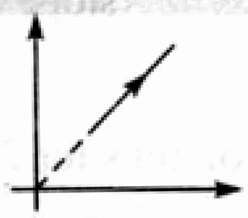
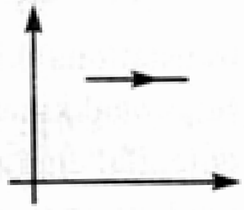
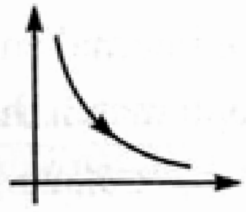
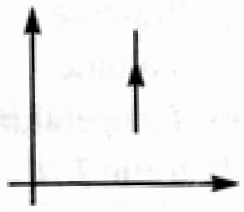
Column I	Column II
(a) x_1	(p) 1.5
(b) x_2	(q) 2.0
(c) x_3	(r) 3.0
(d) x_4	(s) None of these/data insufficient

4. With increase in temperature, match the following two columns.

Column I	Column II
(a) Density of water	(p) will increase
(b) Fraction of a solid floating in a liquid	(q) will decrease
(c) Apparent weight of a solid immersed in water	(r) will remain unchanged
(d) Time period of pendulum	(s) may increase or decrease

5. Corresponding to isobaric process match the following two columns.

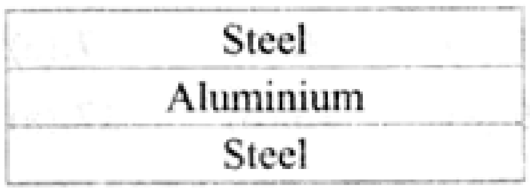
Column I	Column II
(a) P-T graph	(p) 
(b) U-ρ graph	(q) 
(c) T-V graph	(r) 
(d) T-ρ graph	(s) 

Note First physical quantity is along y-axis.

Subjective Questions

1. A cubical vessel contains one gram molecule of nitrogen at a pressure of 2 atm and temperature 300 K. If the molecules are assumed to move with the rms velocity.
   (a) Find the number of collisions per unit area per second which the molecules may make with the wall of the vessel.
   (b) Further if the vessel now thermally insulated moved with a constant speed v and then suddenly stopped results in a rise of temperature of 2°C, find v.

2. The volume of a diatomic gas ($\gamma = 7/5$) is increased two times in a polytropic process with molar heat capacity $C = R$. How many times will the rate of collision of molecules against the wall of the vessel be reduced as a result of this process?
3. A perfectly conducting vessel of volume $V = 0.4\text{ m}^3$ contains an ideal gas at constant temperature $T = 273$ K. A portion of the gas is let out and the pressure of the gas falls by $\Delta P = 0.24$ atm. (Density of the gas at STP is $\rho = 1.2\text{ kg/m}^3$). Find the mass of the gas which escapes from the vessel.
4. A thin-walled cylinder of mass m, height h and cross-sectional area A is filled with a gas and floats on the surface of water. As a result of leakage from the lower part of the cylinder, the depth of its submergence has increased by Δh. Find the initial pressure P_1 of the gas in the cylinder if the atmospheric pressure is P_0 and the temperature remains constant.
5. A cubical box of side 1 m contains helium gas (atomic weight 4) at a pressure of 100 N/m^2. During an observation time of 1 s an atom travelling with the rms speed parallel to one of the edges of the cube, was found to make 500 hits with a particular wall, without any collision with other atoms. Take $R = 8.31$ J/mol-K and $k = 1.38 \times 10^{-23}$ J/K.
   (a) Evaluate the temperature of the gas.
   (b) Evaluate the average kinetic energy per atom.
   (c) Evaluate the total mass of helium gas in the box.
6. An air bubble of volume V is released from the bottom of a lake which has a depth of 11 m. Find the volume of the bubble at the surface of the lake. The water has density 1000 kg/m^3. At the release point of the bubble and at the surface, temperature is 4°C. The atmospheric pressure is $1.01 \times 10^5\text{ N/m}^2$.
7. Find the minimum attainable pressure of an ideal gas in the process $T = T_0 + \alpha V^2$ where T_0 and α are positive constants and V is the volume of one mole of gas.
8. A solid body floats in a liquid at a temperature $t = 50°\text{C}$ being completely submerged in it. What percentage of the volume of the body is submerged in the liquid after it is cooled to $t_0 = 0°\text{C}$, if the coefficient of cubic expansion for the solid is $\gamma_s = 0.3 \times 10^{-5}\,°\text{C}^{-1}$ and of the liquid $\gamma_l = 8 \times 10^{-5}\,°\text{C}^{-1}$.
9. Two vessels connected by a pipe with a sliding plug contain mercury. In one vessel, the height of mercury column is 39.2 cm and its temperature is 0°C, while in the other, the height of mercury column is 40 cm and its temperature is 100°C. Find the coefficient of cubical expansion for mercury. The volume of the connecting pipe should be neglected.
10. Two steel rods and an aluminium rod of equal length l_0 and equal cross-section are joined rigidly at their ends as shown in the figure below. All the rods are in a state of zero tension at 0°C.
    Find the length of the system when the temperature is raised to θ. Coefficient of linear expansion of aluminium and steel are α_a and α_s respectively. Young's modulus of aluminium is Y_a and of steel is Y_s.



11. A metal rod A of 25 cm length expands by 0.050 cm when its temperature is raised from 0° C to 100° C. Another rod B of a different metal of length 40 cm expands by 0.040 cm for the same rise in temperature. A third rod C of 50 cm length is made up of pieces of rods A and B placed end to end expands by 0.03 cm on heating from 0° C to 50° C. Find the lengths of each portion of the composite rod.

ANSWERS

Introductory Exercise 17.1

1. (a) -17.8°C (b) -459.67°F **2.** (a) 160°C (b) -24.6°C **3.** 122°F
4. 574.25 **5.** -40°C **6.** Gains, 15.55 s **7.** It will first increase and then decrease
8. $(\gamma_2 - \gamma_1)\,\Delta T$ **9.** Cool the system

Introductory Exercise 17.2

1. $m_1 > m_2$ **2.** 12 atm **3.** 1.5 kg/m^3 **4.** 8×10^{15} **5.** $P_1 > P_2$
6. Straight line passing through origin

Introductory Exercise 17.3

1. Speed is a scalar quantity while velocity is a vector quantity. **2.** 6.21×10^{-21} J
3. (a) 1368 m/s, 609 m/s (b) 6.21×10^{-21} J **4.** 160 K **5.** 76.5% by mass
6. 103 cm^3 **7.** 6.5×10^3
8. (a) 3.5 mol (b) 43.65 J/mol-K, 72.75 J/mol-K (c) 72.75 J/mol-K, 101.85 J/mol-K
9. (a) 2.81 mol (b) 9.56 kJ (c) 20.8 J/mol-K **10.** True

For JEE Main

Subjective Questions

1. 20°C, -15°C, 80°C, 293K, 258K, 353K **2.** 86°F, 41°F, -4°F, 546°R, 501°R, 456°R
3. $-40^\circ\text{F} = -40^\circ\text{C}$ **4.** 140.2°F **5.** 20°C **6.** 546.30 K **7.** 400° **8.** 177.07°C
9. 53.8°C **10.** (a) 0.068 m (b) 88.49 cm **11.** -0.042% **12.** 192 N
13. 3.1×10^{-4} per $^\circ$C **14.** 2.82×10^{-26} kg **15.** (a) 6.135 mol (b) 1.24 kg/m^3 (c) 19.6 kg/m^3
16. 12.7 atm absolute pressure **17.** 900 m^3 **18.** 5.09 cm **19.** 0.089 **20.** 0.97 MPa
21. 1.13 atm **22.** 22.4 L **23.** 3.36×10^5Pa **24.** 4.1×10^5N/m^2 **25.** 10^{12} rad/s
26. 5 **27.** 1.54 **28.** $7.5\,E$ **29.** (a) 5 (b) 3 **30.** (a) 6.225×10^{-21} J (b) 20.8 J
31. $3R, 2R, 1.5$ **32.** γ **33.** $-\gamma$ **35.** 2.15 km/s **36.** $v_{\text{rms}} = 714$ m/s, $v_{\text{av}} = 700$ m/s
37. 5×10^{21}, 8.3×10^{-3} mol **38.** 3.1×10^{27} **39.** 4.8×10^{-22} J
40. (a) $1.40\,v_0$ (b) v_0 (c) $0.58\,v_0$ or $v_0/\sqrt{3}$ **41.** -253°C **42.** $T_E = 10059$ K, $T_M = 449$ K
43. (a) 6.21×10^{-21} J (b) 3740 J (c) 484 m/s

Objective Questions

1.(b) **2.**(b) **3.**(c) **4.**(a) **5.**(d) **6.**(c) **7.**(a) **8.**(b) **9.**(c) **10.**(a)
11.(a) **12.**(a) **13.**(c) **14.**(b) **15.**(a) **16.**(b) **17.**(a) **18.**(b) **19.**(c) **20.**(d)
21.(d) **22.**(c)

More than One Correct Options

23. (b,d) **24.** (a,d) **25.** (a,c) **26.** (a,c,d) **27.** (a,b) **28.** (a,b,c,d) **29.** (a,d)

For JEE Advanced

Assertion and Reason

1. (d) **2.** (b) **3.** (b) **4.** (d) **5.** (d) **6.** (b) **7.** (c) **8.** (b) **9.** (b) **10.** (a)

Match the Columns

1. (a) → r (b) → p (c) → s (d) → s

2. (a) → p (b) → q (c) → q (d) → p

3. (a) → r (b) → s (c) → q (d) → s

4. (a) → s (b) → s (c) → s (d) → p

5. (a) → q (b) → r (c) → p (d) → r

Subjective Questions

1. (a) 4.2×10^{27} (b) 54.5 m/s **2.** $(2)^{4/3}$ times **3.** 115.2 g

4. $P_1 = \left(P_0 + \frac{mg}{A}\right)\left(1 - \frac{\Delta h}{h}\right)$ **5.** (a) 160 K (b) 3.31×10^{-21} J (c) 3.0×10^{-4} kg

6. 2.089 V **7.** $2R\sqrt{\alpha T_0}$ **8.** 99.99% **9.** 2.0×10^{-4} per °C

10. $l_0\left[1 + \left(\frac{\alpha_a Y_a + 2\alpha_s Y_s}{Y_a + 2Y_s}\right)\theta\right]$ **11.** 10 cm, 40 cm

18

LAWS OF THERMODYNAMICS

Chapter Contents

18.1 The First Law of Thermodynamics

The first law of thermodynamics, is an extension of the principle of conservation of energy. To state energy relationships precisely, we need the concept of a **thermodynamic system.** A thermodynamic system is a system that can interact (and exchange energy) with its surroundings, or environment, in at least one ways, one of which is heat transfer. In this chapter the thermodynamic system will be an ideal gas contained in a vessel in most of the cases. A process in which there are changes in the state of a thermodynamic system (P, V and T in case of a gas) is called a **thermodynamic process.**

We now come to the first law.

Let a system changes from an initial equilibrium state i to a final equilibrium state f in a definite way, the heat absorbed by the system being Q and the work done by the system being W. Then we compute the $Q - W$. While Q and W both depend on the thermodynamic path taken between two equilibrium states, their difference $Q - W$ does not. We do this over and over again, using different paths each time. We find that in every case the quantity $Q - W$ is the same. The students may recall from mechanics that when an object is moved from an initial point i to a final point f in a gravitational field in the absence of friction, the work done depends only on the positions of the two points and not at all on the path through which the body is moved.

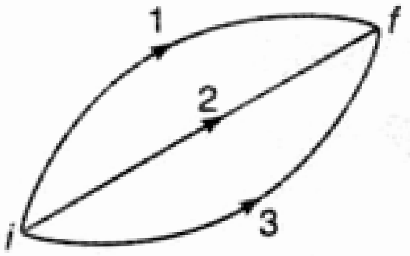


Fig. 18.1

From this we concluded that there is a function of the space coordinates of the body whose final value minus its initial value equals the work done in displacing the body. We called it the potential energy function. In thermodynamics there is a function of the thermodynamic coordinates (P, V and T) whose final value minus its initial value equals the change $Q - W$ in the process. We call this function the **internal energy** function. We have,

$$\Delta U = U_f - U_i = Q - W \qquad \ldots\text{(i)}$$

This equation is known as the first law of thermodynamics.

We describe the energy relations in any thermodynamic process in terms of the quantity of heat Q added to the system and the work W done by the system. Both Q and W may be positive, negative or zero. A positive value of Q represents heat flow into the system, negative Q represents heat flow out of the system. A positive value of W represents work done by the system against its surroundings, such as work done by an expanding gas. Negative W represents work done on the system by its surroundings such as work done during compression of a gas.

Table 18.1 Thermodynamic sign conventions for heat and work.

Process	Convention
Heat added to the system	$Q>0$
Heat removed from the system	$Q<0$
Work done by the system	$W>0$
Work done on the system	$W<0$

Eq. (i) can be written as

$$Q_1 - W_1 = Q_2 - W_2 = \ldots\ldots\ldots$$

or

$$\Delta U_1 = \Delta U_2 = \ldots\ldots\ldots$$

that is the change in the internal energy of the system between two points is path independent. It depends on thermodynamic co-ordinates of the two points. For example, in case of an ideal gas it depends only on the initial and final temperatures.

Often the first law must be used in its differential form, which is

$$dU = dQ - dW \qquad \text{...(ii)}$$

This can also be written as

$$dQ = dU + dW \qquad \text{...(iii)}$$

or

$$Q = \Delta U + W \qquad \text{...(iv)}$$

The first law can be expressed in other words as under.

Suppose a heat Q is given to a system. This heat is partly used by the system in doing work against its surroundings and partly its internal energy gets increased and from energy conservation principle $Q = \Delta U + W$. An another analogous example is from our daily life. Consider a person X. Suppose his monthly income is Rs. 50,000 (Q). He spends Rs. 30,000 (W) as his monthly expenditure. Then obviously the remaining Rs. 20,000 goes to his savings (ΔU). In some month it is also possible that he spends more than his income. In that case he will withdraw it from his bank or his savings will get reduced ($\Delta U < 0$). In the similar manner other combinations can be made.

Sample Example 18.1 *When a system goes from state A to state B, it is supplied with 400 J of heat and it does 100 J of work.*

(a) For this transition, what is the system's change in internal energy?

(b) If the system moves from B to A, what is the change in internal energy?

(c) If in moving from A to B along a different path in which $W'_{AB} = 400$ J of work is done on the system, how much heat does it absorb?

Solution (a) From the first law,

$$\Delta U_{AB} = Q_{AB} - W_{AB} = (400 - 100)\text{ J}$$
$$= 300\text{ J}$$

(b) Consider a closed path that passes through the state A and B. **Internal energy is a state function so ΔU is zero for a closed path.**

Thus,

$$\Delta U = \Delta U_{AB} + \Delta U_{BA} = 0$$

or

$$\Delta U_{BA} = -\Delta U_{AB}$$
$$= -300\text{ J}$$

(c) The change in internal energy is the same for any path, so

$$\Delta U_{AB} = \Delta U'_{AB} = Q'_{AB} - W'_{AB}$$
$$300\text{ J} = Q'_{AB} - (-400\text{ J})$$

and the heat exchanged is

$$Q'_{AB} = -100\text{ J}$$

The negative sign indicates that the system loses heat in this transition.

Exercise *The quantities in the following table represent four different paths for the same initial and final state. Find a, b, c, d, e, f and g.*

Table 18.2

Q (J)	W (J)	ΔU (J)
–80	–120	d
90	c	e
a	40	f
b	–40	g

Ans. $a = 80$ J $b = 0$ $c = 50$ J $d = 40$ J $e = 40$ J $f = 40$ J $g = 40$ J

18.2 Further Explanation of The Three Terms Used in First Law

First law of thermodynamics basically revolves round the three terms Q, ΔU and W. If you substitute these three terms correctly with proper signs in the equation $Q = \Delta U + W$, then you are able to solve most of the problems of first law. Let us take each term one by one. Here, we are taking the system an ideal gas.

(i) Heat transfer (Q or dQ)

For heat transfer, apply

$$Q = nC\Delta T$$

or in differential form

$$dQ = nCdT$$

where C is the molar heat capacity of the gas and n is the number of moles of the gas. Always take,

$$\Delta T = T_f - T_i$$

where T_f is the final temperature and T_i the initial temperature of the gas. Further, we have discussed in chapter 20 , that molar heat capacity of an ideal gas in the process PV^x = constant is,

$$C = \frac{R}{\gamma - 1} + \frac{R}{1-x} = C_V + \frac{R}{1-x}$$

$C = C_V = \frac{R}{\gamma - 1}$ in isochoric process and

$C = C_P = C_V + R$ in isobaric process

Mostly C_P and C_V are used.

(ii) Change in internal energy (U or dU)

For change in internal energy of the gas apply,

$$\Delta U = nC_V\Delta T$$

or in differential form,

$$dU = nC_V dT$$

Students are often confused that the result $\Delta U = nC_V\Delta T$ can be applied only in case of an isochoric process (as C_V is here used). However it is not so. It can be applied in any process, whether it is isobaric, isothermal adiabatic or else.

(iii) Work done (W or dW)

This is the most important of the three.

Work done during volume changes

A gas in a cylinder with a movable piston is a simple example of a thermodynamic system.

Figure shows a gas confined to a cylinder that has a movable piston at one end. If the gas expands against the piston, it exerts a force through a distance and does work on the piston. If the piston compresses the gas as it is moved inward, work is also done—in this case on the gas. The work associated with such volume changes can be determined as follows.

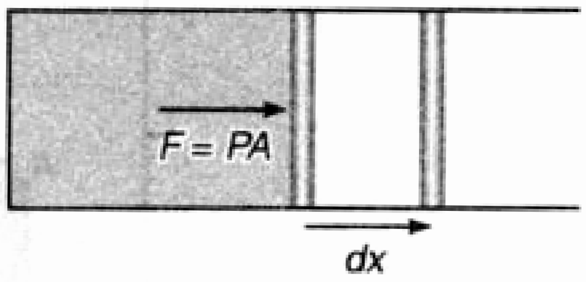


Fig. 18.2

Let the gas pressure on the piston face be P. Then the force on the piston due to gas is PA, where A is the area of the face.

When the piston is pushed outward an infinitesimal distance dx, the work done by the gas is

$$dW = F \cdot dx = PA\,dx$$

which, since the change in volume of the gas is $dV = Adx$, becomes

$$dW = PdV$$

For a finite change in volume from V_i to V_f, this equation is then integrated between V_i to V_f to find the net work

$$W = \int dW = \int_{V_i}^{V_f} PdV$$

Now, there are two methods of finding work done by a gas.

Method 1. This is used when P-V equation is known to us. Suppose P as a function of V is known to us.

$$P = f(V)$$

then work done can be found by,

$$W = \int_{V_i}^{V_f} f(V)\,dV$$

Method 2. The work done by a gas is also equal to the area under P-V graph. Following different cases are possible.

Case 1. When volume is constant

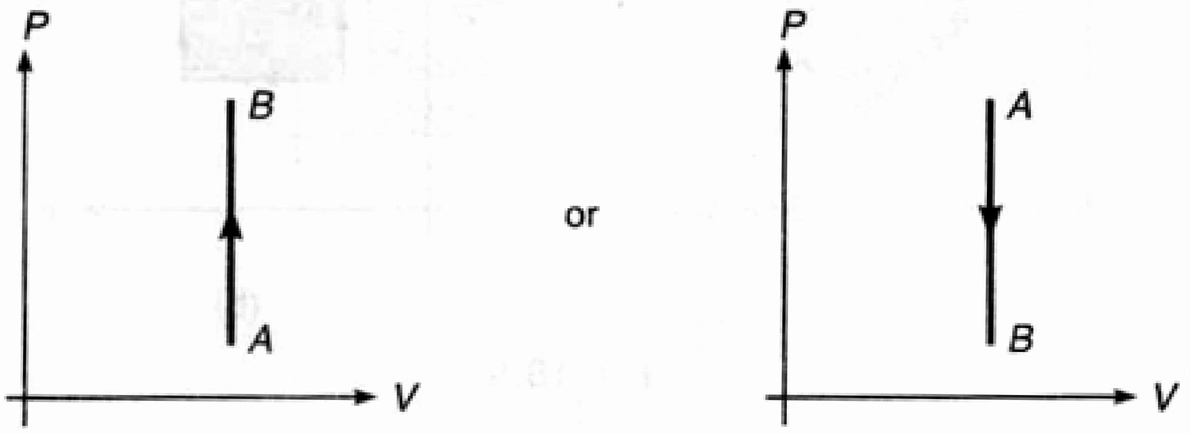


Fig. 18.3

$$V = \text{constant}$$

$$\therefore \quad W_{AB} = 0$$

Case 2. When volume is increasing

V is increasing

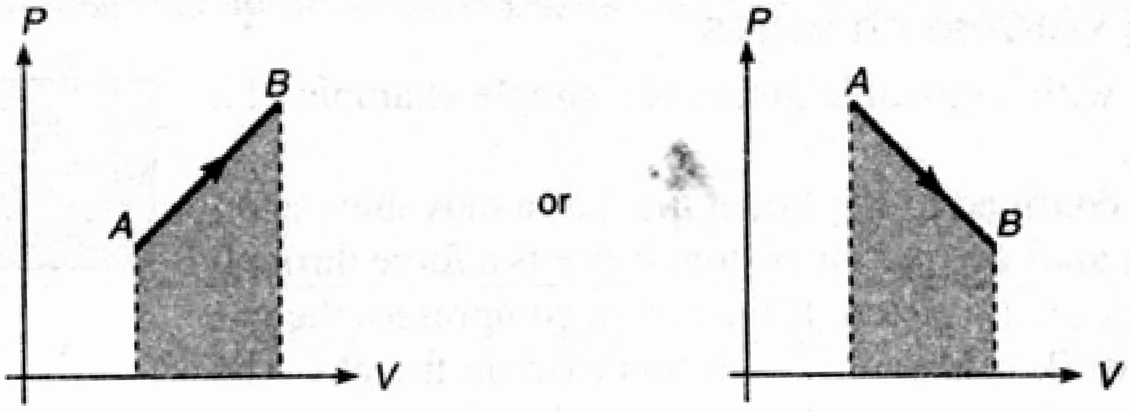


Fig. 18.4

$$\therefore \qquad W_{AB} > 0$$

$$W_{AB} = \text{Shaded area}$$

Case 3. When volume is decreasing

V is decreasing

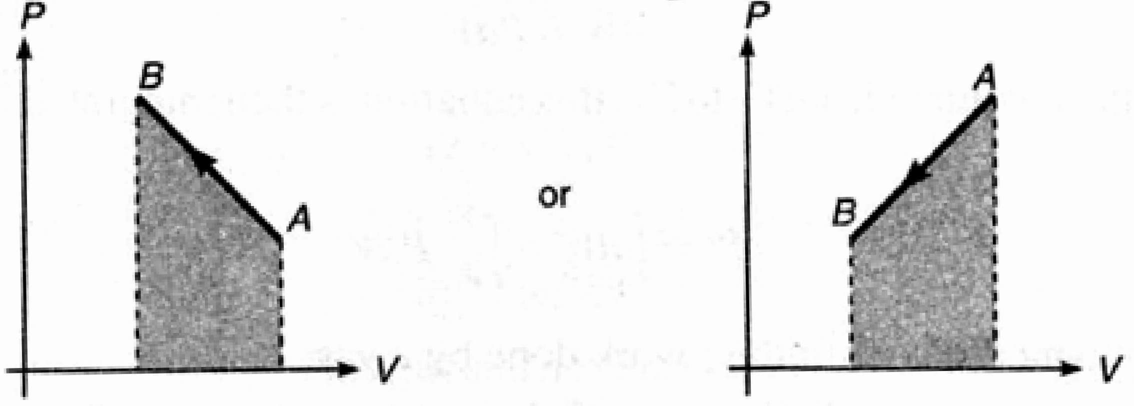
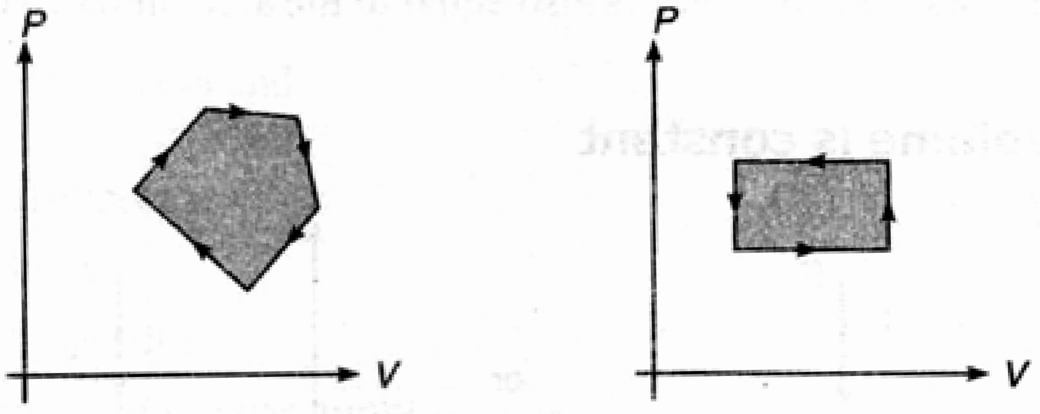


Fig. 18.5

$$\therefore \qquad W_{AB} < 0$$

$$W_{AB} = -\text{Shaded area}$$

Case 4. Cyclic process



(a) (b)

Fig. 18.6

$$W_{\text{clockwise cycle}} = +\text{Shaded area} \qquad \text{[in figure (a)]}$$

$$W_{\text{anticlockwise cycle}} = -\text{Shaded area} \qquad \text{[in figure (b)]}$$

Case 5. Incomplete cycle

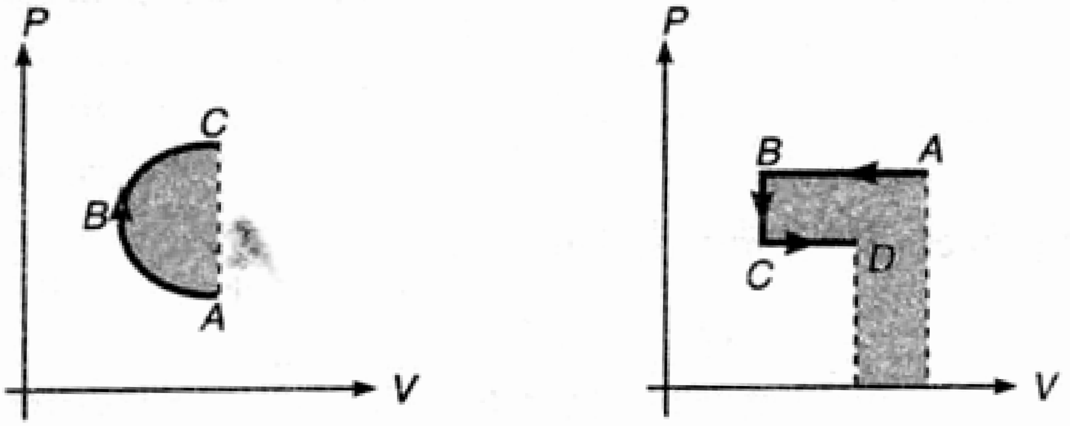


Fig. 18.7

$$W_{ABC} = +\text{Shaded area}$$
$$W_{ABCD} = -\text{Shaded area.}$$

Sample Example 18.2 *A certain amount of an ideal gas passes from state A to B first by means of process 1, then by means of process 2. In which of the process is the amount of heat absorbed by the gas greater?*

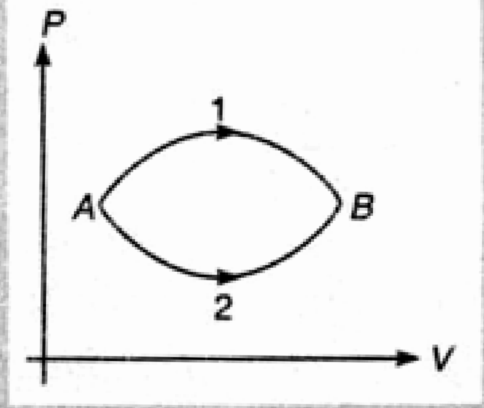


Fig. 18.8

Solution $$Q_1 = W_1 + \Delta U_1$$

and $$Q_2 = W_2 + \Delta U_2$$

U is a state function. Hence, ΔU depends only on the initial and final positions. Therefore,

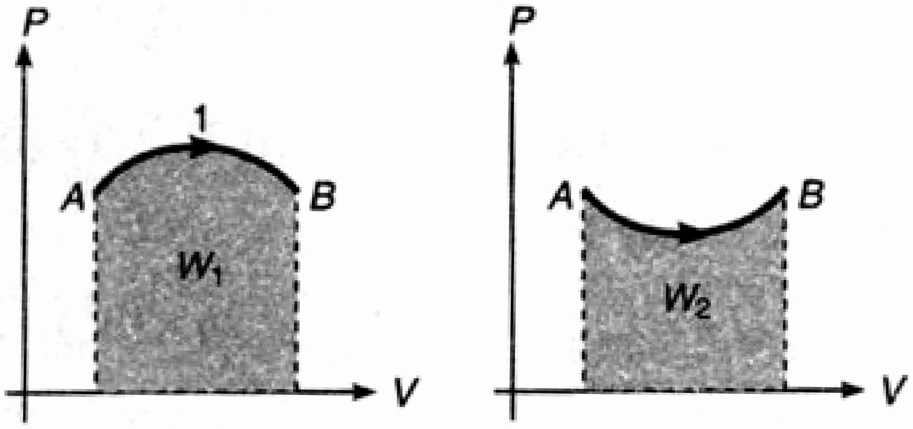


Fig. 18.9

$$\Delta U_1 = \Delta U_2$$

But $$W_1 > W_2$$

as the area under 1 is greater than area under 2. Hence,

$$Q_1 > Q_2$$

Sample Example 18.3 *Find the ratio of* $\frac{\Delta Q}{\Delta U}$ *and* $\frac{\Delta Q}{\Delta W}$ *in an isobaric process. The ratio of molar heat capacities* $\frac{C_P}{C_V}=\gamma$.

Solution In an isobaric process $P=$ constant. Therefore, $C=C_P$.

Now,
$$\frac{\Delta Q}{\Delta U}=\frac{nC_P\Delta T}{nC_V\Delta T}=\frac{C_P}{C_V}=\gamma$$

and
$$\frac{\Delta Q}{\Delta W}=\frac{\Delta Q}{\Delta Q-\Delta U}$$
$$=\frac{nC_P\Delta T}{nC_P\Delta T-nC_V\Delta T}$$
$$=\frac{C_P}{C_P-C_V}=\frac{C_P/C_V}{C_P/C_V-1}$$
$$=\frac{\gamma}{\gamma-1}$$

Sample Example 18.4 *Boiling water: Suppose* 1.0 g *of water vaporizes isobarically at atmospheric pressure* (1.01×10^5 *Pa*). *Its volume in the liquid state is* $V_i=V_{liquid}=1.0\ cm^3$ *and its volume in vapour state is* $V_f=V_{vapour}=1671\ cm^3$. *Find the work done in the expansion and the change in internal energy of the system. Ignore any mixing of the steam and the surrounding air. Take latent heat of vaporization* $L_v=2.26\times10^6\ J/kg$.

Solution Because the expansion takes place at constant pressure, the work done is

$$W=\int_{V_i}^{V_f}P_0dV=P_0\int_{V_i}^{V_f}dV=P_0\,(V_f-V_i)$$
$$=(1.01\times10^5)\,(1671\times10^{-6}-1.0\times10^{-6})$$
$$=169\text{ J}$$
$$Q=mL_v=(1.0\times10^{-3})\,(2.26\times10^6)=2260\text{ J}$$

Hence, from the first law, the change in internal energy

$$\Delta U=Q-W=2260-169=2091\text{ J}$$

Note *The positive value of* ΔU *indicates that the internal energy of the system increases. We see that most* $\left(\frac{2091\text{ J}}{2260\text{ J}}=93\%\right)$ *of the energy transferred to the liquid goes into increasing the internal energy of the system only* $\frac{169\text{ J}}{2260\text{ J}}=7\%$ *leaves the system by work done by the steam on the surrounding atmosphere.*

Introdcutory Exercise 18.1

1. A gas in a cylinder is held at a constant pressure of 1.7×10^5 Pa and is cooled and compressed from $1.20\ \text{m}^3$ to $0.8\ \text{m}^3$. The internal energy of the gas decreases by 1.1×10^5 J.
   (a) Find the work done by the gas.
   (b) Find the magnitude of the heat flow into or out of the gas, and state the direction of heat flow.
   (c) Does it matter whether or not the gas is ideal?

2. A thermodynamic system undergoes a cyclic process as shown in figure.
   (a) over one complete cycle, does the system do positive or negative work.
   (b) over one complete cycle, does heat flow into or out of the system.
   (c) In each of the loops 1 and 2, does heat flow into or out of the system.

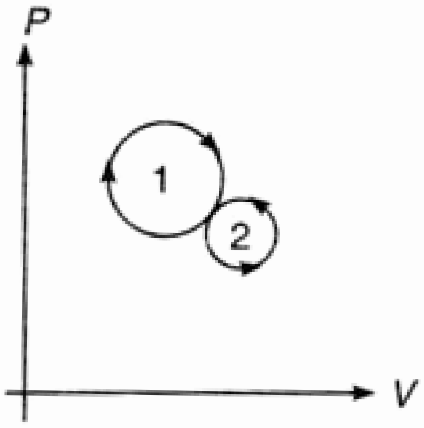


Fig. 18.10

3. A well insulated box contains a partition dividing the box into two equal volumes as shown in figure. Initially the left hand side contains an ideal monoatomic gas and the other half is a vacuum. The partition is suddenly removed so that the gas now is contained throughout the entire box.
   (a) Does the temperature of the gas change?
   (b) Does the internal energy of the system change?
   (c) Does the gas work?

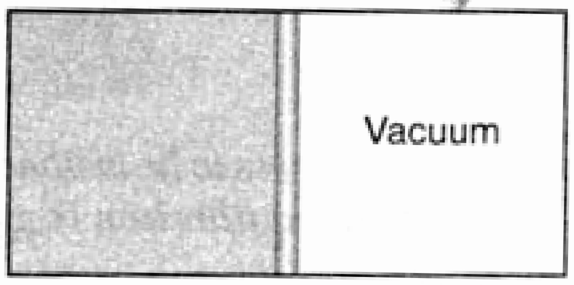


Fig. 18.11

4. How many moles of helium at temperature 300 K and 1.00 atm pressure are needed to make the internal energy of the gas 100 J?
5. A 1.0 kg bar of copper is heated at atmospheric pressure ($1.01\times 10^5\ \text{N/m}^2$). If its temperature increases from 20°C to 50°C, calculate the change in its internal energy. $\alpha = 7.0\times 10^{-6}$ per°C, $\rho = 8.92\times 10^3\ \text{kg/m}^3$ and $c = 387\ \text{J/kg-°C}$.

18.3 Different Thermodynamic Processes

Among the thermodynamic processes we will consider are the following :

(i) An isothermal process during which the system's temperature remains constant.
(ii) An adiabatic process during which no heat is transferred to or from the system.
(iii) An isobaric process during which the pressure of the system is constant.
(iv) An isochoric process during which the system's volume does not change.

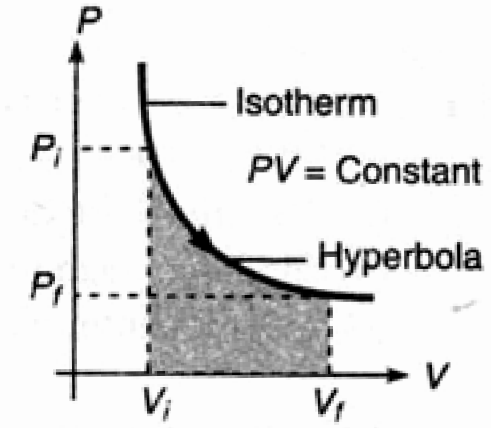
There are, of course, many other processes that do not fit into any of these four categories. We will mostly consider an ideal gas.

(i) Isothermal process

An isothermal process is a constant temperature process. In an isothermal process :

(i) $T = \text{constant}$ or $\Delta T = 0$
(ii) $P \propto \dfrac{1}{V}$ or $PV = \text{constant}$ *i.e.*, P-V graph is a rectangular hyperbola with $P_iV_i = P_fV_f$.
(iii) As $T = \text{constant}$, hence $U = \text{constant}$ for an ideal gas, because U is a function of T only.
(iv) $\Delta U = 0 \quad \therefore \quad Q = W$

Work done in isothermal process :



Isothermal expansion of an ideal gas

Fig. 18.12

$$W=\int_{V_i}^{V_f} P\,dV$$

$$=\int_{V_i}^{V_f}\left(\frac{nRT}{V}\right)dV \quad \left(\text{as } P=\frac{nRT}{V}\right)$$

$$=nRT\int_{V_i}^{V_f}\frac{dV}{V} \quad (\text{as } T=\text{constant})$$

$$=nRT\ln\left(\frac{V_f}{V_i}\right)$$

$$=nRT\ln\left(\frac{P_i}{P_f}\right) \quad (\text{as } P_iV_i=P_fV_f)$$

Thus in an isothermal process :

$$\Delta U=0 \quad \text{and} \quad Q=W=nRT\ln\left(\frac{V_f}{V_i}\right)=nRT\ln\left(\frac{P_i}{P_f}\right)$$

Note *For a process to be isothermal, any heat flow into or out of the system must occur* ***slowly*** *enough, so that thermal equilibrium is maintained.*

(ii) Adiabatic Process

An adiabatic process is defined as one with no heat transfer into or out of a system : $Q=0$. We can prevent heat flow either by surrounding the system with thermally insulating material or by carrying out the process so **quickly** that there is not enough time for appreciable heat flow. From the first law we find that for every adiabatic process,

$$W=-\Delta U \quad (\text{as } Q=0)$$

$$=-nC_V\Delta T$$

$$=-nC_V(T_f-T_i)$$

$$=n\left(\frac{R}{\gamma-1}\right)(T_i-T_f) \quad \left(\text{as } C_V=\frac{R}{\gamma-1}\right)$$

$$=\frac{P_iV_i-P_fV_f}{\gamma-1} \quad (\text{as } nRT=PV)$$

Thus, in an adiabatic process,

$$Q=0 \quad \text{and} \quad W=-\Delta U=\frac{P_iV_i-P_fV_f}{\gamma-1}$$

Note *In adiabatic process $W=-\Delta U$. Therefore, if the work done by a gas is positive (i.e., volume of the gas is increasing), then ΔU will be negative. That is U and hence T will decrease. The cooling of air can be experienced practically during bursting of a tyre. The process is so fast that it can be assumed as adiabatic. As the gas expands. Therefore, it cools. On the other hand the compression stroke in an internal combustion engine is an approximately adiabatic process. The temperature rises as the air fuel mixture in the cylinder is compressed.*

P-V relation : In adiabatic process $dQ = 0$

and $$dW = -\,dU$$

$\therefore$ $$PdV = -\,C_V dT \qquad \text{(for } n = 1\text{)}$$

$\therefore$ $$dT = -\frac{PdV}{C_V} \qquad \ldots\text{(i)}$$

Also, for 1 mole of an ideal gas,

$$d\,(PV) = d\,(RT)$$

or $$PdV + VdP = RdT$$

or $$dT = \frac{PdV + VdP}{R} \qquad \ldots\text{(ii)}$$

From Eqs. (i) and (ii)

$$C_V VdP + (C_V + R)\,PdV = 0$$

or $$C_V VdP + C_P PdV = 0$$

Dividing this equation by PV, we are left with

$$C_V \frac{dP}{P} + C_P \frac{dV}{V} = 0$$

or $$\frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

or $$\int \frac{dP}{P} + \gamma \int \frac{dV}{V} = 0$$

or $$\ln\,(P) + \gamma \ln\,(V) = \text{constant}$$

We can write this in the form

$$PV^{\gamma} = \text{constant}$$

This equation is the condition that must be obeyed by an ideal gas in an adiabatic process. For example, if an ideal gas makes an adiabatic transition from a state with pressure and volume P_i and V_i to a state with P_f and V_f, then

$$P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

The equation $PV^{\gamma} = \text{constant}$ can be written in terms of other pairs of thermodynamic variables by combining it with the ideal gas law $(PV = nRT)$. In doing so we will find that,

$$TV^{\gamma - 1} = \text{constant} \quad \text{and} \quad T^{\gamma} P^{1-\gamma} = \text{constant}$$

Slope of *P-V* graph

In an adiabatic process ($PV^{\gamma} = \text{constant}$), the slope of PV diagram at any point is

$$\frac{dP}{dV} = \frac{d}{dV}\left(\frac{\text{constant}}{V^{\gamma}}\right) = -\gamma\left(\frac{P}{V}\right)$$

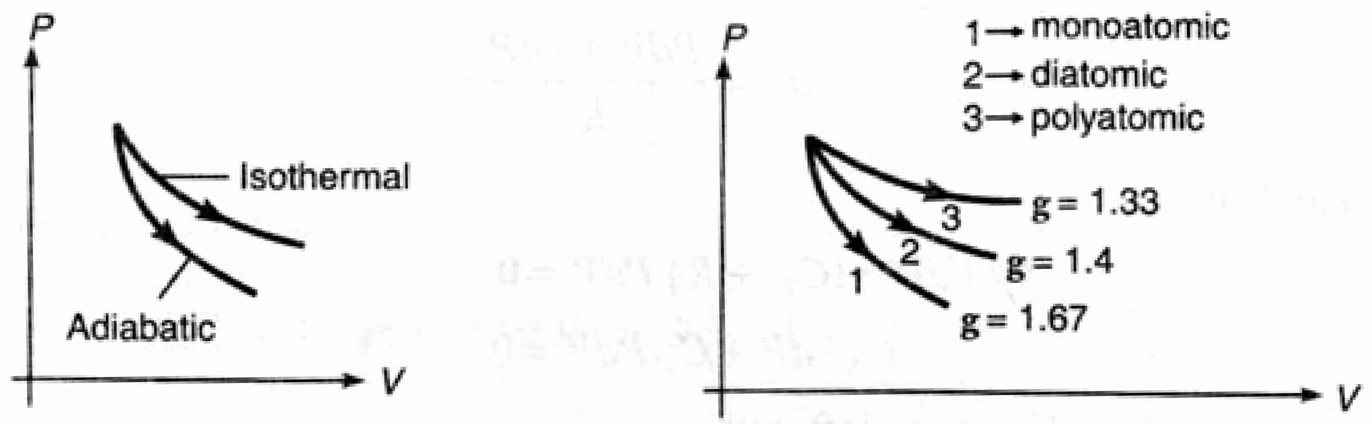
Thus,
$$(\text{Slope})_{\text{adiabatic}} = -\gamma\left(\frac{P}{V}\right)$$

Similarly in an isothermal process (PV = constant), the slope of PV diagram at any point is,

$$\frac{dP}{dV} = \frac{d}{dV}\left(\frac{\text{constant}}{V}\right) = -\frac{P}{V}$$

or
$$(\text{Slope})_{\text{isothermal}} = -\frac{P}{V}$$

Because $\gamma > 1$, the isothermal curve is not as steep as that for the adiabatic expansion.



Adiabatic and isothermal expansion of an ideal gas

Adiabatic expansion of mono, dia and polyatomic gases.

Fig. 18.13

(iii) Isobaric process

An isobaric process is a constant pressure process. In an isobaric process :

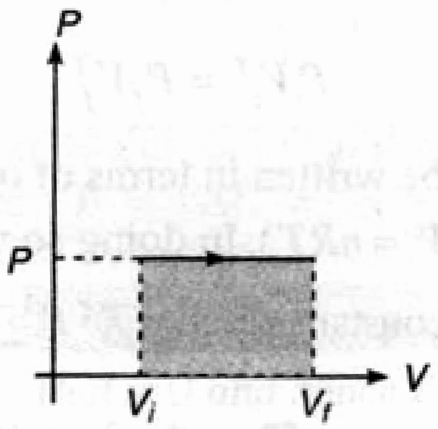
(i) $P = \text{constant}$ or $\Delta P = 0$

(ii) $V \propto T$ or $\frac{V}{T} = \text{constant}$

i.e., V-T graph is a straight line passing through origin.

(iii)
$$Q = nC_P\Delta T, \quad \Delta U = nC_V\Delta T \quad \text{and therefore}$$
$$W = Q - \Delta U = n(C_P - C_V)\Delta T = nR\Delta T$$
$$= nR(T_f - T_i)$$
$$= P(V_f - V_i) \qquad (\text{as } nRT = PV)$$

Thus, in an isobaric process



Isobaric expansion of a gas

Fig. 18.14

$$Q = nC_P\Delta T, \quad \Delta U = nC_V\Delta T \quad \text{and} \quad W = P(V_f - V_i)$$

(iv) Isochoric process

An isochoric process is a constant volume process. In an isochoric process :

(i) $V = \text{constant}$ or $\Delta V = 0$

(ii) $P \propto T$ or $\dfrac{P}{T} = \text{constant}$

i.e., P-T graph is a straight line passing through origin.

(iii)

As $V = \text{constant}$, hence $W = 0$ and from first law of thermodynamics

$$Q = \Delta U = nC_V \Delta T$$

Thus in an isochoric process :

$$W = 0 \quad \text{and} \quad Q = \Delta U = nC_V \Delta T$$

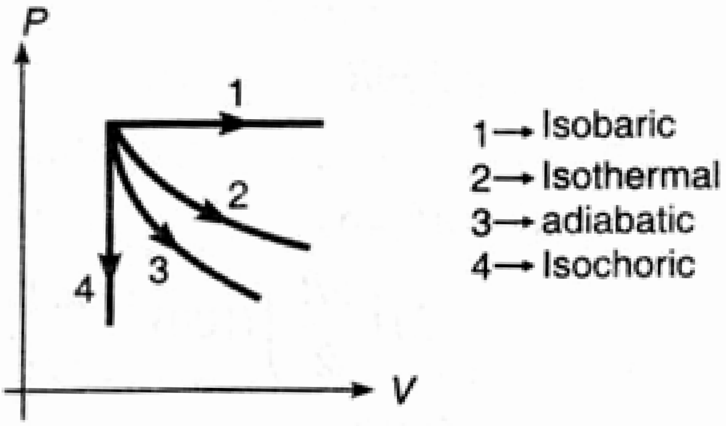


Fig. 18.15

P-V diagram of different processes is shown in one graph.

Table 18.3 shows Q, ΔU and W for different processes discussed above.

Table 18.3

Name of the process	Q	ΔU	W
Isothermal	$Q = W$	0	$nRT \ln\left(\dfrac{V_f}{V_i}\right) = nRT \ln\left(\dfrac{P_i}{P_f}\right)$
Adiabatic	0	$nC_V \Delta T$	$\dfrac{P_iV_i - P_fV_f}{\gamma - 1} = -\Delta U$
Isobaric	$nC_P \Delta T$	$nC_V \Delta T$	$P(V_f - V_i)$
Isochoric	$Q = \Delta U$ $= nC_V \Delta T$	$nC_V \Delta T$	0

Sample Example 18.5 *What is the heat input needed to raise the temperature of 2 moles of helium gas from 0°C to 100°C*

(a) at constant volume,

(b) at constant pressure?

(c) What is the work done by the gas in part (b)?

Give your answer in terms of R.

Solution Helium is monoatomic gas. Therefore,

$$C_V = \frac{3R}{2} \quad \text{and} \quad C_P = \frac{5R}{2}$$

(a) At constant volume,

$$\begin{aligned} Q &= nC_V \Delta T \\ &= (2)\left(\frac{3R}{2}\right)(100) \\ &= 300R \end{aligned}$$

(b) At constant pressure,

$$\begin{aligned} Q &= nC_P \Delta T \\ &= (2)\left(\frac{5R}{2}\right)(100) \\ &= 500R \end{aligned}$$

(c) At constant pressure,

$$\begin{aligned} W &= Q - \Delta U \\ &= nC_P\Delta T - nC_V\Delta T \\ &= nR\Delta T = (2)(R)(100) \\ &= 200R \end{aligned}$$

Sample Example 18.6 *An ideal monoatomic gas at 300 K expands adiabatically to twice its volume. What is the final temperature?*

Solution For an ideal monoatomic gas,

$$\gamma = \frac{5}{3}$$

In an adiabatic process,

$$TV^{\gamma-1} = \text{constant}$$

$\therefore$

$$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

or

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1}$$

$$= (300)\left(\frac{1}{2}\right)^{\frac{5}{3}-1} = 189\text{ K}$$

Sample Example 18.7 *An ideal gas expands isothermally along AB and does 700 J of work.*

(a) How much heat does the gas exchange along AB?

(b) The gas then expands adiabatically along BC and does 400 J of work. When the gas returns to A along CA, it exhausts 100 J of heat to its surroundings. How much work is done on the gas along this path?

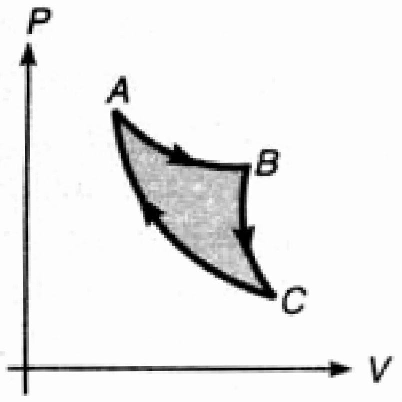


Fig. 18.16

Solution (a) AB is an isothermal process. Hence,

$$\Delta U_{AB} = 0$$

and

$$Q_{AB} = W_{AB} = 700 \text{ J}$$

(b) BC is an adiabatic process. Hence,

$$Q_{BC} = 0$$

$$W_{BC} = 400 \text{ J} \qquad \text{(given)}$$

$$\therefore \quad \Delta U_{BC} = -W_{BC} = -400 \text{ J}$$

ABC is a cyclic process and internal energy is a state function. Therefore,

$$(\Delta U)_{\text{whole cycle}} = 0 = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA}$$

and from first law of thermodynamics,

$$Q_{AB} + Q_{BC} + Q_{CA} = W_{AB} + W_{BC} + W_{CA}$$

Substituting the values,

$$700 + 0 - 100 = 700 + 400 + \Delta W_{CA}$$

$$\therefore \quad \Delta W_{CA} = -500 \text{ J}$$

Negative sign implies that work is done on the gas.

Table 18.4 shows different values in different processes.

Table 18.4

Process	Q (J)	W (J)	ΔU (J)
AB	700	700	0
BC	0	400	–400
CA	–100	–500	400
For complete cycle	600	600	0

Note *Total work done is 600 J, which implies that area of the closed curve is also 600 J.*

Introductory Exercise 18.2

1. One mole of an ideal monoatomic gas is initially at 300 K. Find the final temperature if 200 J of heat are added as follows :
   (a) at constant volume
   (b) at constant pressure
2. Prove that work done by an ideal gas in an adiabatic process is $W = \dfrac{P_i V_i - P_f V_f}{\gamma - 1}$, using the integraion $\int PdV$.

3. When a gas expands along AB it does 500 J of work and absorbs 250 J of heat. When the gas expands along AC, it does 700 J of work and absorbs 300 J of heat.
   (a) How much heat does the gas exchange along BC?
   (b) When the gas makes the transition from C to A along CDA, 800 J of work are done on it from C to D. How much heat does it exchange along CDA?

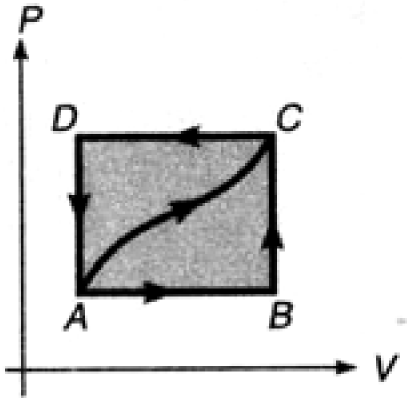


Fig. 18.17

4. One mole of an ideal monoatomic gas occupies a volume of 1.0×10^{-2} m^3 at a pressure of 2.0×10^5 N/m^2.
   (a) What is the temperature of the gas?
   (b) The gas undergoes a quasi-static adiabatic compression until its volume is decreased to 5.0×10^{-3} m^3. What is the new gas temperature?
   (c) How much work is done on the gas during the compression?
   (d) What is the change in the internal energy of the gas?
5. A bullet of mass 10 g travelling horizontally at 200 m/s strikes and embeds in a pendulum bob of mass 2.0 kg.
   (a) How much mechanical energy is dissipated in the collision?
   (b) Assuming that C_v for the bob plus bullet is 3 R, calculate the temperature increase of the system due to the collision. Take the molecular mass of the system to be 200 g/mol.
6. An ideal gas is carried through a thermodynamic cycle consisting of two isobaric and two isothermal processes, as shown in figure. Show that the net work done in the entire cycle is given by the equation.

$$W_{\text{net}} = P_1 (V_2 - V_1) \ln \frac{P_2}{P_1}$$

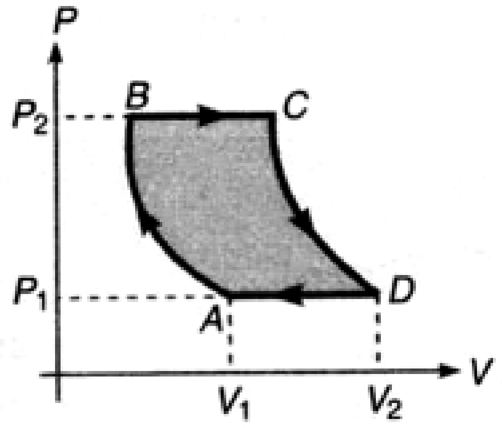


Fig. 18.18

7. Consider the cyclic process depicted in figure. If Q is negative for the process BC, and if ΔU is negative for the process CA, what are the signs of Q, W and ΔU that are associated with each process?

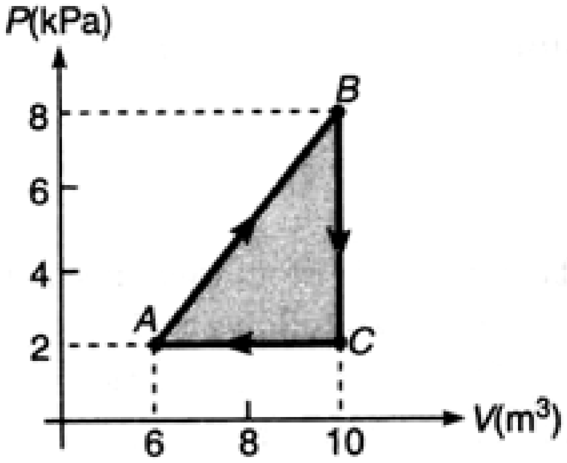


Fig. 18.19

8. An ideal gas is enclosed in a cylinder with a movable piston on top. The piston has mass of 8000 g and an area of 5.00 cm^2 and is free to slide up and down, keeping the pressure of the gas constant. How much work is done as the temperature of 0.200 mol of the gas is raised from 200°C to 300°C?

9. A sample of ideal gas is expanded to twice its original volume of 1.00 m^3 in a quasi-static process for which $P = \alpha V^2$, with $\alpha = 5.00$ atm/m^6, as shown in figure. How much work is done by the expanding gas?

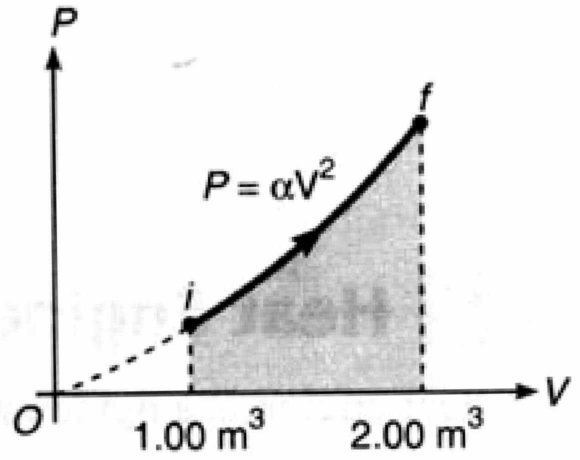


Fig. 18.20

18.4 Efficiency of a Cycle

In a cyclic process.

$$\Delta U = 0 \quad \text{and} \quad Q_{\text{net}} = W_{\text{net}}$$

(from first law of thermodynamics)

First we see what is the meaning of efficiency of a cycle. Suppose 100 J of heat is supplied to a system (in our case it is an ideal gas) and the system does 60 J of work. Then efficiency of the cycle is 60%. Thus, efficiency (η) of a cycle can be defined as

$$\eta = \left(\frac{\text{Work done by the working substance (an ideal gas in our case) during a cycle}}{\text{Heat supplied to the gas during the cycle}} \right) \times 100$$

$$= \frac{W_{\text{Total}}}{|Q_{\text{+ve}}|} \times 100$$

$$= \frac{|Q_{\text{+ve}}| - |Q_{\text{-ve}}|}{|Q_{\text{+ve}}|} \times 100$$

$$= \left\{ 1 - \left| \frac{Q_{\text{-ve}}}{Q_{\text{+ve}}} \right| \right\} \times 100$$

Thus,

$$\eta = \frac{W_{\text{Total}}}{|Q_{\text{+ve}}|} \times 100 = \left\{ 1 - \left| \frac{Q_{\text{-ve}}}{Q_{\text{+ve}}} \right| \right\} \times 100$$

Note (i) *There cann't be a cycle whose efficiency is 100%. Hence, η is always less than 100%.*

Thus, $W_{\text{Total}} \neq Q_{\text{+ve}}$

(ii) *It is just like a shopkeeper. He takes some money from you. (Suppose he takes Rs. 100/- from you). In lieu of this he provides services to you (suppose he provides services of worth Rs. 80/-). Then the efficiency of the shopkeeper is 80%. There cann't be a shopkeeper whose efficiency is 100%. Otherwise what will he save?*

Sample Example 18.8 *In Sample Example* 18.7 *find the efficiency of the given cycle.*

Solution From table 18.4 we can see that $Q_{+\text{ve}}$ during the cycle is 700 J, while the total work done in the cycle is 600 J.

$$\therefore \qquad \eta = \frac{W_{\text{Total}}}{|Q_{+\text{ve}}|} \times 100 = \left(\frac{600}{700}\right) \times 100$$

$$= 85.71\%$$

18.5 Heat Engines

A heat engine is a device which converts heat energy into mechanical energy.

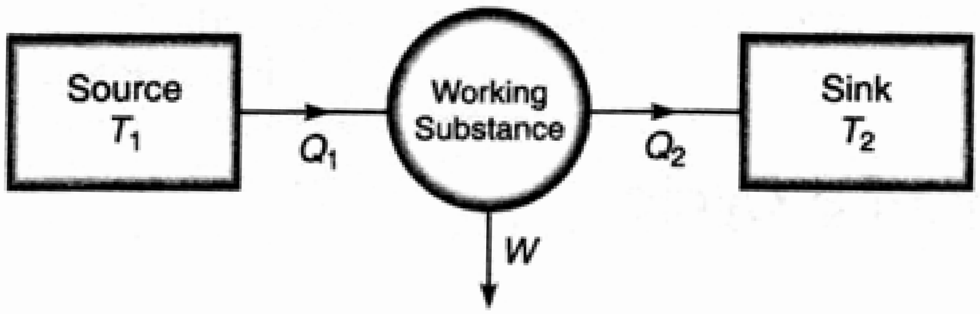


Fig. 18.21

Any heat engine has some working substance (normally a gas in a chamber). In every heat engine the working substance absorbs some heat (Q_1) from a source (at temperature T_1), converts a part of it into work (W) and the rest (Q_2) is rejected to the sink (at temperature T_2).

From conservation of energy.

$$Q_1 = W + Q_2$$

As discussed in article 18.4 **thermal efficiency** of a heat engine is defined as the ratio of net work done per cycle by the engine to the total amount of heat absorbed per cycle by the working substance from the source. It is denoted by η. Thus,

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

As some heat is always rejected to the sink $Q_2 \neq 0$. Therefore, η is always less than 1 *i.e.*, thermal efficiency of a heat engine is always less than 100%.

Types of Heat Engines

In practice, heat engine are of two types :

(a) External combustion engine

In which heat is produced by burning the fuel in a chamber outside the main body (working substance) of the engine. Steam engine is an external combustion engine. The thermal efficiency of a steam engine varies from 10 to 20%.

(b) Internal combustion engine

In which heat is produced by burning the fuel inside the main body of the engine. Petrol engine and diesel engines are internal combustion engine.

Carnot Engine

Carnot cycle consists of the following four stages :

(i) Isothermal expansion (process AB)g
(ii) Adiabatic expansion (process BC)
(iii) Isothermal compression (process CD) and
(iv) Adiabatic compression (process DA)

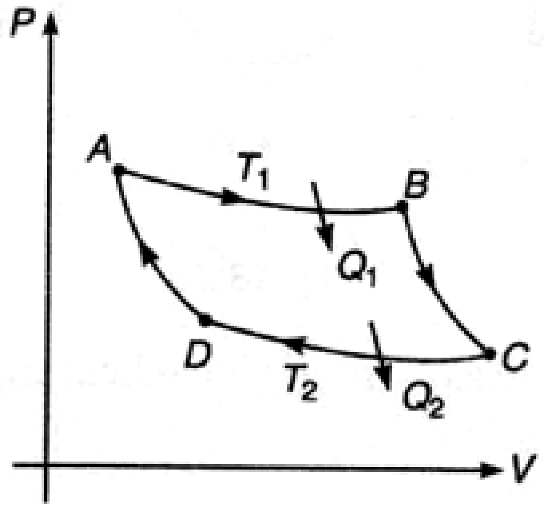


Fig. 18.22

The P-V diagram of the cycle is shown in the figure.

In process AB heat Q_1 is taken by the working substance at constant temperature T_1 and in process CD heat Q_2 is liberated from the working substance at constant temperature T_2. The net work done is area of graph $ABCD$. After doing the calculations for different processes we can show that :

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

Therefore, efficiency of the cycle is,

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

Note *That efficiency of Carnot engine is maximum (not 100%) for given temperatures T_1 and T_2. But still Carnot engine is not a practical engine because many ideal situations have been assumed while designing this engine which can practically not be obtained.*

Otto or Petrol Engine

This engine was made by Otto. This is also a four stroke engine. Four stroke means, in a cycle there are four processes. The working substance in it is 2% petrol and 98% air. The four processes are, charging stroke, compression stroke, working stroke and exhaust stroke. The efficiency of a petrol engine is about 52%.

Diesel Engine

The Diesel engine was made by a German Engineer Diesel. The efficiency of Diesel engine is about 64%.

18.6 Refrigerator

Refrigerator is an apparatus which takes heat from a cold body, work is done on it and the work done together with the heat absorbed is rejected to the source.

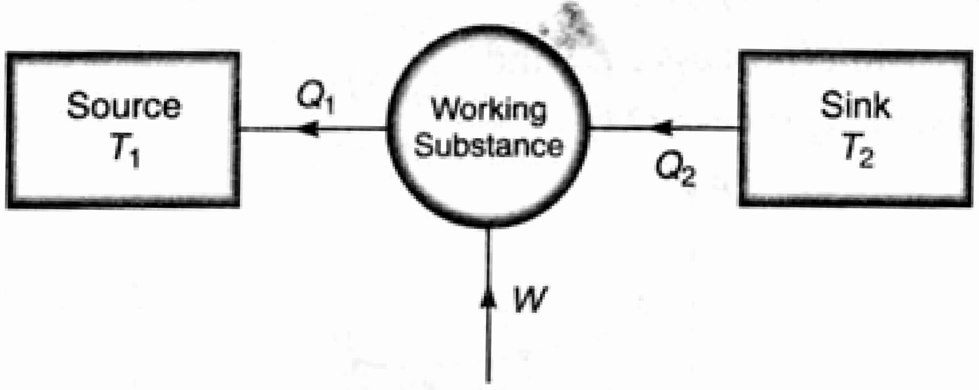


Fig. 18.23

An ideal refrigerator can be regarded as Carnot's ideal heat engine working in the reverse direction.

Coefficient of Performance

(β) of a refrigerator is defined as the ratio of quantity of heat removed per cycle (Q_2) to the work done on the working substance per cycle to remove this heat. Thus,

$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

By doing the calculations we can show that,

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

Here, η is the efficiency of Carnot's cycle.

Sample Example 18.9 *The P-V diagram of* 0.2 *mol of a diatomic ideal gas is shown in figure. Process BC is adiabatic. The value of* γ *for this gas is* 1.4.

(a) *Find the pressure and volume at points A, B and C.*

(b) *Calculate* $\Delta Q, \Delta W$ *and* ΔU *for each of the three processes.*

(c) *Find the thermal efficiency of the cycle.*

Take $1\ atm = 1.0 \times 10^5\ N/m^2$.

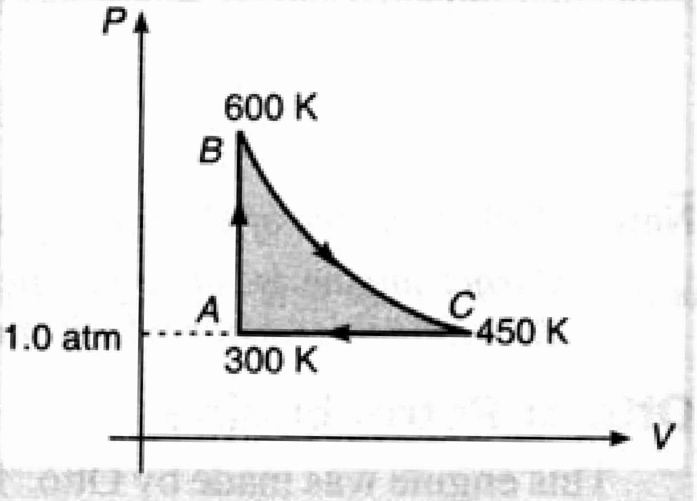


Fig. 18.24

Solution (a) $P_A = P_C = 1\ \text{atm} = 1.01 \times 10^5\ \text{N/m}^2$

Process *AB* is an isochoric process.

$$\therefore \qquad P \propto T \qquad \text{or} \qquad \frac{P_B}{P_A} = \frac{T_B}{T_A}$$

$$\therefore \qquad P_B = \left(\frac{T_B}{T_A}\right) P_A = \left(\frac{600}{300}\right)(1\ \text{atm}) = 2\ \text{atm}$$

$$= 2.02 \times 10^5\ \text{N/m}^2$$

From ideal gas equation $$V = \frac{nRT}{P}$$

$$\therefore \quad V_A = V_B = \frac{nRT_A}{P_A}$$

$$= \frac{(0.2)\,(8.31)\,(300)}{(1.01 \times 10^5)} \approx 5.0 \times 10^{-3}\ \text{m}^3$$

$$= 5\ \text{litre}$$

and $$V_C = \frac{nRT_C}{P_C} = \frac{(0.2)\,(8.31)\,(455)}{(1.01 \times 10^5)}$$

$$= 7.6 \times 10^{-3}\ \text{m}^3$$

$$\approx 7.6\ \text{litre}$$

State	P	V
A	1 atm	5 lt
B	2 atm	5 lt
C	1 atm	7.6 lt

(b) Process *AB* is an isochoric process. Hence,

$$\Delta W_{AB} = 0$$

$$\Delta Q_{AB} = \Delta U_{AB} = nC_V \Delta T = n\left(\frac{5}{2}R\right)(T_B - T_A)$$

$$= (0.2)\left(\frac{5}{2}\right)(8.31)\,(600 - 300) \approx 1246\ \text{J}$$

Process *BC* is an adiabatic process. Hence,

$$\Delta Q_{BC} = 0$$

$$\therefore \quad \Delta W_{BC} = -\,\Delta U_{BC}$$

$$\Delta U_{BC} = nC_V \Delta T = nC_V\ (T_C - T_B)$$

$$= (0.2)\left(\frac{5}{2}R\right)(455 - 600)$$

$$= (0.2)\left(\frac{5}{2}\right)(8.31)\,(-145)\ \text{J}$$

$$\approx -\,602\ \text{J}$$

$$\therefore \quad \Delta W_{BC} = -\,\Delta U_{BC} = 602\ \text{J}$$

Process *CA* is an isobaric process. Hence,

$$\Delta Q_{CA} = nC_P \Delta T = n\left(\frac{7}{2}R\right)(T_A - T_C)$$

$$= (0.2)\left(\frac{7}{2}\right)(8.31)\,(300 - 455)$$

$$\approx -902 \text{ J}$$

$$\Delta U_{CA} = nC_V \Delta T$$

$$= \frac{\Delta Q_{CA}}{\gamma} \qquad \left(\text{as } \gamma = \frac{C_P}{C_V}\right)$$

$$= -\frac{902}{1.4} \approx -644 \text{ J}$$

$$\therefore \quad \Delta W_{CA} = \Delta Q_{CA} - \Delta U_{CA} = -258 \text{ J}$$

Process	ΔQ (in J)	ΔW (in J)	ΔU (in J)
AB	1246	0	1246
BC	0	602	− 602
CA	− 902	− 258	− 644
Total	344	344	0

(c) Efficiency of the cycle

$$\eta = \frac{W_{\text{Total}}}{|Q_{+\text{ve}}|} \times 100$$

$$= \frac{344}{1246} \times 100$$

$$= 27.6\%$$

Introductory Exercise 18.3

1. Three moles of an ideal gas being initially at a temperature $T_i = 273$ K were isothermally expanded 5 times its initial volume and then isochorically heated so that the pressure in the final state become equal to that in the initial state. The total heat supplied in the process is 80 kJ. Find $\gamma \left(= \frac{C_P}{C_V}\right)$ of the gas.

2. As a result of the isobaric heating by $\Delta T = 72$ K, one mole of a certain ideal gas obtains an amount of heat $Q = 1.6$ kJ. Find the work performed by the gas, the increment of its internal energy and γ.

3. A gas undergoes the cycle shown in figure. The cycle is repeated 100 times per minute. Determine the power generated.

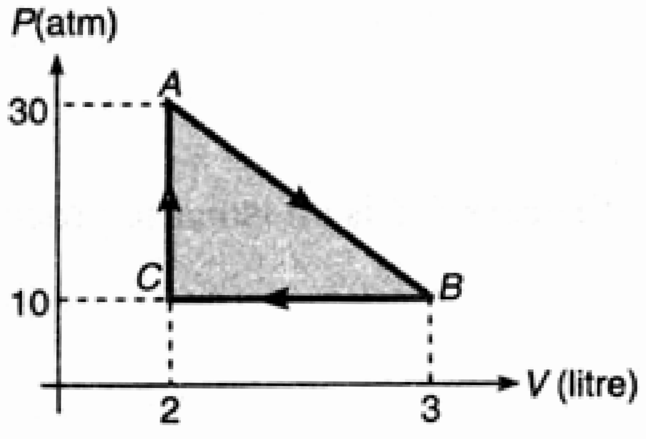


Fig. 18.25

Sample Example 18.10 *Carnot's engine takes in a thousand kilo calories of heat from a reservoir at 827°C and exhausts it to a sink at 27°C. How, much work does it perform ? What is the efficiency of the engine?*

Solution Given, $Q_1 = 10^6$ cal

$$T_1 = (827 + 273) = 1100 \text{ K}$$

and
$$T_2 = (27 + 273) = 300 \text{ K}$$

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

$\therefore$
$$Q_2 = \frac{T_2}{T_1} \cdot Q_1 = \left(\frac{300}{1100}\right)(10^6)$$

$$= 2.72 \times 10^5 \text{ cal}$$

Efficiency of the cycle,

$$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

or
$$\eta = \left(1 - \frac{300}{1100}\right) \times 100$$

$$= 72.72\%$$

Sample Example 18.11 *Calculate the least amount of work that must be done to freeze one gram of water at 0°C by means of a refrigerator. Temperature of surroundings is 27°C. How much heat in passed on the surroundings in this process? Latent heat of fusion $L = 80$ cal/g.*

Solution
$$Q_2 = mL = 1 \times 80 = 80 \text{ cal}$$

$$T_2 = 0°\text{C} = 273 \text{ K}$$

and
$$T_1 = 27°\text{C} = 300 \text{ K}$$

$$\frac{Q_2}{W} = \frac{T_2}{T_1 - T_2}$$

$\therefore$
$$W = \frac{Q_2(T_1 - T_2)}{T_2}$$

$$= \frac{80\,(300 - 273)}{273} = 7.91 \text{ cal}$$ **Ans.**

$$Q_1 = Q_2 + W$$

$$= (80 + 7.91) = 87.91 \text{ cal}$$ **Ans.**

18.7 Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that if two systems, A and B, are in thermal equilibrium with a third system, C, then A and B are in thermal equilibrium with each other. It is analogous to the transitive property in math (if $A = C$ and $B = C$, then $A = B$). Another way of stating the zeroth law is that every object has a certain temperature, and when two objects are in thermal equilibrium, their temperatures are equal. It is called the zeroth law because it came to light after the first and second laws of thermodynamics had already been established and named, but was considered more fundamental and thus was given a lower number zero.

18.8 Second Law of Thermodynamics

Before studying the second law of thermodynamics we will have to understand the concept of entropy.

Entropy

Entropy is an extensive thermodynamic property that is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. In thermodynamics, entropy has the dimension of energy divided by temperature, which has a unit of joules per kelvin (J/K) in the SI units. As a physical system becomes more disordered, and its energy becomes more evenly distributed, that energy becomes less able to do work. For example, a car rolling along a road has kinetic energy that could do work (by carrying or colliding with something). As friction slows it down and its energy is distributed to its surroundings as heat, it loses this ability. The amount of entropy is often thought of as the amount of disorder in a system.

Second law of thermodynamics

The First Law of Thermodynamics, commonly known as the Law of Conservation of Matter, states that matter/energy cannot be created nor can it be destroyed. The quantity of matter/energy remains the same. It can change from solid to liquid to gas to plasma and back again, but the total amount of matter/energy in the universe remains constant.

The second law is a statement that all processes go only in one direction, which is the direction of greater and greater degradation of energy. In other words, to a state of higher and higher entropy. This is also known as the Law of Increased Entropy. While quantity remains the same (First Law), the quality of matter/energy deteriorates gradually over time. How so? Usable energy is inevitably used for productivity, growth and repair. In the process, usable energy is converted into unusable energy. Thus, usable energy is irretrievably lost in the form of unusable energy. The implications of the Second Law of Thermodynamics are considerable. The universe is constantly losing usable energy and never gaining. We logically conclude that the universe is not eternal. The universe had a finite beginning — the moment at which it was at zero entropy (its most ordered possible state). Like a wind-up clock, the universe is winding down, as if at one point it was fully wound up and has been winding down ever since.

There are three alternative statements of second law of thermodynamics.

Clausius statement of the second law It is impossible to transfer heat from a cooler to a hotter body.

Kelvin-Planck statement of the second law It is impossible to build a heat engine that has 100% efficiency.

Entropy statement of the second law It is impossible for any system in a way that entropy is destroyed. Therefore in any process change in entropy ($S_f - S_i$) may be positive or zero. It cannot be negative.

or $\Delta S \geq 0$ Always

Note *Actual statements may be different. We have given them in simple form for better understanding.*

18.9 Reversible And Irreversible Processes

Irreversible Process

Most thermodynamic processes proceed naturally from one direction to another. In other words, they have a preferred direction. Heat flows from a hotter object to a colder one. Gases expand to fill a room, but will not spontaneously contract to fill a smaller space.

The process is said to be an irreversible process if it cannot return the system and the surroundings to their original conditions when the process is reversed. The irreversible process is not at equilibrium throughout the process.

For example, when we are driving the car uphill, it consumes a lot of fuel and this fuel is not returned when we are driving down the hill. The basic concept is that most of the thermodynamic processes have a preferred direction just as heat always flows from hotter object to colder object. Once a gas is released in a room, it expands in room and never contracts without indulgence of any external force etc.

Many factors contribute in making any process irreversible. *The most common of these are:*

(i) Friction

(ii) Unrestrained expansion of a fluid

(iii) Heat transfer through a finite temperature difference

(iv) Mixing of two different substances

Reversible Process

In some systems, the reverse occurs. Normally it happens when that system is close to thermal equilibrium. This equilibrium has to be inside the system itself and also within the system and its surroundings. When this stage is reached, even a small change can change the direction of the process and therefore such a reversible process is also known as an equilibrium process.

For Example

A very simple example can be of two metaljars A and B which are at a thermal equilibrium and are in contact with each other. Now when we heat jar A slightly, heat starts to flow from Jar A to Jar B. This is the direction of this process. Now this process can be reversed just by cooling Jar A slightly. When Jar A is cooled, heat flows from Jar B to Jar A till thermal equilibrium is reached.

Note *One of the important uses of second law of thermodynamics is to determine whether a given process is reversible or irreversible. Any process which is in agreement with second law of thermodynamics is irreversible.*

Extra Points

- In the above discussion we have seen that :

$$W = \int_{V_i}^{V_f} P\,dV$$

From this equation it seems as if work done can be calculated only when P-V equation is known and the limits V_i and V_f are known to us. But it is not so. We can calculate work done even if we know the limits of temperature.

For example, the temperature of n moles of an ideal gas is increased from T_0 to $2T_0$ through a process $P = \frac{\alpha}{T}$ and we are interested in finding the work done by the gas. Then

$$PV = nRT \qquad \text{(ideal gas equation)}\ldots\text{(i)}$$

and

$$P = \frac{\alpha}{T} \qquad \ldots\text{(ii)}$$

Dividing Eq. (i) by Eq. (ii), we get $V = \frac{nRT^2}{\alpha}$

or

$$dV = \frac{2nRT}{\alpha}\,dT$$

$\therefore$

$$W = \int_{V_i}^{V_f} P\,dV$$

$$= \int_{T_0}^{2T_0} \left(\frac{\alpha}{T}\right)\left(\frac{2nRT}{\alpha}\right) dT = 2nRT_0$$

So, we have found the work done without putting the limits of volume.

- Sometimes the piston (which is massless) is attached to a spring of force constant k and a mass m is placed over the piston. The area of the piston is A. The gas expands. To make the calculation easy we assume that initially the spring was in its natural length. We are required to find the work done by the gas. As the piston is massless, net force on it at every instant is zero.

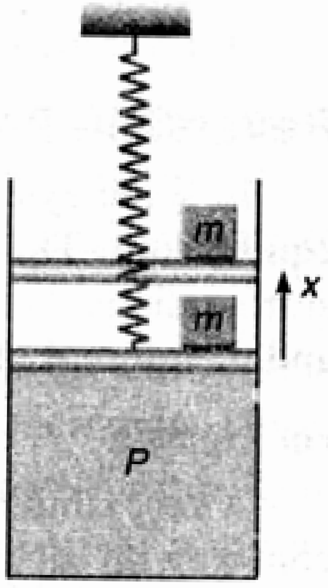


Fig. 18.26

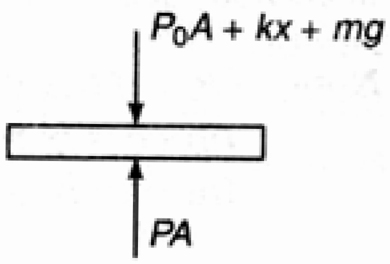


Fig. 18.27

$\therefore$

$$PA = kx + mg + P_0A$$

or

$$P = P_0 + \frac{kx}{A} + \frac{mg}{A}$$

$$dW = PdV = P\,(Adx)$$

$$= (AP_0 + kx + mg)\,dx$$

$\therefore$

$$W = \int_0^x P\,dV$$

or

$$W = \int_0^x (AP_0 + kx + mg)\,dx$$

$$= P_0Ax + \frac{1}{2}kx^2 + mgx \qquad (\text{as } Ax = \Delta V)$$

or

$$W = P_0\Delta V + \frac{1}{2}kx^2 + mgx$$

The result can be stated in a different manner as under.

The gas does work against the atmospheric pressure P_0 (which is constant), the spring force kx (which varies linearly with x) and the gravity force mg (which is again constant).

$\therefore$ $$W_1 = \text{Work done against } P_0 = P_0 \Delta V$$

$$W_2 = \text{Work done against } kx = \frac{1}{2}kx^2$$

and $$W_3 = \text{Work done against } mg = mgx$$

So that $$W_{\text{Total}} = W_1 + W_2 + W_3 = P_0 \Delta V + \frac{1}{2}kx^2 + mgx$$

- From point number (2). We may conclude that work done by a gas is zero if the other side of the piston is vacuum.

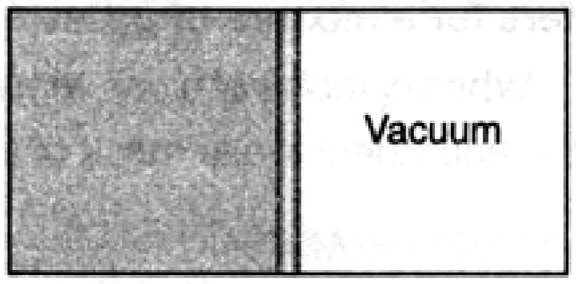


Fig. 18.28

- $\boldsymbol{C_V = \frac{dU}{dT}}$**:** Let us derive the relation $C_V = \frac{dU}{dT}$. Where U = internal energy of 1 mole of the gas.

  Consider 1 mole ($n = 1$) of an ideal monoatomic gas which undergoes an isochoric process (V = constant). From the first law of thermodynamics.

$$dQ = dW + dU \qquad \text{...(i)}$$

Here, $$dW = 0 \quad \text{as} \quad V =$$

$$dQ = CdT = C_V dT \qquad (\text{In } dQ = nC_V dT, n = 1 \text{ and } C = C_V)$$

Substituting in Eq. (i), we have

$$C_V dT = dU$$

or $$C_V = \frac{dU}{dT}$$ **Hence Proved**

- $\boldsymbol{C_P - C_V = R}$**:** To prove this relation (also known as **Mayor's formula**) let us consider 1 mole of an ideal gas which undergoes an isobaric (P = constant) process. From first law of thermodynamics,

$$dQ = dW + dU$$

Here, $$dQ = C_P dT \qquad (\text{as } n = 1 \text{ and } C = C_P)$$

$$dU = C_V dT$$

and $$dW = PdV = Pd\left(\frac{RT}{P}\right) \qquad \left(V = \frac{RT}{P}\right)$$

$$= d\,(RT) \qquad (\text{as } P = \qquad)$$

$$= R \cdot dT$$

Substituting these values in equation (i)

We have $$C_P dT = R \cdot dT + C_V dT$$

or $$C_P - C_V = R$$ **Hence proved**

- $C_V = \dfrac{R}{\gamma - 1}$: We have already derived,

$$C_P - C_V = R$$

dividing this equation by C_V, we have

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

or $$\gamma - 1 = \frac{R}{C_V} \qquad \left(\text{as } \frac{C_P}{C_V} = \gamma\right)$$

$\therefore$ $$C_V = \frac{R}{\gamma - 1}$$ **Hence Proved**

- **Thermodynamic parameters for a mixture of gases :**

(i) Equivalent molar mass : When n_1 moles of a gas with molar mass M_1 are mixed with n_2 moles of a gas with molar mass M_2, the equivalent molar mass of the mixture is given by

$$M = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

(ii) Internal energy of the mixture : The total energy of the mixture is

$$U = U_1 + U_2$$

(iii) C_V of the mixture :

$$U = U_1 + U_2$$

$\therefore$ $$dU = dU_1 + dU_2$$

or $$nC_V dT = n_1 C_{V_1} dT + n_2 C_{V_2} dT \qquad \text{...(ii)}$$

or $$(n_1 + n_2) C_V = n_1 C_{V_1} + n_2 C_{V_2} \qquad (\text{as } n = n_1 + n_2)$$

$\therefore$ $$C_V = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2}$$

(iv) C_P of the mixture :

$$C_P = C_V + R$$

or $$C_P = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2} + R$$

$$= \frac{n_1 (C_{V_1} + R) + n_2 (C_{V_2} + R)}{n_1 + n_2}$$

$$= \frac{n_1 C_{P_1} + n_2 C_{P2}}{n_1 + n_2}$$

Thus, $$C_P = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2}$$

(v) γ of the mixture : From Eq. (ii)

$$(n_1 + n_2) C_V = n_1 C_{V_1} + n_2 C_{V_2}$$

or $$\frac{(n_1+n_2)R}{\gamma-1}=\frac{n_1R}{\gamma_1-1}+\frac{n_2R}{\gamma_2-1}$$

or $$\frac{n_1+n_2}{\gamma-1}=\frac{n_1}{\gamma_1-1}+\frac{n_2}{\gamma_2-1}$$

Thus, γ of the mixture is given by above equation.

- Bulk modulus of a gas is given by

$$B=-\frac{(dP)}{(dV/V)}=V\left(-\frac{dP}{dV}\right)$$

$\left(-\frac{dP}{dV}\right)=\gamma\left(\frac{P}{V}\right)$ in an adiabatic process. Hence, adiabatic bulk modulus of an ideal gas is

$$B_s=\gamma P$$

Similarly,

$$\left(-\frac{dP}{dV}\right)=\left(\frac{P}{V}\right) \text{ in an isothermal process.}$$

Hence, isothermal bulk modulus of an ideal gas is,

$$B_T=P$$

- **Polytropic process**

When P and V bear the relation PV^x = constant, where $x \neq 1$ or γ the process is called a polytropic one. In this process the molar heat capacity is,

$$C=C_V+\frac{R}{1-x}=\frac{R}{\gamma-1}+\frac{R}{1-x}$$

Let us now derive this relation. The molar heat capacity is defined as :

$$C=\frac{\Delta Q}{\Delta T} \text{ for 1 mole}$$

$$=\frac{\Delta U+\Delta W}{\Delta T}$$

$$=\frac{\Delta U}{\Delta T}+\frac{\Delta W}{\Delta T} \qquad \left(\frac{\Delta U}{\Delta T}=C_V\right)$$

$$\therefore \qquad C=C_V+\frac{\Delta W}{\Delta T} \qquad \text{...(i)}$$

Here, $$\Delta W=\int_{V_i}^{V_f}PdV=\int_{V_i}^{V_f}kV^{-x}dV=\left[\frac{kV^{-x+1}}{-x+1}\right]_{V_i}^{V_f}$$

$$=\frac{kV_f^{-x+1}-kV_i^{-x+1}}{-x+1}$$

$$=\frac{P_fV_f^xV_f^{-x+1}-P_iV_i^xV_i^{-x+1}}{1-x}$$

$$= \frac{P_f V_f - P_i V_i}{1-x} = \frac{RT_f - RT_i}{1-x}$$

$$= \frac{R\Delta T}{1-x}$$

$$\therefore \qquad \frac{\Delta W}{\Delta T} = \frac{R}{1-x}$$

Substituting in Eq. (i), we get the **result** *i.e.*,

$$\therefore \qquad C = C_V + \frac{R}{1-x} = \frac{R}{\gamma - 1} + \frac{R}{1-x}$$

Slope of *P-V* diagram

Slope of *P-V* diagram (also known as **indicator diagram**) at any point is

$$\frac{dP}{dV} = -x\frac{P}{V}$$

It x is negative, slope is positive and vice-versa.

Exercise *Derive the relation* $\frac{dP}{dV} = -x\frac{P}{V}$ *for the process* PV^x = *constant.*

▪ Variation of pressure with elevation and depth

Suppose atmospheric pressure at sea level ($y = 0$) is P_0. We are interested in finding the air pressure with elevation in the earth's atmosphere, assuming the temperature to be constant throughout.

We begin with the pressure relation that we use in the chapter of fluid mechanics,

$$\frac{dP}{dy} = -\rho g$$

The density ρ is given by,
$$\rho = \frac{PM}{RT}$$

$$\therefore \qquad \frac{dP}{dy} = -\left(\frac{PM}{RT}\right) g$$

$$\text{or} \qquad \int_{P_0}^{P} \frac{dP}{P} = -\int_0^y \left(\frac{Mg}{RT}\right) dy \qquad \text{...(i)}$$

$$\text{or} \qquad \int_{P_0}^{P} \frac{dP}{P} = -\frac{Mg}{RT}\int_0^y dy \qquad (\text{as } T = \text{constant})$$

$$\text{or} \qquad P = P_0 e^{-\left(\frac{Mg}{RT}\right)y}$$

i.e., pressure of air decreases exponentially with height (y).

With depth : We have already studied, how the pressure varies with depth (h) of water. In increases linearly with depth. The pressure at a depth h is,

$$P = P_0 + \rho_w gh$$

The P *versus y* or *P versus h* graph is shown in figure.

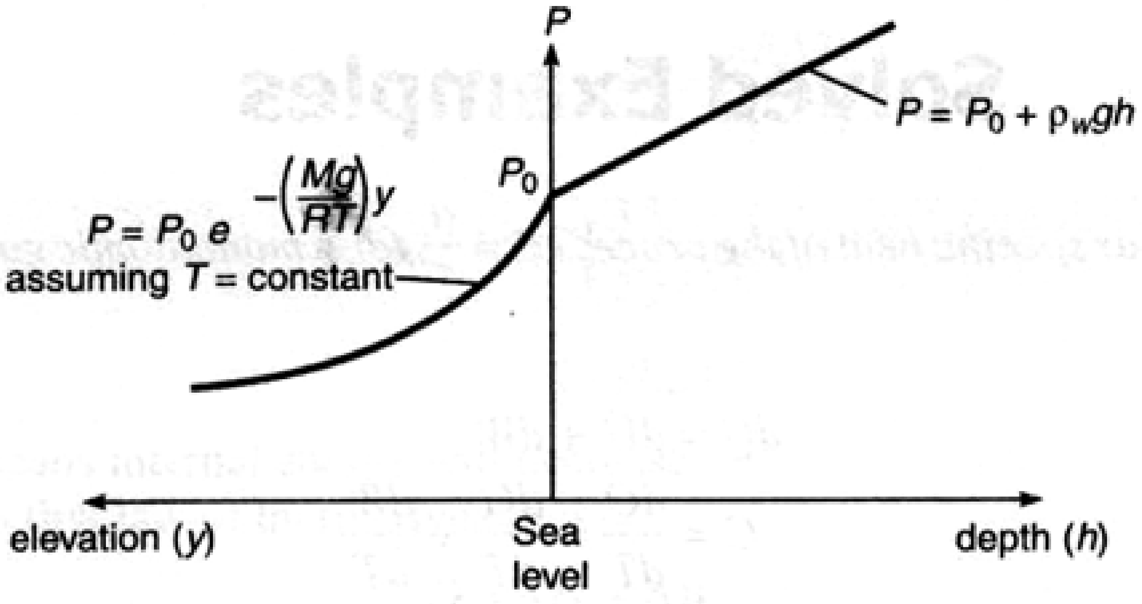


Fig. 18.29

Note *Suppose in some question* $T \neq$ constant, *but it is given a function of elevation y, then Eq. (i), will become*

$$\int_{P_0}^{P} \frac{dP}{P} = -\frac{Mg}{R}\int_0^y \frac{dy}{T}$$

Here, T is the given function of y, so it is inside the integration.

Solved Examples

Example 1 *Find the molar specific heat of the process* $P = \frac{a}{T}$ *for a monoatomic gas, a being constant.*

Solution We know that

$$dQ = dU + dW$$

Specific heat

$$C = \frac{dQ}{dT} = \frac{dU}{dT} + \frac{dW}{dT} \qquad \text{...(i)}$$

Since,

$$dU = C_V dT \qquad \text{...(ii)}$$

$$C = C_V + \frac{dW}{dT}$$

$$= C_V + \frac{PdV}{dT}$$

$$PV = RT$$

∴ For the given process,

$$V = \frac{RT}{P} = \frac{RT^2}{a}$$

$$\frac{dV}{dT} = \frac{2RT}{a}$$

∴

$$C = C_V + P\left(\frac{2RT}{a}\right)$$

$$= C_V + 2R$$

$$= \frac{3}{2}R + 2R = \frac{7}{2}R$$

Example 2 *At* $27°C$ *two moles of an ideal monoatomic gas occupy a volume* V*. The gas expands adiabatically to a volume* $2V$*. Calculate*

(a) final temperature of the gas

(b) change in its internal energy and

(c) the work done by the gas during the process.

[$R = 8.31\,J/mol\text{-}K$*]*

Solution (a) In case of adiabatic change

$$PV^{\gamma} = \text{constant with } PV = nRT$$

So that

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \text{ with } \gamma = \left(\frac{5}{3}\right)$$

i.e.,

$$300 \times V^{2/3} = T(2V)^{2/3}$$

or $$T = \frac{300}{(2)^{2/3}} = 189\text{ K}$$

(b) As $$\Delta U = nC_V\Delta T = \frac{nR\Delta T}{(\gamma - 1)} \qquad \left[\text{as } C_V = \frac{R}{(\gamma - 1)}\right]$$

So, $$\Delta U = 2 \times \left(\frac{3}{2}\right) \times 8.31\,(189 - 300)$$

$$= -2767.23\text{ J}$$

Negative sign means internal energy will decrease.
(c) According to first law of thermodynamics

$$Q = \Delta U + \Delta W$$

And as for adiabatic change $\Delta Q = 0$,

$$\Delta W = -\Delta U = 2767.23\text{ J}$$

Example 3 *The density versus pressure graph of one mole of an ideal monoa- tomic gas undergoing a cyclic process is shown in figure. The molecular mass of the gas is M.*

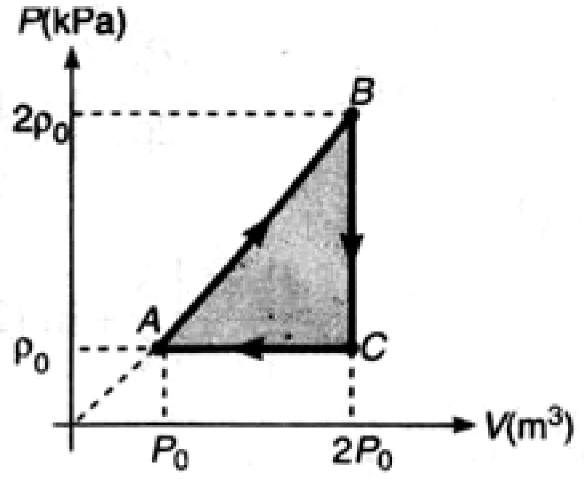


Fig. 18.30

(a) *Find the work done in each process.*
(b) *Find heat rejected by gas in one complete cycle.*
(c) *Find the efficsency of the cycle.*

Solution (a) As $n = 1$, $m = M$

Process *AB* : $\rho \propto P$, *i.e.* It is an isothermal process (T = constant), because $\rho = \dfrac{PM}{RT}$.

$$\therefore \qquad W_{AB} = RT_A \ln\left(\frac{P_A}{P_B}\right) = RT_A \ln\left(\frac{1}{2}\right)$$

$$= -\frac{P_0 M}{\rho_0}\ln(2)$$

$$\Delta U_{AB} = 0$$

and $$Q_{AB} = W_{AB} = -\frac{P_0 M}{\rho_0}\ln(2)$$

Process *BC* is an isobaric process (P = constant)

$$W_{BC} = P_B\,(V_C - V_B) = 2P_0\left(\frac{M}{\rho_C} - \frac{M}{\rho_B}\right) = \frac{2P_0M}{2\rho_0} = \frac{P_0M}{\rho_0}$$

$$\Delta U_{BC} = C_V\Delta T$$

$$= \left(\frac{3}{2}R\right)\left[\frac{2P_0M}{\rho_0R} - \frac{2P_0M}{2\rho_0R}\right] = \frac{3P_0M}{2\rho_0}$$

$$Q_{BC} = W_{BC} + \Delta U_{BC} = \frac{5P_0M}{2\rho_0}$$

Process *CA* : As ρ = constant $\therefore$ V = constant.

So, it is an isochoric process.

$$W_{CA} = 0$$

$$\Delta U_{CA} = C_V\Delta T$$

$$= \left(\frac{3}{2}R\right)(T_A - T_C)$$

$$= \left(\frac{3}{2}R\right)\left[\frac{P_0M}{\rho_0R} - \frac{2P_0M}{\rho_0R}\right] = -\frac{3P_0M}{2\rho_0}$$

$$Q_{CA} = \Delta U_{CA} = -\frac{3P_0M}{2\rho_0}$$

(b) Heat rejected by gas $= |Q_{AB}| + |Q_{CA}|$

$$= \frac{P_0M}{\rho_0}\left[\frac{3}{2} + \ln(2)\right]$$ **Ans.**

(c) Efficiency of the cycle (in fraction)

$$\eta = \frac{\text{Total work done}}{\text{Heat supplied}} = \frac{W_{\text{Total}}}{Q_{+\text{ve}}}$$

$$= \frac{\dfrac{P_0M}{\rho_0}[1 - \ln(2)]}{\dfrac{5}{2}\left(\dfrac{P_0M}{\rho_0}\right)}$$

$$= \frac{2}{5}[1 - \ln(2)]$$ **Ans.**

Example 4 *Two moles of a diatomic ideal gas is taken through PT = constant. Its temperature is increased from T to 2T. Find the work done by the system ?*

Solution

$$W = \int P\,dV$$

Here,

$$PT = P_1T_1 = P_2T_2 = c$$ (constant)

$$\therefore \qquad PT = c \qquad P\cdot\frac{PV}{nR} = c$$

$$\therefore \qquad P^2V = ncR \Rightarrow P = \sqrt{\frac{ncR}{V}}$$

$$\therefore \qquad \int PdV = \sqrt{ncR}\int_{V_1}^{V_2}\frac{1}{\sqrt{V}}\,dV$$

$$\sqrt{ncR}\,[2(\sqrt{V_2}-\sqrt{V_1})] = 2[\sqrt{nR\cdot P_2T_2V_2}-\sqrt{nRP_1T_1V_1}\,]$$

$$= 2nR\,(T_2 - T_1) = 8RT_0$$

Example 5 *An ideal monoatomic gas at temperature 27° C and pressure 10^6 N/m^2 occupies 10 litre volume. 10,000 cal of heat is added to the system without changing the volume. Calculate the final temperature of the gas. Given : $R = 8.31$ J/(mol-K) and $J = 4.18$ J/cal.*

Solution For n mole of gas, we have $PV = nRT$

Here, $P = 10^6 \text{N/m}^2$, $V = 10$ litre $= 10^{-2}\text{m}^3$ and $T = 27°\text{C} = 300\,\text{K}$

$$\therefore \qquad n = \frac{PV}{RT} = \frac{10^6\times10^{-2}}{8.31\times300} = 4.0$$

For "monoatomic" gas, $C_V = \frac{3}{2}R$

Thus, $$C_V = \frac{3}{2}\times 8.31 \text{ J/mol-K}$$

$$= \frac{3}{2}\times\frac{8.31}{4.18} \approx 3 \text{ cal/(mol-K)}$$

Let ΔT be the rise in temperature when n mole of the gas is given Q cal of heat at constant volume. Then,

$$Q = nC_V\Delta T$$

or $$\Delta T = \frac{Q}{nC_V} = \frac{10{,}000\text{ cal}}{4.0\text{ mole}\times 3\text{ cal (mol-K)}} = 833\text{ K}$$

Example 6 *One mole of a monoatomic ideal gas is taken through the cycle shown in figure.*

$A\rightarrow B$ Adiabatic expansion
$B\rightarrow C$ Cooling at constant volume
$C\rightarrow D$ Adiabatic compression.
$D\rightarrow A$ Heating at constant volume

The pressure and temperature at A, B etc., are denoted by $P_A, T_A; P_B, T_B$ etc. respectively.

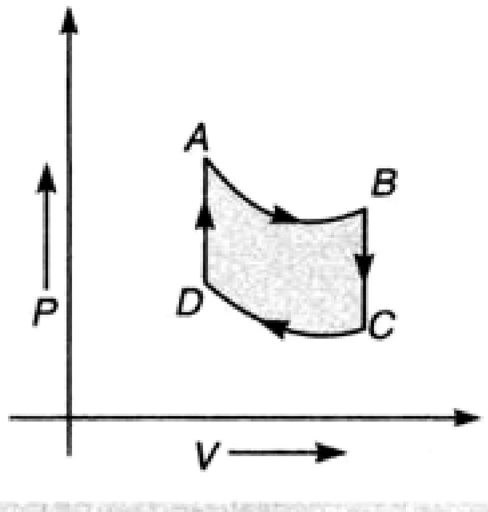


Fig. 18.31

Given $T_A = 1000K, P_B = \left(\frac{2}{3}\right)P_A$ *and* $P_C = \left(\frac{1}{3}\right)P_A$. *Calculate*

(a) the work done by the gas in the process $A \rightarrow B$

(b) the heat lost by the gas in the process $B \rightarrow C$ *and*

Given $\left(\frac{2}{3}\right)^{0.4} = 0.85$ *and* $R = 8.31$ *J/mol-K*

Solution (a) As for adiabatic change $PV^{\gamma} = \text{constant}$

i.e., $$P\left(\frac{nRT}{P}\right)^{\gamma} = \text{constant} \qquad [\text{as } PV = nRT]$$

i.e., $$\frac{T^{\gamma}}{P^{\gamma-1}} = \text{constant so} \left(\frac{T_B}{T_A}\right)^{\gamma} = \left(\frac{P_B}{P_A}\right)^{\gamma-1} \quad \text{where } \gamma = \frac{5}{3}$$

i.e., $$T_B = T_A\left(\frac{2}{3}\right)^{1-\frac{1}{\gamma}} = 1000\left(\frac{2}{3}\right)^{2/5} = 850\,\text{K}$$

So, $$W_{AB} = \frac{nR[T_F - T_I]}{[1-\gamma]} = \frac{1 \times 8.31[1000 - 850]}{\left[\left(\frac{5}{3}\right) - 1\right]}$$

i.e., $$W_{AB} = \left(\frac{3}{2}\right) \times 8.31 \times 150 = 1869.75\,\text{J}$$

(b) For $B \rightarrow C, V = \text{constant}$ so $\Delta W = 0$

So, from first law of thermodynamics

$$\Delta Q = \Delta U + \Delta W = nC_V\Delta T + 0$$

or $$\Delta Q = 1 \times \left(\frac{3}{2}R\right)(T_C - 850) \qquad \text{as } C_V = \frac{3}{2}R$$

Now, along path $BC, V = \text{constant}; P \propto T$

i.e., $$\frac{P_C}{P_B} = \frac{T_C}{T_B}$$

$$T_C = \frac{\left(\frac{1}{3}\right)P_A}{\left(\frac{2}{3}\right)P_A} \times T_B = \frac{T_B}{2} = \frac{850}{2} = 425\,\text{K} \qquad \text{...(ii)}$$

So, $$\Delta Q = 1 \times \frac{3}{2} \times 8.31\,(425 - 850) = -5297.625\,\text{J}$$

[Negative heat means, heat is lost by the system]

Example 7 *A gas undergoes a process such that* $P \propto \frac{1}{T}$. *If the molar heat capacity for this process is* $C = 33.24$ *J/mol-K, find the degree of freedom of the molecules of the gas.*

Solution As $$P \propto \frac{1}{T}$$

or $$PT = \text{constant} \qquad \ldots\text{(i)}$$

We have for one mole of an ideal gas

$$PV = RT \qquad \ldots\text{(ii)}$$

From Eqs. (i) and (ii)

$$P^2V = \text{constant}$$

or $$PV^{1/2} = K \text{ (say)} \qquad \ldots\text{(iii)}$$

From first law of thermodynamics,

$$\Delta Q = \Delta U + \Delta W$$

or $$C\Delta T = C_V \Delta T + \Delta W$$

or $$C = C_V + \frac{\Delta W}{\Delta T} \qquad \ldots\text{(iv)}$$

Here, $$\Delta W = \int P dV = K \int_{V_i}^{V_f} V^{-1/2} dV$$

$$= \frac{P_f V_f - P_i V_i}{1 - (1/2)} = \frac{R\,(T_f - T_i)}{1/2} = \frac{R\Delta T}{1/2}$$

∴ $$\frac{\Delta W}{\Delta T} = 2R$$

Substituting in Eq. (iv), we have

$$C = C_V + 2R = \frac{R}{\gamma - 1} + 2R$$

Substituting the values,

$$33.24 = R\left(\frac{1}{\gamma - 1} + 2\right) = 8.31\left(\frac{1}{\gamma - 1} + 2\right)$$

Solving this we get

$$\gamma = 1.5$$

Now, $$\gamma = 1 + \frac{2}{F}$$

or degree of freedom

$$F = \frac{2}{\gamma - 1} = \frac{2}{1.5 - 1} = 4$$

Alternate Solution : In the process PV^x = constant, molar heat capacity is given by

$$C = \frac{R}{\gamma - 1} + \frac{R}{1 - x}$$

The given process is $PV^{1/2} = \text{constant}$

or
$$x = \frac{1}{2}$$

$\therefore$
$$C = \frac{R}{\gamma-1} + \frac{R}{1-\frac{1}{2}} = \frac{R}{\gamma-1} + 2R$$

Now, we may proceed in the similar manner.

Example 8 *A gaseous mixture enclosed in a vessel consists of one g mole of a gas A with* $\gamma = \left(\frac{5}{3}\right)$ *and some amount of gas B with* $\gamma = \frac{7}{5}$ *at a temperature T. The gases A and B do not react with each other and are assumed to be ideal. Find the number of g moles of the gas B if* γ *for the gaseous mixture is* $\left(\frac{19}{13}\right)$.

Solution As for an ideal gas, $C_P - C_V = R$ and $\gamma = \left(\frac{C_P}{C_V}\right)$

So,
$$C_V = \frac{R}{(\gamma-1)}$$

$\therefore$
$$(C_V)_1 = \frac{R}{\left(\frac{5}{3}\right)-1} = \frac{3}{2}R; \quad (C_V)_2 = \frac{R}{\left(\frac{7}{5}\right)-1} = \frac{5}{2}R$$

and
$$(C_V)_{\text{mix}} = \frac{R}{\left(\frac{19}{13}\right)-1} = \frac{13}{6}R$$

Now, from conservation of energy,

i.e.,
$$\Delta U = \Delta U_1 + \Delta U_2$$
$$(n_1+n_2)(C_V)_{\text{mix}}\,\Delta T = [n_1(C_V)_1 + n_2(C_V)_2]\,\Delta T$$

i.e.,
$$(C_V)_{\text{mix}} = \frac{n_1(C_V)_1 + n_2(C_V)_2}{n_1+n_2}$$

We have
$$\frac{13}{6}R = \frac{1\times\frac{3}{2}R + n_2\frac{5}{2}R}{1+n_2}$$
$$= \frac{(3+5n_2)R}{2(1+n_2)}$$

or
$$13 + 13n_2 = 9 + 15n_2,$$

i.e.,
$$n_2 = 2 \text{ g mole}$$

Example 9 *An ideal gas having initial pressure P, volume V and temperature T is allowed to expand adiabatically until its volume becomes* $5.66\,V$, while its temperature falls to $T/2$

(a) *How many degrees of freedom do the gas molecules have ?*

(b) *Obtain the work done by the gas during the expansion as a function of the initial pressure P and volume V.*

Given that $(5.66)^{0.4} = 2$

Solution (a) For adiabatic expansion

$$TV^{\gamma-1} = \text{constant}$$

i.e.,
$$TV^{\gamma-1} = T'V'^{\gamma-1} = \frac{T}{2}(5.66V)^{\gamma-1}$$

i.e.,
$$(5.66)^{\gamma-1} = 2$$

i.e.,
$$\gamma = 1.4$$

This is the value of γ of a diatomic gas. Hence the degree of freedom per molecule of a diatomic gas $= 5$.

(b) Work done during adiabatic process for one mole gas is

$$W = \frac{1}{1-\gamma}[P'V' - PV]$$

From relation,
$$\frac{PV}{T} = \frac{P'V'}{T'}$$

we get
$$P' = \frac{T'}{T}\cdot\frac{PV}{V'} = \frac{1}{2}\times\frac{1}{5.66}P = \frac{P}{11.32}$$

$\therefore$
$$W = \frac{1}{1-1.4}\left[\frac{P}{11.32}\times\frac{V}{5.66} - PV\right]$$

$$= \frac{1}{0.4}\left[1 - \frac{1}{11.32\times 5.66}\right]PV$$

$$= 2.461\,PV$$

Example 10 *Plot P-V, V-T and* ρ*-T graph corresponding to the P-T graph for an ideal gas shown in figure.*

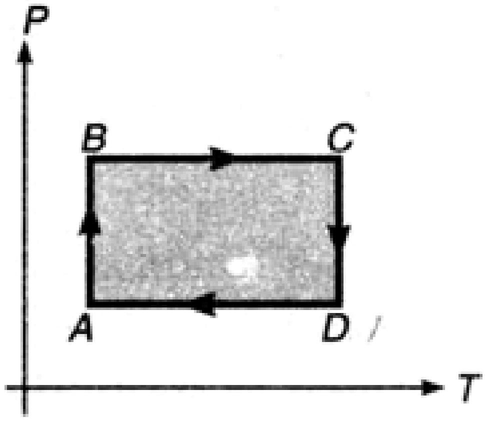


Fig. 18.32

Solution Process *AB* is an isothermal process with $T = \text{constant}$ and $P_B > P_A$.

***P-V* graph :** $P \propto \frac{1}{V}$ i.e., *P-V* graph is a hyperbola with $P_B > P_A$ and $V_B < V_A$.

***V-T* graph :** $T = \text{constant}$. Therefore, *V-T* graph is a straight line parallel to *V*-axis with $V_B < V_A$.

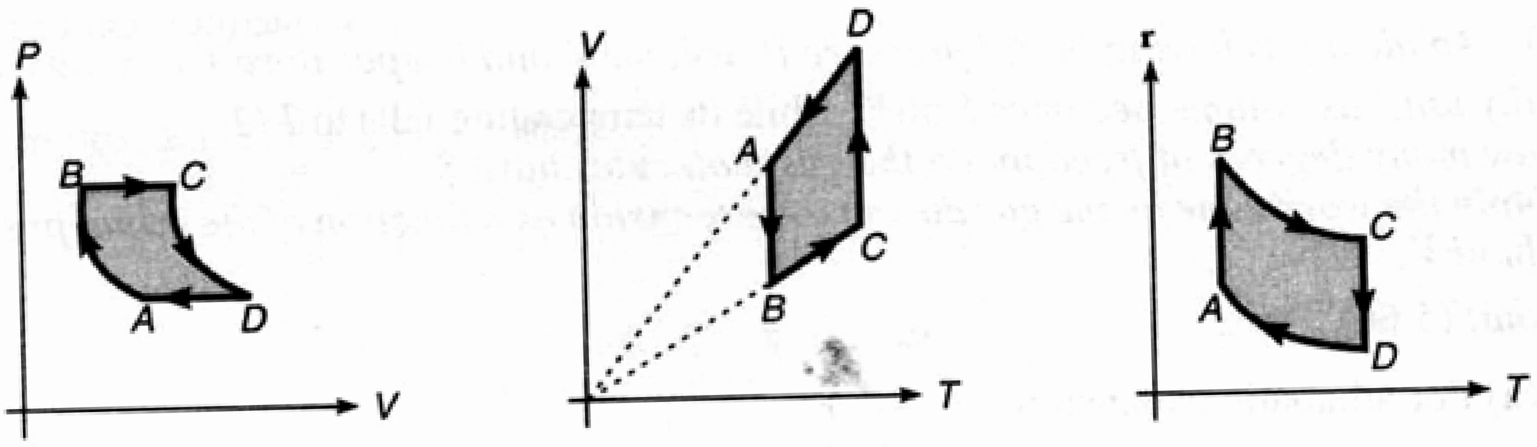


Fig. 18.33

ρ-*T* graph : $\rho = \dfrac{PM}{RT}$ or $\rho \propto P$.

As T is constant. Therefore, ρ-T graph is a straight line parallel to ρ-axis with $\rho_B > \rho_A$ as $P_B > P_A$.

Process *BC* is an isobaric process with $P =$ constant and $T_C > T_B$.

***P-V* graph :** As P is constant. Therefore, P-V graph is a straight line parallel to V-axis with $V_C > V_B$ (because $V \propto T$ in an isobaric process)

***V-T* graph :** In isobaric process $V \propto T$, *i.e.*, V-T graph is a straight line passing through origin, with $T_C > T_B$ and $V_C > V_B$.

ρ-*T* graph : $\rho \propto \dfrac{1}{T}$ (when $P =$ constant), *i.e.*, ρ-T graph is a hyperbola with $T_C > T_B$ and $\rho_C < \rho_B$.

There is no need of discussing *C-D* and *D-A* processes. As they are opposite to *AB* and *BC* respectively. The corresponding three graphs are shown above.

EXERCISES

For JEE Main

Subjective Questions

First Law of Thermodynamics

1. In a certain chemical process, a lab technician supplies 254 J of heat to a system. At the same time, 73 J of work are done on the system by its surroundings. What is the increase in the internal energy of the system?
2. One mole of an ideal monoatomic gas is initially at 300 K. Find the final temperature if 200 J of heat are added as follows :

   (a) at constant volume, (b) at constant pressure.
3. Show how internal energy U varies with T in isochoric, isobaric and adiabatic process?
4. A closed vessel 10 litres in volume contains a diatomic gas under a pressure of $10^5\,\text{N/m}^2$. What amount of heat should be imparted to the gas to increase the pressure in the vessel five times ?
5. A diatomic ideal gas is heated at constant volume until its pressure becomes three times. It is again heated at constant pressure until its volume is doubled. Find the molar heat capacity for the whole process.
6. Two moles of a certain gas at a temperature $T_0 = 300$ K were cooled isochorically so that the pressure of the gas got reduced 2 times. Then as a result of isobaric process, the gas is allowed to expand till its temperature got back to the initial value. Find the total amount of heat absorbed by gas in this process.
7. Five moles of an ideal monoatomic gas with an initial temperature of 127°C expand and in the process absorb 1200 J of heat and do 2100 J of work. What is the final temperature of the gas ?
8. An ideal gas expands while the pressure is kept constant. During this process, does heat flow into the gas or out of the gas? Justify your answer.
9. Find the change in the internal energy of 2 kg of water as it is heated from 0° C to 4° C. The specific heat capacity of water is 4200 J / kg - K and its densities at 0° C and 4° C are $999.9\,\text{kg/m}^3$ and $1000\,\text{kg/m}^3$ respectively. Atmospheric pressure $= 10^5$ Pa.
10. Calculate the increase in the internal energy of 10 g of water when it is heated from 0° C to 100° C and converted into steam at 100 kPa. The density of steam $= 0.6\,\text{kg/m}^3$. Specific heat capacity of water = 4200 J/kg-° C and the latent heat of vaporization of water $= 2.5 \times 10^6$ J/kg.
11. One gram of water ($1\,\text{cm}^3$) becomes $1671\,\text{cm}^3$ of steam when boiled at a constant pressure of 1 atm (1.013×10^5 Pa). The heat of vaporization at this pressure is $L_v = 2.256 \times 10^6$ J/kg. Compute (a) the work done by the water when it vaporizes and (b) its increase in internal energy.
12. A gas in a cylinder is held at a constant pressure of 2.30×10^5 Pa and is cooled and compressed from $1.70\,\text{m}^3$ to $1.20\,\text{m}^3$. The internal energy of the gas decreases by 1.40×10^5 J. (a) Find the work done by the gas. (b) Find the absolute value $|Q|$ of the heat flow into or out of the gas and state the direction of the heat flow. (c) Does it matter whether or not the gas is ideal ? Why or why not?

Cyclic Process and Efficiency of Cycle

13. An ideal gas is taken through a cyclic thermodynamic process through four steps. The amounts of heat involved in these steps are $Q_1 = 5960$ J, $Q_2 = -5585$ J, $Q_3 = -2980$ J and $Q_4 = 3645$ J respectively. The corresponding quantities of work involved are $W_1 = 2200$ J, $W_2 = -825$ J, $W_3 = -1100$ J and W_4 respectively.

(a) Find the value of W_4.

(b) What is the efficiency of the cycle ?

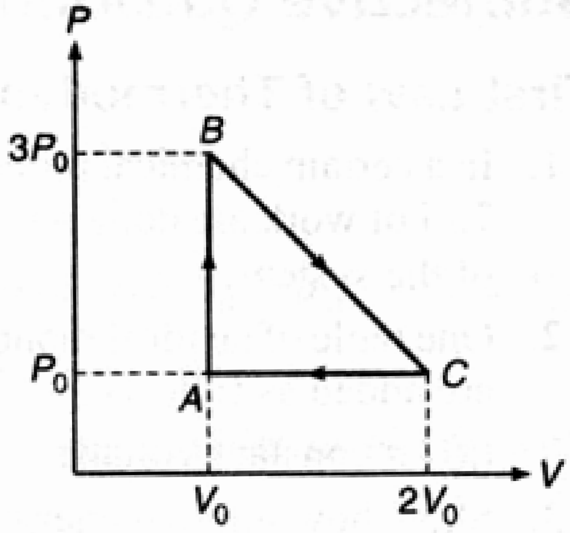
14. One mole of an ideal monoatomic gas is taken round the cyclic process $ABCA$ as shown in figure. Calculate:

(a) The work done by the gas.

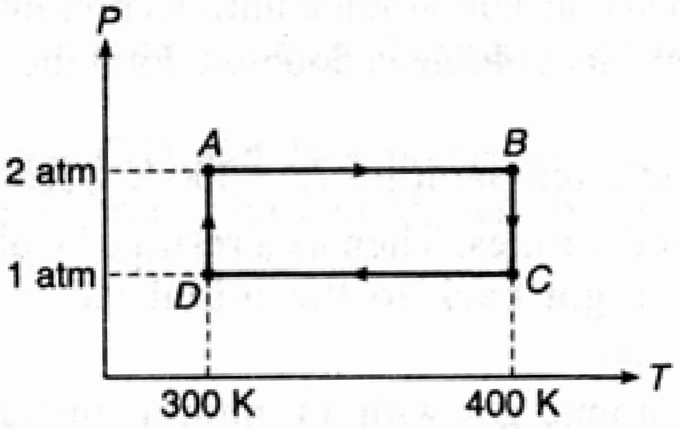
(b) The heat rejected by the gas in the path CA and heat absorbed in the path AB.

(c) The net heat absorbed by the gas in the path BC.

(d) The maximum temperature attained by the gas during the cycle.



15. Two moles of helium gas undergo a cyclic process as shown in figure. Assuming the gas to be ideal, calculate the following quantities in this process.

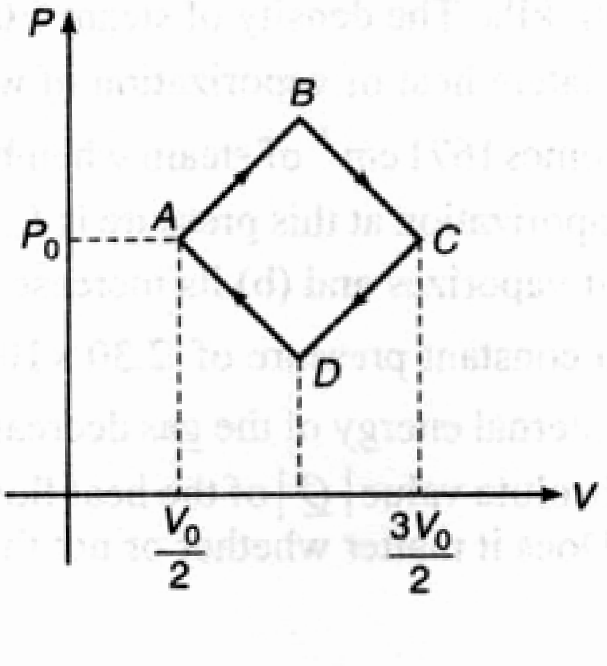


(a) The net change in the heat energy.

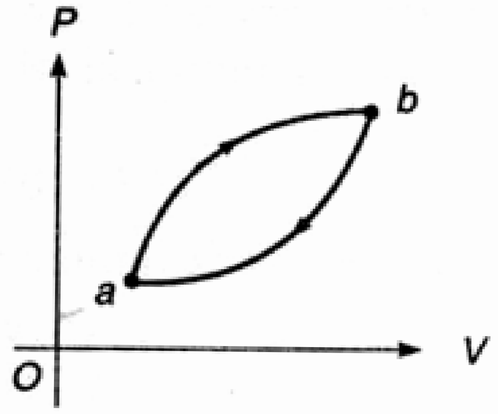
(b) The net work done.

(c) The net change in internal energy.

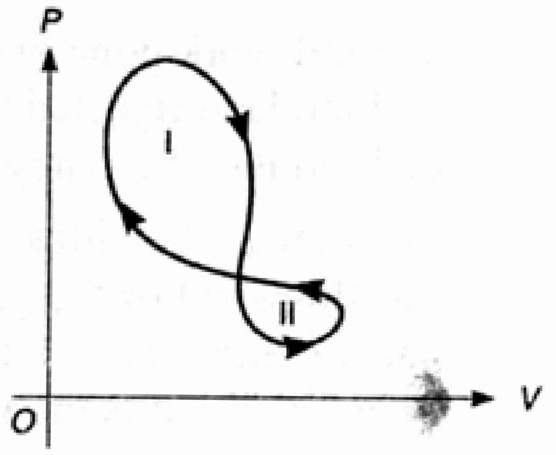
16. n moles of a monoatomic gas are taken around in a cyclic process consisting of four processes along $ABCDA$ as shown. All the lines on the P-V diagram have slope of magnitude P_0 / V_0. The pressure at A and C is P_0 and the volumes at A and C are $V_0/2$ and $3V_0/2$ respectively. Calculate the percentage efficiency of the cycle.



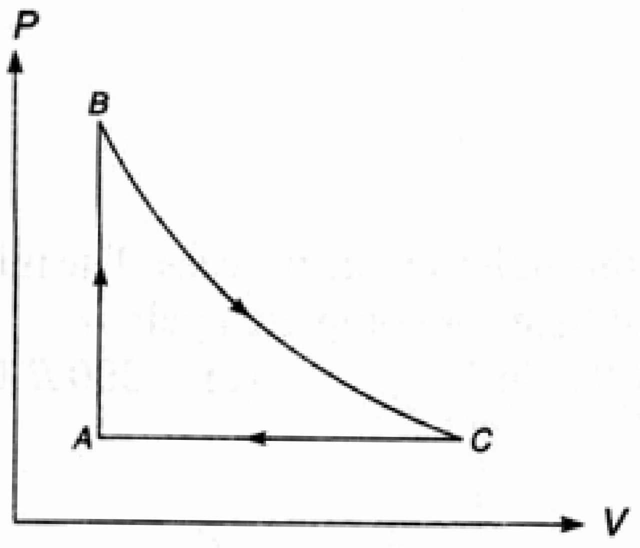
17. A system is taken around the cycle shown in figure from state a to state b and then back to state a. The absolute value of the heat transfer during one cycle is 7200 J. (a) Does the system absorb or liberate heat when it goes around the cycle in the direction shown in the figure ? (b) What is the work W done by the system in one cycle ? (c) If the system goes around the cycle in a counter-clock wise direction, does it absorb or liberate heat in one cycle? What is the magnitude of the heat absorbed or liberated in one counterclockwise cycle ?



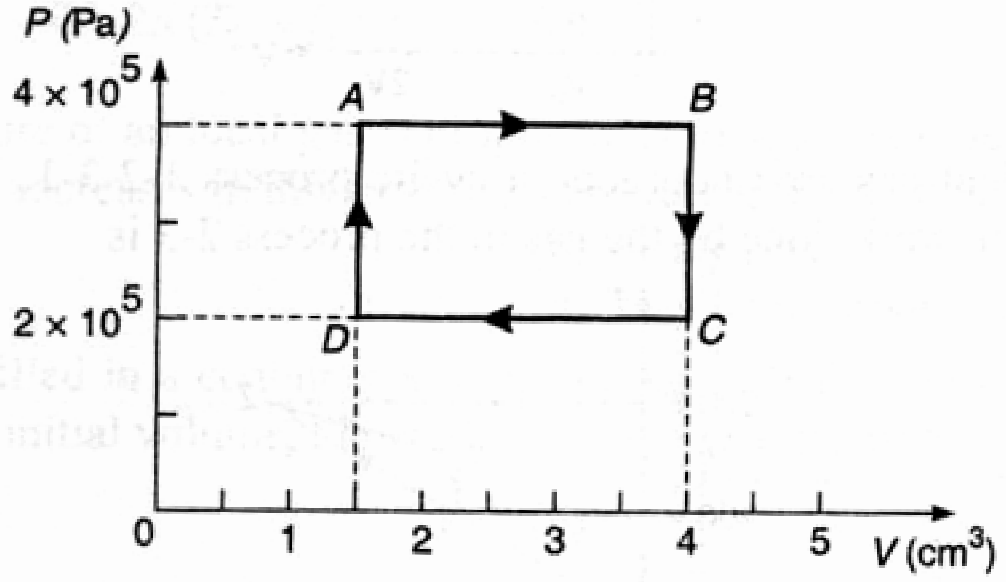
18. A thermodynamic system undergoes a cyclic process as shown in figure. The cycle consists of two closed loops, loop I and loop II. (a) Over one complete cycle, does the system do positive or negative work ? (b) In each of loops I and II, is the net work done by the system positive or negative ? (c) Over one complete cycle, does heat flow into or out of the system ? (d) In each of loops I and II, does heat flow into or out of the system ?



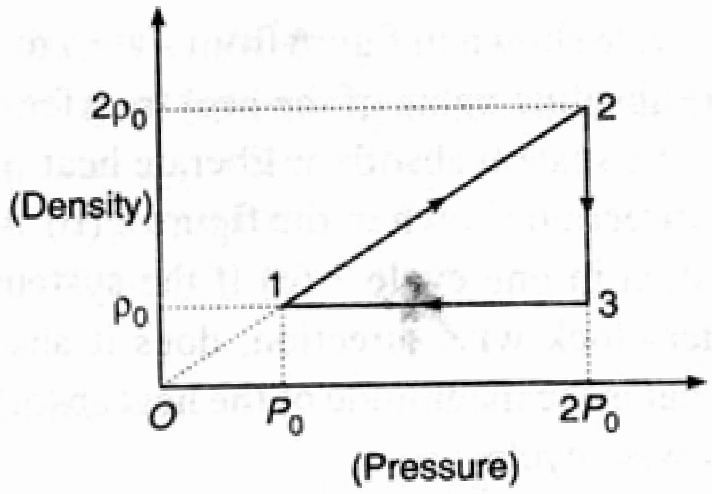
19. 1.0 k-mol of a sample of helium gas is put through the cycle of operations shown in figure. BC is an isothermal process and $P_A = 1.00$ atm, $V_A = 22.4\ \text{m}^3$, $P_B = 2.00$ atm. What are T_A, T_B and V_C?



20. For the thermodynamic cycle shown in figure find (a) net output work of the gas during the cycle, (b) net heat flow into the gas per cycle.



21. The density (ρ) *versus* pressure (P) graph of an ideal gas (monoatomic) undergoing a cyclic process is shown in figure. The gas taken has molecular mass M and one mole of gas is taken.



(a) Find work done in each process.
(b) Find heat rejected by gas in one complete cycle.
(c) Find the efficiency of the cycle.

22. Two moles of an ideal monoatomic gas go through the cycle *abc*. For the complete cycle 800 J of heat flows out of the gas. Process *ab* is at constant pressure and process *bc* is at constant volume. States *a* and *b* have temperatures $T_a = 200$ K and $T_b = 300$ K. (a) Sketch the *P-V* diagram for the cycle. (b) What is the work *W* for the process *ca* ?

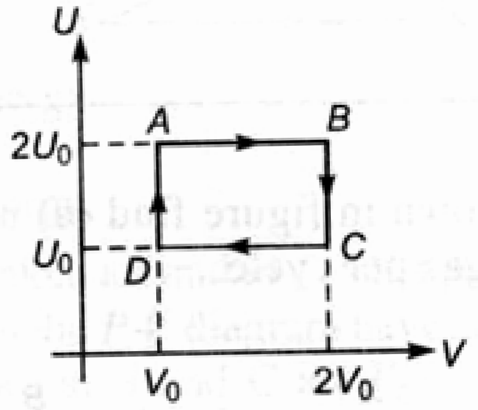
23. A monoatomic gas is expanded adiabatically from volume V_0 to $2V_0$ and then is brought back to the initial state through an isothermal and isochoric process respectively. Plot the *P-V* diagram of the complete cycle and find the efficiency of the cycle.

Objective Questions

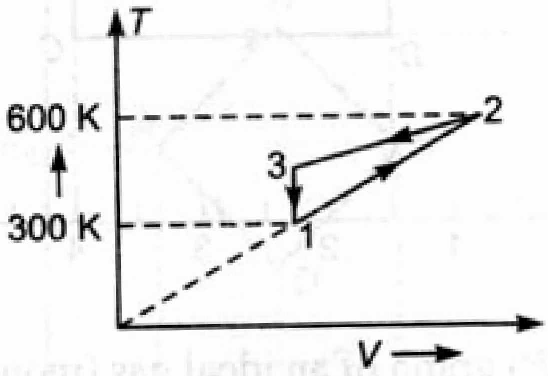
Single Correct Option

1. 1 mole of an ideal gas is taken through a cyclic process. The minimum temperature during the cycle is 300 K. Then net exchange of heat for complete cycle is

(a) 600 R ln 2 (b) 300 R ln 2 (c) −300 R ln 2 (d) 900 R ln 2



2. Two moles of an ideal gas are undergone a cyclic process 1-2-3-1. If net heat exchange in the process is − 300 J, the work done by the gas in the process 2-3 is



(a) −500 J (b) − 5000 J (c) − 3000 J (d) None of these

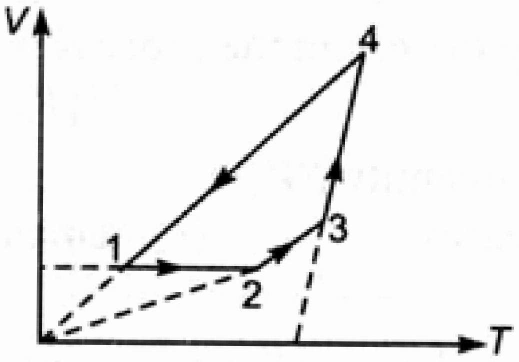
3. Two cylinders fitted with pistons contain equal amount of an ideal diatomic gas at 300 K. The piston of A is free to move, while that of B is held fixed. The same amount of heat is given to the gas in each cylinder. If the rise in temperature of the gas in A is 30 K, then the rise in temperature of gas in B is

(a) 30 K (b) 18 K (c) 50 K (d) 42 K

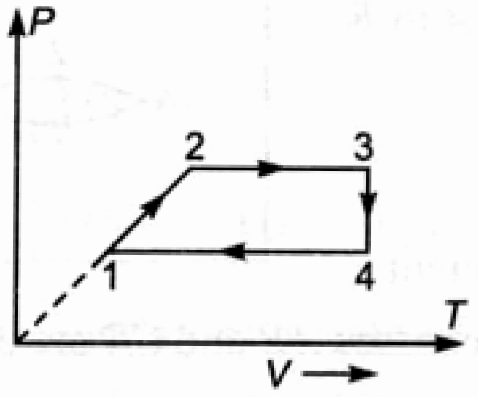
4. A gas follows a process $TV^{n-1} = \text{constant}$ where T = absolute temperature of the gas and V = volume of the gas. The bulk modulus of the gas in the process is given by

(a) $(n-1)P$ (b) $P/(n-1)$ (c) nP (d) P/n

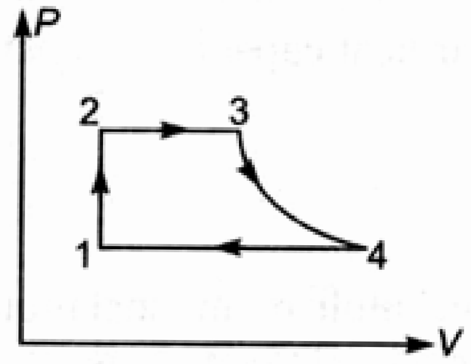
5. A cyclic process 1-2-3-4-1 is depicted on V-T diagram. The P-T and P-V diagrams for this cyclic process are given below. Select the correct choices



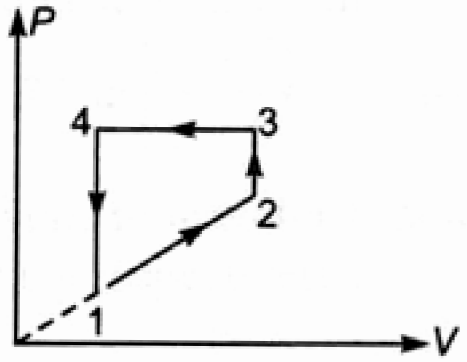
(a)



(b)



(c)



(d) None of these

6. One mole of an ideal gas at temperature T_1 expands slowly according to the law P/V = constant. Its final temperature is T_2. The work done by the gas is

(a) $R(T_2 - T_1)$ (b) $2R(T_2 - T_1)$ (c) $\frac{R}{2}(T_2 - T_1)$ (d) $\frac{2R}{3}(T_2 - T_1)$

7. In a process the pressure of an ideal gas is proportional to square of the volume of the gas. If the temperature of the gas increases in this process, then work done by this gas :

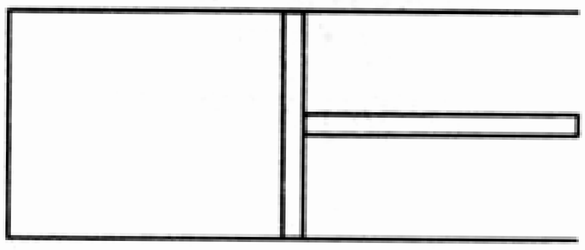
(a) is positive (b) is negative

(c) is zero (d) may be positive or negative

8. n moles of a gas are filled in a container at temperature T. If the gas is slowly and isothermally compressed to half its initial volume, the work done by the atmosphere on the gas is

(a) $\frac{nRT}{2}$ (b) $-\frac{nRT}{2}$

(c) $nRT \ln 2$ (d) $-nRT \ln 2$



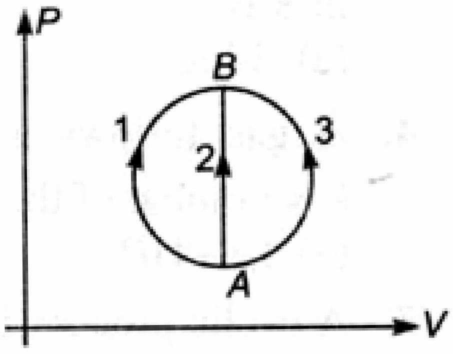
9. 600 J of heat is added to a monoatomic gas in a process in which the gas performs a work of 150 J. The molar heat capacity for the process is

(a) $3R$ (b) $4R$ (c) $2R$ (d) $6R$

10. A gas undergoes A to B through three different processes 1, 2 and 3 as shown in the figure. The heat supplied to the gas is Q_1, Q_2 and Q_3 respectively, then

(a) $Q_1 = Q_2 = Q_3$ (b) $Q_1 < Q_2 < Q_3$

(c) $Q_1 > Q_2 > Q_3$ (d) $Q_1 = Q_3 > Q_2$



11. The internal energy of a gas is given by $U = 2PV$. It expands from V_0 to $2V_0$ against a constant pressure P_0. The heat absorbed by the gas in the process is

(a) $2P_0V_0$ (b) $4P_0V_0$ (c) $3P_0V_0$ (d) P_0V_0

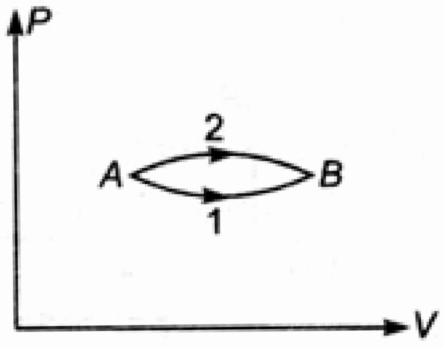
12. For an adiabatic compression the quantity PV

(a) increases (b) decreases (c) remains constant (d) depends on γ

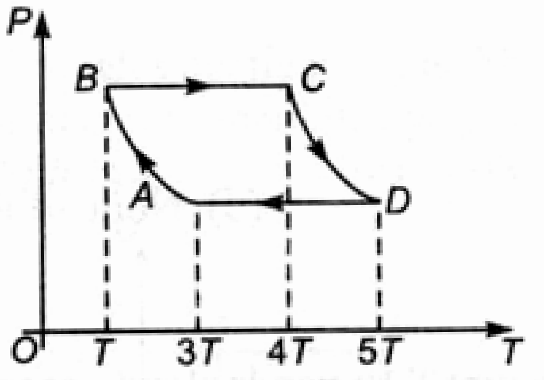
13. The figure shows two paths for the change of state of a gas from A to B. The ratio of molar heat capacities in path 1 and path 2 is

(a) < 1 (b) > 1

(c) 1 (d) Data insufficient



14. P-T diagram of one mole of an ideal monoatomic gas is shown. Processes AB and CD are adiabatic. Work done in the complete cycle is



(a) 2.5 RT (b) $-2RT$ (c) 1.5 RT (d) $-3.5\ RT$

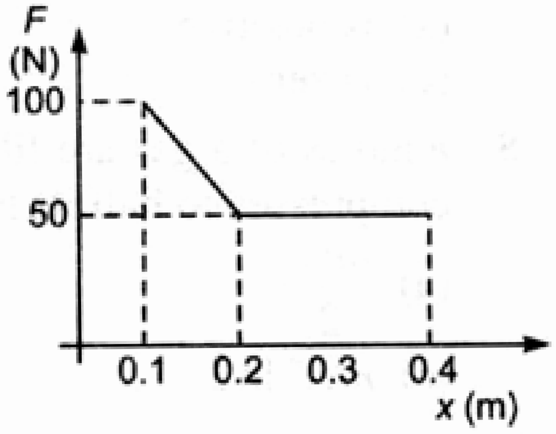
15. An ideal monoatomic gas undergoes a process in which its internal energy U and density ρ vary as $U\rho$ = constant. The ratio of change in internal energy and the work done by the gas is

(a) $\frac{3}{2}$ (b) $\frac{2}{3}$ (c) $\frac{1}{3}$ (d) $\frac{3}{5}$

16. The given figure shows the variation of force applied by ideal gas on a piston which undergoes a process during which piston position changes from 0.1 to 0.4 m. If the internal energy of the system at the end of the process is 2.5 J higher, then the heat absorbed during the process is

(a) 15 J (b) 17.5 J

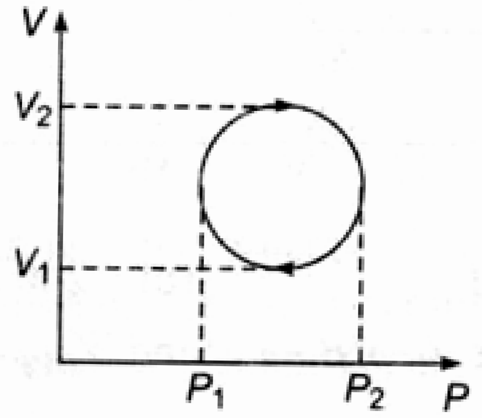
(c) 20 J (d) 22.5 J



17. A gas can expand through two processes : (i) isobaric, (ii) P/V = constant. Assuming that the initial volume is same in both processes and the final volume which is two times the initial volume is also same in both processes, which of the following is true?

(a) Work done by gas in process (i) is greater than the work done by the gas in process (ii)
(b) Work done by gas in process (i) is smaller than the work done by the gas in process (ii)
(c) Final pressure is greater in process (i)
(d) Final temperature is greater in process (i)

18. The cyclic process form a circle on a PV diagram as shown in figure. The work done by the gas is



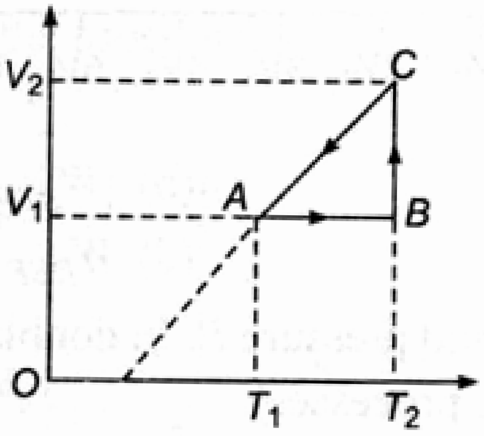
(a) $\frac{\pi}{4}(P_2 - P_1)^2$ (b) $\frac{\pi}{4}(V_2 - V_1)^2$

(c) $\frac{\pi}{2}(P_2 - P_1)(V_2 - V_1)$ (d) $\frac{\pi}{4}(P_2 - P_1)(V_2 - V_1)$

19. The equation of a state of a gas is given by $P(V-b) = nRT$. If 1 mole of a gas is isothermally expanded from volume V and $2V$, the work done during the process is

(a) $RT \ln\left|\frac{2V-b}{V-b}\right|$ (b) $RT \ln\left|\frac{V-b}{V}\right|$ (c) $RT \ln\left|\frac{V-b}{2V-b}\right|$ (d) $RT \ln\left|\frac{V}{V-b}\right|$

20. A cyclic process for 1 mole of an ideal gas is shown in the V-T diagram. The work done in AB, BC and CA respectively is



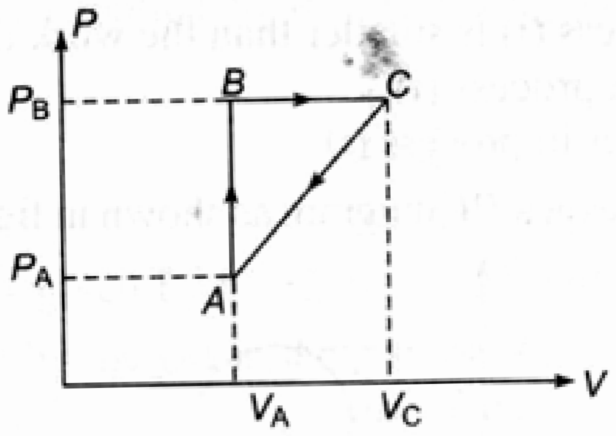
(a) $0, RT_2 \ln\left|\frac{V_2}{V_1}\right|, R(T_1 - T_2)$ (b) $R(T_1 - T_2), 0, RT_1 \ln\left|\frac{V_1}{V_2}\right|$

(c) $0, RT_1 \ln\left|\frac{V_1}{V_2}\right|, R(T_1 - T_2)$ (d) $0, RT_2 \ln\left|\frac{V_2}{V_1}\right|, R(T_2 - T_1)$

21. An ideal gas of adiabatic exponent γ is expanded so that the amount of heat transferred to the gas is equal to the decrease of its internal energy. Then the equation of the process in terms of the variables T and V is

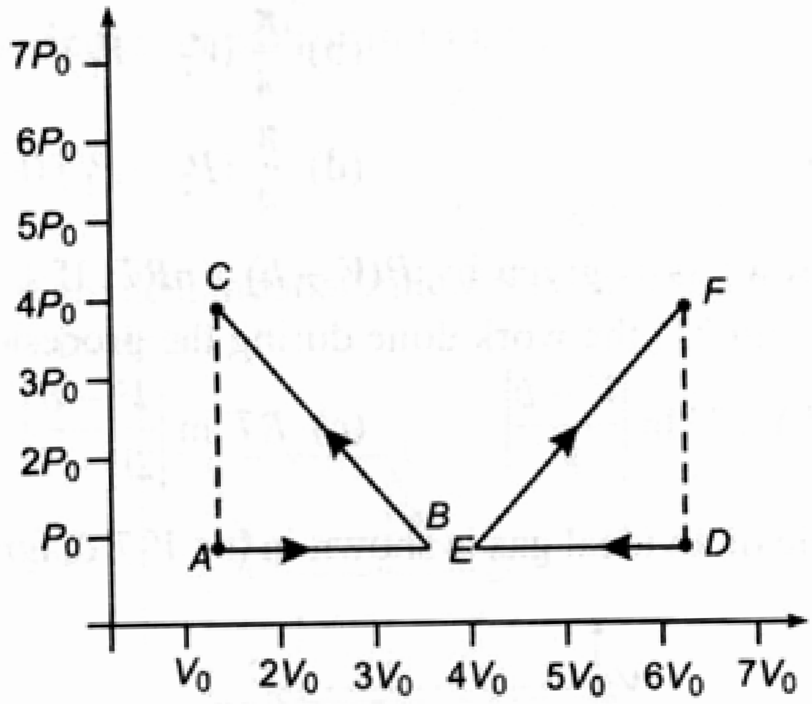
(a) $TV^{\frac{(\gamma-1)}{2}} = C$ (b) $TV^{\frac{(\gamma-2)}{2}} = C$ (c) $TV^{\frac{(\gamma-1)}{4}} = C$ (d) $TV^{\frac{(\gamma-2)}{4}} = C$

22. A thermodynamical process is shown in the figure with $P_A = 3 \times P_{\text{atm}}$, $V_A = 2 \times 10^{-4}\ \text{m}^3$, $P_B = 8 \times P_{\text{atm}}$, $V_C = 5 \times 10^{-4}\ \text{m}^3$. In the process AB and BC, 600 J and 200 J heat are added to the system. Find the change in internal energy of the system in the process CA. [1 $P_{\text{atm}} = 10^5\ \text{N/m}^2$]



(a) 560 J (b) –560 J (c) –240 J (d) +240 J

23. If W_{ABC} is the work done in process $A \to B \to C$ and W_{DEF} is work done in process $D \to E \to F$ as shown in the figure, then



(a) $|W_{DEF}| > |W_{ABC}|$ (b) $|W_{DEF}| < |W_{ABC}|$

(c) $W_{DEF} = W_{ABC}$ (d) $W_{DEF} = -W_{ABC}$

24. An ideal gas has initial volume V and pressure P. In doubling its volume the minimum work done will be in the process (of the given processes)

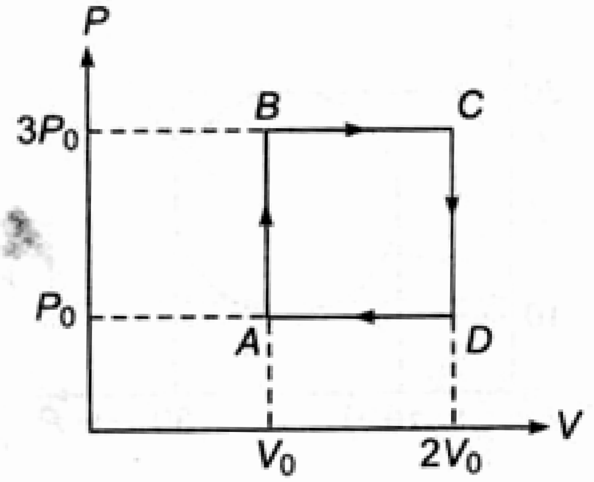
(a) isobaric process (b) isothermal process

(c) adiabatic process (d) same in all given processes

25. Ten moles of a diatomic perfect gas are allowed to expand at constant pressure. The initial volume and temperature are V_0 and T_0 respectively. If $\frac{7}{2}RT_0$ heat is transferred to the gas then the final volume and temperature are

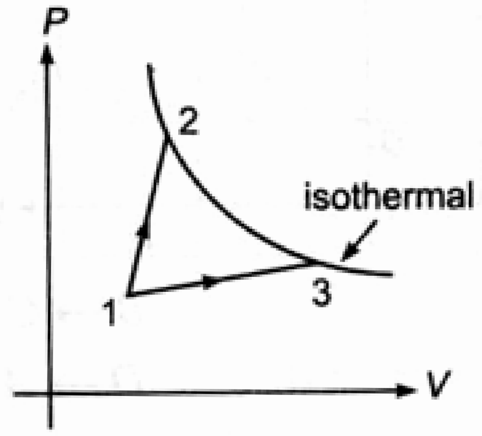
(a) $1.1V_0, 1.1T_0$ (b) $0.9V_0, 0.9T_0$ (c) $1.1V_0, \frac{10}{11}T_0$ (d) $0.9V_0, \frac{10}{9}T_0$

26. An ideal monoatomic gas is carried around the cycle *ABCDA* as shown in the figure. The efficiency of the gas cycle is



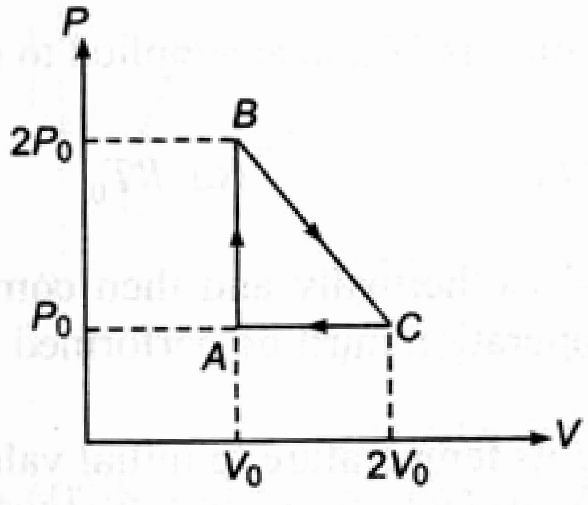
(a) $\frac{4}{21}$ (b) $\frac{2}{21}$ (c) $\frac{4}{31}$ (d) $\frac{2}{31}$

27. A gas takes part in two processes in which it is heated from the same initial state 1 to the same final temperature. The processes are shown on the *P-V* diagram by the straight lines 1-3 and 1-2. 2 and 3 are the points on the same isothermal curve. Q_1 and Q_2 are the heat transfer along the two processes. Then



(a) $Q_1 = Q_2$ (b) $Q_1 < Q_2$ (c) $Q_1 > Q_2$ (d) Insufficient data

28. In the process shown in figure, the internal energy of an ideal gas decreases by $\frac{3P_0V_0}{2}$ in going from point *C* to *A*. Heat transfer along the process *CA* is

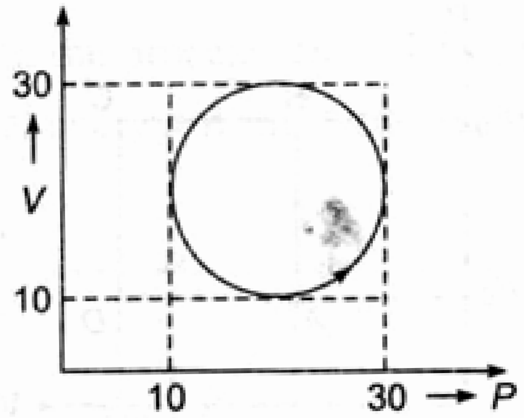


(a) $(-3\,P_0V_0)$ (b) $(-5\,P_0V_0/2)$ (c) $(-3\,P_0V_0/2)$ (d) zero

29. A closed system receives 200 kJ of heat at constant volume. It then rejects 100 kJ of heat while it has 50 kJ of work done on it at constant pressure. If an adiabatic process can be found which will restore the system to its initial state, the work done by the system during this process is

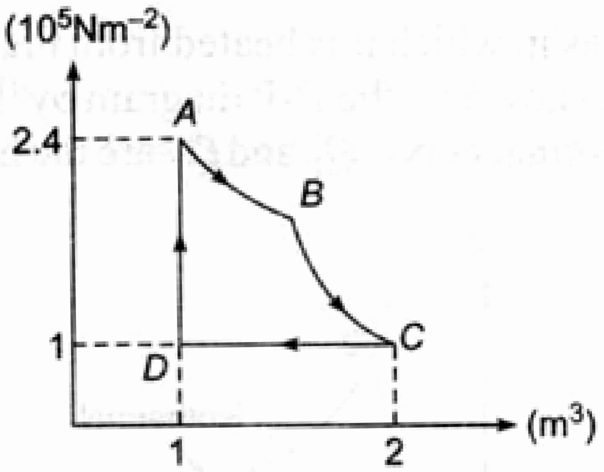
(a) 100 kJ (b) 50 kJ (c) 150 kJ (d) 200 kJ

30. Heat energy absorbed by a system in going through a cyclic process is shown in the figure [V in litres and P in k Pa] is



(a) $10^7\,\pi$ J (b) $10^4\,\pi$ J (c) $10^2\,\pi$ J (d) $10^3\,\pi$ J

31. 100 moles of an ideal monatomic gas undergoes the thermodynamic process as shown in the figure



$A \to B$: isothermal expansion $B \to C$: adiabatic expansion

$C \to D$: isobaric compression $D \to A$: isochoric process

The heat transfer along the process AB is 9×10^4 J.The net work done by the gas during the cycle is [Take $R = 8\ \text{JK}^{-1}\ \text{mol}^{-1}$)

(a) -0.5×10^4 J (b) $+0.5\times10^4$ J (c) -5×10^4 J (d) $+5\times10^4$ J

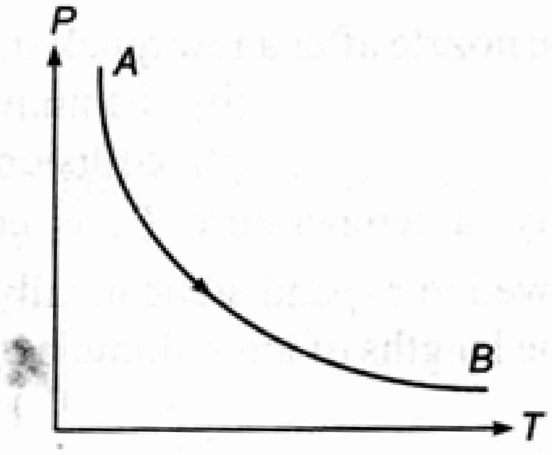
32. One mole of an ideal monoatomic gas at temperature T_0 expands slowly according to the law $\frac{P}{V}$ = constant. If the final temperature is $2T_0$, heat supplied to the gas is

(a) $2RT_0$ (b) $\frac{3}{2}RT_0$ (c) RT_0 (d) $\frac{1}{2}RT_0$

33. A mass of gas is first expanded isothermally and then compressed adiabatically to its original volume. What further simplest operation must be performed on the gas to restore it to its original state ?

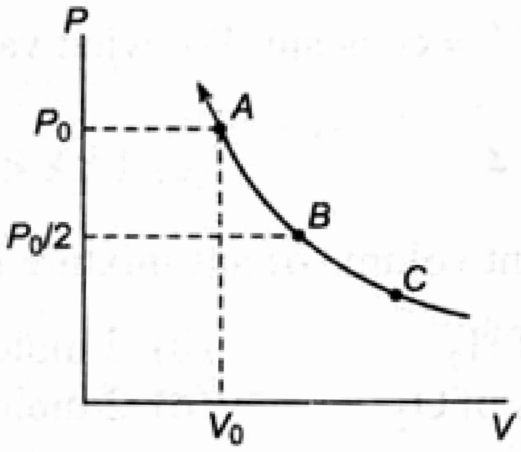
(a) An isobaric cooling to bring its temperature to initial value
(b) An isochoric cooling to bring its pressure to its initial value
(c) An isothermal process to take its pressure to its initial value
(d) An isochoric heating to bring its temperature to initial value

34. Two moles of an ideal monoatomic gas are expanded according to the equation PT = constant from its initial state (P_0, V_0) to the final state due to which its pressure becomes half of the initial pressure. The change in internal energy is



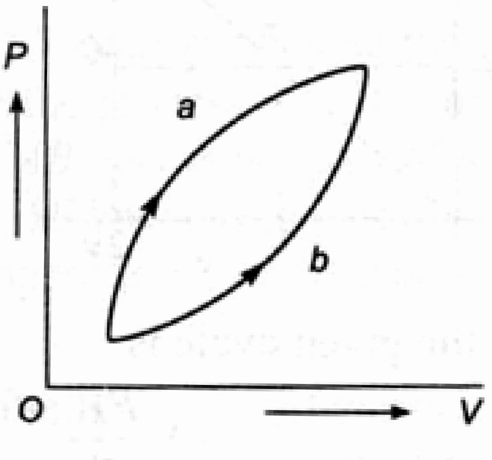
(a) $\frac{3P_0V_0}{4}$ (b) $\frac{3P_CV_0}{2}$ (c) $\frac{9P_0V_0}{2}$ (d) $\frac{5P_0V_0}{2}$

35. The state of an ideal gas is changed through an isothermal process at temperature T_0 as shown in figure. The work done by gas in going from state B to C is double the work done by gas in going from state A to B. If the pressure in the state B is $\frac{P_0}{2}$, then the pressure of the gas in state C is



(a) $\frac{P_0}{3}$ (b) $\frac{P_0}{4}$ (c) $\frac{P_0}{6}$ (d) $\frac{P_0}{8}$

36. Figure shows two processes a and b for a given sample of a gas. If $\Delta Q_1, \Delta Q_2$ are the amounts of heat absorbed by the system in the two cases and $\Delta U_1, \Delta U_2$ are changes in internal energies respectively, then



(a) $\Delta Q_1 = \Delta Q_2; \Delta U_1 = \Delta U_2$ (b) $\Delta Q_1 > \Delta Q_2; \Delta U_1 > \Delta U_2$
(c) $\Delta Q_1 < \Delta Q_2; \Delta U_1 < \Delta U_2$ (d) $\Delta Q_1 > \Delta Q_2; \Delta U_1 = \Delta U_2$

37. A Carnot engine works between 600 K and 300 K. The efficiency of the engine is
(a) 50% (b) 70% (c) 20% (d) 80%

38. Air in a cylinder is suddenly compressed by a piston which is then maintained at the same position. As the time passes pressure of the gas
(a) increases
(b) decreases
(c) remains the same
(d) may increase or decrease depending on the nature of the gas

39. A cycle pump becomes hot near the nozzle after a few quick strokes even if they are smooth because
(a) the volume of air decreases
(b) the number of air molecules increases
(c) the compression is adiabatic
(d) collision between air particles increases

40. A monoatomic ideal gas, initially at temperature T_1, is enclosed in a cylinder fitted with a frictionless piston. The gas is allowed to expand adiabatically to a temperature T_2 by releasing the piston suddenly. If L_1 and L_2 are the lengths of gas column before and after expansion respectively, then $\frac{T_1}{T_2}$ is given by
(a) $\left(\frac{L_1}{L_2}\right)^{2/3}$
(b) $\frac{L_1}{L_2}$
(c) $\frac{L_2}{L_1}$
(d) $\left(\frac{L_2}{L_1}\right)^{2/3}$

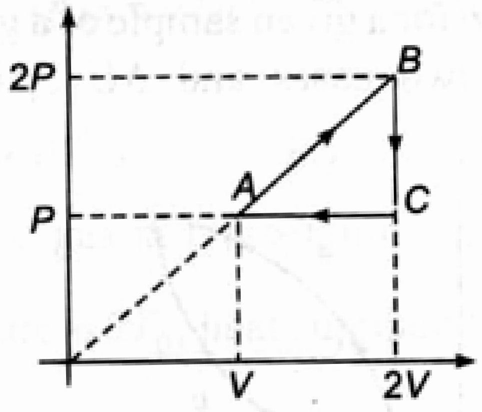
41. In an adiabatic change, the pressure P and temperature T of a diatomic gas are related by the relation $P \propto T^{\alpha}$ where α equals
(a) 1.67
(b) 0.4
(c) 0.6
(d) 3.5

42. A diatomic gas obeys the law PV^x = constant. For what value of x, it has negative molar specific heat ?
(a) $x > 1.4$
(b) $x < 1.4$
(c) $1 < x < 1.4$
(d) $0 < x < 1$

43. The molar specific heat at constant volume of gas mixture is $\frac{13R}{6}$. The gas mixture consists of
(a) 2 moles of O_2 and 4 moles of H_2
(b) 2 moles of O_2 and 4 moles of argon
(c) 2 moles of argon and 4 moles of O_2
(d) 2 moles of CO_2 and 4 moles of argon

Passage : (Q. 44 and 45)

One mole of a monoatomic ideal gas is taken along the cycle ABCA as shown in the diagram.

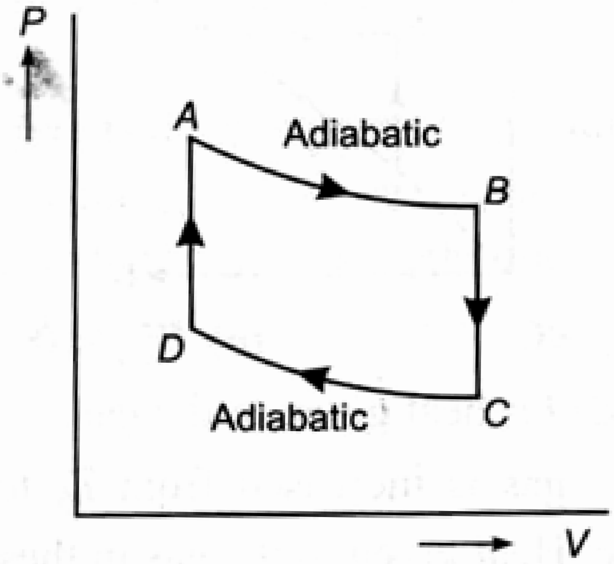


44. The net heat absorbed by the gas in the given cycle is
(a) PV
(b) $\frac{PV}{2}$
(c) $2PV$
(d) $4PV$

45. The ratio of specific heat in the process CA to the specific heat in the process BC is
(a) 2
(b) $\frac{5}{3}$
(c) 4
(d) None of these

Passage : (Q. 46 - Q. 48)

One mole of a monoatomic ideal gas is taken through the cycle ABCDA as shown in the figure. $T_A = 1000\,K$ *and* $2P_A = 3P_B = 6P_C$.



$$\left[Assume \left(\frac{2}{3}\right)^{0.4} = 0.85 \; and \; R = \frac{25}{3} JK^{-1} mol^{-1} \right]$$

46. The temperature at B is

(a) 350 K (b) 1175 K (c) 850 K (d) 577 K

47. Work done by the gas in the process $A \rightarrow B$ is

(a) 5312.5 J (b) 1875 J (c) zero (d) 8854 J

48. Heat lost by the gas in the process $B \rightarrow C$ is

(a) 5312.5 J (b) 1875 J (c) zero (d) 8854 J

49. An ideal gas is taken from the state A (pressure P, volume V) to the state B (pressure $\frac{P}{2}$, volume $2V$) along a straight line path in the P-V diagram. Select the correct statement(s) from the following.

(a) The work done by the gas in the process A to B is negative
(b) In the T-V diagram, the path AB becomes a part of a parabola
(c) In the P-T diagram, the path AB becomes a part of a hyperbola
(d) In going from A to B, the temperature T of the gas first increases to a maximum value and then decreases

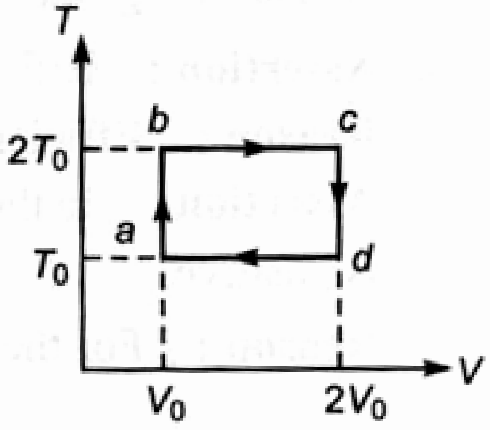
50. In the process PV^2 = constant, if temperature of gas is increased

(a) change in internal energy of gas is positive
(b) work done by gas is positive
(c) heat is given to the gas
(d) heat is taken out from the gas

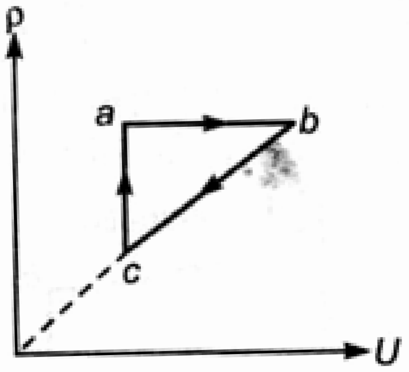
51. T-V diagram of two moles of a monoatomic gas is as shown in figure :

For the process *abcda* choose the correct options given below :

(a) $\Delta U = 0$
(b) work done by gas > 0
(c) heat given to the gas is $4RT_0$
(d) heat given to the gas is $2RT_0$



52. Density (ρ) versus internal energy (U) graph of a gas is as shown in figure. Choose the correct options



(a) $Q_{bc} = 0$ (b) $W_{bc} = 0$ (c) $W_{ca} < 0$ (d) $Q_{ab} > 0$

Here W is work done by gas and Q is heat given to the gas.

53. Temperature of a monoatomic gas is increased from T_0 to $2T_0$ in three different processes : isochoric, isobaric and adiabatic. Heat given to the gas in these three processes are Q_1, Q_2 and Q_3 respectively. Then choose the correct option.

(a) $Q_1 > Q_3 > Q_2$ (b) $Q_2 > Q_1 > Q_3$ (c) $Q_1 > Q_2 > Q_3$ (d) $Q_2 > Q_3 > Q_1$

For **JEE Advanced**

Assertion and Reason

Directions : *Choose the correct option.*

*(a) If both **Assertion** and **Reason** are true and the **Reason** is correct explanation of the **Assertion.***

*(b) If both **Assertion** and **Reason** are true but **Reason** is not the correct explanation of **Assertion.***

*(c) If **Assertion** is true, but the **Reason** is false.*

*(d) If **Assertion** is false but the **Reason** is true.*

1. Assertion : In adiabatic expansion, temperature of gas always decreases.

Reason : In adiabatic process exchange of heat is zero.

2. Assertion : In a thermodynamic process, initial volume of gas is equal to final volume of gas. Work done by gas in this process should be zero.

Reason : Work done by gas in isochoric process is zero.

3. Assertion : First law of thermodynamics can be applied for ideal gases only.

Reason : First law is simply, law of conservation of energy.

4. Assertion : When ice melts, work is done by atmosphere on (ice + water) system.

Reason : On melting of ice volume decreases.

5. Assertion : Between two thermodynamic states, the value of $(Q - W)$ is constant for any process.

Reason : Q and W are path functions.

6. Assertion : Efficiency of a heat engine can't be greater than efficiency of Carnot's engine.

Reason : Efficiency of any engine is never 100%.

7. Assertion : In the process $PT =$ constant, if temperature of gas is increased work done by the gas is positive.

Reason : For the given process $V \propto T$

8. **Assertion :** In free expansion of a gas inside an adiabatic chamber Q, W and ΔU all are zero.

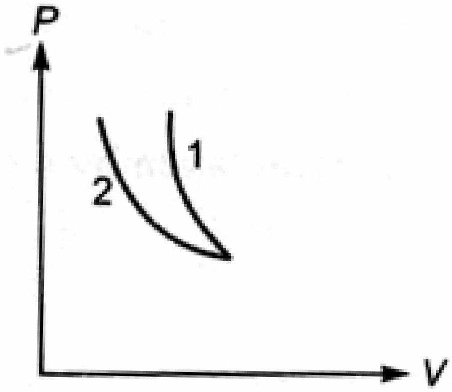
   Reason : In such an expansion $P \propto \frac{1}{V}$.

9. **Assertion :** For an ideal gas in a cyclic process and in an isothermal process change in internal energy is zero.

   Reason : In both processes there is no change in temperature.

10. **Assertion :** Isothermal and adiabatic, two processes are shown on P-V diagram. Process-1 is adiabatic and process-2 is isothermal.

    Reason : At a given point, slope of adiabatic process $= \gamma \times$ slope of isothermal process.

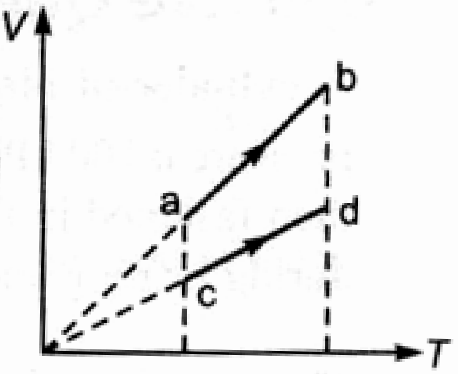


Match the Columns

1. Temperature of 2 moles of a monoatomic gas is increased from T to $2T$. Match the following two columns.

Column I	Column II
(a) Work done by gas in isobaric process	(p) $3RT$
(b) Change in internal energy in isobaric process	(q) $4RT$
(c) Work done by gas in adiabatic process	(r) $2RT$
(d) Change in internal energy in an adiabatic process	(s) None of these

2. For V-T diagrams of two processes $a-b$ and $c-d$ shown in figure for same gas match the following two columns.



Column I	Column II
(a) Work-done	(p) is more in process ab
(b) Change in internal energy	(q) is more in process ca
(c) Heat exchange	(r) is same in both processes
(d) Molar heat capacity	(s) Can't say anything

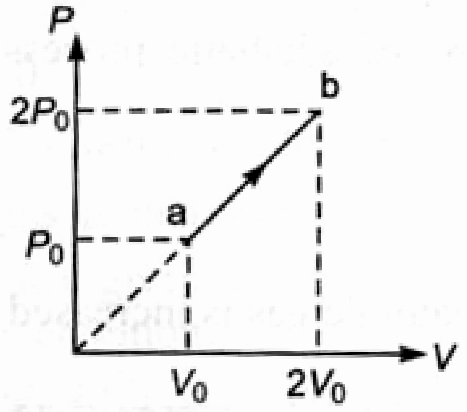
3. Temperature of a monoatomic gas is increased by ΔT in process $P^2V =$ constant. Match the following two columns.

Column I	Column II
(a) Work done by gas	(p) $2nR\Delta T$
(b) Change in internal energy of gas	(q) $5nR\Delta T$
(c) Heat taken by the gas	(r) $3nR\Delta T$
(d) Work done on the gas	(s) None of these

4. Match the following two columns.

Column I	Column II
(a) Isobaric expansion	(p) $W > \Delta U$
(b) Isochoric cooling	(q) $W < \Delta U$
(c) Adiabatic expansion	(r) $Q = \Delta U$
(d) Isothermal expansion	(s) $Q < \Delta U$

5. Heat taken by a gas in process *a*-*b* is $6P_0V_0$. Match the following columns.



Column I	Column II
(a) W_{ab}	(p) $2P_0V_0$
(b) ΔU_{ab}	(q) $4P_0V_0$
(c) Molar heat capacity in given process	(r) $2R$
(d) C_V of gas	(s) None of these

Subjective Questions

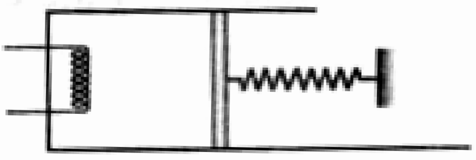
1. A cylinder of ideal gas is closed by an 8 kg movable piston of area $60\,\text{cm}^2$. The atmospheric pressure is 100 kPa. When the gas is heated from 30° C to 100° C the piston rises 20 cm. The piston is then fastened in the place and the gas is cooled back to 30° C. If ΔQ_1 is the heat added to the gas during heating and ΔQ_2 is the heat lost during cooling, find the difference.

2. Three moles of an ideal gas $\left(C_P = \dfrac{7}{2}R\right)$ at pressure P_0 and temperature T_0 is isothermally expanded to twice its initial volume. It is then compressed at a constant pressure to its original volume.
   (a) Sketch *P*-*V* and *P*-*T* diagram for complete process.
   (b) Calculate net work done by the gas.
   (c) Calculate net heat supplied to the gas during complete process.
   (Write your answer in terms of gas constant = R)

3. Two moles of a gas ($\gamma = 5/3$) are initially at temperature 27°C and occupy a volume of 20 litres. The gas is first expanded at constant pressure until the volume is doubled. Then it is subjected to an adiabatic change until the temperature returns to its initial value.

(a) Sketch the process on a *P-V* diagram.
(b) What are final volume and pressure of the gas?
(c) What is the work done by the gas?

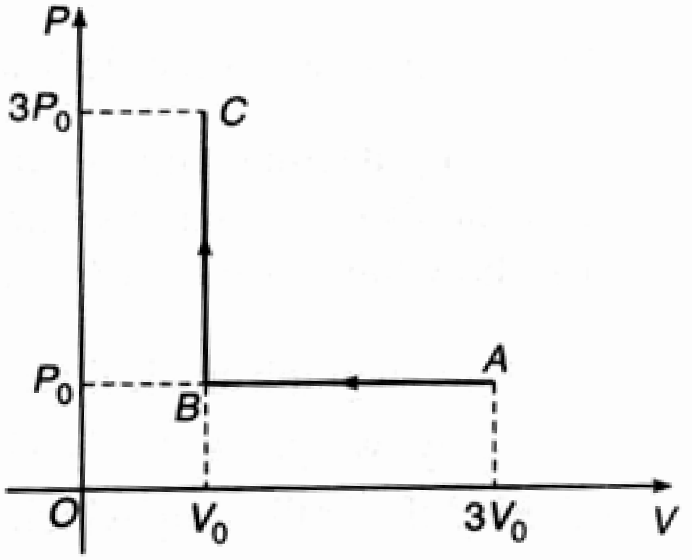
4. A ideal monoatomic gas is confined by a spring loaded massless piston of cross-section $8.0\times10^{-3}\,\text{m}^2$. Initially the gas is at 300 K and occupies a volume of $2.4\times10^{-3}\,\text{m}^3$ and the spring is in its relaxed state. The gas is heated by an electric heater until the piston moves out slowly without friction by 0.1m. Calculate :
(a) the final temperature of the gas and
(b) the heat supplied by the heater.



The force constant of the spring is 8000 N/m, atomspheric pressure is $1.0\times10^5\,\text{N/m}^2$. The cylinder and the piston are thermally insulated.

5. An ideal diatomic gas $\left(\gamma=\frac{7}{5}\right)$ undergoes a process in which its internal energy relates to the volume as $U=\alpha\sqrt{V}$, where α is a constant.
(a) Find the work performed by the gas to increase its internal energy by 100 J.
(b) Find the molar specific heat of the gas.

6. *P-V* diagram of an ideal gas for a process *ABC* is as shown in the figure.
(a) Find total heat absorbed or released by the gas during the process *ABC*.
(b) Change in internal energy of the gas during the process *ABC*.
(c) Plot pressure *versus* density graph of the gas for the process *ABC*.



7. For an ideal gas the molar heat capacity varies as $C=C_V+3aT^2$. Find the equation of the process in the variables (T,V) where a is a constant.

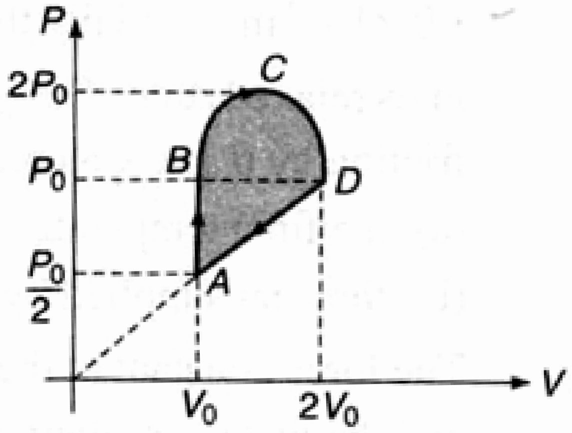
8. One mole of an ideal monoatomic gas undergoes the process $P=\alpha T^{1/2}$, where α is a constant.
(a) Find the work done by the gas if its temperature increases by 50 K.
(b) Also, find the molar specific heat of the gas.

9. One mole of a gas is put under a weightless piston of a vertical cylinder at temperature T. The space over the piston opens into atmosphere. Initially piston was in equilibrium. How much work should be performed by some external force to increase isothermally the volume under the piston to twice the volume? (Neglect friction of piston).

10. An ideal monoatomic gas undergoes a process where its pressure is inversely proportional to its temperature.
(a) Calculate the molar specific heat for the process.
(b) Find the work done by two moles of gas if the temperature changes from T_1 to T_2.

11. The volume of one mole of an ideal gas with the adiabatic exponent γ is changed according to the relation $V = \frac{a}{T}$, where a is a constant. Find the amount of heat absorbed by the gas in the process, if the temperature is increased by ΔT.

12. Two moles of a monoatomic ideal gas undergo a cyclic process $ABCDA$ as shown in figure. BCD is a semicircle. Find the efficiency of the cycle.



13. Pressure P, volume V and temperature T for a certain gas are related by

$$P = \frac{\alpha T - \beta T^2}{V}$$

where α and β are constants. Find the work done by the gas if the temperature changes from T_1 to T_2 while the pressure remains the constant.

14. An ideal gas has a specific heat at constant pressure $C_P = \frac{5R}{2}$. The gas is kept in a closed vessel of volume V_0 at temperature T_0 and pressure P_0. An amount of $10\,P_0V_0$ of heat is supplied to the gas.

(a) Calculate the final pressure and temperature of the gas.

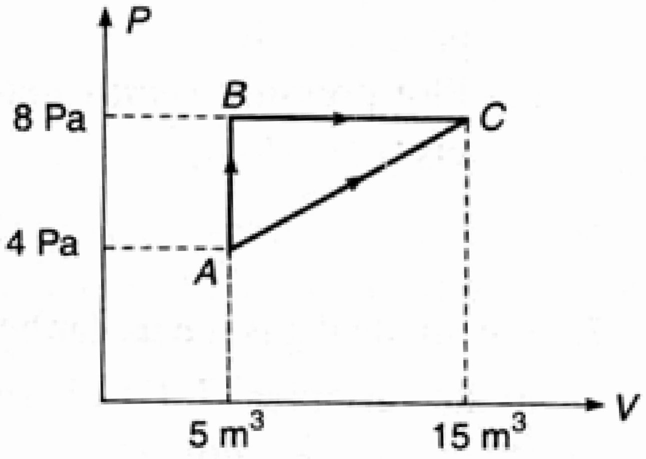
(b) Show the process on P-V diagram.

15. In the given graph an ideal gas changes its state from state A to state C by two paths ABC and AC.

(a) Find the path along which work done is less.

(b) The internal energy of gas at A is 10 J and the amount of heat supplied in path AC is 200 J. Calculate the internal energy of gas at C.

(c) The internal energy of gas at state B is 20 J. Find the amount of heat supplied to the gas to go from A to B.

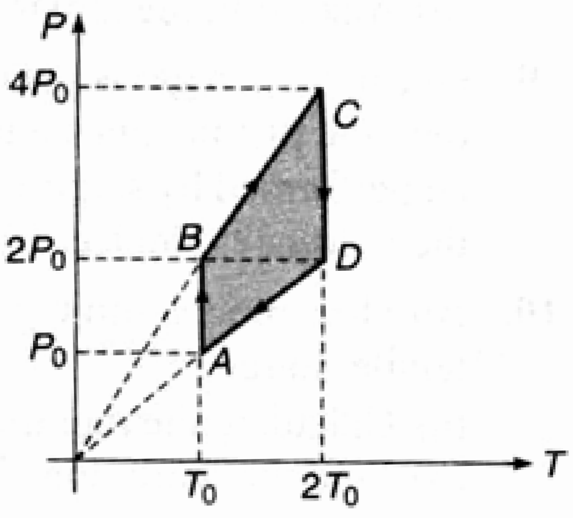


16. Pressure versus temperature (P-T) graph of n moles of an ideal gas is shown in figure. Plot the corresponding:

(a) density versus volume (ρ-V) graph,

(b) pressure versus volume (P-V) graph and

(c) density versus pressure (ρ-P) graph.



ANSWERS

Introductory Exercise 18.1

1. (a) -6.8×10^4 J (b) 1.78×10^5 J, out of gas (c) No

2. (a) Positive (b) Into the system (c) In loop 1, into the system, In loop 2, out of the system

3. (a) No (b) No (c) No **4.** 2.67×10^{-2} mol **5.** 11609.99762 J

Introductory Exercise 18.2

1. (a) 316 K (b) 310 K **3.** (a) -150 J (b) -400 J

4. (a) 241 K (b) 383 K (c) 1770 J (d) 1770 J **5.** (a) 200 J (b) 0.80°C

7.

Process	Q	W	ΔU
BC	−	0	−
CA	−	−	−
AB	+	+	+

8. 166 J **9.** 1.18 MJ

Introductory Exercise 18.3

1. 1.4 **2.** 0.6 kJ, 1.0 kJ, 1.6 **3.** 1.68×10^3 W

For JEE Main

Subjective Questions

1. 327 J **2.** (a) 316 K (b) 310 K **3.** $\Delta U = \frac{nR\Delta T}{\gamma - 1}$ for all processes **4.** 10^4 J

5. $C = 3.1R$ **6.** 2.49 kJ **7.** 113°C **8.** Into gas **9.** (33599.98) J

10. 2.75×10^4 J **11.** (a) 169 J (b) 2087 J

12. (a) -1.15×10^5 J (b) 2.55×10^5 J out of gas (c) No **13.** (a) 765 J (b) 10.82%

14. (a) P_0V_0 (b) $\frac{5}{2}P_0V_0$, $3P_0V_0$ (c) $\frac{P_0V_0}{2}$ (d) $\frac{25P_0V_0}{8R}$ **15.** (a) 1153 J (b) 1153 J (c) zero

16. 18.18% **17.** (a) absorbs (b) 7200 J (c) liberates 7200 J

18. (a) positive (b) I→ positive, II→ negative (c) into the system
(d) I→ into the system II→ out of the system.

19. $T_A = 273$ K, $T_B = 546$ K, $V_C = 44.8\ \text{m}^3$ **20.** (a) 0.50 J (b) 0.50 J

21. (a) $W_{12} = \frac{-P_0M}{\rho_0}\ln(2)$, $W_{23} = \frac{P_0M}{\rho_0}$, $W_{31} = 0$ (b) $\frac{P_0M}{\rho_0}\left(\frac{3}{2} + \ln 2\right)$ (c) $\frac{2}{5}(1 - \ln 2)$

22. (b) -2460 J **23.** 10.82%

Objective Questions

1.(b) **2.**(d) **3.**(d) **4.**(c) **5.**(a,b) **6.**(c) **7.**(a) **8.**(c) **9.**(c) **10.**(c)
11(c) **12.**(a) **13.**(a) **14.**(a) **15.**(a) **16.**(c) **17.**(b) **18.**(d) **19.**(a) **20.**(a)
21.(a) **22.**(b) **23.**(d) **24.**(c) **25.**(a) **26.**(a) **27.**(c) **28.**(b) **29.**(c) **30.**(c)
31.(d) **32.**(a) **33.**(b) **34.**(b) **35.**(d) **36.**(d) **37.**(a) **38.**(b) **39.**(c) **40.**(d)
41.(d) **42.**(c) **43.**(c) **44.**(b) **45.**(b) **46.**(c) **47.**(b) **48.**(a) **49.**(b,d) **50.**(a,c)
51.(a,b) **52.**(c,d) **53.**(b)

For JEE Advanced

Assertion and Reason

1. (b) 2. (d) 3. (d) 4. (a) 5. (b) 6. (d) 7. (c) 8. (b) 9. (a) 10. (a or b)

Match the Columns

1. (a) → r (b) → p (c) → s (d) → p
2. (a) → s (b) → s (c) → s (d) → r
3. (a) → p (b) → s (c) → s (d) → s
4. (a) → q (b) → p,r (c) → p (d) → p
5. (a) → s (b) → s (c) → r (d) → s

Subjective Questions

1. 136 J 2. (b) $3RT_0 \ln(2) - \frac{3}{2}RT_0$ (c) $3RT_0 \ln(2) - \frac{21}{4}RT_0$

3. (b) 113.1 L, 0.44×10^5 N/m^2 (c) 12479 J 4. (a) 800 K (b) 720 J

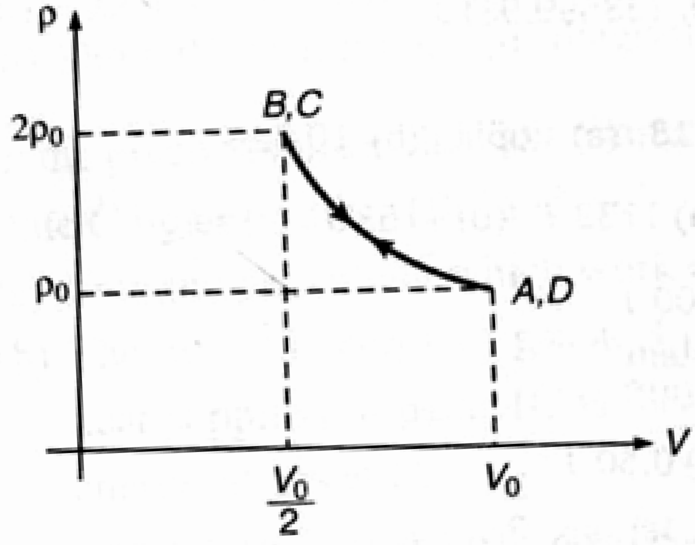
5. (a) 80 J (b) $\frac{9R}{2}$ 6. (a) $Q_{ABC} = -2P_0V_0$ (b) $\Delta U_{ABC} = 0$ 7. $Ve^{-\left(\frac{3a}{2R}\right)T^2}$ = constant

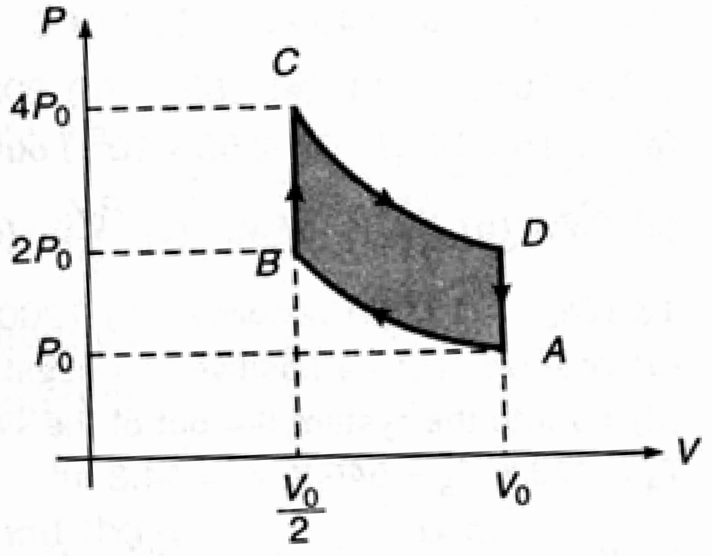
8. (a) 207.75 J (b) $2R$ 9. $RT(1 - \ln 2)$ 10. $\frac{7R}{2}$, $4R(T_2 - T_1)$

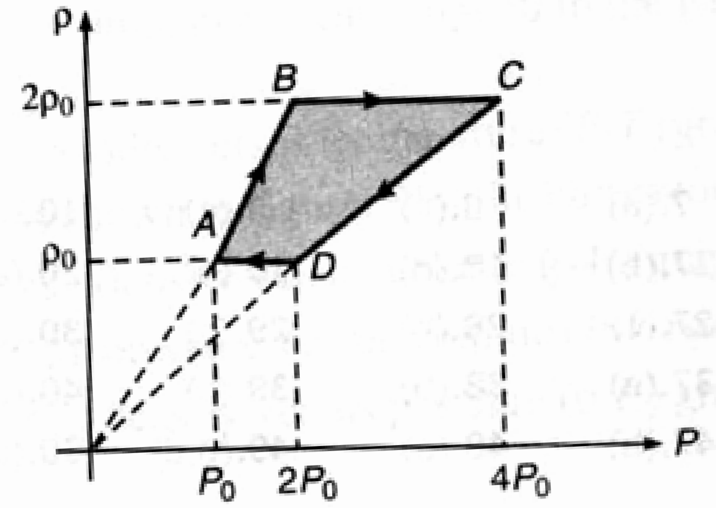
11. $\frac{(2-\gamma)R\Delta T}{(\gamma - 1)}$ 12. 25.8% 13. $\alpha(T_2 - T_1) - \beta(T_2^2 - T_1^2)$ 14. (a) $\frac{23}{3}P_0, \frac{23}{3}T_0$

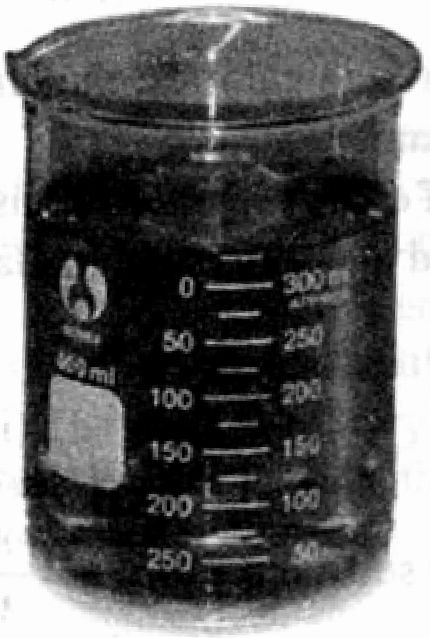
15. (a) AC (b) 150 J (c) 10 J

16.









19

CALORIMETRY & HEAT TRANSFER

Chapter Contents

19.1 Specific Heat

When heat energy flows into a substance, the temperature of the substance usually rises. An exception occurs during a change in phase, as when water freezes or evaporates. The amount of heat required to produce the same temperature increase for a given amount of substance varies from one substance to another. The relationship between heat exchanged and the corresponding temperature change is characterized by the **specific heat** c of a substance. If the temperature of a substance of mass m changes from T to $T + dT$ when it exchanges an amount of heat dQ with its surroundings then its specific heat is

$$c = \frac{1}{m} \cdot \frac{dQ}{dT} \qquad \text{...(i)}$$

The SI unit of specific heat is J/kg-K. Because heat is so frequently measured in calories, the unit cal/g-°C is also used quite often. The specific heat capacity of water is approximately 1 cal/g-°C.

From Eq. (i), we can define the specific heat of a substance as "the amount of energy needed to raise the temperature of unit mass of that substance by 1°C (or 1 K)". A closely related quantity is the **Molar heat capacity** $\boldsymbol{C}$. It is defined as,

$$C = \frac{1}{n} \cdot \frac{dQ}{dT} \qquad \text{...(ii)}$$

where n is the number of moles of the substance. If M is the molecular mass of the substance, then $n = \dfrac{m}{M}$ where m is the mass of the substance and,

$$C = \frac{M}{m} \cdot \frac{dQ}{dT} \qquad \text{...(iii)}$$

The SI unit of molar heat capacity C is, J/mol-K and it can be defined as "the amount of energy needed to raise the temperature of one mole of a substance by 1°C (or 1 K) sometimes the product of mc is also written as C, simply the **heat capacity**, which is defined as the energy needed to raise the temperature of the whole substance by 1°C (or K)".

Thus,
$$C = mc = \frac{dQ}{dT} \qquad \text{...(iv)}$$

The SI units of C are J/K.

Note 1. *In general, if c varies with temperature over the interval, then the corresponding expression for Q is,*

$$Q = m\int_{T_1}^{T_2} c \cdot dT$$

2. *The specific heat of water is much larger than that of most other substances. Consequently, for the same amount of added heat, the temperature change of a given mass of water is generally less than that for the same mass of another substance. For this reason a large body of water moderates the climate of nearby land. In the winter the water cools off more slowly than the surrounding land and tends to warm the land. In the summer, the opposite effect occurs, as the water heats up more slowly than the land.*

Sample Example 19.1 *When 400 J of heat are added to a 0.1 kg sample of metal, its temperature increases by 20°C. What is the specific heat of the metal?*

Solution Using
$$c=\frac{1}{m}\cdot\frac{\Delta Q}{\Delta T}$$

we have
$$c=\left(\frac{1}{0.1}\right)\left(\frac{400}{20}\right)$$
$$=200\ \text{J/kg-°C}$$

19.2 Phase Changes, Latent Heat

Suppose that we slowly heat a cube of ice whose temperature is below 0°C at atmospheric pressure, what changes do we observe in the ice? Initially we find that its temperature increases according to equation

$$Q=mc\,(T_2-T_1)$$

Once 0°C is reached, the additional heat does not increase the temperature of the ice. Instead, the ice melts and temperature remains at 0°C. The temperature of the water then starts to rise and eventually reaches 100°C, whereupon the water vaporizes into steam at this same temperature.

During phase transitions (solid to liquid or liquid to gas) the added heat causes a change in the positions of the molecules relative to one another, without affecting the temperature.

The heat necessary to change a unit mass of a substance from one phase to another is called the **latent heat (L).** Thus, the amount of heat required for melting and vaporizing a substance of mass m are given by,

$$Q=mL \qquad \text{...(i)}$$

For a solid-liquid transition, the latent heat is known as the **latent heat of fusion (L_f)** and for the liquid-gas transition, it is known as the **latent heat of vaporization (L_v).**

For water at 1 atmosphere latent heat of fusion is 80.0 cal/g. This simply means 80.0 cal of heat are required to melt 1.0 g of water or 80.0 cal heat is liberated when 1.0 g of water freezes at 0°C. Similarly latent heat of vaporization for water at 1 atmosphere is 539 cal/g.

Figure shows how the temperature varies when we add heat continuously to a specimen of ice with an initial temperature below 0°C. Suppose we have taken 1 g of ice at –20°C specific heat of ice is 0.53 cal/g-°C.

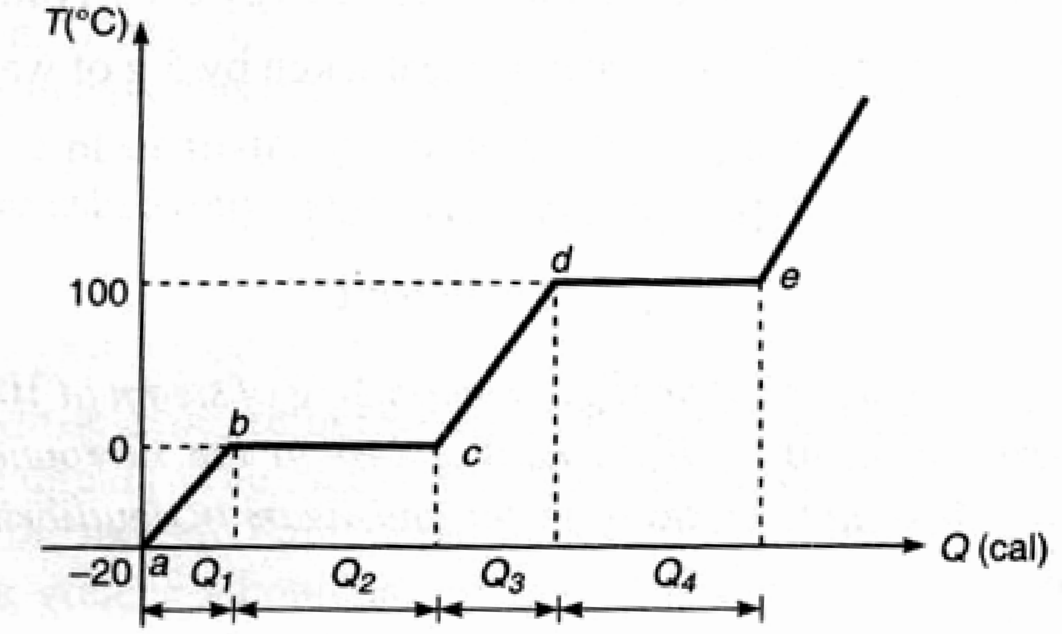


Fig. 19.1

In the figure :

***a* to *b* :** Temperature of ice increases until it reaches its melting point 0°C.

$$Q_1=mc_{\text{ice}}\,[0-(-20)]=(1)\,(0.53)\,(20)=10.6\,\text{cal}$$

***b* to *c* :** Temperature remains constant until all the ice has melted.

$$Q_2 = mL_f = (1)\,(80) = 80\,\text{cal}$$

***c* to *d* :** Temperature of water again rises until it reaches its boiling point 100°C.

$$Q_3 = mc_{\text{water}}\,[100 - 0] = (1)\,(1.0)\,(100) = 100\,\text{cal}$$

***d* to *e* :** Temperature is again constant until all the water is transformed into the vapour phase.

$$Q_4 = mL_v = (1)\,(539) = 539\,\text{cal}$$

Thus, the net heat required to convert 1 g of ice at $-20°\text{C}$ into steam at 100°C is

$$Q = Q_1 + Q_2 + Q_3 + Q_4 = 729.6\,\text{cal}$$

Sample Example 19.2 *How much heat is required to convert 8.0 g of ice at -15°C to steam at 100°C? (Given $c_{ice} = 0.53$ cal/g-°C, $L_f = 80$ cal/g and $L_v = 539$ cal/g, and $c_{water} = 1$ cal/g-°C)*

Solution

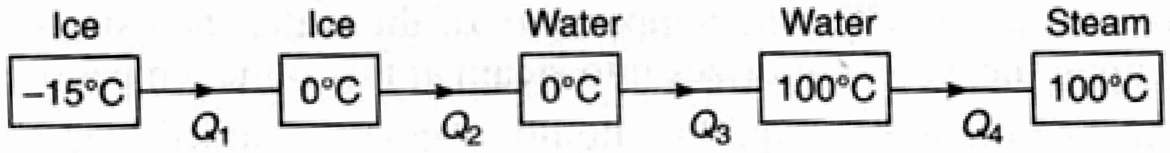


Fig. 19.2

$$Q_1 = mc_{\text{ice}}\,(T_f - T_i) = (8.0)\,(0.53)\,[0 - (-15)] = 63.6\,\text{cal}$$
$$Q_2 = mL_f = (8)\,(80) = 640\,\text{cal}$$
$$Q_3 = mc_{\text{water}}\,(T_f - T_i) = (8.0)\,(1.0)\,[100 - 0] = 800\,\text{cal}$$
$$Q_4 = mL_v = (8.0)\,(539) = 4312\,\text{cal}$$

∴ Net heat required

$$Q = Q_1 + Q_2 + Q_3 + Q_4 = 5815.6\,\text{cal}$$

Sample Example 19.3 *10 g of water at 70°C is mixed with 5 g of water at 30°C. Find the temperature of the mixture in equilibrium.*

Solution Let $t°\text{C}$ be the temperature of the mixture. From energy conservation,

Heat given by 10 g of water = Heat taken by 5 g of water

or $$m_1 c_{\text{water}}\,|\Delta t_1| = m_2 c_{\text{water}}\,|\Delta t_2|$$

∴ $$(10)\,(70 - t) = 5\,(t - 30)$$

∴ $$t = 56.67°\text{C}$$

Sample Example 19.4 *In a container of negligible mass 30 g of steam at 100°C is added to 200 g of water that has a temperature of 40°C. If no heat is lost to the surroundings, what is the final temperature of the system? Also find masses of water and steam in equilibrium. Take $L_v = 539$ cal/g and $c_{water} = 1$ cal/g-°C.*

Solution Let Q be the heat required to convert 200 g of water at 40°C into 100°C, then

$$\begin{aligned} Q &= mc\Delta T \\ &= (200)\,(1.0)\,(100 - 40) \\ &= 12{,}000\,\text{cal} \end{aligned}$$

Now, suppose m_0 mass of steam converts into water to liberate this much amount of heat, then

$$m_0 = \frac{Q}{L} = \frac{12000}{539} = 22.26\,\text{g}$$

Since it is less than 30 g, the temperature of the mixture is 100°C. **Ans.**

$$\text{Mass of steam in the mixture} = 30 - 22.26 = 7.74\,\text{g}$$ **Ans.**

and $$\text{mass of water in the mixture} = 200 + 22.26 = 222.26\,\text{g}$$ **Ans.**

Introductory Exercise 19.1

Take $c_{\text{ice}} = 0.53$ cal/g-°C, $c_{\text{water}} = 1.0$ cal/g-°C, $(L_f)_{\text{water}} = 80$ cal/g and $(L_v)_{\text{water}} = 529$ cal/g unless given in the question.

1. In a container of negligible mass 140 g of ice initially at −15° C is added to 200 g of water that has a temperature of 40°C. If no heat is lost to the surroundings, what is the final temperature of the system and masses of water and ice in mixture?
2. The temperatures of equal masses of three different liquids *A*, *B* and *C* are 12°C, 19°C and 28°C respectively. The temperature when *A* and *B* are mixed is 16°C and when *B* and *C* are mixed is 23°C. What would be the temperature when *A* and *C* are mixed?
3. Equal masses of ice (at 0°C) and water are in contact. Find the temperature of water needed to just melt the complete ice.
4. A closely thermally insulated vessel contains 100 g of water at 0°C. If the air from this vessel is rapidly pumped out, intensive evaporation will produce cooling and as a result of this water freeze. How much ice will be formed by this method? If latent heat of fusion is 80 cal/g and of evaporation 560 cal/g.
   [**Hint :** If m g ice is formed, $mL_f = (100 - m)\,L_v$]
5. A nuclear power plant generates 500 MW of waste heat that must be carried away by water pumped from a lake. If the water temperature is to rise by 10°C, what is the required flow rate in kg/s?

19.3 Heat Transfer

Heat can be transferred from one place to the other by any of three possible ways : **conduction, convection** and **radiation.** In the first two processes, a medium is necessary for the heat transfer. Radiation, however, does no have this restriction. This is also the fastest mode of heat transfer, in which heat is transferred from one place to the other in the form of electromagnetic radiation. In competition examinations problems are asked only in first and last. So, we will discuss conduction and radiation in detail.

Conduction

Figure shows a rod whose ends are in thermal contact with a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2. The sides of the rod are covered with insulating medium, so the transport of heat is along the rod, not through the sides. The molecules at the hot reservoir have greater vibrational energy. This energy is transferred by collisions to the atoms at the end face of the rod. These atoms in turn transfer energy to their neighbours further along the rod. Such transfer of heat through a substance in which heat is transported without direct mass transport is called conduction.

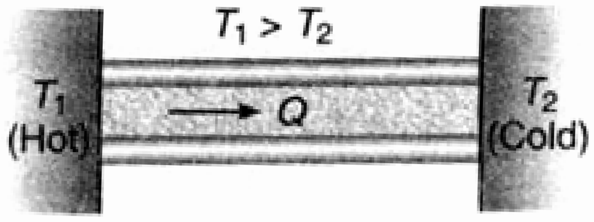


Fig. 19.3

Most metals use another, more effective mechanism to conduct heat. The free electrons, which move throughout the metal can rapidly carry energy from the hotter to cooler regions, so metals are generally good conductors of heat. The presence of 'free' electrons also causes most metals to be good electrical conductors. A metal rod at 5°C feels colder than a piece of wood at 5°C because heat can flow more easily from your hand into the metal.

Heat transfer occurs only between regions that are at different temperatures, and the rate of heat flow is $\frac{dQ}{dt}$. This rate is also called the **heat current**, denoted by H. Experiments show that the heat current is proportional to the cross-section area A of the rod and to the temperature gradient $\frac{dT}{dx}$, which is the rate of change of temperature with distance along the bar. In general

$$H = \frac{dQ}{dt} = -kA\frac{dT}{dx} \qquad \text{...(i)}$$

The negative sign is used to make $\frac{dQ}{dt}$ a positive quantity since $\frac{dT}{dx}$ is negative. The constant k, called the **thermal conductivity** is a measure of the ability of a material to conduct heat.

A substance with a large thermal conductivity k is a good heat conductor. The value of k depends on the temperature, increasing slightly with increasing temperature, but k can be taken to be practically constant throughout a substance if the temperature difference between its ends is not too great.

Let us apply Eq. (i) to a rod of length L and constant cross sectional area A in which a steady state has been reached. In a steady state the temperature at each point is constant in time. Hence,

$$-\frac{dT}{dx} = T_1 - T_2$$

Therefore, the heat ΔQ transferred in time Δt is

$$\Delta Q = kA\left(\frac{T_1 - T_2}{L}\right)\Delta t \qquad \text{...(ii)}$$

Thermal Resistance (R)

Eq. (ii) in differential form can be written as

$$\frac{dQ}{dt} = H = \frac{\Delta T}{l/kA} = \frac{\Delta T}{R} \qquad \text{...(iii)}$$

Here, ΔT = temperature difference (TD) and

$R = \frac{l}{kA}$ = thermal resistance of the rod.

• *Important Points in* CONDUCTION

1. Consider a section *ab* of a rod as shown in figure. Suppose Q_1 heat enters into the section at '*a*' and Q_2 leaves at '*b*', then $Q_2 < Q_1$. Part of the energy $Q_1 - Q_2$ is utilized in raising the temperature of section *ab* and the remaining is lost to atmosphere through *ab*. If heat is continuously supplied from the left end of the rod, a stage comes when temperature of the section becomes constant. In that case, $Q_1 = Q_2$ if rod is insulated from the surroundings (or loss through *ab* is zero). This is called the **steady state** condition. Thus, in steady state temperature of different sections of the rod becomes constant (but not same).

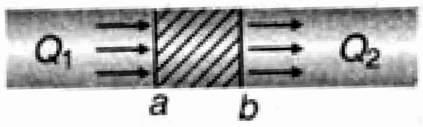


Fig. 19.4