'\bar{R}TC+C'(\bar{R}T)^2+D'(\bar{R}T)^3}{\bar{v}^3}+\ldots
\end{aligned} \tag{10.70}$$

Comparing this equation with Eq. (10.67) and rearranging

$$B' = \frac{B}{\bar{R}T}, \quad C' = \frac{C-B^2}{(\bar{R}T)^2},$$

$$D' = \frac{D - 3BC + 2B^3}{(\bar{R}T)^3}, \text{ and so on}$$

Therefore

$$Z = \frac{p\bar{v}}{\bar{R}T} = 1 + B'p + C'p^2 + \ldots$$

$$= 1 + \frac{B}{\bar{R}T}p + \frac{C - B^2}{(\bar{R}T)^2}p^2 + \ldots \qquad (10.71)$$

The terms $B/\bar{v}$, $C/\bar{v}^2$ etc. of the virial expansion arise on account of molecular interactions. If no such interactions exist (at very low pressures) $B = 0$, $C = 0$, etc., $Z = 1$ and $p\bar{v} = \bar{R}T$.

10.6 LAW OF CORRESPONDING STATES

For a certain gas, the compressibility factor Z is a function of p and T [Eq. (10.71)], and so a plot can be made of lines of constant temperature on coordinates of p and Z (Fig. 10.3). From this plot Z can be obtained for any value of p and T, and the volume can then be obtained from the Equation $pv = ZRT$. The advantage of using Z instead of a direct plot of v is a smaller range of values in plotting.

For each substance, there is a compressibility factor chart. It would be very convenient if one chart could be used for all substances. The general shapes of the vapour dome and of the constant temperature lines on the p–v plane are similar for all substances, although the scales may be different. This similarity can be exploited by using dimensionless properties called *reduced properties*. The reduced pressure is the ratio of the existing pressure to the critical pressure of the substance, and similarly for reduced temperature and reduced volume. Then

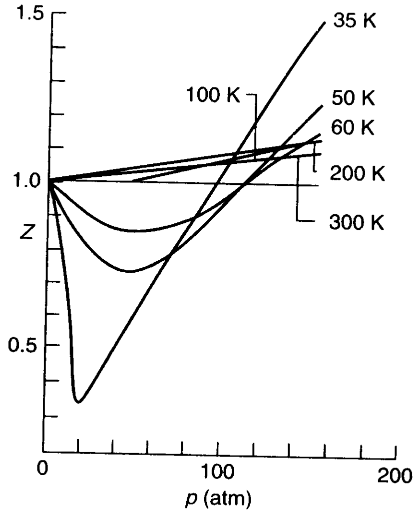


Fig. 10.3 *Variation of the compressibility factor of hydrogen with pressure at constant temperature*

$$p_r = \frac{p}{p_c},\ T_r = \frac{T}{T_c},\ v_r = \frac{v}{v_c}$$

where subscript r denotes the reduced property, and subscript c denotes the property at the critical state.

At the same pressure and temperature the specific or molal volumes of different gases are different. However, it is found from experimental data that at the same reduced pressure and reduced temperature, the reduced volumes of different gases are approximately the same. Therefore, for all substances

$$v_r = f(p_r, T_r) \qquad (10.72)$$

Now

$$v_r = \frac{v}{v_c} = \frac{ZRTp_c}{Z_cRT_cp} = \frac{Z}{Z_c} \cdot \frac{T_r}{p_r} \qquad (10.73)$$

where $Z_c = \frac{p_c v_c}{RT_c}$. This is called the critical compressibility factor. Therefore from Eqs (10.72) and (10.73),

$$Z = f(p_r, T_r, Z_c) \qquad (10.74)$$

Experimental values of Z_c for most substances fall within a narrow range 0.20–0.30. Therefore, Z_c may be taken to be a constant and Eq. (10.74) reduces

$$Z = f(p_r, T_r) \qquad (10.75)$$

When T_r is plotted as a function of reduced pressure and Z, a single plot, known as *the generalized compressibility chart*, is found to be satisfactory for a great variety of substances. Although necessarily approximate, the plots are extremely useful in situations where detailed data on a particular gas are lacking but its critical properties are available.

The relation among the reduced properties, p_r, T_r, and v_r, is known as the law of *corresponding states*. It can be derived from the various equations of state, such as those of van der Waals, Berthelot, and Dieterici. For a van der Waals gas,

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

where a, b, and R are the characteristic constants of the particular gas.

$$\therefore \qquad p=\frac{RT}{v-b}-\frac{a}{v^2}$$

or

$$pv^3-(pb+RT)v^2+av-ab=0$$

It is therefore a cubic in v and for given values of p and T has three roots of which only one need be real. For low temperatures, three positive real roots exist for a certain range of pressure. As the temperature increases the three real roots approach one another and at the critical temperature they become equal. Above this temperature only one real root exists for all values of p. The critical isotherm T_c at the critical state on the p–v plane (Fig. 10.4), where the three real roots of the van der Waals equation coincide, not only has a zero slope, but also its slope changes at the critical state (point of inflection), so that the first and second derivatives of p with respect to v at $T = T_c$ are each equal to zero. Therefore

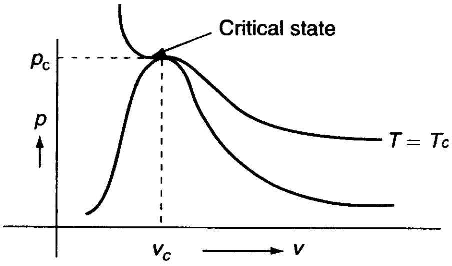


Fig. 10.4 *Critical properties on p–v diagram*

$$\left(\frac{\partial p}{\partial v}\right)_{T=T_c}=-\frac{RT_c}{(v_c-b)^2}+\frac{2a}{v_c^3}=0 \qquad (10.76)$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_{T=T_c}=\frac{2\cdot RT_c}{(v_c-b)^3}-\frac{6a}{v_c^4}=0 \qquad (10.77)$$

From these two equations, by rearranging and dividing, $b=\frac{1}{3}v_c$.

Substituting the values of b in Eq. (10.76)

$$R=\frac{8a}{9T_cv_c}$$

Substituting the values of b and R in Eq. (10.60)

$$\left(p_c+\frac{a}{v_c^2}\right)\left(\frac{2}{3}v_c\right)=\frac{8a}{9T_cv_c}\cdot T_c$$

$$a=3p_c\,v_c^2$$

Therefore, the value of R becomes

$$R=\frac{8}{3}\frac{p_cv_c}{T_c}$$

The values of a, b, and R have thus been expressed in terms of critical properties. Substituting these in the van der Waals equation of state

$$\left(p+\frac{3p_c v_c^2}{v^2}\right)\left(v-\frac{1}{3}v_c\right) = \frac{8}{3}\frac{p_c v_c}{T_c}T$$

or,

$$\left(\frac{p}{p_c}+\frac{3v_c^2}{v^2}\right)\left(\frac{v}{v_c}-\frac{1}{3}\right) = \frac{8}{3}\frac{T}{T_c}$$

Using the reduced parameters,

$$\therefore \qquad \left(p_r+\frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r \qquad (10.78)$$

In the reduced equation of state (10.78) the individual coefficients a, b and R for a particular gas have disappeared. So this equation is an expression of the *law of corresponding states* because it reduces the properties of all gases to one formula. It is a 'law' to the extent that real gases obey van der Waals equation. Two different substances are considered to be in 'corresponding states', if their pressures, volumes and temperatures are of the same fractions (or multiples) of the critical pressure, volume and temperature of the two substances. The *generalized compressibility* chart in terms of reduced properties is shown in Fig. 10.5(a) and (b). It is very useful in predicting the properties of substances for which more precise data are not available. The value of Z at the critical state of a van der Waals gas is 0.375 $\left(\text{since } R = \frac{8}{3}\frac{p_c v_c}{T_c}\right)$. At very low pressures Z approaches unity, as a real gas approaches the ideal gas behaviour. Equation (10.78) can also be written in the following form

$$\left(p_r v_r+\frac{3}{v_r}\right)(3v_r - 1) = 8T_r v_r$$

$$\therefore \qquad p_r v_r = \frac{8T_r v_r}{3v_r - 1} - \frac{3}{v_r} \qquad (10.79)$$

Figure 10.6 shows the law of corresponding states in reduced coordinates, $(p_r v_r)$ vs. p_r. Differentiating Eq. (10.79) with respect to p_r and making it equal to zero, it is possible to determine the minima of the isotherms as shown below.

$$\frac{\partial}{\partial p_r}\left[\frac{8T_r v_r}{3v_r - 1} - \frac{3}{v_r}\right]_{T_r} = 0$$

or

$$\frac{\partial}{\partial v_r}\left[\frac{8T_r v_r}{3v_r - 1} - \frac{3}{v_r}\right]_{T_r}\left[\frac{\partial v_r}{\partial p_r}\right]_{T_r} = 0$$

Since

$$\left[\frac{\partial v_r}{\partial p_r}\right]_{T_r} \neq 0$$

$$\frac{\partial}{\partial v_r}\left[\frac{8T_r v_r}{3v_r - 1} - \frac{3}{v_r}\right]_{T_r} = 0$$

$$\therefore \qquad \frac{8T_r}{(3v_r - 1)^2} = \frac{3}{v_r^2}$$

or

$$\frac{3(3v_r - 1)^2}{v_r^2} = 8T_r = \left[p_r + \frac{3}{v_r^2}\right](3v_r - 1)$$

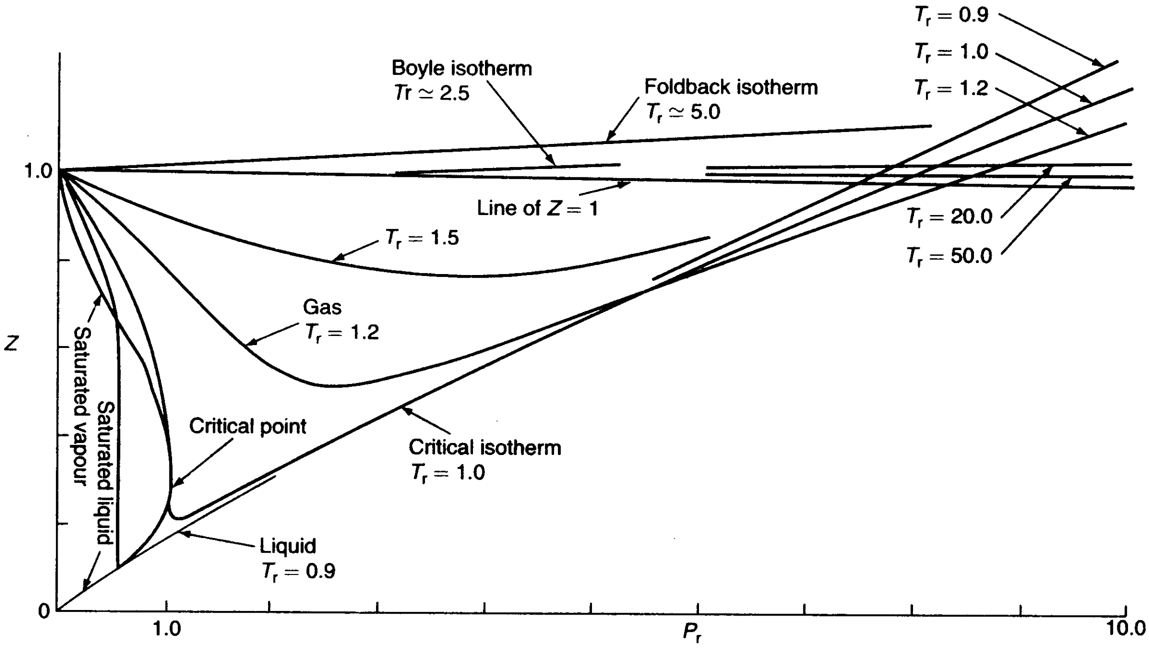


Fig. 10.8 *(a) Generalized compressibility chart*

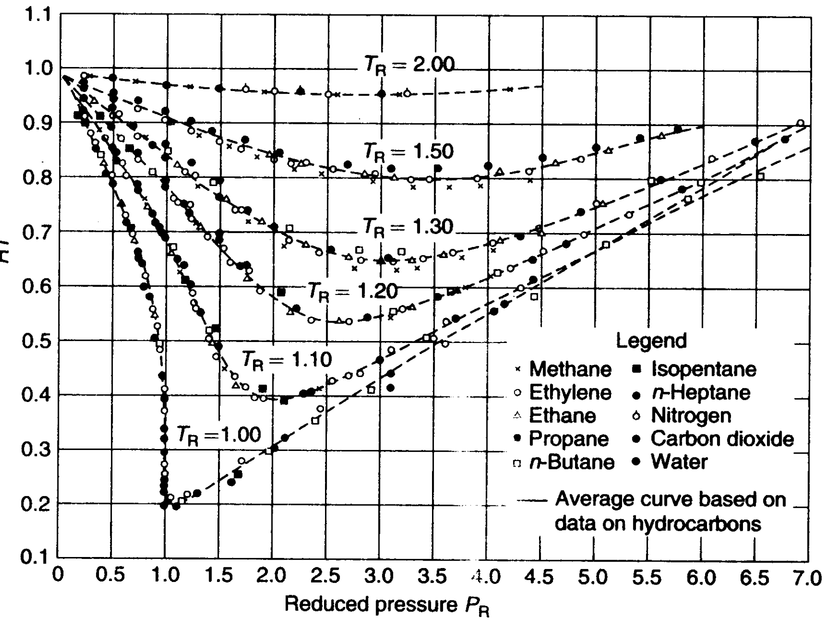


Fig. 10.8 *(b) Generalized compressibility chart*

Simplifying $(p_r v_r)^2 - 9(p_r v_r) + 6p_r = 0$

This is the equation of a parabola passing through the minima of the isotherms (Fig. 10.6).

When $p_r = 0,$

$$p_r v_r = 0, 9$$

Again
$$p_r = \frac{9(p_r v_r) - (p_r v_r)^2}{6}$$

$$\frac{dp_r}{d(p_r v_r)} = 9 - 2\,(p_r\, v_r) = 0$$

$$\therefore \quad p_r\, v_r = 4.5$$

$$p_r = \frac{9 \times 4.5 \times (4.5)^2}{6} = 3.375$$

The parabola has the vertex at $p_r v_r = 4.5$ and $p_r = 3.375$, and it intersects the ordinate at 0 and 9.

Each isotherm up to that marked T_B has a minimum (Fig. 10.6). The T_B isotherm has an initial horizontal portion ($p_r v_r$ = constant) so that Boyle's law is obeyed fairly accurately up to moderate pressures. Hence, the corresponding temperature is called the *Boyle temperature* for that gas. The Boyle temperature T_B can be determined by making

$$\left[\frac{\partial(p_r v_r)}{\partial p_r}\right]_{T_r = T_B} = 0 \ \text{when}\ p_r = 0$$

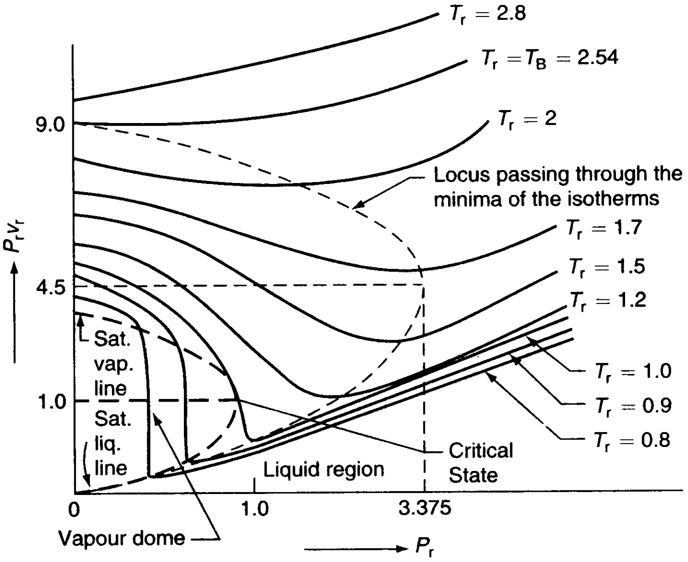


Fig. 10.6 *Law of corresponding states in reduced coordinates*

Above the Boyle temperature, the isotherms slope upward and show no minima.

As T_r is reduced below the critical (i.e. for $T_r < 1$), the gas becomes liquefied, and during phase transition isotherms are vertical. The minima of all these isotherms lie in the liquid zone.

Van der Waals equation of state can be expressed in the virial form as given below

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$$\left(pv+\frac{a}{v}\right)\left(1-\frac{b}{v}\right)=RT$$

$$\therefore \quad pv+\frac{a}{v}=RT\left(1-\frac{b}{v}\right)^{-1}$$

$$=RT\left[1+\frac{b}{v}+\frac{b^2}{v^2}+\frac{b^3}{v^3}+\cdots\right] \quad \left(\text{where } \frac{b}{v}<1\right)$$

$$\therefore \quad pv=RT\left[1+\left(b-\frac{a}{RT}\right)\frac{1}{v}+\frac{b^2}{v^2}+\frac{b^3}{v^3}+\cdots\right] \tag{10.80}$$

$\therefore$ The second virial coefficient $B = b - a/RT$, the third virial coefficient $C = b^2$, etc.

From Eq. (10.71), on mass basis

$$pv=RT\left(1+\frac{B}{\bar{R}T}p+\frac{C-B^2}{\bar{R}T^2}p^2+\ldots\right)$$

To determine Boyle temperature, T_B

$$\left[\frac{\partial(pv)}{\partial p}\right]_{\substack{T=C\\ p=0}}=0=\frac{B}{\bar{R}T}$$

$$\therefore \quad B=0$$

or

$$T_B=\frac{a}{bR}, \text{ because } B=b-\frac{a}{RT}$$

The point at which B is equal to zero gives the Boyle temperature. The second virial coefficient is the most important. Since $\left[\frac{\partial(pv)}{\partial p}\right]_{p=0} = B$, when B is known, the behaviour of the gas at moderate pressures is completely determined. The terms which contain higher power (C/v^2, D/v^3, etc.) becomes significant only at very high pressures.

10.7 OTHER EQUATIONS OF STATE

van der Waals equation is one of the oldest equations of state introduced in 1899, where the constants a and b are related to the critical state properties as found earlier,

$$a=3p_c{v^2}_c=\frac{27}{64}\frac{R^2T_c^2}{p_c},\ b=\frac{1}{3}v_c=\frac{1}{8}\frac{RT_c}{p_c}$$

The Beattie-Bridgeman equation developed in 1928 is given in Eq. 10.79, which has five constants. It is essentially an empirical curve fit of data, and is reasonably accurate when values of specific volume are greater than v_c.

Benedict, Webb, and Rubin extended the Beattie-Bridgeman equation of state to cover a broader range of states as given below:

$$p=\frac{\bar{R}T}{v}+\left(B\bar{R}T-A-\frac{c}{T^2}\right)\frac{1}{\bar{v}^2}+\frac{(b\bar{R}T-a)}{\bar{v}^3}+\frac{a}{\bar{v}^6}$$

$$+\frac{c}{\bar{v}^3T^2}\left(1+\frac{\gamma}{\bar{v}^2}\right)\exp\left(-\frac{\gamma}{\bar{v}^2}\right)$$

It has eight constants and is quite successful in predicting the $p-v-T$ behaviour of light hydrocarbons.

The Redlich-Kwong equation proposed in 1949 and given by Eq. 10.77 has the constants a and b in terms of critical properties as follows:

$$a = 0.4275\ \frac{R^2T_c^{2.5}}{p_c},\quad b = 0.0867\ \frac{RT_c}{p_c}$$

The values of the constants for the van der Waals, Redlich-Kwong and Benedict-Webb-Rubin equations of state are given in Table 10.1, while those for the Beattie-Bridgeman equation of state are given in Table 10.2. Apart from these, many other multi-constant equations of state have been proposed. With the advent of high speed computers, equations having 50 or more constants have been developed for representing the $p-v-T$ behaviour of different substances.

Table 10.1

Constants for the van der Waals, Redlich-Kwong, and Benedict-Webb-Rubin Equations of State

1. van der Waals and Redlich-Kwong: Constants for pressure in bars, specific volume in m³/k mol, and temperature in K

	van der Waals		*Redlich-Kwong*	
Substance	*a* $bar\left(\frac{m^3}{k\,mol}\right)^2$	*b* $\frac{m^3}{k\,mol}$	*a* $bar\left(\frac{m^3}{k\,mol}\right)^2 K^{1/2}$	*b* $\frac{m^3}{k\,mol}$
Air	1.368	0.0367	15.989	0.02541
Butane (C_4H_{10})	**13.86**	**0.1162**	**289.55**	**0.08060**
Carbon dioxide (CO_2)	3.647	0.0428	64.43	0.02963
Carbon monoxide (CO)	**1.474**	**0.0395**	**17.22**	**0.02737**
Methane (CH_4)	2.293	0.0428	32.11	0.02965
Nitrogen (N_2)	**1.366**	**0.0386**	**15.53**	**0.02677**
Oxygen (O_2)	1.369	0.0317	17.22	0.02197
Propane (C_3H_8)	**9.349**	**0.0901**	**182.23**	**0.06242**
Refrigerant 12	10.49	0.0971	208.59	0.06731
Sulfur dioxide (SO_2)	**6.883**	**0.0569**	**144.80**	**0.03945**
Water (H_2O)	5.531	0.0305	142.59	0.02111

Source: Calculated from critical data.

2. Benedict-Webb-Rubin: Constants for pressure in bars, specific volume in m³/k mol, and temperature in K

Substance	***a***	***A***	***b***	***B***	***c***	***C***	α	γ
C_4H_{10}	1.9073	10.218	0.039998	0.12436	3.206×10^5	1.006×10^6	1.101×10^{-3}	0.0340
CO_2	**0.1386**	**2.7737**	**0.007210**	**0.04991**	1.512×10^4	1.404×10^5	8.47×10^{-5}	**0.00539**
CO	0.0371	1.3590	0.002632	0.05454	1.054×10^3	8.676×10^3	1.350×10^{-4}	0.0060
CH_4	**0.0501**	**1.8796**	**0.003380**	**0.04260**	2.579×10^3	2.287×10^4	1.244×10^{-4}	**0.0060**
N_2	0.0254	1.0676	0.002328	0.04074	7.381×10^2	8.166×10^1	$1.272 \times 10,^{-4}$	0.0053

Source: H.W. Coopper, and J.C. Goldfrank, Hydrocarbon Processing, 45 (12); 141 (1967).

Table 10.2

(a) The Beattie-Bridgeman equation of state is

$$P = \frac{R_u T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^2}\right)\left(\bar{v} + B\right) - \frac{A}{\bar{v}}\ \text{, where } A = A_0\left(1 - \frac{a}{\bar{v}}\right) \text{ and } B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

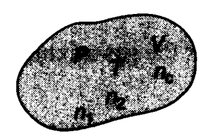
When P is in kPa, $\bar{v}$ is in m^3/k mol, T is in K, and $R_u = 8.314$ kPa · m^3/(k mol · K), the five constants in the Beattie-Bridgeman equation are as follows:

Gas	A_0	a	B_0	b	c
Air	131.8441	0.01931	0.04611	– 0.001101	4.34×10^4
Argon, Ar	**130.7802**	**0.02328**	**0.03931**	**0.0**	5.99×10^4
Carbon dioxide, CO_2	507.2836	0.07132	0.10476	0.07235	6.60×10^5
Helium, He	**2.1886**	**0.05984**	**0.01400**	**0.0**	**40**
Hydrogen, H_2	20.0117	– 0.00506	0.02096	– 0.04359	504
Nitrogen, N_2	**136.2315**	**0.02617**	**0.05046**	**– 0.00691**	4.20×10^4
Oxygen, O_2	151.0857	0.02562	0.04624	0.004208	4.80×10^4

Source: Gordon J. Van Wylen and Richard E. Sonntag, Fundamentals of Classical Thermodynamics, English/S.I. Version, 3d Ed., Wiley New York, 1986, p. 46. Table 3.3.

10.8 PROPERTIES OF MIXTURES OF GASES—DALTON'S LAW OF PARTIAL PRESSURES

Let us imagine a homogeneous mixture of inert ideal gases at a temperature T, a pressure p, and a volume V. Let us suppose there are n_1 moles of gas A_1, n_2 moles of gas A_2, ... and upto n_c moles of gas A_c (Fig. 10.7). Since there is no chemical reaction, the mixture is in a state of equilibrium with the equation of state



Mixture of gases

$$pV = (n_1 + n_2 + \dots n_c)\ \bar{R}T$$

where $\bar{R} = 8.3143$ kJ/kg mol K

$$\therefore \quad p = \frac{n_1\bar{R}T}{V} + \frac{n_2\bar{R}T}{V} + \dots + \frac{n_c\bar{R}T}{V}$$

The expression $\frac{n_K\bar{R}T}{V}$ represents the pressure that the Kth gas would exert if it occupied the volume V alone at temperature T. This is called the *partial pressure* of the Kth gas and is denoted by p_K. Thus

$$p_1 = \frac{n_1\bar{R}T}{V},\ p_2 = \frac{n_2\bar{R}T}{V},\ \dots,\ p_c = \frac{n_c\bar{R}T}{V}$$

and

$$p = p_1 + p_2 + \dots + p_c \tag{10.81}$$

This is known as *Dalton's law of partial pressures* which states that the total pressure of a mixture of ideal gases is equal to the sum of the partial pressures.

Now

$$V = (n_1 + n_2 + \dots + n_c)\cdot\frac{\bar{R}T}{p}$$

$$= \Sigma n_K \cdot \frac{\bar{R}T}{p}$$

and the partial pressure of the *K*th gas is

$$p_K = \frac{n_k \bar{R} T}{V}$$

Substituting the value of V

$$p_K = \frac{n_K \bar{R} T \cdot p}{\Sigma n_K \cdot \bar{R} T} = \frac{n_K \bar{R} T}{\Sigma n_K} \cdot p$$

Now

$$\Sigma n_K = n_1 + n_2 + \ldots + n_c$$

$$= \text{Total number of moles of gas}$$

The ratio $\frac{n_k}{\Sigma n_k}$ is called the *mole fraction of the K*th gas, and is denoted by x_K.

Thus

$$x_1 = \frac{n_1}{\Sigma n_K}, x_2 = \frac{n_2}{\Sigma n_K}, \ldots, x_c = \frac{n_c}{\Sigma n_K}$$

and

$$p_1 = x_1 p, p_2 = x_2 p, \ldots, p_c = x_c p$$

or

$$p_K = x_K \times p \tag{10.82}$$

Also

$$x_1 + x_2 + \ldots + x_c = 1 \tag{10.83}$$

In a mixture of gases, if all but one mole fraction is determined, the last can be calculated from the above equation. Again, in terms of masses

$$p_1 V = m_1 R_1 T$$

$$p_2 V = m_2 R_2 T$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$p_c V = m_c R_c T$$

Adding, and using Dalton's law

$$pV = (m_1 R_1 + m_2 R_2 + \ldots + m_c R_c) T \tag{10.84}$$

where

$$p = p_1 + p_2 + \ldots + p_c$$

For the gas mixture

$$pV = (m_1 + m_2 + \ldots + m_c) R_m T \tag{10.85}$$

where R_m is the gas constant for the mixture. From Eqs (10.84) and (10.85)

$$R_m = \frac{m_1 R_1 + m_2 R_2 + \ldots + m_c R_c}{m_1 + m_2 + \ldots + m_c} \tag{10.86}$$

The gas constant of the mixture is thus the weighted mean, on a mass basis, of the gas constants of the components.

The total mass of gas mixture m is

$$m = m_1 + \ldots + m_c$$

If μ denotes the *equivalent molecular* weight of the mixture having n total number of moles.

$$n\mu = n_1 \mu_1 + n_2 \mu_2 + \ldots + n_c \mu_c$$

$\therefore$

$$\mu = x_1 \mu_1 + x_2 \mu_2 + \ldots + x_c \mu_c$$

or

$$\mu = \Sigma x_K \mu_K \tag{10.87}$$

A quantity called the *partial volume* of a component of a mixture is the volume that the component alone would occupy at the pressure and temperature of the mixture. Designating the partial volumes by V_1, V_2, etc.

$$pV_1 = m_1R_1T, pV_2 = m_2R_2T, \dots, pV_c = m_cR_cT$$

or

$$p(V_1 + V_2 + \dots + V_c) = (m_1R_1 + m_2R_2 + \dots + m_cR_c)T \tag{10.88}$$

From Eqs (10.84), (10.85), and (10.88)

$$V = V_1 + V_2 + \dots + V_c \tag{10.89}$$

The total volume is thus equal to the sum of the partial volumes.

The *specific volume of the mixture*, v, is given by

$$v = \frac{V}{m} = \frac{V}{m_1 + m_2 + \dots + m_c}$$

or

$$\frac{1}{v} = \frac{m_1 + m_2 + \dots + m_c}{V}$$

$$= \frac{m_1}{V} + \frac{m_2}{V} + \dots + \frac{m_c}{V}$$

or

$$\frac{1}{v} = \frac{1}{v_1} + \frac{1}{v_2} + \dots + \frac{1}{v_c} \tag{10.90}$$

where v_1, v_2, ... denote specific volumes of the components, each component occupying the total volume.

Therefore, the density of the mixture $\rho = \rho_1 + \rho_2 + \dots + \rho_c$ (10.91)

10.9 INTERNAL ENERGY, ENTHALPY AND SPECIFIC HEATS OF GAS MIXTURES

When gases at equal pressures and temperatures are mixed adiabatically without work, as by inter-diffusion in a constant volume container, the first law requires that the internal energy of the gaseous system remains constant, and experiments show that the temperature remains constant. Hence, the internal energy of a mixture of gases is equal to the sum of the internal energies of the individual components, each taken at the temperature and volume of the mixture (i.e. sum of the 'partial' internal energies). This is also true for any of the thermodynamic properties like H, C_v, C_p, S, F, and G, and is known as *Gibbs theorem*. Therefore, on a mass basis

$$mu_m = m_1u_1 + m_2u_2 + \dots + m_cu_c$$

$$u_m = \frac{m_1u_1 + m_2u_2 + \dots + m_cu_c}{m_1 + m_2 + \dots + m_c} \tag{10.92}$$

which is the average specific internal energy of the mixture.

Similarly, the total enthalpy of a gas mixture is the sum of the 'partial' enthalpies

$$mh_m = m_1h_1 + m_2h_2 + \dots + m_ch_c$$

and

$$h_m = \frac{m_1h_1 + m_2h_2 + \dots + m_ch_c}{m_1 + m_2 + \dots + m_c} \tag{10.93}$$

From the definitions of specific heats, it follows that

$$c_{vm} = \frac{m_1c_{v_1} + m_2c_{v_2} + \dots + m_cc_{v_c}}{m_1 + m_2 + \dots + m_c} \tag{10.94}$$

and

$$c_{pm} = \frac{m_1c_{p_1} + m_2c_{p_2} + \dots + m_cc_{p_c}}{m_1 + m_2 + \dots + m_c} \tag{10.95}$$

10.10 ENTROPY OF GAS MIXTURES

Gibbs theorem states that the total entropy of a mixture of gases is the sum of the partial entropies. The partial entropy of one of the gases of a mixture is the entropy that the gas would have if it occupied the whole volume alone at the same temperature. Let us imagine a number of inert ideal gases separated from one another by suitable partitions, all the gases being at the same temperature T and pressure p. The total entropy (initial)

$$S_i = n_1 s_1 + n_2 s_2 + \dots + n_c s_c \quad = \Sigma\, n_K s_K$$

From property relation

$$T\mathrm{d}s = \mathrm{d}h - v\mathrm{d}p = c_p \mathrm{d}T - v\mathrm{d}p$$

$$\therefore \qquad \mathrm{d}\bar{s} = \bar{c}_p \frac{\mathrm{d}T}{T} - \bar{R}\frac{\mathrm{d}p}{p}$$

The entropy of 1 mole of the Kth gas at T and p

$$\bar{s}_K = \int c_{p_K} \frac{\mathrm{d}T}{T} - \bar{R}\ln p + \bar{s}_{0K}$$

where s_{0K} is the constant of integration.

$$\therefore \qquad S_i = \bar{R}\,\Sigma\, n_K \left(\frac{1}{\bar{R}}\int \bar{c}_{p_K} \frac{\mathrm{d}T}{T} + \frac{\bar{s}_{0K}}{\bar{R}} - \ln p\right)$$

Let

$$\sigma_K = \frac{1}{\bar{R}}\int \bar{c}_{p_K} \frac{\mathrm{d}T}{T} + \frac{\bar{s}_{0K}}{\bar{R}}$$

then

$$S_i = \bar{R}\,\Sigma\, n_k(\sigma_K - \ln p) \tag{10.96}$$

After the partitions are removed, the gases diffuse into one another at the same temperature and pressure, and by Gibbs theorem, the entropy of the mixture, S_f, is the sum of the partial entropies, with each gas exerting its respective partial pressure. Thus

$$S_f = \bar{R}\,\Sigma\, n_K(\sigma_K - \ln p_K)$$

Since

$$p_K = x_K\, p$$

$$S_f = \bar{R}\,\Sigma\, n_K(\sigma_K - \ln x_K - \ln p) \tag{10.97}$$

A change in entropy due to the diffusion of any number of inert ideal gases is

$$S_f - S_i = -\bar{R}\,\Sigma\, n_K \ln x_K \tag{10.98}$$

or

$$S_f - S_i = -\bar{R}\,(n_1 \ln x_1 + n_2 \ln x_2 + \dots + n_c \ln x_c)$$

Since the mole fractions are less than unity, $(S_f - S_i)$ is always positive, conforming to the Second Law. Again

$$S_f - S_i = -\bar{R}\left(n_1 \ln\frac{p_1}{p} + n_2 \ln\frac{p_2}{p} + \dots + n_c \ln\frac{p_c}{p}\right) \tag{10.99}$$

which indicates that each gas undergoes in the diffusion process a *free expansion* from total pressure p to the respective partial pressure at constant temperature.

Similarly, on a mass basis, the entropy change due to diffusion

$$S_f - S_i = -\,\Sigma m_K\, R_K \ln\frac{p_K}{p}$$

$$= -\left(m_1 R_1 \ln\frac{p_1}{p} + m_2 R_2 \ln\frac{p_2}{p} + \dots + m_c R_c \ln\frac{p_1}{p}\right)$$

10.11 GIBBS FUNCTION OF A MIXTURE OF INERT IDEAL GASES

From the equations

$$d\bar{h} = \bar{c}_p \, dT$$

$$d\bar{s} = \bar{c}_p \frac{dT}{T} - \bar{R}\frac{dp}{p}$$

the enthalpy and entropy of 1 mole of an ideal gas at temperature T and pressure p are

$$\bar{h} = \bar{h}_0 + \int c_p \, dT$$

$$\bar{s} = \int \bar{c}_p \frac{dT}{T} + \bar{s}_0 - \bar{R} \ \ln p$$

Therefore, the molar Gibbs function

$$\bar{g} = \bar{h} - T\bar{s}$$

$$= \bar{h}_0 + \int \bar{c}_p dT - T\int \bar{c}_p \frac{dT}{T} - T\bar{s}_0 + \bar{R}T \ln p$$

Now $\int d(uv) = \int u dv + \int v du = uv$

Let $u = \frac{1}{T}, v = \int c_p \, dT$

Then $\frac{1}{T} \int c_p \, dT = \int \frac{1}{T} \ c_p \, dT + \int c_p \, dT \left(-\frac{1}{T^2}\right) dT$

$$= \int \frac{1}{T} \ c_p \, dT - \int \frac{\int c_p dT}{T^2} \ dT$$

$$\int c_p \, dT - T\int c_p \frac{dT}{T} = - T\int \frac{\int c_p dT}{T^2} \ dT$$

Therefore

$$\bar{g} = \bar{h}_0 - T\int \frac{\int \bar{c}_p dT}{T^2} \ dT - T\bar{s}_0 + \bar{R}T \ \ln p$$

$$= \bar{R}T \left(\frac{\bar{h}_0}{\bar{R}T} - \frac{1}{\bar{R}} \int \frac{\int \bar{c}_p dT}{T^2} dT - \frac{\bar{s}_0}{\bar{R}} + \ln p \right)$$

Let

$$\phi = \frac{\bar{h}_0}{\bar{R}T} - \frac{1}{\bar{R}} \int \frac{\int \bar{c}_p dT}{T^2} dT - \frac{\bar{s}_0}{\bar{R}} \tag{10.100}$$

Thus

$$\bar{g} = \bar{R}T \ (\phi + \ln p) \tag{10.101}$$

where ϕ is a function of temperature only.

Let us consider a number of inert ideal gases separated from one another at the same T and p

$$G_i = \Sigma \, n_K \, g_K$$

$$= \bar{R}T \ \Sigma \, n_K(\phi_K + \ln p)$$

After the partitions are removed, the gases will diffuse, and the partial Gibbs function of a particular gas is the value of G, if that gas occupies the same volume at the same temperature exerting a partial pressure p_K. Thus

$$G_f = \bar{R}T\, \Sigma\, n_K(\phi_K + \ln p_K)$$

$$= \bar{R}T\, \Sigma\, n_K\, (\phi_K + \ln p + \ln x_K)$$

Therefore

$$G_f - G_i = \bar{R}T\, \Sigma\, n_K \ln x_K \tag{10.102}$$

Since $x_K < 1$, $(G_f - G_i)$ is negative because G decreases due to diffusion. Gibbs function of a mixture of ideal gases at T and p is thus

$$G = \bar{R}T\Sigma\, n_K\, (\phi_K + \ln p + \ln x_K) \tag{10.103}$$

Solved Examples

Example 10.1

Two vessels, A and B, both containing nitrogen, are connected by a valve which is opened to allow the contents to mix and achieve an equilibrium temperature of 27°C. Before mixing the following information is known about the gases in the two vessels.

Vessel A	*Vessel B*
$p = 1.5$ *MPa*	$p = 0.6$ *MPa*
$t = 50°C$	$t = 20°C$
Contents = 0.5 *kg mol*	*Contents* = 2.5 *kg*

Calculate the final equilibrium pressure, and the amount of heat transferred to the surroundings. If the vessel had been perfectly insulated, calculate the final temperature and pressure which would have been reached. Take $\gamma = 1.4$.

Solution For the gas in vessel A (Fig. Ex. 10.1)

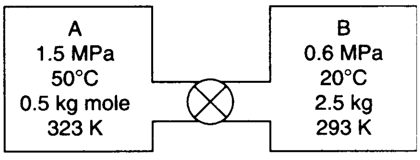


Fig. Ex. 10.1

$$p_A V_A = n_A \bar{R}\, T_A$$

where V_A is the volume of vessel A

$$1.5 \times 10^3 \times V_A = 0.5 \times 8.3143 \times 323$$

$$V_A = 0.895 \text{ m}^3$$

The mass of gas in vessel A

$$m_A = n_A\, \mu_A$$

$$= 0.5 \text{ kg mol} \times 28 \text{ kg/kg mol} = 14 \text{ kg}$$

Characteristic gas constant R of nitrogen

$$R = \frac{8.3143}{28} = 0.297 \text{ kJ/kg K}$$

For the vessel B

$$p_B V_B = m_B\, R T_B$$

$$0.6 \times 10^3 \times V_B = 2.5 \times 0.297 \times 293$$

$$\therefore \quad V_B = 0.363 \text{ m}^3$$

Total volume of A and B

$$V = V_A + V_B = 0.895 + 0.363$$

$$= 1.258 \text{ m}^3$$

Total mass of gas

$$m = m_A + m_B = 14 + 2.5 = 16.5 \text{ kg}$$

Final temperature after mixing

$$T = 27 + 273 = 300 \text{ K}$$

For the final condition after mixing

$$pV = mRT$$

where p is the final equilibrium pressure

$$\therefore \quad p \times 1.258 = 16.5 \times 0.297 \times 300$$

$$\therefore \quad p = \frac{16.5 \times 0.297 \times 300}{1.258}$$

$$= 1168.6 \text{ kPa}$$

$$= 1.168 \text{ MPa}$$

$$c_v = \frac{R}{\gamma - 1} = \frac{0.297}{0.4} = 0.743 \text{ kJ/kg K}$$

Since there is no work transfer, the amount of heat transfer

$$Q = \text{change of internal energy}$$

$$= U_2 - U_1$$

Measuring the internal energy above the datum of absolute zero (at $T = 0$ K, $u = 0$ kJ/kg)

Initial internal energy U_1 (before mixing)

$$= m_A c_v T_A + m_B c_v T_B$$

$$= (14 \times 323 + 2.5 \times 293) \times 0.743$$

$$= 3904.1 \text{ kJ}$$

Final internal energy U_2 (after mixing)

$$= mc_v T$$

$$= 16.5 \times 0.743 \times 300$$

$$= 3677.9 \text{ kJ}$$

$$\therefore \quad Q = 3677.9 - 3904.1 = -226.2 \text{ kJ}$$ *Ans.*

If the vessels were insulated

$$U_1 = U_2$$

$$m_A c_v T_A + m_B c_v T_B = mc_v T$$

where T would have been the final temperature.

$$\therefore \quad T = \frac{m_A T_A + m_B T_B}{m}$$

$$= \frac{14 \times 323 + 2.5 \times 293}{16.5} = 318.5 \text{ K}$$

or $$t = 45.5°\text{C}$$ *Ans.*

The final pressure

$$p = \frac{mRT}{V} = \frac{16.5 \times 0.297 \times 318.5}{1.258}$$

$$= 1240.7 \text{ kPa}$$

$$= 1.24 \text{ MPa}$$

Example 10.2

A certain gas has $c_p = 1.968$ *and* $c_v = 1.507$ *kJ/kg K. Find its molecular weight and the gas constant.*

A constant volume chamber of 0.3 *m*^{3} *capacity contains* 2 *kg of this gas at* 5°*C. Heat is transferred to the gas until the temperature is* 100°*C. Find the work done, the heat transferred, and the changes in internal energy, enthalpy and entropy.*

Solution Gas constant,

$$R = c_p - c_v = 1.968 - 1.507$$

$$= 0.461 \text{ kJ/kg K} \qquad \textit{Ans.}$$

Molecular weight,

$$\mu = \frac{\bar{R}}{R} = \frac{8.3143}{0.461} = 18.04 \text{ kg/kg mol} \qquad \textit{Ans.}$$

At constant volume

$$Q_{1-2} = mc_v (t_2 - t_1)$$

$$= 2 \times 1.507 (100 - 5)$$

$$= 286.33 \text{ kJ} \qquad \textit{Ans.}$$

Change in internal energy

$$W_{1-2} = \int_1^2 p\mathrm{d}v = 0 \qquad \textit{Ans.}$$

$$U_2 - U_1 = Q_{1-2} = 286.33 \text{ kJ} \qquad \textit{Ans.}$$

Change in enthalpy

$$H_2 - H_1 = mc_p (t_2 - t_1)$$

$$= 2 \times 1.968 (100 - 5) = 373.92 \text{ kJ} \qquad \textit{Ans.}$$

Change in entropy

$$S_2 - S_1 = mc_v \ln \frac{T_2}{T_1} = 2 \times 1.507 \ln \frac{373}{268}$$

$$= 0.886 \text{ kJ/K} \qquad \textit{Ans.}$$

Example 10.3

(*a*) *The specific heats of a gas are given by* $c_p = a + kT$ *and* $c_v = b + kT$*, where a, b, and k are constants and T is in K. Show that for an isentropic expansion of this gas*

$$T^b v^{a-b} e^{kT} = \text{constant}$$

(*b*) 1.5 *kg of this gas occupying a volume of* 0.06 *m*^{3} *at* 5.6 *MPa expands isentropically until the temperature is* 240°*C. If* $a = 0.946$, $b = 0.662$, *and* $k = 10^{-4}$, *calculate the work done in the expansion.*

Solution (a) $c_p - c_v = a + kT - b - kT$

$$= a - b = R$$

Now $$ds = c_v \frac{dT}{T} + R\frac{dv}{v}$$

$$= (b + kT)\frac{dT}{T} + (a - b)\frac{dv}{v} = b\frac{dT}{T} + k\,dT + (a - b)\frac{dv}{v}$$

For an isentropic process

$$b \ln T + kT + (a - b) \ln v = \text{constant}$$

$$\therefore \quad T^b \cdot v^{a-b} e^{kT} = \text{constant} \qquad \text{(Q.E.D.)}$$

(b)

$$R = a - b = 0.946 - 0.662 = 0.284 \text{ kJ/kg K}$$

$$T_2 = 240 + 273 = 513 \text{ K}$$

$$T_1 = \frac{p_1 V_1}{mR} = \frac{5.6\times10^3\times0.06}{1.5\times0.284} = 788.73 \text{ K} = 789 \text{ K}$$

$$TdS = dU + \text{đ}W = 0$$

$$\therefore \quad W_{1-2} = -\int_{T_1}^{T_2} mc_v\,dT$$

$$= 1.5\int_{513}^{789}(0.662 + 0.0001T)\,dT$$

$$= 1.5\,[0.662\,(789 - 513) + 10^{-4}\times 0.5\,\{(789)^2 - (513)^2\}]$$

$$= 1.5\,(182.71 + 19.97)$$

$$= 304 \text{ kJ}$$

Ans.

Example 10.4

Show that for an ideal gas, the slope of the constant volume line on the T–s diagram is more than that of the constant pressure line.

Solution We have, for 1 kg of ideal gas

$$Tds = du + pdv \quad = c_v\,dT + pdv$$

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

Also $$Tds = dh - vdp \quad = c_p\,dT - vdp$$

$$\therefore \quad \left(\frac{\partial T}{\partial s}\right)_p = \frac{T}{c_p}$$

Since $$c_p > c_v, \quad \frac{T}{c_v} > \frac{T}{c_p}$$

$$\therefore \quad \left(\frac{\partial T}{\partial s}\right)_v > \left(\frac{\partial T}{\partial s}\right)_p$$

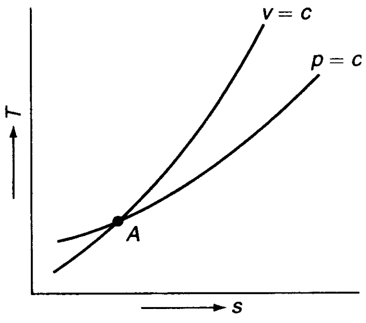


Fig. Ex. 10.4

This is shown in Fig. Ex. 10.4. The slope of the constant volume line passing through point *A* is steeper than that of the constant pressure line passing through the same point. (Q.E.D.)

Example 10.5

0.5 kg of air is compressed reversibly and adiabatically from 80 kPa, 60°C to 0.4 MPa, and is then expanded at constant pressure to the original volume. Sketch these processes on the p–v and T–s planes. Compute the heat transfer and work transfer for the whole path.

Solution The processes have been shown on the $p-v$ and $T-s$ planes in Fig. Ex. 10.5. At state 1

$$p_1V_1 = mRT_1$$

$\therefore$ V_1 = volume of air at state 1

$$= \frac{mRT_1}{p_1} = \frac{1\times 0.287\times 333}{2\times 80} = 0.597\ \text{m}^3$$

Since the process 1–2 is reversible and adiabatic

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

$$\therefore \quad \frac{T_2}{T_1} = \left(\frac{400}{80}\right)^{(1.4-1)/1.4} = (5)^{2/7}$$

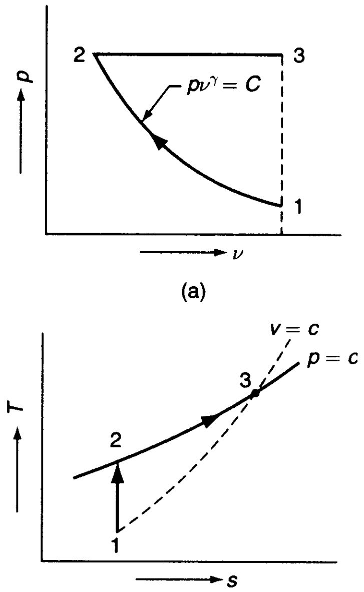
$$\therefore \quad T_2 = 333 \times (5)^{2/7} = 527\ \text{K}$$

For process 1–2, work done

$$W_{1-2} = \frac{p_1V_1 - p_2V_2}{\gamma-1} = \frac{mR(T_1-T_2)}{\gamma-1}$$

$$= \frac{1/2\times 0.287\,(333-527)}{0.4}$$

$$= -\ 69.6\ \text{kJ}$$



(a)

(b)

[redacted]

Again $\quad p_1 v_1^{\gamma} = p_2\, v_2^{\gamma}$

$$\therefore \quad \left(\frac{v_2}{v_1}\right)^{\gamma} = \frac{p_1}{p_2} = \frac{80}{400} = \frac{1}{5}$$

$$\therefore \quad \frac{v_2}{v_1} = \left(\frac{1}{5}\right)^{1/1.4} = \frac{1}{3.162} = \frac{V_2}{V_1}$$

$$\therefore \quad V_2 = \frac{0.597}{3.162} = 0.189\ \text{m}^3$$

For process 2–3, work done

$$W_{2-3} = p_2(V_1 - V_2) = 400\,(0.597 - 0.189)$$

$$= 163.2\ \text{kJ}$$

$\therefore$ Total work transfer

$$W = W_{1-2} + W_{2-3}$$

$$= -\ 69.6 + 163.2 = 93.6\ \text{kJ}$$ *Ans.*

For states 2 and 3

$$\frac{p_2V_2}{T_2} = \frac{p_3V_3}{T_3}$$

$$\therefore \qquad T_3 = T_2 \cdot \frac{V_3}{V_2} = 527 \times 3.162 = 1667 \text{ K}$$

Total heat transfer

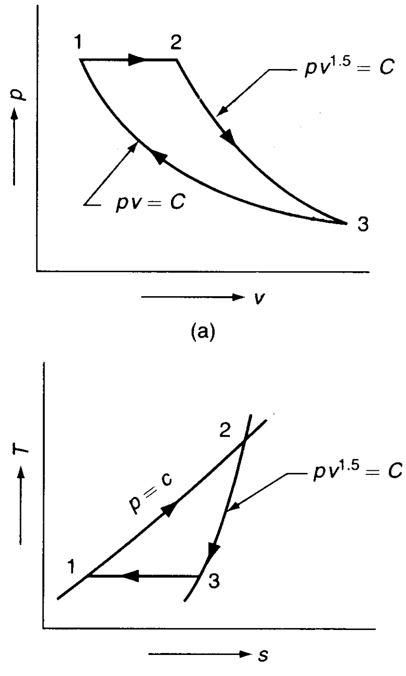
$$Q = Q_{1-2} + Q_{2-3} = Q_{2-3} = mc_p\,(T_3 - T_2)$$
$$= 1/2 \times 1.005\,(1667 - 527)$$
$$= 527.85 \text{ kJ}$$

Ans.

Example 10.6

A mass of air is initially at 260°C *and* 700 *kPa, and occupies* 0.028 *m*^{3}. *The air is expanded at constant pressure to* 0.084 *m*^{3}. *A polytropic process with n* = 1.50 *is then carried out, followed by a constant temperature process which completes a cycle. All the processes are reversible.* (*a*) *Sketch the cycle in the p–v and T–s planes.* (*b*) *Find the heat received and heat rejected in the cycle.* (*c*) *Find the efficiency of the cycle.*

Solution (a) The cycle is sketched on the p–v and T–s planes in Fig. Ex. 10.6.



(a)

(b)

Fig. Ex. 10.6

Given $p_1 = 700$ kPa, $T_1 = 260 + 273 = 533 \text{ K} = T_3$

$V_1 = 0.028 \text{ m}^3$

$V_2 = 0.084 \text{ m}^3$

From the ideal gas equation of state

$$p_1V_1 = mRT_1$$

$$m = \frac{700 \times 0.028}{0.287 \times 533} = 0.128 \text{ kg}$$

Now $$\frac{T_2}{T_1} = \frac{p_2V_2}{p_1V_1} = \frac{0.0084}{0.028} = 3$$

$$\therefore \qquad T_2 = 3 \times 533 = 1599 \text{ K}$$

Again $$\frac{p_2}{p_2} = \left(\frac{T_2}{T_3}\right)^{n/(n-1)} = \left(\frac{1599}{533}\right)^{1.5/0.5} = (3)^3 = 27$$

Heat transfer in process 1–2

$$Q_{1-2} = mc_p\,(T_2 - T_1)$$
$$= 0.128 \times 1.005\,(1599 - 533)$$
$$= 137.13 \text{ kJ}$$

Heat transfer in process 2–3

$$Q_{2-3} = \Delta U + \int p\,dv$$
$$= mc_v\,(T_3 - T_2) + \frac{mR\,(T_2 - T_3)}{n-1}$$
$$= mc_v\,\frac{n-\gamma}{n-1}\,(T_3 - T_2)$$
$$= 0.128 \times 0.718 \times \frac{1.5-1.4}{1.5-1}\,(533 - 1599)$$
$$= 0.128 \times 0.718 \times \frac{0.1}{0.5}\,(-\,1066) \qquad = -\,19.59 \text{ kJ}$$

For process 3–1

$$đQ = dU + đW = đW$$

$$\therefore \quad Q_{3-1} = W_{3-1} = \int_3^1 p\mathrm{d}V = mRT_1 \ln \frac{V_1}{V_3}$$

$$= mRT_1 \ln \frac{p_3}{p_1} = 0.128 \times 0.287 \times 533 \ln \left(\frac{1}{27}\right)$$

$$= -\,0.128 \times 0.287 \times 533 \times 3.2959$$

$$= -\,64.53 \text{ kJ}$$

(b) Heat received in the cycle

$$Q_1 = 137.13 \text{ kJ}$$

Heat rejected in the cycle

$$Q_2 = 19.59 + 64.53 = 84.12 \text{ kJ}$$ *Ans.*

(c) The efficiency of the cycle

$$\eta_{\text{cycle}} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{84.12}{137.13} = 1 - 0.61$$

$$= 0.39, \text{ or } 39\%$$ *Ans.*

Example 10.7

A mass of 0.25 kg of an ideal gas has a pressure of 300 kPa, a temperature of 80°C, and a volume of 0.07 m³. The gas undergoes an irreversible adiabatic process to a final pressure of 300 kPa and final volume of 0.10 m³, during which the work done on the gas is 25 kJ. Evaluate the c_p and c_v of the gas and the increase in entropy of the gas.

Solution From

$$p_1V_1 = mRT_1$$

$$R = \frac{300 \times 0.07}{0.25 \times (273 + 80)} = 0.238 \text{ kJ/kg K}$$

Final temperature

$$T_2 = \frac{p_2V_2}{mR} = \frac{300 \times 0.1}{0.25 \times 0.238} = 505 \text{ K}$$

Now

$$Q = (U_2 - U_1) + W = mc_v(T_2 - T_1) + W$$

$$0 = 0.25\, c_v(505 - 353) - 25$$

$$\therefore \quad c_v = \frac{25}{0.25 \times 152} = 0.658 \text{ kJ/kg K}$$

Now

$$c_p - c_v = R$$

$$c_p = 0.658 + 0.238 = 0.896 \text{ kJ/kg K}$$

Entropy change

$$S_2 - S_1 = mc_v \ln \frac{p_2}{p_1} + mc_p \ln \frac{v_2}{v_1}$$

$$= mc_p \ln \frac{V_2}{V_1} = 0.25 \times 0.896 \ln \frac{0.10}{0.07}$$

$$= 0.224 \times 0.3569 = 0.08 \text{ kJ/kg K}$$ *Ans.*

Example 10.8

A mixture of ideal gases consists of 3 *kg of nitrogen and* 5 *kg of carbondioxide at a pressure of* 300 *kPa and a temperature of* 20°C. *Find (a) the mole fraction of each constituent, (b) the equivalent molecular weight of the mixture, (c) the equivalent gas constant of the mixture, (d) the partial pressures and the partial volumes, (e) the volume and density of the mixture, and (f) the* c_p *and* c_v *of the mixture.*

If the mixture is heated at constant volume to 40°C, *find the changes in internal energy, enthalpy and entropy of the mixture. Find the changes in internal energy, enthalpy and entropy of the mixture if the heating is done at constant pressure. Take* γ *for* CO_2 *and* N_2 *to be* 1.286 *and* 1.4 *respectively.*

Solution (a) Since mole fraction $x_i = \dfrac{n_i}{\Sigma n_i}$

$$x_{N_2} = \frac{\frac{3}{28}}{\frac{3}{28}+\frac{5}{44}} = 0.485$$

$$x_{CO_2} = \frac{\frac{5}{44}}{\frac{3}{28}+\frac{5}{44}} = 0.515 \qquad \textit{Ans.}$$

(b) Equivalent molecular weight of the mixture

$$\begin{aligned} M &= x_1\,\mu_1 + x_2\,\mu_2 \\ &= 0.485 \times 28 + 0.515 \times 44 \\ &= 36.25 \text{ kg/kg mol} \qquad \textit{Ans.} \end{aligned}$$

(c) Total mass,

$$m = m_{N_2} + m_{CO_2} = 3 + 5 = 8 \text{ kg}$$

Equivalent gas constant of the mixture

$$\begin{aligned} R &= \frac{m_{N_2}R_{N_2} + m_{CO_2}R_{CO_2}}{m} \\ &= \frac{3\times\frac{8.3143}{28} + 5\times\frac{8.3143}{44}}{8} = \frac{0.89+0.94}{8} \\ &= 0.229 \text{ kJ/kg K} \qquad \textit{Ans.} \end{aligned}$$

(d)

$$p_{N_2} = x_{N_2}\cdot p = 0.485 \times 300 = 145.5 \text{ kPa}$$

$$p_{CO_2} = x_{CO_2}\cdot p = 0.515 \times 300 = 154.5 \text{ kPa}$$

$$V_{N_2} = \frac{m_{N_2}R_{N_2}T}{p} = \frac{3\times\frac{8.3143}{28}\times 293}{300} = 0.87 \text{ m}^3$$

$$V_{CO_2} = \frac{m_{CO_2}R_{CO_2}T}{p} = \frac{5\times\frac{8.3143}{44}\times 293}{300} = 0.923 \text{ m}^3 \qquad \textit{Ans.}$$

(e) Total volume of the mixture

$$V = \frac{mRT}{p} = \frac{m_{N_2} R_{N_2} T}{p_{N_2}} = \frac{m_{CO_2} R_{CO_2} T}{p_{CO_2}}$$

$$\therefore \quad V = \frac{8 \times 0.229 \times 293}{300} = 1.79 \text{ m}^3$$

Density of the mixture

$$\rho = \rho_{N_2} + \rho_{CO_2} = \frac{m}{V} = \frac{8}{1.79}$$

$$= 4.46 \text{ kg/m}^3$$ *Ans.*

(f)

$$c_{pN_2} - c_{vN_2} = R_{N_2}$$

$$\therefore \quad c_{vN_2} = \frac{R_{N_2}}{\gamma - 1} = \frac{8.3143}{28 \times (1.4 - 1)}$$

$$= 0.742 \text{ kJ/kg K}$$

$$\therefore \quad c_{pN_2} = 1.4 \times 0.742$$

$$= 1.039 \text{ kJ/kg K}$$

For CO_2, $\gamma = 1.286$

$$\therefore \quad c_{vCO_2} = \frac{R_{CO_2}}{\gamma - 1} = \frac{8.3143}{44 \times 0.286} = 0.661 \text{ kJ/kg K}$$

$$c_{pCO_2} = 1.286 \times 0.661 = 0.85 \text{ kJ/kg K}$$

For the mixture

$$c_p = \frac{m_{N_2} c_{pN_2} + m_{CO_2} c_{pCO_2}}{m_{N_2} + m_{CO_2}}$$

$$= 3/8 \times 1.039 + 5/8 \times 0.85 = 0.92 \text{ kJ/kg K}$$

$$c_v = \frac{m_{N_2} c_{vN_2} + m_{CO_2} c_{vCO_2}}{m}$$

$$= 3/8 \times 0.742 + 5/8 \times 0.661 = 0.69 \text{ kJ/kg K}$$ *Ans.*

If the mixture is heated at constant volume

$$U_2 - U_1 = mc_v (T_2 - T_1)$$

$$= 8 \times 0.69 \times (40 - 20) = 110.4 \text{ kJ}$$

$$H_2 - H_1 = mc_p (T_2 - T_1)$$

$$= 8 \times 0.92 \times 20 = 147.2 \text{ kJ}$$

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

$$= mc_v \ln \frac{T_2}{T_1} = 8 \times 0.69 \times \ln \frac{313}{293}$$

$$= 0.368 \text{ kJ/kg K}$$

If the mixture is heated at constant pressure, ΔU and ΔH will remain the same. The change in entropy will be

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

$$= mc_p \ln \frac{T_2}{T_1} = 8 \times 0.92 \ln \frac{313}{293}$$

$$= 0.49 \text{ kJ/kg K}$$ *Ans.*

Example 10.9

Find the increase in entropy when 2 kg of oxygen at 60°C are mixed with 6 kg of nitrogen at the same temperature. The initial pressure of each constituent is 103 kPa and is the same as that of the mixture.

Solution

$$x_{O_2} = \frac{p_{O_2}}{p} = \frac{\frac{2}{32}}{\frac{2}{32}+\frac{6}{28}} = 0.225$$

$$x_{N_2} = \frac{p_{N_2}}{p} = 0.775$$

Entropy increase due to diffusion

$$\Delta S = -m_{O_2} R_{O_2} \ln \frac{p_{O_2}}{p} - m_{N_2} R_{N_2} \ln \frac{p_{N_2}}{p}$$

$$= -2\left(\frac{8.3143}{32}\right) \ln 0.225 - 6\left(\frac{8.3143}{28}\right) \ln 0.775$$

$$= 1.2314 \text{ kJ/kg K}$$ *Ans.*

Example 10.10

The gas neon has a molecular weight of 20.183 and its critical temperature, pressure and volume are 44.5 K, 2.73 MPa and 0.0416 m³/kg mol. Reading from a compressibility chart for a reduced pressure of 2 and a reduced temperature of 1.3, the compressibility factor Z is 0.7. What are the corresponding specific volume, pressure, temperature, and reduced volume?

Solution At $p_r = 2$ and $T_r = 1.3$ from chart (Fig. Ex. 10.13),

$$z = 0.7$$

$$p = 2 \times 2.73 = 5.46 \text{ MPa}$$ *Ans.*

$$\frac{T}{T_c} = 1.3$$

$$T = 1.3 \times 44.5 = 57.85 \text{ K}$$ *Ans.*

$$p_v = ZRT$$

$$\therefore \quad v = \frac{0.7 \times 8.3143 \times 57.85}{20.183 \times 5.46 \times 10^3}$$

$$= 3.05 \times 10^{-3} \text{ m}^3/\text{kg}$$

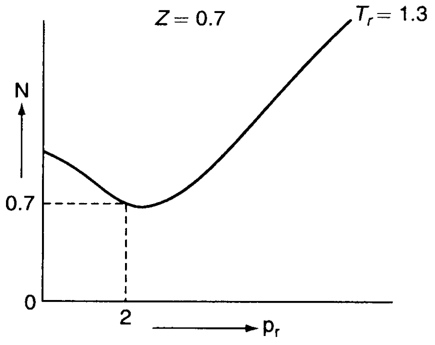


Fig. Ex. 10.10

$$\therefore \quad v_r = \frac{v}{v_c} = \frac{3.05\times10^{-3}\times20.183}{4.16\times10^{-2}}$$

$$= 1.48$$

Ans.

Example 10.11

For the Berthelot equation of state

$$p = \frac{RT}{v-b} - \frac{a}{Tv^2}$$

show that (*a*) $\lim\limits_{\substack{p\to0\\T\to\infty}} (RT - pv) = 0$

(*b*) $\lim\limits_{T\to\infty} \frac{v}{T} = \frac{R}{p}$

(*c*) *Boyle temperature,* $T_B = \sqrt{\frac{a}{bR}}$,

(*d*) *Critical properties* $p_c = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}$, $v_c = 3b$, $T_c = \sqrt{\frac{8a}{27bR}}$,

(*e*) *Law of corresponding states*

$$\left(p_r + \frac{3}{T_r \cdot v_r^2}\right)(3v_r - 1) = 8T_r$$

Solution (a)

$$p = \frac{RT}{v-b} - \frac{a}{Tv^2}$$

$$\therefore \quad RT = \left(p + \frac{a}{Tv^2}\right)(v - b)$$

or

$$\frac{RT}{p} = v + \frac{a}{pvT} - b - \frac{ab}{pv^2T}$$

$$\therefore \quad RT - pv = \frac{a}{vT} - bp - \frac{ab}{v^2T}$$

$$\therefore \quad \lim_{\substack{p\to0\\T\to\infty}} (RT - pv) = 0$$

Proved (a)

(b) Now

$$v = \frac{RT}{p} - \frac{a}{pvT} + b + \frac{ab}{pv^2T}$$

$$\therefore \quad \frac{v}{T} = \frac{R}{p} - \frac{a}{pvT^2} + \frac{b}{T} + \frac{ab}{pv^2T^2}$$

$$\therefore \quad \lim_{T\to\infty} \frac{v}{T} = \frac{R}{p}$$

Proved (b)

(c)

$$pv = RT - \frac{a}{vT} + bp + \frac{ab}{v^2T}$$

The last three terms of the equation are very small, except at very high pressures and small volume. Hence substituting $v = RT/p$

$$pv = RT - \frac{ap}{RT^2} + bp + \frac{abp^2}{R^2T^3}$$

$$\therefore \qquad \left[\frac{\partial(pv)}{\partial p}\right]_T = -\frac{a}{RT^2} + b + \frac{2abp}{R^2T^3} = 0$$

when $p = 0$, $T = T_B$, the Boyle temperature

$$\therefore \qquad \frac{a}{RT_B^2} = b$$

or

$$T_B = \sqrt{\frac{a}{bR}}$$

Proved (c)

(d)

$$p = \frac{RT}{v-b} - \frac{a}{Tv^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_{T=T_c} = -\frac{RT_c}{(v_c-b)^2} + \frac{2a}{T_c \cdot v_c^3} = 0$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_{T=T_c} = \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{T_c \cdot v_c^4} = 0$$

$$\left(p_c + \frac{a}{T_c v_c^2}\right)(v_c - b) = RT_c$$

By solving the three equations, as was done in the case of van der Waals equation of state in Article 10.7

$$p_c = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}, \; v_c = 3b, \text{ and } T_c = \sqrt{\frac{8a}{27bR}}$$

Proved (d)

(e) Solving the above three equations

$$a = \frac{8v_c^3 p_c^2}{R} = 3p_c \cdot v^2{}_c \cdot T_c$$

$$b = \frac{v_c}{3}, \; R = \frac{8}{3}\frac{p_v v_c}{T_c} \quad \text{(so that } Z_c = 3/8\text{)}$$

Substituting in the equation

$$\left(p + \frac{a}{Tv^2}\right)(v - b) = RT$$

$$\left(p + \frac{3p_c v_c^2 T_c}{Tv^2}\right)\left(v - \frac{v_c}{3}\right) = \frac{8p_c v_c}{3T_c} \cdot T$$

$$\left(p_r + \frac{3}{T_r v_r^2}\right)(3v_r - 1) = 8T_r$$

This is the law of corresponding states.

Proved (e)

Review Questions

10.1 What is a mole?

10.2 What is Avogadro's law?

10.3 What is an equation of state?

10.4 What is the fundamental property of gases with respect to the product pv?

10.5 What is universal gas constant?

10.6 Define an ideal gas.

10.7 What is the characteristic gas constant?

10.8 What is Boltzmann constant?

10.9 Why do the specific heats of an ideal gas depend only on the atomic structure of the gas?

10.10 Show that for an ideal gas the internal energy depends only on its temperature.

10.11 Show that the enthalpy of an ideal gas is a function of temperature only.

10.12 Why is there no temperature change when an ideal gas is throttled?

10.13 Show that for an ideal gas, $c_p - c_v = R$.

10.14 Derive the equations used for computing the entropy change of an ideal gas.

10.15 Show that for a reversible adiabatic process executed by an ideal gas, the following relations hold good: (i) pv^γ = constant, (ii) $Tv^{\gamma - 1}$ = constant, and (iii) $Tp^{\frac{1-\gamma}{\gamma}}$ = constant.

10.16 Express the changes in internal energy and enthalpy of an ideal gas in a reversible adiabatic process in terms of the pressure ratio.

10.17 Derive the expression of work transfer for an ideal gas in a reversible isothermal process.

10.18 What is a polytropic process? What are the relations among p, v and T of an ideal gas in a polytropic process?

10.19 Show that the entropy change between states 1 and 2 in a polytropic process, pv^n = constant, is given by the following relations:

(i) $s_2 - s_1 = \dfrac{n-\gamma}{(\gamma-1)(n-1)} R \ln \dfrac{T_2}{T_1}$

(ii) $s_2 - s_1 = \dfrac{n-\gamma}{n(\gamma-1)} R \ln \dfrac{p_2}{p_1}$

(iii) $s_2 - s_1 = -\dfrac{n-\gamma}{\gamma-1} R \ln \dfrac{v_2}{v_1}$

10.20 What are the expressions of work transfer for an ideal gas in a polytropic process, if the gas is: (i) a closed system, and (ii) a steady flow system?

10.21 Derive the expression of heat transfer for an ideal gas in a polytropic process. What is the polytropic specific heat? What would be the direction of heat transfer if (a) $n > \gamma$, and (b) $n < \gamma$?

10.22 Why is the external work supplied to a compressor equal to $-\int_{p_1}^{p_2} v \, dp$?

10.23 Write down the van der Waals equation of state. How does it differ from the ideal gas equation of state. What is the force of cohesion? What is co-volume?

10.24 What are the two-constant equations of state?

10.25 Give the virial expansions for pv in terms of p and v.

10.26 What are virial coefficients? When do they become zero?

10.27 What is the compressibility factor?

10.28 What are reduced properties?

10.29 What is the generalized compressibility chart?

10.30 What is the law of corresponding states?

10.31 Express the van der Waals constants in terms of critical properties.

10.32 Draw the diagram representing the law of corresponding states in reduced coordinates indicating the isotherms and the liquid and vapour phases.

10.33 Define Boyle temperature? How is it computed?

10.34 State Dalton's law of partial pressures.

10.35 How is the partial pressure in a gas mixture related to the mole fraction?

10.36 How are the characteristic gas constant and the molecular weight of a gas mixture computed?

10.37 What is Gibb's theorem?

10.38 Show that in a diffusion process a gas undergoes a free expansion from the total pressure to the relevant partial pressure.

10.39 Show that in a diffusion process at constant temperature the entropy increases and the Gibbs function decreases.

Problems

10.1 What is the mass of air contained in a room 6 m × 9 m × 4 m if the pressure is 101.325 kPa and the temperature is 25°C? *Ans.* 256 kg

10.2 The usual cooking gas (mostly methane) cylinder is about 25 cm in diameter and 80 cm in height. It is charged to 12 MPa at room temperature (27°C). (a) Assuming the ideal gas law, find the mass of gas filled in the cylinder. (b) Explain how the actual cylinder contains nearly 15 kg of gas. (c) If the cylinder is to be protected against excessive pressure by means of a fusible plug, at what temperature should the plug melt to limit the maximum pressure to 15 MPa?

10.3 A certain gas has $c_p = 0.913$ and $c_v = 0.653$ kJ/kg K. Find the molecular weight and the gas constant R of the gas.

10.4 From an experimental determination the specific heat ratio for acetylene (C_2H_2) is found to 1.26. Find the two specific heats.

10.5 Find the molal specific heats of monatomic, diatomic, and polyatomic gases, if their specific heat ratios are respectively 5/3, 7/5 and 4/3.

10.6 A supply of natural gas is required on a site 800 m above storage level. The gas at − 150°C, 1.1 bar from storage is pumped steadily to a point on the site where its pressure is 1.2 bar, its temperature 15°C, and its flow rate 1000 m^3/hr. If the work transfer to the gas at the pump is 15 kW, find the heat transfer to the gas between the two points. Neglect the change in K.E. and assume that the gas has the properties of methane (CH_4) which may be treated as an ideal gas having $\gamma = 1.33$ ($g = 9.75$ m/s^2). *Ans.* 63.9 kW

10.7 A constant volume chamber of 0.3 m^3 capacity contains 1 kg of air at 5°C. Heat is transferred to the air until the temperature is 100°C. Find the work done, the heat transferred, and the changes in internal energy, enthalpy and entropy.

10.8 One kg of air in a closed system, initially at 5°C and occupying 0.3 m^3 volume, undergoes a constant pressure heating process to 100°C. There is no work other than pdv work. Find (a) the work done during the process, (b) the heat transferred, and (c) the entropy change of the gas.

10.9 0.1 m^3 of hydrogen initially at 1.2 MPa, 200°C undergoes a reversible isothermal expansion to 0.1 MPa. Find (a) the work done during the process, (b) the heat transferred, and (c) the entropy change of the gas.

10.10 Air in a closed stationary system expands in a reversible adiabatic process from 0.5 MPa, 15°C to 0.2 MPa. Find the final temperature, and per kg of air, the change in enthalpy, the heat transferred, and the work done.

10.11 If the above process occurs in an open steady flow system, find the final temperature, and per kg of air, the change in internal energy, the heat transferred, and the shaft work. Neglect velocity and elevation changes.

10.12 The indicator diagram for a certain water-cooled cylinder and piston air compressor shows that during compression $pv^{1.3}$ = constant. The compression starts at 100 kPa, 25°C and ends at 600 kPa. If the process is reversible, how much heat is transferred per kg of air?

10.13 An ideal gas of molecular weight 30 and $\gamma = 1.3$ occupies a volume of 1.5 m^3 at 100 kPa and 77°C. The gas is compressed according to the law $pv^{1.25}$ = constant to a pressure of 3 MPa. Calculate the volume and temperature at the end of compression and heating, work done, heat transferred, and the total change of entropy.

10.14 Calculate the change of entropy when 1 kg of air changes from a temperature of 330 K and a volume of 0.15 m^3 to a temperature of 550 K and a volume of 0.6 m^3. If the air expands according to the law, pv^n = constant, between the same end states, calculate the heat given to, or extracted from, the air during the expansion, and show that it is approximately equal to the change of entropy multiplied by the mean absolute temperature.

10.15 0.5 kg of air, initially at 25°C, is heated reversibly at constant pressure until the volume is doubled, and is then heated reversibly at constant volume until the pressure is doubled. For the total path, find the work transfer, the heat transfer, and the change of entropy.

10.16 An ideal gas cycle of three processes uses Argon (Mol. wt. 40) as a working substance. Process 1−2 is a reversible adiabatic expansion from 0.014 m^3, 700 kPa, 280°C to 0.056 m^3. Process 2−3 is a reversible isothermal process. Process 3–1 is a constant pressure process in which heat transfer is zero. Sketch the cycle in the *p*-*v* and *T*-*s* planes, and find (a) the work transfer in process 1–2, (b) the work transfer in process 2–3, and (c) the net work of the cycle. Take $\gamma = 1.67$.

Ans. (a) 8.85kJ (b) 8.96kJ (c) 5.82kJ

10.17 A gas occupies 0.024m^3 at 700 kPa and 95°C. It is expanded in the non-flow process according to the law $pv^{1.2}$ = constant to a pressure of 70 kPa after which it is heated at constant pressure back to its original temperature. Sketch the process on the *p*-*v* and *T*-*s* diagrams, and calculate for the whole process the work done, the heat transferred, and the change of entropy. Take $c_p = 1.047$ and $c_v = 0.775$ kJ/kg K for the gas.

10.18 0.5 kg of air at 600 kPa receives an addition of heat at constant volume so that its temperature rises from 110°C to 650°C. It then expands in a cylinder polytropically to its original temperature and the index of expansion is 1.32. Finally, it is compressed isothermally to its original volume. Calculate (a) the change of entropy during each of the three stages, (b) the pressures at the end of constant volume heat addition and at the end of expansion. Sketch the processes on the *p*-*v* and *T*-*s* diagrams.

10.19 0.5 kg of helium and 0.5 kg of nitrogen are mixed at 20°C and at a total pressure of 100 kPa. Find (a) the volume of the mixture, (b) the partial volumes of the components, (c) the partial pressures of the components, (d) the mole fractions of the components, (e) the specific heats c_p and c_v of the mixture, and (f) the gas constant of the mixture.

Ans. (a) 3.481 m^3 (b) 3.045, 0.436 m^3
(c) 87.5, 12.5 kPa (d) 0.875, 0.125
(e) 3.11, 1.921 kJ/k (f) 1.189 kJ/kgK.

10.20 A gaseous mixture consists of 1 kg of oxygen and 2 kg of nitrogen at a pressure of 150 kPa and a temperature of 20°C. Determine the changes in internal energy, enthalpy and entropy of the mixture when the mixture is heated to a temperature of 100°C (a) at constant volume, and (b) at constant pressure.

10.21 A closed rigid cylinder is divided by a diaphragm into two equal compartments, each of volume 0.1 m^3. Each compartment contains air at a temperature of 20°C. The pressure in one compartment is 2.5 MPa and in the other compartment is 1 MPa. The diaphragm is ruptured so that the air in both the compartments mixes to bring the pressure to a uniform value throughout the cylinder which is insulated. Find the net change of entropy for the mixing process.

10.22 A vessel is divided into three compartments (a), (b), and (c) by two partitions. Part (a) contains oxygen and has a volume of 0.1 m^3, (b) has a volume of 0.2 m^3 and contains nitrogen, while (c) is 0.05 m^3 and holds CO$_2$. All three parts are at a pressure of 2 bar and a temperature of 13°C. When the partitions are removed and the gases mix, determine the change of entropy of each constituent, the final pressure in the vessel and the partial pressure of each gas. The vessel may be taken as being completely isolated from its surroundings.

Ans. 0.0875, 0.0783, 0.0680 kJ/K; 2 bar;
0.5714, 1.1329, 0.2857 bar.

10.23 A Carnot cycle uses 1 kg of air as the working fluid. The maximum and minimum temperatures of the cycle are 600 K and 300 K. The maximum pressure of the cycle is 1 MPa and the volume of the gas doubles during the isothermal heating process. Show by calculation of net work and heat supplied that the efficiency is the maximum possible for the given maximum and minimum temperatures.

10.24 An ideal gas cycle consists of three reversible processes in the following sequence: (a) constant volume pressure rise, (b) isentropic expansion to *r* times the initial volume, and (c) constant pressure decrease in volume. Sketch the cycle on the *p*-*v* and *T*-*s* diagrams. Show that the efficiency of the cycle is

$$\eta_{\text{cycle}} = \frac{r^{\gamma} - 1 - \gamma(r-1)}{r^{\gamma} - 1}$$

Evaluate the cycle efficiency when $\gamma = \frac{4}{3}$ and $r = 8$. *Ans.* ($\eta = 0.378$)

10.25 Using the Dieterici equation of state

$$p = \frac{RT}{v-b} \cdot \exp\left(-\frac{a}{RTv}\right)$$

(a) Show that

$$p_c = \frac{a}{4e^2b^2},\ v_c = 2b,\ T_c = \frac{a}{4Rb}$$

(b) expand in the form

$$pv = RT\left(1 + \frac{B}{v} + \frac{C}{v^2} + \cdots\right)$$

(c) show that $T_B = \dfrac{a}{bR}$

10.26 The number of moles, the pressures, and the temperatures of gases *a*, *b*, and *c* are given below as follows

Gas	*m (kg mol)*	*p (kPa)*	*t (°C)*
N_2	1	350	100
CO	3	420	200
O_2	2	700	300

If the containers are connected, allowing the gases to mix freely, find (a) the pressure and temperature of the resulting mixture at equilibrium, and (b) the change of entropy of each constituent and that of the mixture.

10.27 Calculate the volume of 2.5 kg moles of steam at 236.4 atm. and 776.76 K with the help of compressibility factor versus reduced pressure graph. At this volume and the given pressure, what would the temperature be in K, if steam behaved like a van der Waals gas?

The critical pressure, volume, and temperature of steam are 218.2 atm, 57 cm^3/g mole, and 647.3 K respectively.

10.28 Two vessels, *A* and *B*, each of volume 3 m^3 may be connected together by a tube of negligible volume. Vessel *A* contains air at 7 bar, 95°C while *B* contains air at 3.5 bar, 205°C. Find the change of entropy when *A* is connected to *B*. Assume the mixing to be complete and adiabatic.

Ans. (0.975 kJ/kg K)

10.29 An ideal gas at temperature T_1 is heated at constant pressure to T_2 and then expanded reversibly, according to the law pv^n = constant, until the temperature is once again T_1. What is the required value of *n*, if the changes of entropy during the separate processes are equal?

Ans. $\left(n = \frac{2\gamma}{\gamma+1}\right)$

10.30 A certain mass of sulphur dioxide (SO_2) is contained in a vessel of 0.142 m^3 capacity, at a pressure and temperature of 23.1 bar and 18°C respectively. A valve is opened momentarily and the pressure falls immediately to 6.9 bar. Sometime later the temperature is again 18°C and the pressure is observed to be 9.1 bar. Estimate the value of specific heat ratio. *Ans.* 1.29

10.31 A gaseous mixture contains 21% by volume of nitrogen, 50% by volume of hydrogen, and 29% by volume of carbon-dioxide. Calculate the molecular weight of the mixture, the characteristic gas constant *R* for the mixture and the value of the reversible adiabatic index γ. (At 10°C, the c_p values of nitrogen, hydrogen, and carbon dioxide are 1.039, 14.235, and 0.828 kJ/kg K respectively.)

A cylinder contains 0.085 m^3 of the mixture at 1 bar and 10°C. The gas undergoes a reversible non-flow process during which its volume is reduced to one-fifth of its original value. If the law of compression is $pv^{1.2}$ = constant, determine the work and heat transfers in magnitude and sense and the change in entropy.

Ans. 19.64 kg/kg mol, 0.423 kJ/kg K,
1.365, − 16 kJ, − 7.24 kJ, − 0.31 kJ/kg K

10.32 Two moles of an ideal gas at temperature *T* and pressure *p* are contained in a compartment. In an adjacent compartment is one mole of an ideal gas at temperature 2*T* and pressure *p*. The gases mix adiabatically but do not react chemically when a partition separating the compartments is withdrawn. Show that the entropy increase due to the mixing process is given by

$$R\left(\ln\frac{27}{4}+\frac{\gamma}{\gamma-1}\ln\frac{32}{27}\right)$$

provided that the gases are different and that the ratio of specific heat γ is the same for both gases and remains constant.

What would the entropy change be, if the mixing gases were of the same species?

10.33 n_1 moles of an ideal gas at pressure p_1 and temperature *T* are in one compartment of an insulated container. In an adjoining compartment, separated by a partition, are n_2 moles of an ideal gas at pressure p_2 and temperature *T*. When the partition is removed, calculate (a) the final pressure of the mixture, (b) the entropy change when the gases are identical, and (c) the entropy change when the gases are different. Prove that the entropy change in (c) is the same as that produced by two independent free expansions.

10.34 Assume that 20 kg of steam are required at a pressure of 600 bar and a temperature of 750°C in order to conduct a particular experiment. A 140-litre heavy duty tank is available for storage.

Predict if this is an adequate storage capacity using:

(a) the ideal gas theory,

(b) the compressibility factor chart,

(c) the van der Waals equation with $a = 5.454$ (litre)^2 atm/(g mol)^2, $b = 0.03042$ litres/g mol for steam,
(d) the Mollier chart
(e) the steam tables.

Estimate the error in each.

Ans. (a) 157.75*l*, (b) 132.5*l*, (c) 124.94*l*, (d) 137.29*l*

10.35 Estimate the pressure of 5 kg of CO_2 gas which occupies a volume of 0.70 m^3 at 75°C, using the Beattie-Bridgeman equation of state.

Compare this result with the value obtained using the generalized compressibility chart. Which is more accurate and why?

For CO_2 with units of atm, litres/g mol and K, $A_0 = 5.0065$, $a = 0.07132$, $B_0 = 0.10476$, $b = 0.07235$, $C \times 10^{-4} = 66.0$.

10.36 Measurements of pressure and temperature at various stages in an adiabatic air turbine show that the states of air lie on the line $pv^{1.25}$ = constant. If kinetic and gravitational potential energy are neglected, prove that the shaft work per kg as a function of pressure is given by the following relation

$$W = 3.5\, p_1 v_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{1/5}\right]$$

Take γ for air as 1.4.

10.37 Air flows steadily into a compressor at a temperature of 17°C and a pressure of 1.05 bar and leaves at a temperature of 247°C and a pressure of 6.3 bar. There is no heat transfer to or from the air as it flows through the compressor; changes in elevation and velocity are negligible. Evaluate the external work done per kg of air, assuming air as an ideal gas for which $R = 0.287$ kJ/kg K and $\gamma = 1.4$. Evaluate the minimum external work required to compress the air adiabatically from the same initial state to the same final pressure and the isentropic efficiency of the compressor.

Ans. – 225kJ/kg, – 190kJ/kg, 84.4%

10.38 A slow-speed reciprocating air compressor with a water jacket for cooling approximates a quasi-static compression process following a path $pv^{1.3}$ = const. If air enters at a temperature of 20°C and a pressure of 1 bar, and is compressed to 6 bar at a rate of 1000 kg/h, determine the discharge temperature of air, the power required and the heat transferred per kg. *Ans.* 443k, 51.82 kW, 36 kJ/kg

10.39 A single-acting two-stage reciprocating air compressor with complete intercooling delivers 6 kg/min at 15 bar pressure. Assume an intake condition of 1 bar and 15°C and that the compression and expansion processes are polytropic with $n = 1.3$. Calculate: (a) the power required, (b) the isothermal efficiency.

Ans. (a) 26.15 kW (b) 85.6%

10.40 A two-stage air compressor receives 0.238 m^3/s of air at 1 bar and 27°C and discharges it at 10 bar. The polytropic index of compression is 1.35. Determine (a) the minimum power necessary for compression, (b) the power needed for single-stage compression to the same pressure, (c) the maximum temperature for (a) and (b), and (d) the heat removed in the intercooler. *Ans.* (a) 63.8 kW, (b) 74.9 kW, (c) 404.2 k, 544.9 k, (d) 28.9 kW

10.41 A mass of an ideal gas exists initially at a pressure of 200 kPa, temperature 300 K, and specific volume 0.5 m^3/kg. The value of γ is 1.4. (a) Determine the specific heats of the gas. (b) What is the change in entropy when the gas is expanded to pressure 100 kPa according to the law $pv^{1.3}$ = const? (c) What will be the entropy change if the path is $pv^{1.5}$ = const. (by the application of a cooling jacket during the process)? (d) What is the inference you can draw from this example?

Ans. (a) 1.166, 0.833 kJ/kg K, (b) 0.044 kJ/kg K (c) – 0.039 kJ/kg K (d) Entropy increases when $n < \gamma$ and decreases when $n > \gamma$

10.42 (a) A closed system of 2 kg of air initially at pressure 5 atm and temperature 227°C, expands reversibly to pressure 2 atm following the law $pv^{1.25}$ = const. Assuming air as an ideal gas, determine the work done and the heat transferred. *Ans.* 193 kJ, 72 kJ

(b) If the system does the same expansion in a steady flow process,what is the work done by the system? *Ans.* 241 kJ

10.43 Air contained in a cylinder fitted with a piston is compressed reversibly according to the law $pv^{1.25}$ = const.Themassofairinthecylinderis0.1kg. The initial pressure is 100 kPa and the initial temperature 20°C. The final volume is 1/8 of the initial volume. Determine the work and the heat transfer. *Ans.* – 22.9 kJ, – 8.7 kJ

10.44 Air is contained in a cylinder fitted with a frictionless piston. Initially the cylinder contains 0.5 m^3 of air at 1.5 bar, 20°C. The air is then compressed reversibly according to the law pv^n = constant until the final pressure is 6 bar, at which point the temperature is 120°C. Determine: (a) the polytropic index *n*, (b) the final volume of air, (c) the work done on the air and the heat transfer, and (d) the net change in entropy.

Ans. (a) 1.2685, (b) 0.1676 m^3 (c) – 95.3 kJ, – 31.5 kJ, (d) 0.0153 kJ/K

10.45 The specific heat at constant pressure for air is given by

$$c_p = 0.9169 + 2.577 \times 10^{-4}T - 3.974 \times 10^{-8} T^2 \text{ kJ/kg K}$$

Determine the change in internal energy and that in entropy of air when it undergoes a change of state from 1 atm and 298 K to a temperature of 2000 K at the same pressure.

Ans. 1470.4 kJ/kg, 2.1065 kJ/kg K

10.46 A closed system allows nitrogen to expand reversibly from a volume of 0.25 m^3 to 0.75 m^3 along the path $pv^{1.32}$ = const. The original pressure of the gas is 250 kPa and its initial temperature is 100°C. (a) Draw the *p-v* and *T-s* diagrams. (b)What are the final temperature and the final pressure of the gas? (c) How much work is done and how much heat is transferred? (d) What is the entropy change of nitrogen?

Ans. (b) 262.44 K, 58.63 kPa, (c) 57.89 kJ, 11.4 kJ, (d) 0.0362 kJ/K

10.47 Methane has a specific heat at constant pressure given by $c_p = 17.66 + 0.06188\, T$ kJ/kg mol K when 1 kg of methane is heated at constant volume from 27 to 500°C. If the initial pressure of the gas is 1 atm, calculate the final pressure, the heat transfer, the work done and the change in entropy.

Ans. 2.577 atm, 1258.5 kJ/kg, 0, 2.3838 kJ/kg K

10.48 Air is compressed reversibly according to the law $pv^{1.25}$ = const. from an initial pressure of 1 bar and volume of 0.9 m^3 to a final volume of 0.6 m^3. Determine the final pressure and the change of entropy per kg of air.

Ans. 1.66 bar, – 0.0436 kJ/kg K

10.49 In a heat engine cycle, air is isothermally compressed. Heat is then added at constant pressure, after which the air expands isentropically to its original state. Draw the cycle on *p-v* and *T-s* coordinates. Show that the cycle efficiency can be expressed in the following form

$$\eta = 1 - \frac{(\gamma - 1)\ln r}{\gamma[r^{\gamma-1/\gamma} - 1]}$$

where *r* is the pressure ratio, p_2/p_1. Determine the pressure ratio and the cycle efficiency if the initial temperature is 27°C and the maximum temperature is 327°C. *Ans.* 13.4, 32.4%

10.50 What is the minimum amount of work required to separate 1 mole of air at 27°C and 1 atm pressure (assumed composed of 1/5 O_2 and 4/5 N_2) into oxygen and nitrogen each at 27°C and 1 atm pressure? *Ans.* 1250 J

10.51 A closed adiabatic cylinder of volume 1 m^3 is divided by a partition into two compartments 1 and 2. Compartment 1 has a volume of 0.6 m^3 and contains methane at 0.4 MPa, 40°C, while compartment 2 has a volume of 0.4 m^3 and contains propane at 0.4 MPa, 40°C. The partition is removed and the gases are allowed to mix. (a) When the equilibrium state is reached, find the entropy change of the universe. (b) What are the molecular weight and the specific heat ratio of the mixture?

The mixture is now compressed reversibly and adiabatically to 1.2 MPa. Compute (c) the final temperature of the mixture, (d) the work required per unit mass, and (e) the specific entropy change for each gas. Take c_p of methane and propane as 35.72 and 74.56 kJ/kg mol K respectively.

Ans. (a) 0.8609 kJ/K, (b) 27.2, 1.193 (c) 100.9°C, (d) 396 kJ, (e) 0.255 kJ/kg K

10.52 An ideal gas cycle consists of the following reversible processes: (i) isentropic compression, (ii) constant volume heat addition, (iii) isentropic expansion, and (iv) constant pressure heat rejection. Show that the efficiency of this cycle is given by

$$\eta = 1 - \frac{1}{r_k^{\gamma-1}}\left[\frac{\gamma(a^{1/\gamma} - 1)}{a - 1}\right]$$

where r_k is the compression ratio and *a* is the ratio of pressures after and before heat addition.

An engine operating on the above cycle with a compression ratio of 6 starts the compression with air at 1 bar, 300 K. If the ratio of pressures after and before heat addition is 2.5, calculate the efficiency and the m.e.p. of the cycle. Take $\gamma = 1.4$ and $c_v = 0.718$ kJ/kg K. *Ans.* 0.579, 2.5322 bar

10.53 The relation between *v*, *p* and *v* for many gases is of the form $u = a + bpv$ where *a* and *b* are constants. Show that for a reversible adiabatic process pv^{γ} = constant, where $\gamma = (b + 1)/b$.

10.54 (a) Show that the slope of a reversible adiabatic process on *p-v* coordinates is

$$\frac{\mathrm{d}p}{\mathrm{d}v} = -\frac{1}{kv}\frac{c_p}{c_v} \text{ where } k = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$$

(b) Hence, show that for an ideal gas, pv^{γ} = constant, for a reversible adiabatic process.

10.55 A certain gas obeys the Clausius equation of state $p(v - b) = RT$ and has its internal energy given by $u = c_v T$. Show that the equation for a reversible adiabatic process is $p(v - b)^{\gamma}$ = constant, where $\gamma = c_p/c_v$.

10.56 (a) Two curves, one representing a reversible adiabatic process undergone by an ideal gas and the other an isothermal process by the same gas, intersect at the same point on the *p-v* diagram. Show that the ratio of the slope of the adiabatic curve to the slope of the isothermal curve is equal to γ. (b) Determine the ratio of work done during a reversible adiabatic process to the work done during an isothermal process for a gas having $\gamma = 1.6$. Both processes have a pressure ratio of 6.

10.57 Two containers *p* and *q* with rigid walls contain two different monatomic gases with masses m_p and m_q, gas constants R_p and R_q, and initail temperatures T_p and T_q respectively, are brought in contact with each other and allowed to exchange energy until equilibrium is achieved. Determine: (a) the final temperature of the two gases and (b) the change of entropy due to this energy exchange.

10.58 The pressure of a certain gas (photon gas) is a function of temperature only and is related to the energy and volume by $p(T) = (1/3)\,(U/V)$. A system consisting of this gas confined by a cylinder and a piston undergoes a Carnot cycle between two pressures p_1 and p_2. (a) Find expressions for work and heat of reversible isothermal and adiabatic processes. (b) Plot the Carnot cycle on *p-v* and *T-s* diagrams. (c) Determine the efficiency of the cycle in terms of pressures. (d) What is the functional relation between pressure and temperature?

10.59 The gravimetric analysis of dry air is approximately: oxygen = 23%, nitrogen = 77%. Calculate: (a) the volumetric analysis, (b) the gas constant, (c) the molecular weight, (d) the respective partial pressures, (e) the specific volume at 1 atm, 15°C, and (f) How much oxygen must be added to 2.3 kg air to produce a mixture which is 50% oxygen by volume?

Ans. (a) 21% O_2, 79% N_2, (b) 0.288 kJ/kg K, (d) 21 kPa for O_2, (e) 0.84 m³/kg, (f) 1.47 kg

10.60 A vessel of volume $2V$ is divided into two equal compartments. These are filled with the same ideal gas, the temperature and pressure on one side of the partition being (p_1, T_1) and on the other (p_2, T_2). Show that if the gases on the two sides are allowed to mix slowly with no heat entering, the final pressure and temperature will be given by

$$p = \frac{p_1 + p_2}{2}, \quad T = \frac{T_1 T_2 (p_1 + p_2)}{p_1 T_2 + p_2 T_1}$$

Further, show that the entropy gain is

$$\Delta S = V\left[\left(\frac{c_p}{R}\right)\left\{\frac{p_1}{T_2}\ln\frac{T}{T_1} + \frac{p_2}{T_2}\ln\frac{T}{T_2}\right\} - \frac{p_1}{T_1}\ln\frac{p}{p_1} - \frac{p_2}{T_2}\ln\frac{p}{p_2}\right]$$

10.61 An ideal gas with a constant volume of c_p = 29.6 J/gmol-K is made to undergo a cycle consisting of the following reversible processes in a closed system:

Process 1–2: The gas expands adiabatically from 5 MPa, 550 K to 1 MPa;

Process 2–3: The gas is heated at constant volume until 550 K;

Process 3–1: The gas is compressed isothermally back to its initial condition.

Calculate the work, the heat and the change of entropy of the gas for each of the three processes. Draw the *p-v* and *T-s* diagrams.

Ans. W_{1-2} = 4260 J/gmol, $Q_{1-2} = 0$, $\Delta s_{1-2} = 0$, $W_{2-3} = 0$, Q_{2-3} = 4260 J/gmol, Δs_{2-3} = 9.62 J/gmol-K, W_{3-1} = – 5290 J/mol = Q_{3-1}, Δs_{3-1} = – 9.62 J/gmol-K, $W_{net} - Q_{net}$ = – 1030 Jg/gmol, $\oint \mathrm{d}S = 0$.

10.62 Air in a closed system expands reversibly and adiabatically from 3 MPa. 200°C to two times its initial volume, and then cools at constant volume until the pressure drops to 0.8 MPa. Calculate the work done and heat transferred per kg of air. Use $c_p = 1.017$ and $c_v = 0.728$ kJ/kgK.

Ans: 82.7 kJ/kg, – 78.1 kJ/kg

10.63 A vessel is divided into three compartments (a), (b) and (c) by two partitions. Part (a) contains hydrogen and has a volume of 0.1 m^3, part (b) contains nitrogen and has a volume of 0.2 m^3 and part (c) contains carbon dioxide and has a volume of 0.05 m^3. All the three parts are at a pressure of 2 bar and a temperature of 13°C. The partitions are removed and the gases are allowed to mix. Determine (a) the molecular weight of the mixture, (b) the characteristics gas constant for the mixture, (c) the partial pressures of each gas, (d) the reversible adiabatic index γ, and (e) the entropy change due to diffusion. The specific heats of hydrogen, nitrogen and carbon dioxide are 14.235, 1.039 and 0.828 kJ/kg K respectively.

The above gas mixture is then reversibly compressed to a pressure of 6 bar according to the law $pv^{1.2}$ = constant, (f) Determine the work and heat interactions in magnitude and sense, and (g) the change in entropy.

Ans. (a) 22.8582 (b) 0.3637 kJ/kg K (c) $p_{H_2} = 0.5714, p_{N_2} = 1.1428, p_{CO_2} = 0.2858$ bar (d) 1.384 (e) 0.3476 kJ/kgK (f) – 70.455 kJ, – 33.772 kJ (g) – 0.1063 kJ/K.

10.64 A four cylinder single-stage air compressor has a bore of 200 mm and a stroke of 300 mm and runs at 400 rpm. At a working pressure of 721.3 kPa it delivers 3.1 m^3 of air per min at 270°C. Calculate (a) the mass flow rate, (b) the free air delivery (FAD) (c) effective swept volume, (d) volumetric efficiency. Take the inlet condition as that of the free air at 101.3 kPa, 21°C. *Ans.* (a) 0.239 kg/s (b) 0.199 m^3/s (c) 0.299 m^3, (d) 79.2%

10.65 Predict the pressure of nitrogen gas at $T = 175$ K and $v = 0.00375$ m^3/kg on the basis of (a) the ideal gas equation of state, (b) the van der Waals equation of state, (c) the Beattie-Bridgeman equation of state and (d) the Benedict-Webb-Rubin equation of state. Compare the values obtained with the experimentally determined value of 10,000 kPa. *Ans.* (a) 13,860 kPa (b) 9468 kPa (c) 10,110 kPa (d) 10,000 kPa

10.66 The pressure in an automobile tyre depends on the temperature of the air in the tyre. When the air temperature is 25°C, the pressure gauge reads 210 kPa. If the volume of the tyre is 0.025 m^3, determine the pressure rise in the tyre when the air temperature in the tyre rises to 50°C. Also find the amount of air that must be bled off to restore pressure to its original value at this temperature. Take atmospheric pressure as 100 kPa.

10.67 Two tanks are connected by a valve. One tank contains 2 kg of CO gas at 77°C and 0.7 bar. The other tank holds 8 kg of the same gas at 27°C and 1.2 bar. The valve is opened and the gases are allowed to mix while receiving energy by heat transfer from the surroundings. The final equilibrium temperature is 42°C. Using the ideal gas model, determine (a) the final equilibrium pressure, (b) the heat transfer for the process.

Ans. (a) 1.05 bar (b) 37.25 kJ

C H A P T E R

11

Thermodynamic Relations, Equilibrium and Third Law

11.1 SOME MATHEMATICAL THEOREMS

Theorem 1 If a relation exists among the variables x, y, and z, then z may be expressed as a function of x and y, or

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y$$

If
$$\left(\frac{\partial z}{\partial x}\right)_y = M, \quad \text{and} \quad \left(\frac{\partial z}{\partial y}\right)_x = N$$

then
$$\mathrm{d}z = M\,\mathrm{d}x + N\,\mathrm{d}y,$$

where z, M and N are functions of x and y. Differentiating M partially with respect to y, and N with respect to x

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \cdot \partial y}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \cdot \partial x}$$

$$\therefore \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{11.1}$$

This is the *condition of exact* (*or perfect*) *differential.*

Theorem 2 If a quantity f is a function of x, y, and z, and a relation exists among x, y and z, then f is a function of any two of x, y, and z. Similarly, any one of x, y, and z may be regarded to be a function of f and any one of x, y, and z. Thus, if

$$x = x\,(f, y)$$

$$\mathrm{d}x = \left(\frac{\partial x}{\partial f}\right)_y \mathrm{d}f + \left(\frac{\partial x}{\partial y}\right)_f \mathrm{d}y$$

Similarly, if
$$y = y(f, z)$$

$$\mathrm{d}y = \left(\frac{\partial y}{\partial f}\right)_z \mathrm{d}f + \left(\frac{\partial y}{\partial z}\right)_f \mathrm{d}z$$

Substituting the expression of dy in the preceding equation

$$\mathrm{d}x = \left(\frac{\partial x}{\partial f}\right)_y \mathrm{d}f + \left(\frac{\partial x}{\partial y}\right)_f \left[\left(\frac{\partial y}{\partial f}\right)_z \mathrm{d}f + \left(\frac{\partial y}{\partial z}\right)_f \mathrm{d}z\right] = \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z\right] \mathrm{d}f + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \mathrm{d}z$$

Again
$$\mathrm{d}x = \left(\frac{\partial x}{\partial f}\right)_z \mathrm{d}f + \left(\frac{\partial x}{\partial z}\right)_f \mathrm{d}z$$

$$\therefore \quad \left(\frac{\partial x}{\partial z}\right)_f = \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f$$

$$\therefore \quad \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1 \tag{11.2}$$

Theorem 3 Among the variables x, y, and z, any one variable may be considered as a function of the other two. Thus

$$x = x(y, z)$$

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

Similarly,

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

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

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

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

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

or

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1 \tag{11.3}$$

Among the thermodynamic variables p, V and T, the following relation holds good

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

11.2 MAXWELL'S EQUATIONS

A pure substance existing in a single phase has only two independent variables. Of the eight quantities p, V, T, S, U, H, F (Helmholtz function), and G (Gibbs function) *any one may be expressed as a function of any two others.*

For a pure substance undergoing an infinitesimal reversible process

(a) $dU = TdS - pdV$
(b) $dH = dU + pdV + Vdp = TdS + Vdp$
(c) $dF = dU - TdS - SdT = -pdV - SdT$
(d) $dG = dH - TdS - SdT = Vdp - SdT$

Since U, H, F and G are thermodynamic properties and exact differentials of the type

$$dz = M\,dx + N\,dy, \text{ then}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Applying this to the four equations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{11.4}$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{11.5}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{11.6}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \tag{11.7}$$

These four equations are known as *Maxwell's equations.*

11.3 TdS EQUATIONS

Let entropy S be imagined as a function of T and V. Then

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore \quad TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

Since $T\left(\frac{\partial S}{\partial T}\right)_V = C_v$, heat capacity at constant volume, and

$\left(\frac{\partial S}{\partial T}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$, Maxwell's third equation,

$$TdS = C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \tag{11.8}$$

This is known as the *first TdS equation.*

If $S = S(T, p)$

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

$$\therefore \quad TdS = T\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp$$

Since $\quad T\left(\frac{\partial S}{\partial T}\right)_p = C_p$, and $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

then
$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp \tag{11.9}$$

This is known as the *second TdS equation*.

11.4 DIFFERENCE IN HEAT CAPACITIES

Equating the first and second *TdS* equations

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp = C_v\, dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$(C_p - C_v)\, dT = T\left(\frac{\partial p}{\partial T}\right)_V dV + T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$\therefore \quad dT = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_p - C_v} dV + \frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p - C_v} dp$$

Again
$$dT = \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial T}{\partial p}\right)_V dp$$

$$\therefore \quad \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_p - C_v} = \left(\frac{\partial T}{\partial V}\right)_p \text{ and } \frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p - C_v} = \left(\frac{\partial T}{\partial p}\right)_V$$

Both these equations give

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p.$$

But
$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$$

$$\therefore \quad C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T \tag{11.10}$$

This is a very important equation in thermodynamics. It indicates the following important facts.

(a) Since $\left(\frac{\partial V}{\partial T}\right)_p^2$ is always positive, and $\left(\frac{\partial p}{\partial V}\right)_T$ for any substance is negative, $(C_p - C_v)$ is always positive.

Therefore, C_p is always greater than C_v.

(b) As $T \to 0\,K$, $C_p \to C_v$ or at absolute zero, $C_p = C_v$.

(c) When $\left(\frac{\partial V}{\partial T}\right)_p = 0$ (e.g., for water at 4°C, when density is maximum, or specific volume minimum), $C_p = C_v$.

(d) For an ideal gas, $pV = mRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{mR}{p} = \frac{V}{T}$$

and

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{mRT}{V^2}$$

$\therefore$

$$C_p - C_v = mR$$

or

$$c_p - c_v = R$$

Equation (11.10) may also be expressed in terms of volume expansivity (β), defined as

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

and isothermal compressibility (k_T), defined as

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T$$

$$C_p - C_v = \frac{TV\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p\right]^2}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}$$

$\therefore$

$$C_p - C_v = \frac{TV\beta^2}{k_T} \qquad (11.11)$$

11.5 RATIO OF HEAT CAPACITIES

At constant S, the two TdS equations become

$$C_p dT_s = T\left(\frac{\partial V}{\partial T}\right)_p dp_s$$

$$C_v dT_s = -T\left(\frac{\partial p}{\partial T}\right)_V dV_s$$

$\therefore$

$$\frac{C_p}{C_v} = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial p}{\partial V}\right)_S = \frac{\left(\frac{\partial p}{\partial V}\right)_S}{\left(\frac{\partial p}{\partial V}\right)_T} = \gamma$$

Since $\gamma > 1$,

$$\left(\frac{\partial p}{\partial V}\right)_S > \left(\frac{\partial p}{\partial V}\right)_T$$

Therefore, the slope of an isentrope is greater than that of an isotherm on $p - v$ diagram (Fig. 11.1). For reversible and adiabatic compression, the work done is

$$W_s = h_{2s} - h_1 = \int_1^{2S} v\,dp = \text{Area } 1\text{–}2S\text{–}3\text{–}4\text{–}1$$

For reversible and isothermal compression, the work done would be

$$W_T = h_{2T} - h_1 = \int_1^{2T} v\,dp = \text{Area } 1\text{–}2T - 3 - 4 - 1$$

$$\therefore \quad W_T < W_S$$

For polytropic compression with $1 < n < \gamma$, the work done will be between these two values. So, isothermal compression requires minimum work. (See Sec. 10.4)

The adiabatic compressibility (k_s) is defined as

$$k_s = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

$$\therefore \quad \frac{C_p}{C_v} = \frac{-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T}{-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_s} = \gamma$$

or $$\gamma = \frac{k_T}{k_s} \tag{11.12}$$

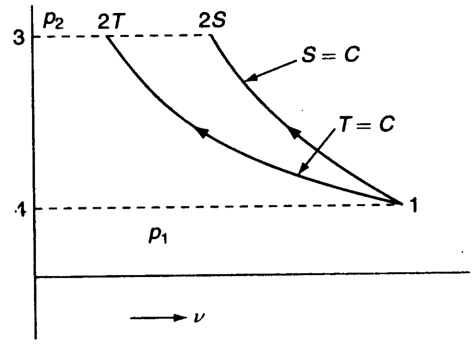


Fig. 11.1 *Compression work in different reversible processes*

11.6 ENERGY EQUATION

For a system undergoing an infinitesimal reversible process between two equilibrium states, the change of internal energy is

$$dU = TdS - pdV$$

Substituting the first *TdS* equation

$$dU = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dV - pdV$$

$$= C_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV \tag{11.13}$$

If $$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{11.14}$$

This is known as the *energy equation*. Two applications of the equation are given below:

(a) For an ideal gas, $$p = \frac{n\bar{R}T}{V}$$

$$\therefore \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{n\bar{R}}{V} = \frac{p}{T}$$

$$\therefore \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\cdot\frac{p}{T} - p = 0$$

U does not change when V changes at $T = C$.

$$\left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial U}\right)_T = 1$$

$$\therefore \qquad \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Since
$$\left(\frac{\partial p}{\partial V}\right)_T \neq 0, \left(\frac{\partial U}{\partial p}\right)_T = 0$$

U does not change either when p changes at $T = C$. So the internal energy of an ideal gas is a function of temperature only, as shown earlier in Chapter 10.

Another important point to note is that in Eq. (11.13), for an ideal gas

$pV = n\bar{R}T$ and
$$T\left(\frac{\partial p}{\partial T}\right)_v - p = 0$$

Therefore
$$dU = C_v\, dT$$

holds good for an ideal gas in any process (even when the volume changes). But for any other substance

$$dU = C_v\, dT$$

is true only when the volume is constant and $dV = 0$.

Similarly
$$dH = TdS + Vdp$$

and
$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$\therefore \qquad dH = C_p\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp \tag{11.15}$$

$$\therefore \qquad \left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{11.16}$$

As shown for internal energy, it can be similarly proved from Eq. (11.16) that the enthalpy of an ideal gas is not a function of either volume or pressure

$$\left[\text{i.e.} \left(\frac{\partial H}{\partial p}\right)_T = 0 \text{ and } \left(\frac{\partial H}{\partial V}\right)_T = 0\right]$$

but a function of temperature alone.

Since for an ideal gas, $pV = n\bar{R}T$

and
$$V - T\left(\frac{\partial V}{\partial T}\right)_p = 0$$

the relation $dH = C_p\, dT$ is true for any process (even when the pressure changes). However, for any other substance the relation $dH = C_p\, dT$ holds good only when the pressure remains constant or $dp = 0$.

(b) Thermal radiation in equilibrium with the enclosing walls possesses an energy that depends only on the volume and temperature. The energy density (u), defined as the ratio of energy to volume, is a function of temperature only, or

$$u = \frac{U}{V} = f(T) \text{ only.}$$

The electromagnetic theory of radiation states that radiation is equivalent to a photon gas and it exerts a pressure, and that the pressure exerted by the black-body radiation in an enclosure is given by

$$p = \frac{u}{3}$$

Black-body radiation is thus specified by the pressure, volume, and temperature of the radiation.

Since $$U = uV \text{ and } p = \frac{u}{3}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = u \text{ and } \left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{3}\frac{du}{dT}$$

By substituting in the energy Eq. (11.13)

$$u = \frac{T}{3}\frac{du}{dT} - \frac{u}{3}$$

$\therefore$ $$\frac{du}{u} = 4\frac{dT}{T}$$

or $$\ln u = \ln T^4 + \ln b$$

or $$u = bT^4$$

where b is a constant. This is known as the *Stefan-Boltzmann Law.*

Since $$U = uV = VbT^4$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_v = 4VbT^3$$

and $$\left(\frac{\partial p}{\partial T}\right)_V = \frac{1}{3}\frac{du}{dT} = \frac{4}{3}bT^3$$

from the first *TdS* equation

$$TdS = C_v\, dT + T\left(\frac{\partial p}{\partial T}\right)_V dV = 4VbT^3\, dT + \frac{4}{3}bT^4 \cdot dV$$

For a reversible isothermal change of volume, the heat to be supplied reversibly to keep temperature constant

$$Q = \frac{4}{3}bT^4 \Delta V$$

For a reversible adiabatic change of volume

$$\frac{4}{3}bT^4\, dV = -4VbT^3\, dT$$

$\therefore$ $$\frac{dV}{V} = -3\frac{dT}{T}$$

or $$VT^3 = \text{const.}$$

If the temperature is one-half the original temperature, the volume of black-body radiation is to be increased adiabatically eight times its original volume so that the radiation remains in equilibrium with matter at that temperature.

11.7 JOULE-KELVIN EFFECT

A gas is made to undergo continuous throttling process by a valve, as shown in Fig. 11.2. The pressures and temperatures of the gas in the insulated pipe upstream and downstream of the valve are measured with suitable manometers and thermometers.

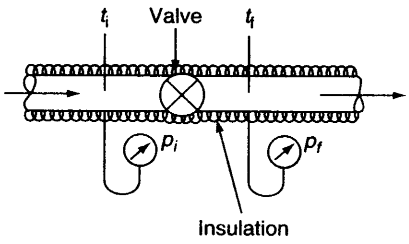


Fig. 11.2 *Joule-Thomson expansion*

Let p_i and T_i be the arbitrarily chosen pressure and temperature before throttling and let them be kept constant. By operating the valve manually, the gas is throttled successively to different pressures and temperatures p_{f1}, T_{f1}; p_{f2}, T_{f2}; p_{f3}, T_{f3} and so on. These are then plotted on the $T - p$ coordinates as shown in Fig. 11.3. All the points represent equilibrium states of some constant mass of gas, say, 1 kg, at which the gas has the *same enthalpy*.

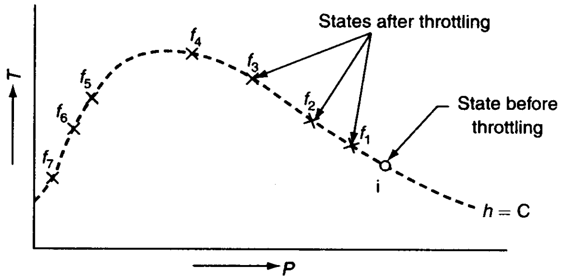


Fig. 11.3 *Isenthalpic states of a gas*

The curve passing through all these points is an isenthalpic curve or an *isenthalpe*. It is not the graph of a throttling process, but the graph through points of equal enthalpy.

The initial temperature and pressure of the gas (before throttling) are then set to new values, and by throttling to different states, a *family of isenthalpes* is obtained for the gas, as shown in Figs. 11.4 and 11.5. The curve passing through the maxima of these isenthalpes is called the *inversion curve*.

The numerical value of the slope of an isenthalpe on a $T - p$ diagram at any point is called the *Joule-Kelvin coefficient* and is denoted by μ_J. Thus the locus of all points at which μ_J is zero is the inversion curve. The region inside the inversion curve where μ_J is positive is called the *cooling region* and the region outside where μ_J is negative is called the *heating region*. So,

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

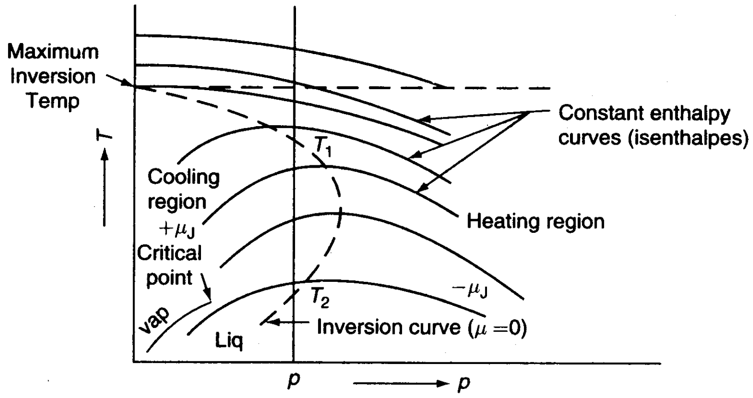


Fig. 11.4 *Isenthalpic curves and the inversion curve*

The difference in enthalpy between two neighbouring equilibrium states is

$$dh = Tds + vdp$$

and the second TdS equation (per unit mass)

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

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

The second term in the above equation stands only for a real gas, because for an ideal gas, $dh = c_p\, dT$.

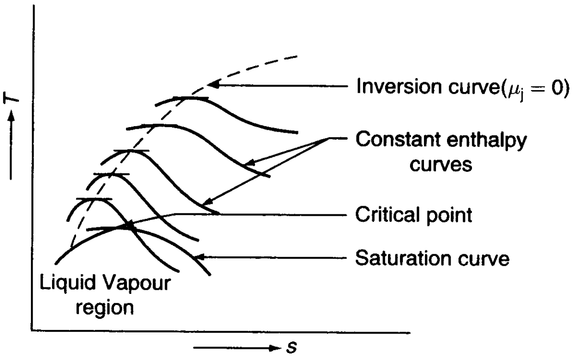


Fig. 11.5 *Inversion and saturation curves on T – s plot*

$$\mu_J = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] \tag{11.17}$$

For an ideal gas

$$pv = RT$$

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

$$\therefore \quad \mu_J = \frac{1}{c_p}\left(T \cdot \frac{v}{T} - v\right) = 0$$

There is no change in temperature when an ideal gas is made to undergo a Joule-Kelvin expansion (i.e. throttling).

For achieving the effect of cooling by Joule-Kelvin expansion, the initial temperature of the gas must be below the point where the inversion curve intersects the temperature axis, i.e. below the *maximum inversion temperature*. For nearly all substances, the maximum inversion temperature is above the normal ambient temperature, and hence cooling can be obtained by the Joule-Kelvin effect. In the case of hydrogen and helium, however, the gas is to be precooled in heat exchangers below the maximum inversion temperature before it is throttled. For liquefaction, the gas has to be cooled below the critical temperature.

Let the initial state of gas before throttling be at A (Fig. 11.6). The change in temperature may be positive, zero, or negative, depending upon the final pressure after throttling. If the final pressure lies between A and B, there will be a rise in temperature or heating effect. If it is at C, there will be no change in temperature. If the final pressure is below p_C, there will be a cooling effect, and if the final pressure is p_D, the temperature drop will be $(T_A - T_D)$.

Maximum temperature drop will occur if the initial state lies on the inversion curve. In Fig. 11.6, it is $(T_B - T_D)$.

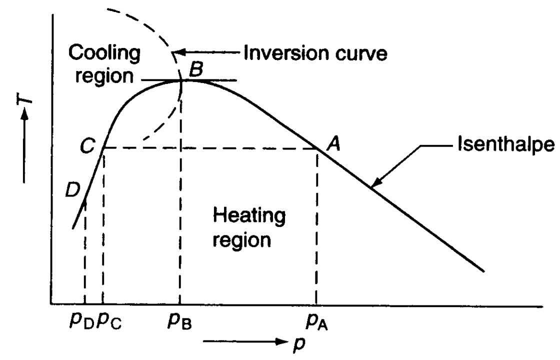


Fig. 11.6 *Maximum cooling by Joule-Kelvin expansion*

The volume expansivity is

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

So the Joule-Kelvin coefficient μ_J is given by, from Eq. (11.17)

$$\mu_J = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

or
$$\mu_J = \frac{v}{c_p}\,[\beta T - 1]$$

For an ideal gas, $\beta = \frac{1}{T}$ and $\mu_J = 0$

There are two inversion temperatures for each pressure, e.g. T_1 and T_2 at pressure p (Fig. 11.4).

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

$$s = (1 - x)\, s^{(i)} + x s^{(f)}$$
$$v = (1 - x)\, v^{(i)} + x v^{(f)}$$

where s and v are linear function 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
$$dg = -s\,dT + v\,dp$$

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:

(a) There are changes of entropy and volume.

(b) 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

$$T\{s^{(f)} - s^{(i)}\} = T\,\frac{dp}{dT}\cdot\{v^{(f)} - v^{(i)}\}$$

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

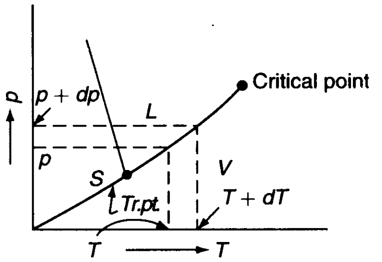


Fig. 11.7 *First order phase transition*

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 $T + \mathrm{d}T$ and $p + \mathrm{d}p$ (Fig. 11.7)

$$g^{(i)} + \mathrm{d}g^{(i)} = g^{(f)} + \mathrm{d}g^{(f)}$$

Subtracting

$$\mathrm{d}g^{(i)} = \mathrm{d}g^{(f)}$$

or

$$-s^{(i)}\,\mathrm{d}T + v^{(i)}\,\mathrm{d}p = -s^{(f)}\,\mathrm{d}T + v^{(f)}\,\mathrm{d}p$$

$$\therefore \quad \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{l}{T\left[v^{(f)} - v^{(i)}\right]}$$

For *fusion*

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l_{\text{fu}}}{T(v'' - v')}$$

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*

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{l_{\text{vap}}}{T(v''' - v'')}$$

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

$$\therefore \quad l_{\text{vap}} = T\,\frac{\mathrm{d}p}{\mathrm{d}T}\,(v''' - v'')$$

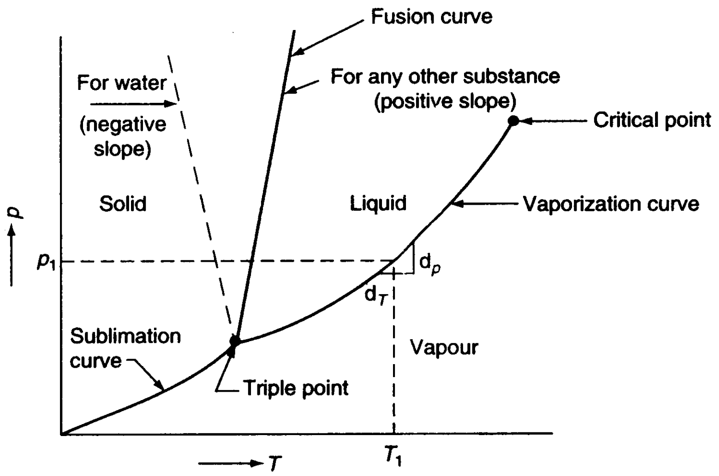


Fig. 11.8 *Phase diagram for water and any other substance on p-T coordinates*

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

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

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

or

$$l_{\text{vap}} = \frac{RT^2}{p} \frac{dp}{dT} \tag{11.19}$$

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

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

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

$$\frac{\bar{h}_{\text{fg}}}{T_{\text{B}}} \cong 88 \text{ kJ/kgmol K}$$

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

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

or

$$\int_{101.325}^{\text{P}} \frac{dp}{p} = \frac{88T_{\text{B}}}{\bar{R}} \int_{\text{T}_{\text{B}}}^{\text{T}} \frac{dT}{T^2}$$

$$\ln \frac{p}{101.325} = -\frac{88T_{\text{B}}}{\bar{R}} \left(\frac{1}{T} - \frac{1}{T_{\text{B}}} \right)$$

$\therefore$

$$p = 101.325 \exp \left[\frac{88}{\bar{R}} \left(1 - \frac{T_{\text{B}}}{T} \right) \right] \tag{11.21}$$

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_{sub} is the latent heat of sublimation.

Since $v''' >> v'$, and vapour pressure is low, $v''' = \dfrac{RT}{p}$

$$\frac{dp}{dT} = \frac{l_{\text{sub}}}{T \cdot \frac{RT}{p}}$$

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

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

At the triple point (Fig. 9.12),

$$l_{\text{sub}} = l_{\text{vap}} + l_{\text{fus}} \tag{11.22}$$

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\text{vap}} = \frac{p_{\text{tp}}\,l_{\text{vap}}}{\bar{R}T_{\text{tp}}^2}$$

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\text{sub}} = \frac{p_{\text{tp}}\,l_{\text{sub}}}{\bar{R}T_{\text{tp}}^2}$$

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

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\text{sub}} > \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\text{vap}}$$

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:

$$\mathrm{d}u = c_v\,\mathrm{d}T + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]\mathrm{d}v \tag{11.23}$$

$$\mathrm{d}h = c_p\,\mathrm{d}T + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]\mathrm{d}p \tag{11.24}$$

$$\mathrm{d}s = \frac{1}{T}\left[c_v\,\mathrm{d}T + T\left(\frac{\partial p}{\partial T}\right)_v \mathrm{d}v\right]$$

$$= \frac{1}{T}\left[c_p\,\mathrm{d}T - T\left(\frac{\partial v}{\partial T}\right)_p \mathrm{d}v\right] \tag{11.25}$$

Integrations of the differential relations of the properties p, v and T in the above equations are carried out with the help of an equation of state. The changes in properties are independent of the path and depend only on the end states. Let us consider that the change in enthalpy per unit mass of a gas from a reference state 0 at p_0, T_0 having enthalpy, h_0 to some other state B at p, T with enthalpy h is to be calculated (Fig. 11.9). The reversible path $0B$ may be replaced for convenience by either path 0–a–B or path 0–b–B, both also being reversible.

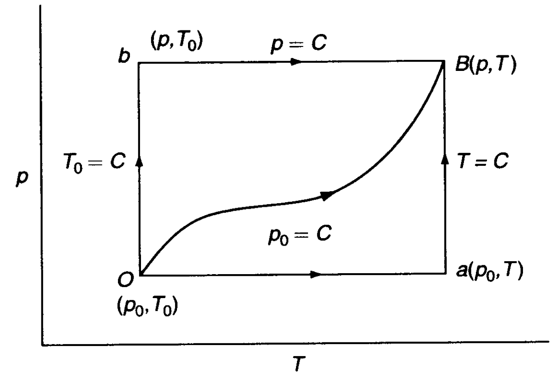


Fig. 11.9 Processes connecting states (p_0, T_0) and (p, T)

Path 0–*a*–*B*:
From Eq. 11.24,

$$h_a - h_0 = \int_{T_0}^{T} c_p \, dT$$

$$h - h_a = \int_{p_0}^{p} \left[v - T\left(\frac{\partial v}{\partial T}\right)_p \right]_T dp$$

On addition,

$$h - h_0 = \left[\int_{T_0}^{T} c_p dT\right]_{p_0} + \left\{\int_{p_0}^{p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp\right\}_T \tag{11.26}$$

Similarly, for
Path 0-*b*-*B*:

$$h - h_0 = \left\{\int_{p_0}^{p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp\right\}_{T_0} + \left[\int_{T_0}^{T} c_p \, dT\right]_p \tag{11.27}$$

Equation (11.26) is preferred to Eq. (11.27) since c_p at lower pressure can be conveniently measured.
Now,

$$\int_{p_0 v_a}^{pv} d\,(pv) = \int_{v_a}^{v} p \, dv + \int_{p_0}^{p} v \, dp$$

$$\int_{p_0}^{p} v \, dp = pv - p_0 v_a - \left[\int_{v_a}^{v} p dv\right]_T \tag{11.28}$$

Again,

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

$$\therefore \qquad \left[\frac{\partial v}{\partial T}\right]_p = -\left[\frac{\partial p}{\partial T}\right]_v \left[\frac{\partial v}{\partial p}\right]_T$$

Substituting in Eq. (11.26),

$$h - h_0 = \left[\int_{T_0}^{T} c_p dT\right]_{p_0} + pv - p_0 v_a - \left[\int_{v_a}^{v} p dv\right]_T + \left\{\int_{p_0}^{p} T\left(\frac{\partial p}{\partial T}\right)_p \left(\frac{\partial v}{\partial p}\right)_T dp\right\}_T$$

$$= \left[\int_{T_0}^{T} c_p dT\right]_{p_0} + pv - p_0 v_a - \left\{\int_{v_a}^{v}\left[p - T\left(\frac{\partial p}{\partial T}\right)_v\right] dv\right\}_T \tag{11.29}$$

To find the entropy change, Eq. (11.25) is integrated to yield:

$$s - s_0 = \left[\int_{T_0}^{T} c_p \frac{dT}{T}\right]_{p_0} - \left[\int_{p_0}^{p}\left(\frac{\partial v}{\partial T}\right)_p dp\right]_T$$

$$= \left[\int_{T_0}^{T} c_p \frac{dT}{T}\right]_{p_0} - \left[-\int_{p_0}^{p}\left(\frac{\partial p}{\partial T}\right)_u \left(\frac{\partial v}{\partial p}\right)_T dp\right]_T$$

$$= \left[\int_{T_0}^{T} c_p \frac{dT}{T}\right]_{p_0} + \left[\int_{v_a}^{v}\left(\frac{\partial p}{\partial T}\right)_v dv\right]_T \tag{11.30}$$

11.10 GENERAL THERMODYNAMIC CONSIDERATIONS ON AN EQUATION OF STATE

Certain general characteristics are common to all gases. These must be clearly observed in the developing and testing of an equation of state. It is edifying to discuss briefly some of the more important ones:

(i) Any equation of state must reduce to the ideal gas equation as pressure approaches zero at any temperature. This is clearly seen in a generalized compressibility factor chart in which all isotherms converge to the point $z = 1$ at zero pressure. Therefore,

$$\lim_{p \to 0} \left[\frac{pv}{RT} \right] = 1 \text{ at any temperature}$$

Also, as seen from Fig. 10.6, the reduced isotherms approach the line $z = 1$ as the temperature approaches infinity, or:

$$\lim_{T \to \infty} \left[\frac{pv}{RT} \right] = 1 \text{ at any pressure.}$$

(ii) The critical isotherm of an equation of state should have a point of inflection at the critical point on p–v coordinates, or

$$\left[\frac{\partial p}{\partial v} \right]_{T=T_c} = 0 \text{ and } \left[\frac{\partial^2 p}{\partial v^2} \right]_{T=T_c} = 0$$

(iii) The isochores of an equation of state on a p–T diagram should be essentially straight, or:

$$\left[\frac{\partial p}{\partial T} \right]_v = \text{constant}, \left[\frac{\partial^2 p}{\partial T^2} \right]_v = 0 \text{ as } p \to 0, \text{ or as } T \to \infty.$$

An equation of state can predict the slope of the critical isochores of a fluid. This slope is identical with the slope of the vaporization curve at the critical point. From the Clapegron equation, $dp/dT = \Delta s/\Delta v$, the slope of the vaporization curve at the critical point becomes:

$$\frac{dp}{dT} = \left[\frac{\partial s}{\partial v} \right]_{T_c} = \left[\frac{\partial p}{\partial T} \right]_{v_c} \quad \text{(by Maxwell's equation)}$$

Therefore, the vapour-pressure slope at the critical point, dp/dT, is equal to the slope of the critical isochore $(\partial p/\partial T)_{v_c}$ (Fig. 11.10).

(iv) The slopes of the isotherms of an equation of state on a Z–p compressibility factor chart as p approaches zero should be negative at lower temperatures and positive at higher temperatures. At the Boyle temperature, the slope is zero as p approaches zero, or

$$\lim_{p \to 0} \left[\frac{\partial z}{\partial p} \right]_T = 0 \text{ at } T = T_B$$

An equation of state should predict the Boyle temperature which is about 2.54 T_c for many gases.

An isotherm of maximum slope on the Z–p plot as p approaches zero, called the *foldback isotherm*, which is about $5T_c$ for many gases, should be predicted by an equation of state, for which:

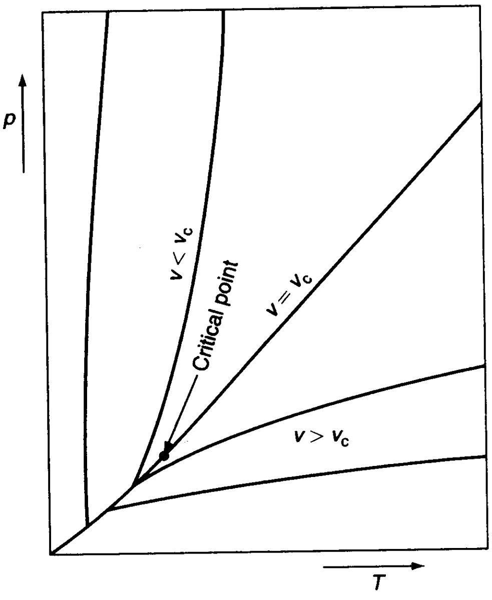


Fig. 11.10 *Pressure-temperature diagram with isochoric lines*

$$\lim_{p\to 0}\left[\frac{\partial^2 z}{\partial T\cdot\partial p}\right] = 0 \text{ at } T = T_F$$

where T_F is the foldback temperature (Fig. 10.10 a). As temperature increases beyond T_F the slope of the isotherm decreases, but always remains positive.

(v) An equation of state should predict the Joule-Thomson coefficient, which is

$$\mu_J = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = \frac{RT^2}{pc_p}\left(\frac{\partial z}{\partial T}\right)_p$$

For the inversion curve, $\mu_J = 0$,

or,
$$\left(\frac{\partial z}{\partial T}\right)_p = 0$$

11.11 MIXTURES OF VARIABLE COMPOSITION

Let us consider a system containing a mixture of substances 1, 2, 3 ... K. If some quantities of a substance are added to the system, the energy of the system will increase. Thus for a system of variable composition, the internal energy depends not only on S and V, but also on the number of moles (or mass) of various constituents of the system.

Thus
$$U = U(S, V, n_1, n_2, ..., n_K)$$

where $n_1, n_2, ..., n_K$ are the number of moles of substances 1, 2, ..., K. The composition may change not only due to addition or subtraction, but also due to chemical reaction and inter-phase mass transfer. For a small change in U, assuming the function to be continuous.

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_1,n_2,...,n_K} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_1,n_2,...,n_K} dV + \left(\frac{\partial U}{\partial n_1}\right)_{S,V,n_2,...,n_K} dn_1 + \left(\frac{\partial U}{\partial n_2}\right)_{S,V,n_1,n_3,...,n_K} dn_2$$
$$+ ... + \left(\frac{\partial U}{\partial n_K}\right)_{S,V,n_1,n_2,...,n_{K-1}} dn_K$$

or
$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^{K}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i$$

where subscript i indicates any substance and subscript j any other substance except the one whose number of moles is changing.

If the composition does not change

$$dU = TdS - pdV$$

$$\therefore \quad \left(\frac{\partial U}{\partial S}\right)_{V,n_i} = T, \text{ and } \left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -p$$

$$\therefore \quad dU = TdS - pdV + \sum_{i=1}^{K}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i \qquad (11.31)$$

Molal *chemical potential*, μ, of component i is defined as

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j}$$

signifying the change in internal energy per unit mole of component *i* when *S*, *V*, and the number of moles of all other components are constant.

$$\therefore \qquad dU = TdS - pdV + \sum_{i=1}^{K} \mu_i \, dn_i$$

or

$$TdS = dU + pdV - \sum_{i=1}^{K} \mu_i \, dn_i \tag{11.32}$$

This is known as *Gibbs entropy equation.*

In a similar manner

$$G = G(p, T, n_1, n_2, ..., n_K)$$

or

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \sum_{i=1}^{K}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i$$

$$= Vdp - SdT + \sum_{i=1}^{K}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i \tag{11.33}$$

Since

$$G = U + pV - TS$$

$$d(U + pV - TS) = VdP - SdT + \sum_{i=1}^{K}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i$$

or

$$dU + pdV + Vdp - TdS - SdT = Vdp - SdT + \sum_{i=1}^{K}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i$$

or

$$dU = TdS - pdV + \sum_{i=1}^{K}\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} dn_i$$

Comparing this equation with Eq. (11.31)

$$\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} = \mu_i$$

∴ Equation (11.33) becomes

$$dG = Vdp - SdT + \sum_{i=1}^{K} \mu_i \, dn_i$$

Similar equations can be obtained for changes in *H* and *F*.

Thus

$$dU = TdS - pdV + \sum_{i=1}^{K} \mu_i \, dn_i$$

$$dG = Vdp - SdT + \sum_{i=1}^{K} \mu_i \, dn_i$$

$$dH = TdS + Vdp + \sum_{i=1}^{K} \mu_i \, dn_i \tag{11.34}$$

$$dF = -SdT - pdV + \sum_{i=1}^{K} \mu_i \, dn_i$$

where

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j} \tag{11.35}$$

Chemical potential is an intensive property.

Let us consider a homogeneous phase of a multi-component system, for which

$$dU = TdS - pdV + \sum_{i=1}^{K} \mu_i \, dn_i$$

If the phase is enlarged in size, U, S, and V will increase, whereas T, p and μ will remain the same. Thus

$$\Delta U = T\Delta S - p\Delta V + \Sigma \mu_i \, \Delta n_i$$

Let the system be enlarged to K-times the original size. Then

$$\Delta U = KU - U = (K-1)U$$
$$\Delta S = KS - S = (K-1)S$$
$$\Delta V = (K-1)V$$
$$\Delta n_i = (K-1)\, n_i$$

Substituting

$$(K-1)\, U = T(K-1)\, S - p\,(K-1)\, V + \Sigma \mu_i \,(K-1)\, n_i$$

$$\therefore \quad U = TS - pV + \Sigma \, \mu_i n_i$$

$$\therefore \quad G_{T,p} = \Sigma \, \mu_i n_i \tag{11.36}$$

Let us now find a relationship if there is a simultaneous change in intensive property. Differentiating Eq. (11.36)

$$dG = \Sigma \, n_i \, d\mu_i + \Sigma \, \mu_i dn_i \tag{11.37}$$

at constant T and p, with only μ changing.

When T and p change

$$dG = -SdT + Vdp + \Sigma \mu_i dn_i \tag{11.38}$$

Combining Eqs (11.37) and (11.38)

$$-SdT + Vdp - \Sigma \, n_i \, d\,\mu_i = 0 \tag{11.39}$$

This is known as *Gibbs-Duhem equation*, which shows the necessary relationship for simultaneous changes in T, p, and μ.

Now

$$G_{T \cdot p} = \Sigma \, \mu_i n_i = \mu_1 n_1 + \mu_2 n_2 \dots + \mu_K n_K$$

For a phase consisting of only one constituent

$$G = \mu n$$

or

$$\mu = \frac{G}{n} = g$$

i.e. the chemical potential is the molar Gibbs function and is a function of T and p only.

For a single phase, multi-component system, μ_i is a function of T, p, and the mole fraction x_i.

11.12 CONDITIONS OF EQUILIBRIUM OF A HETEROGENEOUS SYSTEM

Let us consider a heterogeneous system of volume V, in which several homogeneous phases ($\phi = a, b, ..., r$) exist in equilibrium. Let us suppose that each phase consists of i ($= 1, 2, ..., C$) constituents and that the number of constituents in any phase is different from the others.

Within each phase, a change in internal energy is accompanied by a change in entropy, volume and composition, according to

$$dU_\phi = T_\phi\, dS_\phi - p_\phi\, dV_\phi + \sum_{i=1}^{C} (\mu_i\, dn_i)_\phi$$

A change in the internal energy of the entire system can, therefore, be expressed as

$$\sum_{\phi=a}^{r} dU_\phi = \sum_{\phi=a}^{r} T_\phi\, dS_\phi - \sum_{\phi=a}^{r} p_\phi\, dV_\phi + \sum_{\phi=a}^{r} \sum_{i=1}^{c} (\mu_i\, dn_i)_\phi \tag{11.40}$$

Also, a change in the internal energy of the entire system involves changes in the internal energy of the constituent phases.

$$dU = dU_a + dU_b + ... + dU_r = \sum_{\phi=a}^{r} dU_\phi$$

Likewise, changes in the volume, entropy, or chemical composition of the entire system result from contributions from each of the phases

$$dV = dV_a + dV_b + ... + dV_r = \sum_{\phi=a}^{r} dV_\phi$$

$$dS = dS_a + dS_b + ... + dS_r = \sum_{\phi=a}^{r} dS_\phi$$

$$dn = dn_a + dn_b + ... + dn_r = \sum_{\phi=a}^{r} dn_\phi$$

In a closed system in equilibrium, the internal energy, volume, entropy, and mass are constant.

$$\therefore \qquad dU = dV = dS = dn = 0$$

or

$$\begin{aligned} dU_a &= -(dU_b + ... + dU_r) = -\sum_j dU_j \\ dV_a &= -\sum_j dV_j \\ dS_a &= -\sum_j dS_j \\ dn_a &= -\sum_j dn_j \end{aligned} \tag{11.41}$$

where subscript j includes all phases except phase a.

Equation (11.40) can be written in terms of j independent variables and the dependent variable a Eq. (11.41).

$$\left[T_a\, dS_a + \sum_j T_j\, dS_j\right] - \left[p_a\, dV_a + \sum_j p_j\, dV_j\right] + \left[\sum_i (\mu_i\, dn_i)_a + \sum_j \sum_j (\mu_i\, dn_i)_j\right] = 0$$

Substituting from Eq. (11.41)

$$\left[-T_a \sum_j dS_j + \sum_j T_j\, dS_j\right] - \left[-p_a \sum_j dV_j + \sum_j p_j \times dV_j\right] + \left[-\sum_j \sum_t \mu_{ia}\, dn_{ij} + \sum_j \sum_i (\mu_i\, dn_i)_j\right] = 0$$

where subscript *j a* refers to component *i* of phase *a*.

Rearranging and combining the coefficients of the independent variables, dS_j, dV_j and dn_j, gives

$$\sum_j (T_j - T_a)dS_j - \sum_j (p_j - p_a)dV_j + \sum_j \sum_i (\mu_{ij} - \mu_{ia})\, dn_{ij} = 0$$

But since dS_j, dV_j, and dn_j are independent, their coefficients must each be equal to zero.

$$\therefore \qquad T_j = T_a, \quad p_j = p_a, \quad \mu_{ij} = \mu_{ia} \qquad (11.42)$$

These equations represent conditions that exist when the system is in thermal, mechanical, and chemical equilibrium. The temperature and pressure of phase *a* must be equal to those of all other phases, and the chemical potential of the *i*th component in phase *a* must be equal to the chemical potential of the same component in all other phases.

11.13 GIBBS PHASE RULE

Let us consider a heterogeneous system of *C* chemical constituents which do not combine chemically with one another. Let us suppose that there are ϕ phases, and every constituent is present in each phase. The constituents are denoted by subscripts and the phases by superscripts. The Gibbs function of the whole heterogeneous system is

$$G_{T,p} = \sum_{i=1}^{C} n_i^{(1)} \mu_i^{(1)} + \sum_{i=1}^{C} n_i^{(2)} \mu_i^{(2)} + \ldots + \sum_{i=1}^{C} n_i^{(\phi)} \mu_i^{(\phi)}$$

G is a function of *T*, *p*, and the *n*'s of which there are $C\phi$ in number. Since there are no chemical reactions, the only way in which the *n*'s may change is by the transport of the constituents from one phase to another. In this case the total number of moles of each constituent will remain constant.

$$n_1^{(1)} + n_1^{(2)} + \ldots + n_1^{(\phi)} = \text{constant}$$

$$n_2^{(1)} + n_2^{(2)} + \ldots + n_2^{(\phi)} = \text{constant}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$n_C^{(1)} + n_C^{(2)} + \ldots + n_C^{(\phi)} = \text{constant}$$

These are the *equations of constraint.*

At chemical equilibrium, *G* will be rendered a minimum at constant *T* and *p*, subject to these equations of constraint. At equilibrium, from Eq. (11.42).

$$\begin{aligned} \mu_{ij} &= \mu_{ia} \\ \mu_1^{(1)} = \mu_1^{(2)} &= \ldots = \mu_1^{(\phi)} \\ \mu_2^{(1)} = \mu_2^{(2)} &= \ldots = \mu_2^{(\phi)} \\ &\ldots\ldots\ldots\ldots\ldots \\ \mu_c^{(1)} = \mu_c^{(2)} &= \ldots = \mu_c^{(\phi)} \end{aligned} \qquad (11.43)$$

These are known as the *equations of phase equilibrium*. The equations of the phase equilibrium of one constituent are $(\phi - 1)$ in number. Therefore, for *C* constituents, there are $C(\phi - 1)$ such equations.

When equilibrium has been reached, there is no transport of matter from one phase to another. Therefore, in each phase, $\Sigma x = 1$. For ϕ phases, there are ϕ such equations available.

The state of the system at equilibrium is determined by the temperature, pressure, and $C\phi$ mole fractions. Therefore

Total number of variables $= C\phi + 2$.

Among these variables, there are $C(\phi - 1)$ equations of phase equilibrium and ϕ equations of $\Sigma x = 1$ type. Therefore

Total number of equations $= C(\phi - 1) + \phi$

If the number of variables is equal to the number of equations, the system is *nonvariant*. If the number of variables exceeds the number of equations by one, then the system is called *monovariant* and is said to have a variance of 1.

The excess of variables over equations is called the *variance, f*. Thus

$$f = (C\phi + 2) - [C(\phi - 1) + \phi]$$

or

$$f = C - \phi + 2 \tag{11.44}$$

This is known as the *Gibbs Phase Rule* for a non-reactive system. The variance 'f' is also known as the *degree of freedom*.

For a pure substance existing in a single phase, $C = 1$, $\phi = 1$, and therefore, the variance is 2. There are two properties required to be known to fix up the state of the system at equilibrium.

If $C = 1$, $\phi = 2$, then $f = 1$, i.e. only one property is required to fix up the state of a single-component two-phase system.

If $C = 1$, $\phi = 3$, then $f = 0$. The state is thus unique for a substance; and refers to the triple point where all the three phases exist in equilibrium.

11.14 TYPES OF EQUILIBRIUM

The thermodynamic potential which controls equilibrium in a system depends on the particular *constraints* imposed on the system. Let $đQ$ be the amount of heat transfer involved between the system and the reservoir in an infinitesimal irreversible process (Fig. 11.11). Let dS denote the entropy change of the system and dS_0 the entropy change of the reservoir. Then, from the entropy principle

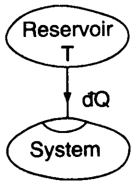


Fig. 11.11 *Heat interaction between a system and its surroundings*

$$dS_0 + dS > 0$$

Since

$$dS_0 = -\frac{đQ}{T} - \frac{đQ}{T} + dS > 0$$

or

$$đ\,Q - TdS < 0$$

During the infinitesimal process, the internal energy of the system changes by an amount dU, and an amount of work pdV is performed. So, by the first law

$$đQ = dU + pdV$$

Thus the inequality becomes

$$dU + pdV - TdS < 0 \tag{11.45}$$

If the constraints are constant U and V, then the Eq. (11.46) reduces to

$$dS > 0$$

The condition of constant U and V refers to an isolated system. Therefore, entropy is the critical parameter to determine the state of thermodynamic equilibrium of an isolated system. The entropy of an isolated system always increases and reaches a maximum value when equilibrium is reached.

If the constraints imposed on the system are constant T and V, the Eq. (11.45) reduces to

$$dU - d(TS) < 0$$

or
$$\mathrm{d}(U - TS) < 0$$
$$\mathrm{d}F < 0$$

which expresses that the Helmholtz function decreases, becoming a minimum at the final equilibrium state.

If the constraints are constant T and p, the Eq. (11.46) becomes

$$\mathrm{d}U + \mathrm{d}(pV) - \mathrm{d}(TS) < 0$$
$$\mathrm{d}(U + pV - TS) < 0$$
$$\mathrm{d}G < 0$$

The Gibbs function of a system at constant T and p decreases during an irreversible process, becoming a minimum at the final equilibrium state. For a system constrained in a process to constant T and p, G is the critical parameter to determine the state of equilibrium.

The thermodynamic potential and the corresponding constrained variables are shown below.

$$\begin{array}{ccc} S & U & V \\ H & & F \\ P & G & T \end{array}$$

This trend of G, F, or S establishes four types of equilibrium, namely (a) stable, (b) neutral, (c) unstable, and (d) metastable.

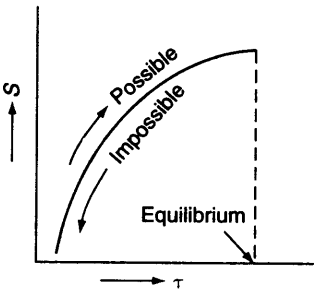


Fig. 11.12 *Possible process for an isolated system*

A system is said to be in a state of *stable* equilibrium if, when the state is perturbed, the system returns to its original state. A system is not in equilibrium if there is a spontaneous change in the state. If there is a spontaneous change in the system, the entropy of the system increases and reaches a maximum when the equilibrium condition is reached (Fig. 11.12). Both A and B (Fig. 11.13) are assumed to be at the same temperature T. Let there be some spontaneous change; the temperature of A rises to $T + \mathrm{d}T_1$, and that of B decreases to $T - \mathrm{d}T_2$. For simplicity, let the heat capacities of the bodies be the same, so that $\mathrm{d}T_1 = \mathrm{d}T_2 = \mathrm{d}T$. If $\text{đ}Q$ is the heat interaction involved, then the entropy change

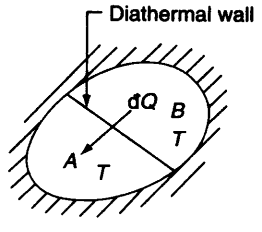


Fig. 11.13 *Spontaneous changes in A and B due to heat interaction*

$$\mathrm{d}S_A = \frac{\text{đ}Q}{T + \mathrm{d}T}, \; \mathrm{d}S_B = -\frac{\text{đ}Q}{T - \mathrm{d}T}$$

$$\therefore \quad \mathrm{d}S = \mathrm{d}S_A + \mathrm{d}S_B = \text{đ}Q \left[\frac{1}{T + \mathrm{d}T} - \frac{1}{T - \mathrm{d}T}\right] = -\frac{2 \cdot \mathrm{d}T}{T^2} \cdot \text{đ}Q$$

So there is a decrease in entropy for the isolated system of A and B together. It is thus clear that the variation in temperature $\mathrm{d}T$ cannot take place. The system, therefore, exists in a stable equilibrium condition. Perturbation of the state produces an absurd situation and the system must revert to the original stable state. It may be observed:

If for all the possible variations in state of the isolated system, there is a negative change in entropy, then the system is in stable equilibrium.

$$\begin{array}{lll} (\mathrm{d}S)_{U,V} > 0 & \text{Spontaneous change} & \\ (\mathrm{d}S)_{U,V} = 0 & \text{Equilibrium} & (11.46) \\ (\mathrm{d}S)_{U,V} < 0 & \text{Criterion of stability} & \end{array}$$

Similarly

$$\begin{array}{lll}(dG)_{p,T} < 0, (dF)_{T,V} < 0 & \text{Spontaneous change} & \\ (dG)_{p,T} = 0, (dF)_{T,V} = 0 & \text{Equilibrium} & (11.47) \\ (dG)_{p,T} > 0, (dF)_{T \times V} > 0 & \text{Criterion of stability} & \end{array}$$

A system is in a state of ***stable equilibrium*** if, for any finite variation of the system at constant T and p, G increases, i.e. the stable equilibrium state corresponds to the minimum value of G.

A system is said to be in a state of ***neutral equilibrium*** when the thermodynamic criterion of equilibrium (G, F, S, U, or H) remains at constant value for all possible variations of finite magnitude. If perturbed, the system does not revert to the original state.

For a system at constant T and p, the criterion of neutral equilibrium is

$$\delta G_{T,p} = 0$$

Similarly

$$\delta F_{T,V} = 0, \delta H_{S,p} = 0, \delta U_{S,V} = 0, \delta S_{U,V} = 0$$

A system is in a state of ***unstable equilibrium*** when the thermodynamic criterion is neither an extremum nor a constant value for all possible variations in the system. If the system is in unstable equilibrium, there will be a spontaneous change accompanied by

$$\delta G_{T,p} < 0, \delta F_{T,V} < 0, \delta U_{S,V} < 0, \delta H_{S,p} < 0, \delta S_{U,V} > 0$$

A system is in a state of ***metastable equilibrium*** if it is stable to small but not to large disturbances. A mixture of oxygen and hydrogen is in a metastable equilibrium. A little spark may start a chemical reaction. Such a mixture is not in its most stable state, even though in the absence of a spark it appears to be stable.

Figure 11.14 shows different types of equilibrium together with their mechanical analogies. S has been used as the criterion for equilibrium.

11.15 LOCAL EQUILIBRIUM CONDITIONS

Let an arbitrary division of an isolated system be considered, such that

$$S = S_1 + S_2, U = U_1 + U_2$$

Then for equilibrium, it must satisfy the condition

$$(\delta S)_{U,V} = 0$$

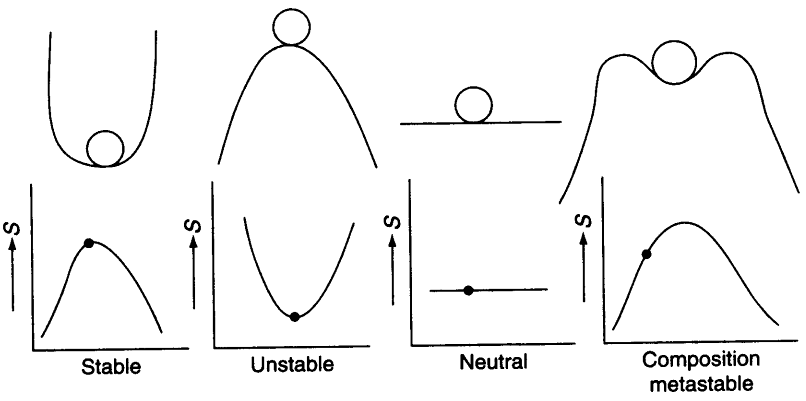


Fig. 11.14 *Types of equilibrium*

to first order in small displacements (otherwise δS could be made positive because of higher order terms). Now to the first order in a very small change

$$\delta_1 S = \left(\frac{\partial S}{\partial U_1}\right)_V \delta U_1 + \left(\frac{\partial S}{\partial U_2}\right)_V \delta U_2 + \left(\frac{\partial S}{\partial U_1}\right)_u \delta V_1 + \left(\frac{\partial S}{\partial V_2}\right)_u \delta V_2$$

Now

$$T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V$$

∴

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}, \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}$$

∴

$$\delta_1 S = \frac{1}{T_1}\,\delta U_1 + \frac{1}{T_2}\,\delta U_2 + \frac{p_1}{T_1}\,\delta V_1 + \frac{p_2}{T_2}\,\delta V_2$$

Again

$$\delta U_1 = -\,\delta U_2 \text{ and } \delta V_1 = -\,\delta V_2$$

∴

$$\delta_1 S = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta U_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\delta V_1 + \text{Second order terms}$$

When

$$\delta_1 S = 0, \text{ at equilibrium}$$

$$T_1 = T_2, p_1 = p_2$$

11.16 CONDITIONS OF STABILITY

At equilibrium, $S = S_{\max}$, $F = F_{\min}$, $G = G_{\min}$, and $SS = 0$, $\delta F = 0$; $\delta G = 0$; these are necessary but not sufficient conditions for equilibrium. To prove that S is a maximum, and G or F a minimum, it must satisfy

$$\delta^2 S < 0, \delta^2 F > 0, \delta^2 G > 0$$

If the system is perturbed, and for any infinitesimal change of the system

$$(\delta S)_{U,V} < 0, (\delta G)_{p,T} > 0, (\delta F)_{T,V} > 0$$

it represents the stability of the system. The system must revert to the original state.

For a spontaneous change, from Eq. (11.46)

$$\delta U + p\delta V - T\delta S < 0$$

For stability

$$\delta U + p\delta V - T\delta S > 0$$

Let us choose $U = U(S, V)$ and expand δU in powers of δV and δS.

$$\delta U = \left(\frac{\partial U}{\partial S}\right)_V \delta S + \frac{1}{2}\left(\frac{\partial^2 U}{\partial S^2}\right)_V (\delta S)^2 + \left(\frac{\partial U}{\partial V}\right)_S \delta V$$

$$+ \frac{1}{2}\left(\frac{\partial^2 U}{\partial V^2}\right)_S (\delta V)^2 + \frac{\partial^2 U}{\partial V \cdot \partial S} \times \delta V \cdot \delta S + \ldots = T\delta S - p\delta V + \frac{1}{2}\left(\frac{\delta^2 U}{\delta S^2}\right)_V (\delta S)^2$$

$$+ \frac{1}{2}\left(\frac{\partial^2 U}{\partial V^2}\right)_S (\delta V)^2 + \frac{\partial^2 U}{\partial V \cdot \partial S}\,\delta V \cdot \delta S + \ldots$$

The third order and higher terms are neglected.

Since $\delta U + p\delta v - T\delta S > 0$, it must satisfy the conditions given below

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0,\ \left(\frac{\partial^2 U}{\partial V^2}\right)_S > 0,\ \frac{\partial^2 U}{\partial V \cdot \partial S} > 0$$

These inequalities indicate how the signs of some important physical quantities become restricted for a system to be stable.

Since

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_v}$$

$\therefore$

$$\frac{T}{C_v} > 0$$

Since $T > 0$ K

$\therefore$

$$C_v > 0 \tag{11.48}$$

which is the condition of *thermal stability*.

Also

$$\left(\frac{\partial U}{\partial V}\right)_S = -p$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial p}{\partial V}\right)_S$$

$\therefore$

$$\left(\frac{\partial p}{\partial V}\right)_S < 0 \tag{11.49}$$

i.e. the adiabatic bulk modulus must be negative.

Similarly, if $F = F(T \cdot V)$, then by Taylor's expansion, and using appropriate substitution

$$\delta F = -S\delta T - p\delta V + \frac{1}{2}\left(\frac{\partial^2 F}{\partial V^2}\right)_T (\delta V)^2 + \frac{1}{2}\left(\frac{\partial^2 F}{\partial T^2}\right)_S (\delta T)^2 + \frac{\partial^2 \cdot F}{\partial V \cdot \partial T} \cdot \delta V \cdot \delta T + \ldots$$

For stability

$$\delta F + S\delta T + p\delta V > 0$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T > 0$$

Again

$$\left(\frac{\partial F}{\partial V}\right)_T = -p$$

$\therefore$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\left(\frac{\partial p}{\partial V}\right)_T$$

$$\therefore \qquad \left(\frac{\partial p}{\partial V}\right)_T < 0 \qquad (11.50)$$

which is known as the condition of *mechanical stability*. The isothermal bulk modulus must also be negative.

Solved Examples

Example 11.1

(a) Derive the equation

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

(b) Prove that C_p of an ideal gas is a function of T only.

(c) In the case of a gas obeying the equation of state

$$\frac{pv}{RT} = 1 + B'p$$

where B' is a function of T only, show that

$$C_p = -\bar{R}\,Tp\frac{d^2}{dT^2}(B'T) + (C_p)_0$$

where $(C_p)_0$ is the value at very low pressures.

Solution

(a)

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

$$\left(\frac{\partial C_p}{\partial p}\right)_p = T\left(\frac{\partial^2 S}{\partial T \cdot \partial p}\right)$$

Now $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$, by Maxwell's relation

$$\therefore \qquad \frac{\partial^2 S}{\partial p \cdot \partial T} = -\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

$$\therefore \qquad \left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

Proved.

(b) For an ideal gas

$$V = \frac{n\bar{R}T}{p}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{n\bar{R}}{p} \text{ and } \left(\frac{\partial^2 V}{\partial T^2}\right)_p = 0$$

$$\therefore \qquad \left(\frac{\partial \bar{C}_p}{\partial p}\right)_T = 0, \text{ i.e. } C_p \text{ is a function of } T \text{ alone.}$$

(c)
$$\frac{p\bar{v}}{\bar{R}T} = 1 + B'p$$

$$\therefore \qquad B'p = \frac{p\bar{v}}{\bar{R}T} - 1$$

$$B'T = \frac{T}{p}\left(\frac{p\bar{v}}{\bar{R}T} - 1\right) = \left(\frac{\bar{v}}{\bar{R}} - \frac{T}{p}\right)$$

$$\left[\frac{\partial}{\partial T}(B'T)\right]_p = + \frac{1}{\bar{R}}\left(\frac{\partial \bar{v}}{\partial T}\right)_p - \frac{1}{p}$$

$$\left[\frac{\partial^2 (B'T)}{\partial T^2}\right]_p = \frac{1}{\bar{R}}\left(\frac{\partial^2 \bar{v}}{\partial T^2}\right)_p = -\frac{1}{\bar{R}T}\left(\frac{\partial \bar{C}_p}{\partial p}\right)_T$$

∴ On integration

$$\bar{C}_p = -\bar{R}Tp\frac{d^2}{dT^2}(B'T) + \bar{C}_{p0}$$

where $\bar{C}_{p0}$ (integration constant) is the value of $\bar{C}_p$ at very low values of pressure.

Example 11.2

The Joule-Kelvin coefficient μ_J is a measure of the temperature change during a throttling process. A similar measure of the temperature change produced by an isentropic change of pressure is provided by the coefficient μ_s, where

$$\mu_s = \left(\frac{\partial T}{\partial p}\right)_S$$

Prove that

$$\mu_s - \mu_J = \frac{V}{C_p}$$

Solution *The Joule-Kelvin coefficient, μ_J, is given by*

$$\frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}$$

Since $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ and by Maxwell's relation

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

$$\mu_j = \frac{-T\left(\frac{\partial S}{\partial p}\right)_T}{T\left(\frac{\partial S}{\partial T}\right)_p} - \frac{V}{C_p}$$

∴ $$\mu_j = -\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial T}{\partial S}\right)_p - \frac{V}{C_p}$$

Since $$\left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial T}{\partial S}\right)_p \left(\frac{\partial p}{\partial T}\right)_S = -1$$

∴ $$\mu_j = +\mu_s - \frac{V}{C_p}$$

∴ $$\mu_s - \mu_j = \frac{V}{C_p}$$ Proved.

Alternative method:

From the second TdS equation

$$TdS = C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \mu_s = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p$$

Now $$\mu_j = \frac{T}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$$

∴ $$\mu_s - \mu_j = \frac{V}{C_p}$$ Proved.

Example 11.3

If the boiling point of benzene at 1 *atm pressure is* 353 *K, estimate the approximate value of the vapour pressure of benzene at* 303 *K.*

Solution Using Clapeyron's equation and Trouton's rule, Eq. (11.21),

$$p = 101.325 \exp\left\{\frac{88}{\bar{R}}\left(1 - \frac{T_B}{T}\right)\right\}$$

$$= 101.325 \exp\left\{\frac{88}{8.3143}\left(1 - \frac{353}{303}\right)\right\}$$

$$= 17.7 \text{ kPa}$$ *Ans.*

Example 11.4

The vapour pressure, in mm of mercury, of solid ammonia is given by

$$\ln p = 23.03 - \frac{3754}{T}$$

and that of liquid ammonia by

$$\ln p = 19.49 - \frac{3063}{T}$$

(*a*) *What is the temperature of the triple point? What is the pressure?* (*b*) *What are the latent heats of sublimation and vaporization?* (*c*) *What is the latent heat of fusion at the triple point?*

Solution At the triple point, the saturated solid and saturated liquid lines meet.

$$23.03 - \frac{3754}{T} = 19.49 - \frac{3063}{T}$$

$$\therefore \quad T = 195.2 \text{ K}$$ *Ans.* (a)

$$\ln p = 23.03 - \frac{3754}{195.2}$$

$$\ln p = 3.80$$

$$p = 44.67 \text{ mm Hg}$$ *Ans.*

With the assumptions, $v''' >> v'$ and $v''' \sim \frac{\bar{R}T}{p}$
Clausius-Clapeyron equation reduces to

$$\frac{dp}{dT} = \frac{p}{\bar{R}T^2} \cdot l_{sub}$$

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

The vapour pressure of solid ammonia is given by

$$\ln p = 23.03 - \frac{3754}{T}$$

$$\therefore \quad \frac{1}{p} \cdot \frac{dp}{dT} = \frac{3754}{T^2}$$

$$\therefore \quad \frac{dp}{dT} = 3754 \frac{p}{T^2} = \frac{p}{\bar{R}T^2} \cdot l_{sub}$$

$$\therefore \quad l_{sub} = 3754 \times 8.3143 = 31{,}200 \text{ kJ/kg mol}$$

The vapour pressure of liquid ammonia is given by

$$\ln p = 19.49 - \frac{3063}{T}$$

$$\therefore \qquad \frac{dp}{dT} = 3063\,\frac{p}{T^2} = \frac{p}{\bar{R}T^2}\cdot l_{\text{vap}}$$

where l_{vap} is the latent heat of vaporization.

$$\therefore \qquad l_{\text{vap}} = 3063 \times 8.3143 = 25{,}500 \text{ kJ/kg mol}$$ *Ans.* (b)

At the triple point

$$l_{\text{sub}} = l_{\text{vap}} + l_{\text{fu}}$$

where l_{fu} is the latent heat of fusion.

$$\therefore \qquad l_{\text{fu}} = l_{\text{sub}} - l_{\text{vap}} = 31{,}200 - 25{,}500 = 5{,}700 \text{ kJ/kg mol}$$

Example 11.5

Explain why the specific heat of a saturated vapour may be negative.

Solution *As seen in Fig. Ex. 11.5, if heat is transferred along the saturation line, there is a decrease in temperature. The slope of the saturated vapour line is negative, i.e. when dS is positive, dT is negative. Therefore, the specific heat at constant saturation*

$$C'''_{\text{sat}} = T\left(\frac{dS'''}{dT}\right)$$

is negative. From the second TdS equation

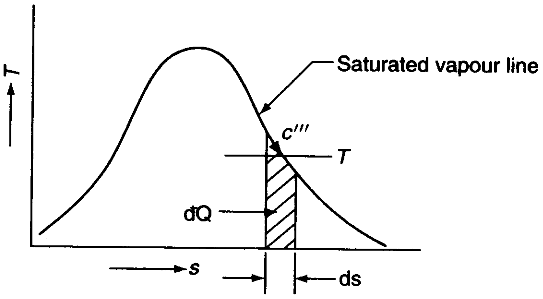


Fig. Ex. 11.5

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$T\frac{dS''}{dT} = C_p - T\left(\frac{\partial V'''}{\partial T}\right)_p\left(\frac{dp}{dT}\right)_{\text{sat}}$$

$$= C_p - T\cdot\frac{n\bar{R}}{p}\cdot\frac{l_{vap}}{T\left(V''' - V''\right)} \quad [\text{using } pV''' = n\bar{R}\,T \text{ and Clapeyron's equation}]$$

$$C'''_{\text{sat}} = C_p\,\frac{V'''}{T}\cdot\frac{l_{\text{vap}}}{V'''} \quad [\because V''' >> V'']$$

$$\therefore \quad C'''_{\text{sat}} = C_p - \frac{l_{\text{vap}}}{T}$$

Now the value of l_{vap}/T for common substances is about 83.74 J/g mol K (*Trouton's rule*), where C_p is less than 41.87 J/g mol K. Therefore, C'''_{sat} can be negative. Proved.

Example 11.6

(a) Establish the condition of equilibrium of a closed composite system consisting of two simple systems separated by a movable diathermal wall that is impervious to the flow of matter.

(*b*) *If the wall were rigid and diathermal, permeable to one type of material, and impermeable to all others, state the condition of equilibrium of the composite system.*

(*c*) *Two particular systems have the following equations of state.*

$$\frac{1}{T_1} = \frac{3}{2}\bar{R}\frac{N_1}{U_1}, \frac{p_1}{T_1} = \frac{N_1}{V_1}\bar{R}$$

and

$$\frac{1}{T_2} = \frac{3}{2}\bar{R}\frac{N_2}{U_2}, \frac{p_2}{T_2} = \bar{R}\frac{N_2}{V_2}$$

where $\bar{R}$ = 8.3143 *kJ/kg mol K, and the subscripts indicate systems* 1 *and* 2. *The mole number of the first system is* $N_1 = 0.5$, *and that of the second is* $N_2 = 0.75$. *The two systems are contained in a closed adiabatic cylinder, separated by a movable diathermal piston. The initial temperatures are* T_1 = 200 *K and* T_2 = 300 *K, and the total volume is* 0.02 *m*^{3}. *What is the energy and volume of each system in equilibrium? What is the pressure and temperature?*

Solution For the composite system, as shown in Fig. Ex. 11.6(a)

$$U_1 + U_2 = \text{constant}$$

$$V_1 = V_2 = \text{constant}$$

The values of U_1, U_2, V_1, and V_2 would change in such a way as to maximize the value of entropy. Therefore, when the equilibrium condition is achieved

$$dS = 0$$

for the whole system. Since

$$S = S_1 + S_2 = S_1(U_1, V_1, \ldots, N_{k1} \ldots) + S_2(U_2, V_2, \ldots, N_{k2} \ldots)$$

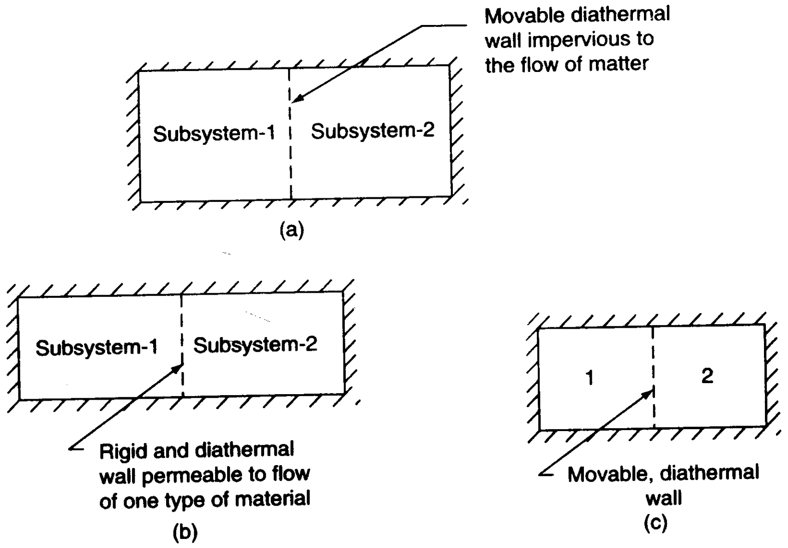


Fig. Ex.11.6

$$\therefore \quad dS = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1 \ldots, N_{k1} \ldots} dU_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1 \ldots, N_{k1} \ldots,} dV_1$$

$$+ \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2 \ldots, N_{k2} \ldots,} dU_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{V_2 \ldots, N_{k2} \ldots} dV_2$$

$$= \frac{1}{T_1} dU_1 + \frac{p_1}{T_1} dV_1 + \frac{1}{T_2} dU_2 + \frac{p_2}{T_2} dV_2$$

Since $dU_1 + dU_2 = 0$ and $dV_1 + dV_2 = 0$

$$\therefore \quad dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 = 0$$

Since the expression must vanish for arbitrary and independent values of dU_1 and dV_1

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \text{ and } \frac{p_1}{T_1} - \frac{p_2}{T_2} = 0$$

or

$$p_1 = p_2 \text{ and } T_1 = T_2$$

$\therefore$ These are the conditions of mechanical and thermal equilibrium.

(b) We will consider the equilibrium state of two simple subsystems (Fig. Ex. 11.6(b)) connected by a rigid and diathermal wall, permeable to one type of material (N_1) and impermeable to all others (N_2, N_3, ... N_r). We thus seek the equilibrium values of U_1 and of U_2, and of N_{1-1} and N_{1-2} (i.e. material N_1 in subsystems 1 and 2 respectively.)

At equilibrium, an infinitesimal change in entropy is zero

$$dS = 0$$

Now

$$dS = dS_1 + dS_2$$

$$= \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1, N_{1-1,\ldots}} dU_1 + \left(\frac{\partial S_1}{\partial N_{1-1}}\right)_{U_1, V_1, N_{1-2,\ldots}} dN_{1-1}$$

$$+ \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2, N_{1-2}} dU_2 + \left(\frac{\partial S_2}{\partial N_{1-2}}\right)_{U_2, V_2, N_{2-2}} dN_{1-2}$$

From the equation

$$TdS = dU + p\,dV - \mu dN$$

$$\therefore \quad \left(\frac{\partial S}{\partial U}\right)_{V, N, \ldots} = \frac{1}{T}, \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

and

$$dN_{1-1} + dN_{1-2} = 0$$

$$dU_1 + dU_2 = 0$$

$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 - \left(\frac{\mu_{1-1}}{T_1} - \frac{\mu_{1-2}}{T_2}\right) dN_{1-1} = 0$$

As dS must vanish for arbitrary values of both dU_1 and dN_{1-1}

$$T_1 = T_2$$

$$\mu_{1-1} = \mu_{1-2}$$

which are the conditions of thermal and chemical equilibrium.

(c) $$N_1 = 0.5 \text{ g mol}, N_2 = 0.75 \text{ g mol}$$

$$T_{1-1} = 200 \text{ K}, T_{1-2} = 300 \text{ K}$$

$$V = V_1 + V_2 = 0.02 \text{ m}^3$$

$$U_1 + U_2 = \text{constant}$$

$$\Delta U_1 + \Delta U_2 = 0$$

Let T_f be the final temperature (Fig. Ex. 11.6(c))

$$(U_{f-1} - U_{i-1}) = -(U_{f-2} - U_{i-2})$$

$$\frac{3}{2}\bar{R}N_1 (T_f - T_{i-1}) = -\frac{3}{2}\bar{R}N_2 (T_f - T_{i-2})$$

$$0.5 (T_f - 200) = -0.75 (T_f - 300)$$

$\therefore$ $$1.25\, T_f = 325$$

or $$T_f = 260 \text{ K}$$ *Ans.*

$$U_{f-1} = \frac{3}{2}\bar{R}\, N_1 T_f = \frac{3}{2} \times 8.3143 \times 0.5 \times 10^{-3} \times 260 = 1.629 \text{ kJ}$$

$$U_{f-2} = \frac{3}{2} \times 8.3143 \times 0.75 \times 10^{-3} \times 260 = 2430 \text{ kJ}$$ *Ans.*

$$V_{f-2} = \frac{\bar{R}N_1 T_{f-1}}{p_{f-1}}$$ At equilibrium $p_{f-1} = p_{f-2} = p_f$

$$V_{f-2} = \frac{\bar{R}N_2 T_{f-2}}{p_{f-2}}$$ $T_{f-1} = T_{f-2} = T_f$

$$V_{f-1} + V_{f-2} = \frac{\bar{R}T_f}{p_f}(N_1 + N_2) = 0.02 \text{ m}^3$$

$$\frac{8.3143 \times 260}{p_f} \times 1.25 \times 10^{-3} = 0.02 \text{ m}^3$$

$\therefore$ $$p_f = \frac{8.3143 \times 260 \times 1.25 \times 10^{-3}}{0.02} \text{ kN/m}^2$$

$$= 135 \text{ kN/m}^2 = 1.35 \text{ bar}$$

$$\therefore \qquad V_{f-1} = \frac{8.3143 \times 0.5 \times 10^{-3} \times 260}{135} = 0.008 \text{ m}^3$$

$$\therefore \qquad V_{f-2} = 0.02 - 0.008 = 0.012 \text{ m}^3 \qquad \textit{Ans.}$$

Example 11.7

Show that for a van der Waals' gas

(*a*) $\left(\frac{\partial c_v}{\partial v}\right)_T = 0$

(*b*) $(s_2 - s_1)_T = R \, ln \, \frac{v_2 - b}{v_1 - b}$

(*c*) $T(v-b)^{R/c_v}$ = *constant, for an isentropic*

(*d*) $c_p - c_v = \frac{R}{1 - 2a(v-b)^2 / RTv^3}$

(*e*) $(h_2 - h_1)_T = (p_2 v_2 - p_1 v_1) + a \left(\frac{1}{v_1} - \frac{1}{v_2}\right)$

Solution (a) From the energy Eq. (11.13)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

$$\frac{\partial^2 U}{\partial V \cdot \partial T} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V + \left(\frac{\partial p}{\partial T}\right)_V - \left(\frac{\partial p}{\partial T}\right)_V$$

$$\frac{\partial^2 U}{\partial V \cdot \partial T} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \frac{\partial^2 U}{\partial T \cdot \partial V} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V = \left(\frac{\partial c_v}{\partial v}\right)_T$$

For a van der Waals' gas

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\therefore \qquad \left(\frac{\partial^2 p}{\partial T^2}\right)_V = 0$$

$$\therefore \qquad \left(\frac{\partial c_v}{\partial v}\right)_T = 0$$

Proved (a)

$\therefore$ c_v is independent of volume.

(b) From the first *Tds* Eq. (11.8)

$$Tds = c_v\, dT + T\left(\frac{\partial p}{\partial T}\right)_V dv$$

and energy Eq. (11.13), $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

$$ds = c_v \frac{dT}{T} + \frac{1}{T}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dv$$

For van der Waals' gas

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{v^2}$$

$$\therefore \qquad ds = c_v \frac{dT}{T} + \frac{1}{T}\left(p + \frac{a}{v^2}\right) dv = c_v \frac{dT}{T} + \frac{R}{v-b}\, dv$$

$$\therefore \qquad (s_2 - s_1)_T = R \ln \frac{v_2 - b}{v_1 - b}$$

Proved (b)

(c) At constant entropy

$$c_v \frac{dT}{T} + \frac{R}{v-b}\, dv = 0$$

or

$$\frac{dT}{T} + \frac{R}{c_v}\frac{dv}{v-b} = 0$$

by integration, $T(v-b)^{R/C_v}$ = constant

Proved (c)

(d)

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial v}{\partial T}\right)_p = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p$$

$$= \left(\frac{a}{v^2} + p\right)\left(\frac{\partial v}{\partial T}\right)_p = \left(\frac{RT}{v-b}\right)\left(\frac{\partial v}{\partial T}\right)_p$$

From the equation

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT$$

$$\therefore \qquad (v-b)(-2av^{-3})\left(\frac{\partial v}{\partial T}\right)_p + \left(p + \frac{a}{v^2}\right)\left(\frac{\partial v}{\partial T}\right)_p = R$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R/(v-b)}{\dfrac{RT}{(v-b)} - \dfrac{2a}{v^3}}$$

$$\therefore \quad c_p - c_v = \frac{R}{1-2a(v-b)^2/RT\,v^3} \qquad \text{Proved (d)}$$

(e)
$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{a}{v^2}$$

$$du_T = \frac{a}{v^2}\,dv_T$$

$$\therefore \quad (u_2 - u_1)_T = a\left(\frac{1}{v_1} - \frac{1}{v_2}\right)$$

$$\therefore \quad (h_2 - h_1)_T = (p_2v_2 - p_1v_1) + a\left(\frac{1}{v_1} - \frac{1}{v_2}\right) \qquad \text{Proved (e)}$$

Example 11.8

The virial equation of state of a gas is given by

$$pv = RT(1 + B'p + C'p^2 + \ldots)$$

Show that

$$\lim_{p\to 0}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right] = RT^2\,\frac{dB'}{dT}$$

Hence, prove that the inversion temperature of a van der Waals' gas is twice the Boyle temperature.

Solution

$$pv = RT(1 + B'p + C'p^2 + \ldots)$$

$$v = \frac{RT}{p} + RTB' + RTpC' + \ldots$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + RT\,\frac{dB'}{dT} + RB' + RTp\,\frac{dC'}{dT} + RpC' + \ldots$$

$$\therefore \quad T\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT}{p} + RT^2\,\frac{dB'}{dT} + RTB' + RT^2p\,\frac{dC'}{dT} + RTpC' + \ldots$$

$$\therefore \quad T\left(\frac{\partial v}{\partial T}\right) - v = RT^2\,\frac{dB'}{dT} + RT^2p\,\frac{dC'}{dT} + \ldots$$

$$\mu_J = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

$$\therefore \quad = \frac{RT^2}{c_p}\left[\frac{dB'}{dT} + p\,\frac{dC'}{dT} + \ldots\right]$$

$$\lim_{p\to 0} \mu_J = \frac{RT^2}{c_p}\frac{dB'}{dT}$$

or
$$\lim_{p\to 0}\left[T\left(\frac{dv}{dT}\right)_p - v\right] = RT^2\,\frac{dB'}{dT}$$
Proved

For a van der Waals' gas, to find Boyle temperature T_B,

$$B = b - \frac{a}{RT} = 0$$

$$\therefore \quad T_B = \frac{a}{bR}$$

$$B' = \frac{B}{RT} = \frac{b}{RT} - \frac{a}{R^2T^2}$$

$$\frac{dB'}{dT} = -\frac{b}{RT^2} + \frac{2a}{R^2T^3}$$

$$\therefore \quad \lim_{p\to 0} \mu_J = \frac{RT^2}{c_p}\left(-\frac{b}{RT^2} + \frac{2a}{R^2T^3}\right) = 0$$

$$\therefore \quad \frac{b}{RT^2} = \frac{2a}{R^2T^3}$$

$$\therefore \quad T_i = \frac{2a}{bR}$$

$$\therefore \quad T_i = 2T_B$$

or Inversion temperature = 2 × Boyle temperature
Proved

Example 11.9

Over a certain range of pressures and temperatures, the equation of a certain substance is given by the relation

$$v = \frac{RT}{p} - \frac{C}{T^3}$$

where C is a constant. Derive an expression for: (a) the change of enthalpy and (b) the change of entropy, of this substance in an isothermal process.

Solution (a) From Eq. (11.15)

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

$$\therefore \quad (h_2 - h_1)_T = \int_1^2 \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

Now,
$$v = \frac{RT}{p} - \frac{C}{T^3}$$

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

$$\therefore \quad T\left(\frac{\partial v}{\partial \mathrm{T}}\right)_p = \frac{RT}{p} + \frac{3C}{T^3}$$

$$\therefore \quad v - \mathrm{T}\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT}{p} - \frac{C}{T^3} - \frac{RT}{p} - \frac{3C}{T^3} = \frac{4C}{T^3}$$

On substitution,

$$(h_2 - h_1)_\mathrm{T} = \int_{p_1}^{p_2} -\frac{4C}{T^3}\,\mathrm{d}p = \frac{4C}{T^3}\,(p_1 - p_2)_\mathrm{T}$$

(b) Using second *T*d*s* equation

$$T\mathrm{d}S = c_\mathrm{p}\,\mathrm{d}T - T\left(\frac{\partial v}{\partial T}\right)_p \mathrm{d}p$$

$$\therefore \quad \mathrm{d}S_\mathrm{T} = -\left(\frac{\partial v}{\partial T}\right)_p \mathrm{d}p_\mathrm{T} = -\left(\frac{R}{p} + \frac{3C}{T^4}\right)\mathrm{d}p_\mathrm{T}$$

$$\therefore \quad (s_2 - s_1)_\mathrm{T} = R\ln\frac{p_1}{p_2} + \frac{3C}{T^4}\,(p_1 - p_2)_\mathrm{T}$$

Example 11.10

Agron gas is compressed reversibly and isothermally at the rate of* 1.5 *kg/s from* 1 *atm,* 300 *K to* 400 *atm. Calculate the power required to run the compressor and the rate at which heat must be removed from the compressor. The gas is assumed to obey the Redlich-Kwong equation of state, for which the constants are:

$$a = 0.42748\frac{\bar{R}^2 T_c^{2.5}}{p_c} \text{ and } b = 0.08664\frac{\bar{R}^2 T_c}{p_c}$$

For argon, T_c = 151 *K and* p_c = 48 *atm. Take* $\bar{R}$ = 0.082 *litre-atm/gmol-K.*

Solution Substituting the values of p_c, T_c and R,

$$a = 0.42748\frac{(82)^2(151)^{2.5}}{48} = 16.8\times10^6\,\frac{\text{atm K}^{1/2}\text{cm}^6}{(\text{g mol})^2}$$

$$b = 0.08664\frac{(82)(151)}{48} = 22.4\,\frac{\text{cm}^3}{\text{g mol}}$$

Substituting the numerical values of p_2, T_2, a, b and R into the Redlich-Kwong equation

$$p=\frac{RT}{v-b}-\frac{a}{T^{1/2}v(v+b)}$$

$$v_2^3-49.24\,v_2^2+335.6\,v_2-43{,}440=0$$

from which we obtain

$$v_2=56.8\ \text{cm}^3/\text{g mol}$$

Since $p_1 = 1$ atm, the volume of the gas at the initial state can be obtained from the ideal gas equation:

$$v_1=\frac{RT_1}{p_1}=\frac{82\times 300}{1}=24{,}600\ \text{cm}^3/\text{g mol}$$

For isothermal compression,

$$\Delta h_{12}=h_2-h_1=\left\{\int_{p_1}^{p_2}\left[v-T\left(\frac{\partial v}{\partial T}\right)_p\right]dp\right\}_T$$

Now, $d(pv) = p\,dv + v\,dp$

$$\int_{p1}^{p_2} v\,dp=p_2v_2-p_1v_1-\left[\int_{v_1}^{v_2}p\,dv\right]_T$$

Since

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

we have

$$\left[\int_{p_1}^{p_2}\left(\frac{\partial v}{\partial T}\right)_p dp\right]_T=-\left[\int_{v_1}^{v_2}\left(\frac{\partial v}{\partial T}\right)_v dv\right]_T$$

Hence,

$$\Delta h_{12}=h_2-h_1=p_2v_2-p_1v_1-\left\{\int_{v_1}^{v_2}\left[p-T\left(\frac{\partial p}{\partial T}\right)\right]_v dv\right\}_T$$

According to Redlich-Kwong equation, we have, $\left(\dfrac{\partial p}{\partial T}\right)=\dfrac{R}{v-b}+\dfrac{a}{2T^{3/2}v(v+b)}$

Thus, $\Delta h_{12}=h_2-h_1=(p_2v_2-p_1v_1)-\left\{\int_{v_1}^{v_2}\left[\dfrac{-3a}{2T^{1/2}v(v+b)}\right]_v dv\right\}_T$

$$=(p_2v_2-p_1v_1)-\frac{1.5a}{T_1^{1/2}}\frac{1}{b}\ln\frac{(v_2+b)/v_2}{(v_1+b)/v_1}$$

Substituting the numerical values,

$$h_2-h_1=-\,1{,}790\ \text{J/g mol}$$

$$\Delta s_{12} = s_2 - s_1 = \left[\int_{p_1}^{p_2} \left(\frac{\partial v}{\partial T}\right)_p \mathrm{d}p\right]_T = \left[\int_{v_1}^{v_2} \left(\frac{\partial p}{\partial T}\right)_v \mathrm{d}v\right]_T$$

For the Redlich-Kwong equation this becomes,

$$s_2 - s_1 = \left\{\int_{v_1}^{v_2} \left[\frac{R}{v-b} + \frac{a}{2T^{3/2} v(v+b)}\right] \mathrm{d}v\right\}_T$$

$$= R \ln \frac{v_2 - b}{v_1 - b} - \frac{a}{2bT_1^{3/2}} \ln \frac{(v_2 + b)/v_2}{(v_1 + b)/v_1}$$

Substituting the numerical values,

$$s_2 - s_1 = -57 \text{ J/gmol-K}$$

$$\dot{Q}_{12} = \dot{m} T_1 (s_2 - s_1)$$

$$= \frac{10^5 \text{ g/h}}{39.8 \text{ g/gmol}} \times 300 \text{ K} \times (-57) \frac{\text{J}}{\text{g mol K}}$$

$$= -4.29 \times 10^7 \text{ J/h}$$

$$= -11.917 \text{ kW (heat removed from the gas)}$$ *Ans.*

$$\dot{W}_{12} = \dot{Q}_{12} + \dot{m}(h_1 - h_2)$$

$$= -4.29 \times 10^7 + \frac{10^5}{39.9} \times 1790$$

$$= -3.84 \times 10^7 \text{ J/h}$$

$$= -10.67 \text{ kW(Work is done on the gas)}$$ *Ans.*

Review Questions

11.1 What is the condition for exact differential?

11.2 Derive Maxwell's equations.

11.3 Write down the first and second *TdS* equations, and derive the expression for the difference in heat capacities, C_p and C_v. What does the expression signify?

11.4 Define volume expansivity and isothermal compressibility.

11.5 Show that the slope of an isentrope is greater than that of an isotherm on p–v plot. How is it meaningful for estimating the work of compression?

11.6 What is the energy equation? How does this equation lead to the derivation of the Stefan-Boltzman law of thermal radiation?

11.7 Show that the internal energy and enthalpy of an ideal gas are functions of temperature only.

11.8 Why are $\mathrm{d}U = C_v\, \mathrm{d}T$ and $\mathrm{d}H = C_p\, \mathrm{d}T$ true for an ideal gas in any process, whereas these are true for any other substance only at constant volume and at constant pressure respectively?

11.9 Explain Joule-Kelvin effect. What is inversion temperature?

11.10 What is Joule-Thomson coefficient? Why is it zero for an ideal gas?

11.11 Why does the hydrogen gas need to be precooled before being throttled to get the cooling effect?

11.12 Why does the maximum temperature drop occur if the state before throttling lies on the inversion curve?

11.13 Why does the Gibbs function remain constant during phase transition?

11.14 What are the characteristics of the first order phase transition?

11.15 Write down the representative equation for phase transition. Why does the fusion line for water have negative slope on the p–T diagram?

11.16 Why is the slope of the sublimation curve at the triple point on the p–T diagram greater than that of the vaporization curve at the same point?

11.17 Explain how thermodynamic properties are evaluated from an equation of state.

11.18 Illustrate how enthalpy change and entropy change of a gas can be estimated with the help of an equation of state.

11.19 State the important thermodynamic criteria which an equation of state should satisfy.

11.20 Explain how the Boyle temperature is yielded when:

$$\lim_{p \to 0} \left(\frac{\partial z}{\partial p} \right)_T = 0$$

11.21 What is foldback temperature?

11.22 Show that for an inversion curve $\left(\frac{\partial z}{\partial T} \right)_p = 0$.

11.23 Define chemical potential of a component in terms of U, H, and G.

11.24 What is the use of the Gibbs entropy equation?

11.25 Explain the significance of the Gibbs-Duhem equation.

11.26 State the conditions of equilibrium of a heterogeneous system.

11.27 What do you understand by phase equilibrium?

11.28 Give the Gibbs phase rule for a nonreactive system. Why is the triple point of a substance nonvariant?

11.29 What are the four types of equilibrium? What is stable equilibrium?

11.30 State the conditions of spontaneous change, equilibrium and criterion of stability for: (a) a system having constant U and V (i.e., isolated), and (b) a system having constant T and p.

11.31 What do you understand by neutral and unstable equilibrium?

11.32 What is metastable equilibrium?

11.33 Show that for a system to be stable, these conditions are satisfied

(a) $C_v > 0$ (thermal stability)

(b) $\left(\frac{\partial p}{\partial V} \right)_T < 0$ (mechanical stability)

Problems

11.1 Derive the following equations

(a) $U = F - T\left(\frac{\partial F}{\partial T} \right)_V = -T^2 \left(\frac{\partial F/T}{\partial T} \right)_V$

(b) $C_v = -T\left(\frac{\partial^2 F}{\partial T^2} \right)_v$

(c) $H = G - T\left(\frac{\partial G}{\partial T} \right)_p = -T^2 \left(\frac{\partial G/T}{\partial T} \right)_p$

(d) $C_p = -T\left(\frac{\partial^2 G}{\partial T^2} \right)_p$

11.2 (a) Derive the equation

$$\left(\frac{\partial c_v}{\partial v} \right)_T = T\left(\frac{\partial^2 p}{\partial T^2} \right)_V$$

(b) Prove that c_v of an ideal gas is a function of T only.

(c) In the case of a gas obeying the equation of state

$$\frac{pv}{RT} = 1 + \frac{B''}{v}$$

where B'' is a function of T only, show that

$$c_v = -\frac{RT}{v}\frac{d^2}{dT^2}(B''T) + (c_v)_0$$

where $(c_v)_0$ is the value at very large volumes.

11.3 Derive the third TdS equation

$$TdS = C_v \left(\frac{\partial T}{\partial p} \right)_v dp + C_p \left(\frac{\partial T}{\partial V} \right)_p dV$$

and show that the three TdS equations may be written as

(a) $TdS = C_v\,dT + \dfrac{\beta T}{k}\,dV$

(b) $TdS = C_p\,dT - V\beta\,Tdp$

(c) $TdS = \dfrac{C_v}{\beta}\,kdp + \dfrac{C_v}{\beta V}\,dV$

11.4 Derive the equations

(a) $C_p = T\left(\dfrac{\partial V}{\partial T}\right)_p\left(\dfrac{\partial p}{\partial T}\right)_s$

(b) $\left(\dfrac{\partial p}{\partial T}\right)_s = \dfrac{C_p}{V\beta T}$

(c) $\dfrac{(\partial p/\partial T)_s}{(\partial p/\partial T)_v} = \dfrac{\gamma}{\gamma - 1}$

11.5 Derive the equations

(a) $C_v = -T\left(\dfrac{\partial p}{\partial T}\right)_v\left(\dfrac{\partial V}{\partial T}\right)_s$

(b) $\left(\dfrac{\partial V}{\partial T}\right)_s = -\dfrac{C_v k}{\beta T}$

(c) $\dfrac{(\partial V/\partial T)_s}{(\partial V/\partial T)_p} = \dfrac{1}{1-\gamma}$

11.6 (a) Prove that the slope of a curve on a Mollier diagram representing a reversible isothermal process is equal to

$$T - \frac{1}{\beta}$$

(b) Prove that the slope of a curve on a Mollier diagram representing a reversible isochoric process is equal to

$$T + \frac{\gamma - 1}{\beta}$$

11.7 (a) Show that

$$\mu_J\, c_p = T^2\left(\frac{\partial V/T}{\partial T}\right)_p$$

For 1 mole of a gas, in the region of moderate pressures, the equation of sate may be written as

$$\frac{p\bar{v}}{\bar{R}T} = 1 + B'p + C'p^2$$

where B' and C' are functions of temperature only.

(b) Show that as $p \to 0$

$$\mu_J\, c_p \to \bar{R}T^2\,\frac{dB'}{dT}$$

(c) Show that the equation of the inversion curve is

$$p = -\frac{dB'/dT}{dC'/dT}$$

11.8 Prove the following functional relationship of the reduced properties for the inversion curve of a van der Waals' gas

$$T_r = \frac{3(3v_r - 1)^2}{4v_r^2} \text{ and } p_r = \frac{9(2v_r - 1)}{v_r^2}$$

Hence, show that

$$\frac{\text{Maximum inversion temperature}}{\text{Critical temperature}} = 6.75$$

and $\dfrac{\text{Minimum inversion temperature}}{\text{Critical temperature}} = 0.75$

11.9 Estimate the maximum inversion temperature of hydrogen if it is assumed to obey the equation of state

$$pV = RT + B_1 p + B_2 p^2 + B_3 p^3 + \ldots$$

For hydrogen, $B_1 \times 10^5 = a + 10^{-2}\,bT + 10^2\,c/T$

where $a = 166$, $b = -7.66$, $c = -172.33$

11.10 The vapour pressure of mercury at 399 K and 401 K is found to be 0.988 mm and 1.084 mm of mercury respectively. Calculate the latent heat of vaporization of liquid mercury at 400 K.

Ans. 61,634.96 kJ/kg mol

11.11 In the vicinity of the triple point, the vapour pressure of liquid ammonia (in atmospheres) is represented by

$$\ln p = 15.16 - \frac{3063}{T}$$

This is the equation of the liquid-vapour boundary curve in a p–T diagram. Similarly, the vapour pressure of solid ammonia is

$$\ln p = 18.70 - \frac{3754}{T}$$

(a) What is the temperature and pressure at the triple point?

(b) What are the latent heats of sublimation and vaporization?

(c) What is the latent heat of fusion at the triple point? *Ans.* 195.2 K, 0.585 atm., 1498 kJ/kg, 1836 kJ/kg, 338 kJ/kg

11.12 It is found that a certain liquid boils at a temperature of 95°C at the top of a hill, whereas it boils at a temperature of 105°C at the bottom. The latent heat is 4.187 kJ/g mole. What is the approximate height of the hill? Assume $T_0 = 300$ K. *Ans.* 394 m

11.13 Show that for an ideal gas in a mixture of ideal gases

$$d\mu_k = \frac{\mu_k - h_k}{T}\, dT + v_k\, dp + RTd \ln x_k$$

11.14 Compute μ_j for a gas whose equation of state is

$$p(v - b) = RT \qquad Ans.\ \mu_J = -b/c_p$$

11.15 Show that

(a) $\left(\dfrac{\partial \beta}{\partial p}\right)_T = -\left(\dfrac{\partial k}{\partial T}\right)_p$

(b) $\left(\dfrac{\partial u}{\partial p}\right)_T = -T\left(\dfrac{\partial v}{\partial T}\right)_p - p\left(\dfrac{\partial v}{\partial p}\right)_T$

11.16 Two particular systems have the following equations of state

$$\frac{1}{T^{(1)}} = \frac{3}{2}\bar{R}\,\frac{N^{(1)}}{U^{(1)}} \text{ and } \frac{1}{T^{(2)}} = \frac{5}{2}\bar{R}\,\frac{N^{(2)}}{U^{(2)}}$$

where $\bar{R} = 8.3143$ kJ/kg mol K. The mole number of the first system is $N^{(1)} = 2$, and that of the second is $N^{(2)} = 3$. The two systems are separated by a diathermal wall, and the total energy in the composite system is 25.120 kJ. What is the internal energy of each system in equilibrium? *Ans.* 7.2 kJ, 17.92 kJ

11.17 Two systems with the equations of state given in Problem 11.16 are separated by a diathermal wall. The respective mole numbers are $N^{(1)} = 2$ and $N^{(2)} = 3$. The initial temperatures are $T^{(1)} = 250$ K and $T^{(2)} = 350$ K. What are the values of $U^{(1)}$ and $U^{(2)}$ after equilibrium has been established? What is the equilibrium temperature? *Ans.* 8.02 kJ, 20.04 kJ, 321.4 K

11.18 Show that the change in latent heat L with temperature is given by the following relation

$$\left(\frac{dL}{dT}\right) = (C_p''' - C_p'') + \frac{L}{T} - \frac{v'''\beta''' - v''\beta''}{v''' - v''}\, L$$

11.19 Show that for a van der Waals' gas, the Joule-Thomson coefficient is given by

$$\mu_j = \frac{v}{c_p}\left[\frac{2a(v-b)^2 - RTbv^2}{RTv^3 - 2a(v-b)^2}\right]$$

11.20 At 273.15 K the specific volumes of water and ice are 0.001 and 0.001091 m³/kg and the latent heat of fusion of ice is 334 kJ/kg. Determine the melting point increase due to increase of pressure by 1 atm (101.325 kPa). *Ans.* −0.00753 K

11.21 Calculate the latent heat of vaporization of steam formed by boiling water under a pressure of 101.325 kPa. At a pressure near this, a rise of temperature of 1 K causes an increase of vapour pressure of 3.62 kPa. *Ans.* 2257 kJ/kg

11.22 It is known that radiation exerts a pressure $p = 1/3\ u$, where u is the energy per unit volume.

(a) Show that $du = TdS + \dfrac{1}{V}\left(Ts - \dfrac{4}{3}u\right) dV$

where s is the entropy per unit volume.

(b) Assuming u and s as functions of temperature only, show that

(i) $u = As^{4/3}$

(ii) $s = \dfrac{4}{3}\, aT^3$

(iii) $u = aT^4$

where A is the constant of integration and $a = 81/256\, A^3$.

(c) Show that the average time radiation remains in a spherical enclosure of radius r is given by

$$t = \frac{4r}{3c}$$

where c is the speed of radiation.

(d) If E_B is the energy emitted per unit area of spherical surface per unit time, show that

$$E_B = \sigma T^4$$

where $\sigma = ac/4$ and T is the temperatur of the surface.

11.23 Show that the inversion temperature of a van der Waals' gas is given by $T_i = 2a/bR$.

11.24 Show that:

(a) $\left(\dfrac{\partial u}{\partial v}\right)_T = T^2\left[\dfrac{\partial (p/T)}{\partial T}\right]_v$

(b) $\left(\dfrac{\partial h}{\partial p}\right)_T = -T^2\left[\dfrac{\partial(v/T)}{\partial T}\right]_p$

11.25 Show that for a van der Waals' gas at low pressures, a Joule-Thomson expansion from pressure p_1 to p_2 produces a temperature change which can be found from the solution of

$$p_1 - p_2 = \frac{c_p}{b}\,(T_1 - T_2) + T_i \ln \frac{T_2 - T_i}{T_1 - T_i}$$

where T_i is the inversion temperature.

11.26 Using the Redlick-Kwong equation of state, develop expressions for the changes in entropy and internal energy of a gas in an isothermal process.

Ans. $(s_2 - s_1)_T = R \ln \dfrac{v_2 - b}{v_1 - b} + \dfrac{a}{2bT^{3/2}} \ln\left[\dfrac{v_2(v_1 + b)}{v_1(v_2 + b)}\right]$

$$(u_2 - u_1)_T = \frac{a}{2bT^{1/2}} \ln\left[\frac{v_2(v_1 + b)}{v_1(v_2 + b)}\right]$$

11.27 Find the change of entropy of a gas following Clausius equation of state at constant temperature

$p(v - b) = RT$ *Ans.* $R \ln \dfrac{v_2 - b}{v_1 - b}$

11.28 (a) Show that for a van der Waals' gas

$$\beta = \frac{Rv^2(v - b)}{RTv^3 - 2a(v - b)^2}$$

$$k_T = \frac{v^2(v - b)^2}{RTv^3 - 2a(v - b)^2}$$

(b) What is the value of k_T/β expressed in its simplest form?

(c) What do the above relations become when $a = 0$, $b = 0$ (ideal gas)?

11.29 (a) Show that

(i) $\left(\dfrac{\partial u}{\partial p}\right)_v = \dfrac{k}{\beta}\cdot c_v$ (ii) $\left(\dfrac{\partial u}{\partial v}\right)_p = \dfrac{c_p}{v_B} - p$

(b) Hence show that the slope of a reversible adiabatic process on p–v coordinates is

$$\frac{dp}{dv} = -\frac{\gamma}{kv}$$

where k is the isothermal compressibility.

11.30 According to Berthelot, the temperature effect of the second virial coefficient is given by

$$B'(T) = \frac{b}{T} - \frac{a}{T^3}$$

where a and b are constants. Show that according to Berthelot,

$$T_{inv}/T_B = \sqrt{3}$$

11.31 The following expressions for the equation of state and the specific heat c_p are obeyed by a certain gas:

$$v = \frac{RT}{p} + \alpha T^2 \quad \text{and} \quad c_p = A + BT + Cp$$

where α, A, B, C are constants. Obtain an expression for (a) the Joule-Thomson coefficient, and (b) the specific heat c_v.

Ans. (a) $\mu_J = \dfrac{\alpha T^2}{A + BT + Cp}$

(b) $c_v = A + BT + \dfrac{CRT}{v - \alpha T^2} - R\left(\dfrac{v + \alpha T^2}{v - \alpha T^2}\right)$

11.32 Determine the maximum Joule-Thomson inversion temperature in terms of the critical temperature T_c predicted by the

(a) van der Waals equations
(b) Redlich–Kwong equation
(c) Dieterici equation

Ans. (a) 6.75 T_c, (b) 5.34 T_c (c) 8T_c

11.33 From the virial form of the equation of state of a gas

$$v = \frac{RT}{p} + RTB'(T) + RTC'(T)p + \ldots$$

show that the Joule-Thomson coefficient is

$$\mu_J = \frac{RT^2}{c_p}\left[\frac{dB'}{dT} + \frac{dC'}{dT}p + \ldots\right]$$

(b) For a van der Waals gas

$$B'(T) = \frac{bRT - a}{R^2T^2}$$

Show that the limiting value of μ_J at low pressure is

$$\mu_J = \frac{1}{c_p}\left(\frac{2a}{RT} - b\right)$$

11.34 Show that $k_T - k_s = \dfrac{Tv\beta^2}{c_p}$

11.35 For a simple compressible system, show that

(a) $\left[\dfrac{\partial u}{dv}\right]_T = T^2\left[\dfrac{\partial p/T}{\partial T}\right]_v$

(b) $\left[\frac{\partial h}{\partial p}\right]_T = -T^2\left[\frac{\partial v/T}{\partial T}\right]_p$

11.36 The liquid-vapour equilibrium curve for nitrogen over the range from the triple point to the normal boiling point may be expressed by the relation:

$$\log p = A - BT - \frac{C}{T}$$

where p is the vapour pressure in mm Hg, T is the temperature in K, and $A = 7.782$, $B = 0.006265$, and $C = 341.6$.

(a) Derive an expression for the enthalpy of vaporization h_{fg} in terms of A, B, C, T and v_{fg}.

(b) Calculate h_{fg} for nitrogen at 71.9 K with v_{fg} = 11,530 cm³/gmol. *Ans.* 5,790 J/gmol

11.37 For a gas obeying the van der Waals equation of state, show that:

(a) $c_p - c_v = \frac{R}{1 - 2a(v-b)^2/RTv^3}$

(b) $\left[\frac{\partial c_v}{\partial v}\right]_T = T\left[\frac{\partial^2 p}{\partial T^2}\right]_v = 0$ to prove that c_v is a function of temperature only.

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

$$= R^2T\left[\frac{2av^3 - 6abv^{-4}}{\left(p - av^{-2} + 2abv^{-3}\right)^3}\right]$$

to prove that c_p for a van der Waals gas is not a function of temperature only.

(d) The relation between T and v is given by:

$T(v-b)^{R/c_v}$ = constant

(e) The relation between p and v is given by:

$\left[p + \frac{a}{v^2}\right](v-b)^{1+R/c_v}$ = constant.

11.38 Nitrogen at a pressure of 250 atm and a temperature of 400 K expands reversibly and adiabatically in a turbine to an exhaust pressure of 5 atm. The flow rate is 1 kg/s. Calculate the power output if nitrogen obeys the Redlich–Kwong equation of state. For nitrogen at 1 atm take.

$c_p = 6.903 - 0.3753 \times 10^{-3}T + 1.930 \times 10^{-6}T^2$
$- 6.861 \times 10^{-9}T^3$

where c_p is in cal/gmol-K and T is in K.

For nitrogen, $T_c = 126.2$ K,
$p_c = 33.5$ atm. *Ans.* 272 kW

Hints: See Fig. P-11.34

$h_1 - h_2 = (h_1 - h_4) + (h_4 - h_3) + (h_3 - h_2)$ and

$s_1 - s_2 = 0 = (s_1 - s_4) + (s_4 - s_3) + (s_3 - s_2)$

$a = 15.4 \times 10^6$ atm/K$^{1/2}$ cm^6/(g mol)^2, b = 26.8 cm³/gmol

By trial-and-error, v_1 = 143 cm³/g mol, v_4 = 32,800 cm³/g mol

$T_2 = 124$ K, $h_1 - h_2 = 7.61$ kJ/g mol.

CHAPTER 12

Vapour Power Cycles

12.1 SIMPLE STEAM POWER CYCLE

A power cycle continuously converts heat (energy released by the burning of fuel) into work (shaft work), in which a working fluid repeatedly performs a succession of processes. In the vapour power cycle the working fluid, which is water, undergoes a change of phase. Figure 12.1 gives the schematic of a simple steam power plant working on the vapour power cycle. Heat is transferred to water in the boiler from an external source (furnace, where fuel is continuously burnt) to raise steam, the high pressure, high temperature steam leaving the boiler expands in the turbine to produce shaft work, the steam leaving the turbine condenses into water in the condenser (where cooling water circulates), rejecting heat, and then the water is pumped back to the boiler. Figure 12.2 shows how a unit mass of the working fluid, sometimes in the

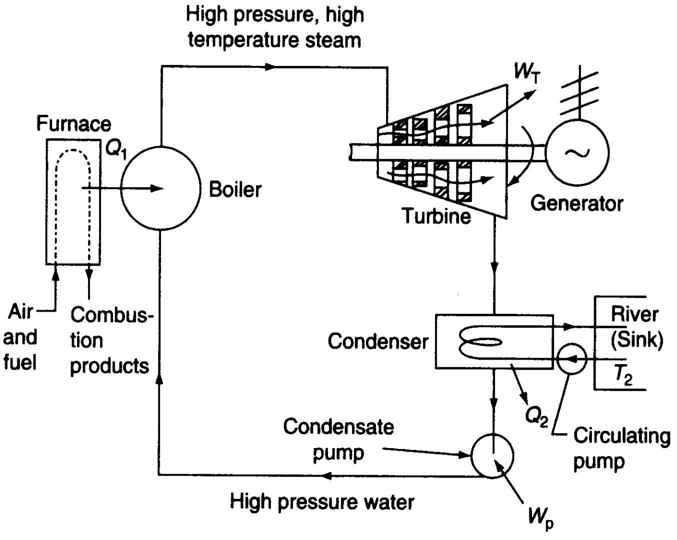


Fig. 12.1 *Simple steam power plant*

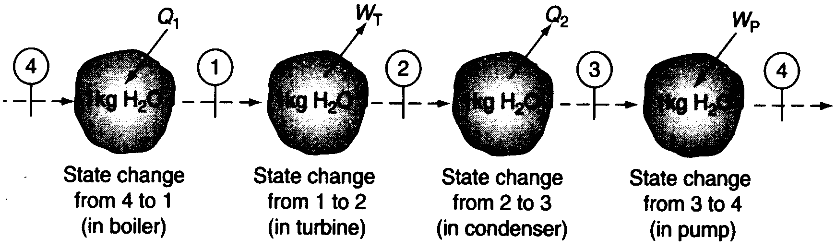


Fig. 12.2 *One kg H_2O executing a heat engine cycle*

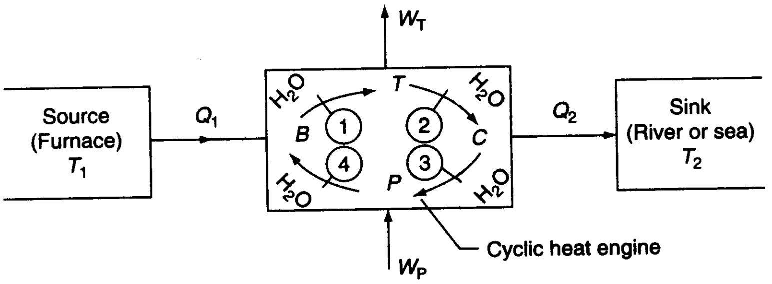


Fig. 12.3 *Cyclic heat engine with water as the working fluid*

liquid phase and sometimes in the vapour phase, undergoes various external heat and work interactions in executing a power cycle. Since the fluid is undergoing a cyclic process, there will be no net change in its internal energy over the cycle, and consequently the net energy transferred to the unit mass of the fluid as heat during the cycle must equal the net energy transfer as work from the fluid. Figure 12.3 shows the cyclic heat engine operating on the vapour power cycle, where the working substance, water, follows along the B-T-C-P (Boiler-Turbine-Condenser-Pump) path, interacting externally as shown, and converting net heat input to net work output continuously. By the first law

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

or

$$Q_1 - Q_2 = W_T - W_P$$

where Q_1 = heat transferred to the working fluid (kJ/kg)
Q_2 = heat rejected from the working fluid (kJ/kg)
W_T = work transferred from the working fluid (kJ/kg)
W_P = work transferred into the working fluid (kJ/kg)

The efficiency of the vapour power cycle would be given by

$$\eta_{\text{cycle}} = \frac{W_{\text{net}}}{Q_1} = \frac{W_T - W_P}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \tag{12.1}$$

12.2 RANKINE CYCLE

For each process in the vapour power cycle, it is possible to assume a hypothetical or ideal process which represents the basic intended operation and involves no extraneous effects. For the steam boiler, this would be a reversible constant pressure heating process of water to form steam, for the turbine the ideal process would be a reversible adiabatic expansion of steam, for the condenser it would be a reversible constant pressure heat rejection as the steam condenses till it becomes saturated liquid, and for the pump, the ideal process would be the reversible adiabatic compression of this liquid ending at the initial pressure. When all these four processes are ideal, the cycle is an ideal cycle, called a *Rankine cycle*. This is a reversible cycle. Figure 12.4 shows the flow diagram of the Rankine cycle, and in Fig. 12.5, the cycle has been

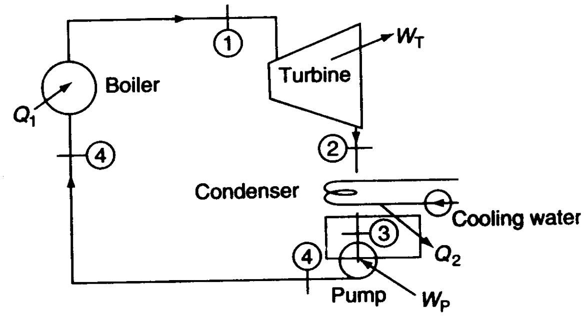
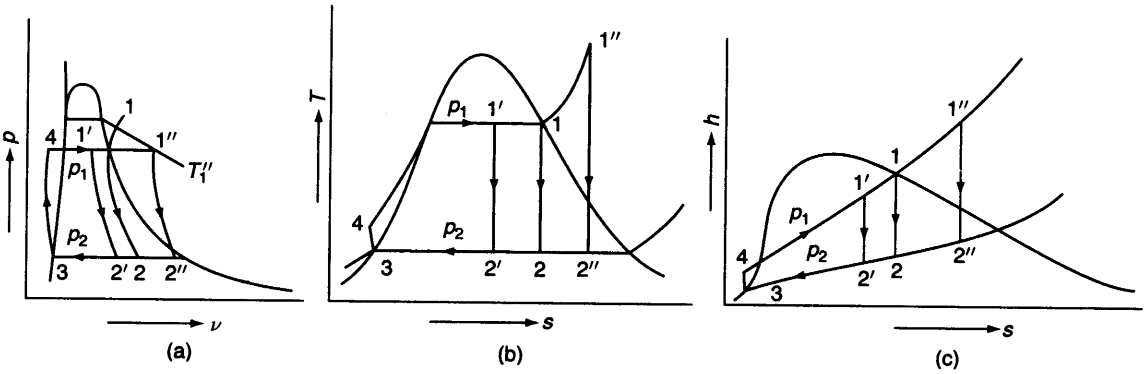


Fig. 12.4 *A simple steam plant*



[illegible] *Rankine cycle on p–v, T–s and h–s diagrams*

plotted on the p–v, T–s, and h–s planes. The numbers on the plots correspond to the numbers on the flow diagram. For any given pressure, the steam approaching the turbine may be dry saturated (state 1) wet (state 1′), or superheated (state 1″), but the fluid approaching the pump is, in each case, saturated liquid (state 3). Steam expands reversibly and adiabatically in the turbine from state 1 to state 2 (or 1′ to 2′, or 1″ to 2″), the steam leaving the turbine condenses to water in the condenser reversibly at constant pressure from state 2 (or 2′, or 2″) to state 3, the water at state 3 is then pumped to the boiler at state 4 reversibly and adiabatically, and the water is heated in the boiler to form steam reversibly at constant pressure from state 4 to state 1 (or 1′ or 1″).

For purposes of analysis the Rankine cycle is assumed to be carried out in a steady flow operation. Applying the steady flow energy equation to each of the processes on the basis of unit mass of fluid, and neglecting changes in kinetic and potential energy, the work and heat quantities can be evaluated in terms of the properties of the fluid.

For 1 kg fluid

The S.F.E.E. for the boiler (control volume) gives

$$h_4 + Q_1 = h_1$$

$$\therefore \quad Q_1 = h_1 - h_4 \tag{12.2}$$

The S.F.E.E. for the turbine as the control volume gives

$$h_1 = W_T + h_2$$

$$\therefore \quad W_T = h_1 - h_2 \tag{12.3}$$

Similarly, the S.F.E.E. for the condenser is

$$h_2 = Q_2 + h_3$$

$$\therefore \quad Q_2 = h_2 - h_3 \tag{12.4}$$

and the S.F.E.E. for the pump gives

$$h_3 + W_p = h_4$$

$$\therefore \quad W_p = h_4 - h_3 \tag{12.5}$$

The efficiency of the Rankine cycle is then given by

$$\eta = \frac{W_{net}}{Q_1} = \frac{W_T - W_P}{Q_1} = \frac{(h_1 - h_2) - (h_4 - h_3)}{h_1 - h_4} \tag{12.6}$$