Chemical Engineering

Thermodynamics

Comprehensive Theory

with Solved Examples and Practice Questions

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Thermodynamics

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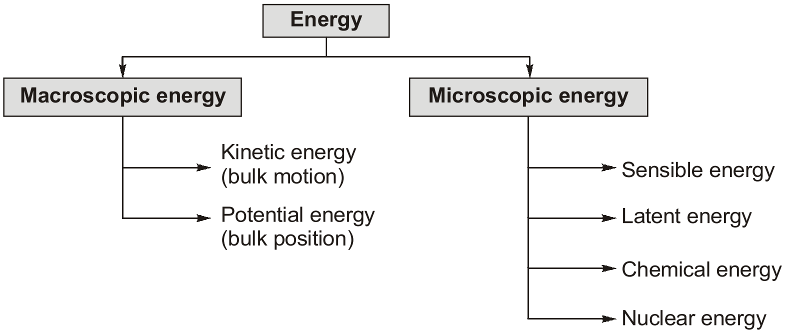
CHAPTER 02

Energy and Energy Interactions

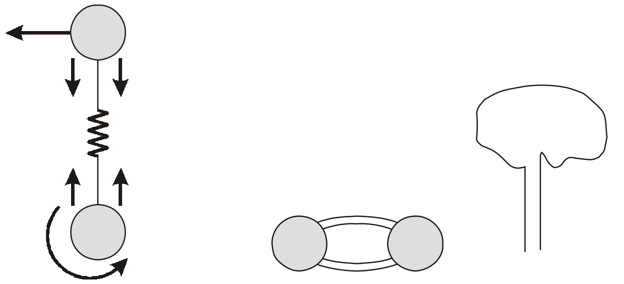
2.1 INTRODUCTION

- Energy can exist in numerous forms such as thermal, mechanical, kinetic, potential, electrical, magnetic, chemical and nuclear, and their sum constitutes total energy *E* of the system. Thermodynamics provides no information about the absolute value of the total energy. It deals only with the change of the total energy.
- In thermodynamics, the various forms of energy are considered in two groups, macroscopic and microscopic forms of energy.
- The energy possessed by the system as a whole with respect to an external reference frame constitute macroscopic forms of energy, such as kinetic and potential energies.
- The energy possessed by the system with respect to then molecular structure and molecular level interactions constitute microscopic forms of energy. The sum of all microscopic forms of energy of a system is called its internal energy and is denoted by *U*.



NOTE

Sensible energy → due to molecular kinetic energy and is temperature dependent.
Latent energy → associated with phase of the system and comes into picture during phase change.
Chemical energy → associated with atomic bonds in a molecule.
Nuclear energy → associated with strong bonds within the nucleus.



Sensible and latent energy Chemical energy Nuclear energy

Figure 2.1 Internal energy of a system is sum of all microscopic energies

- Energy interaction for a closed system with its surroundings can take place in two ways:
  (a) by work transfer (b) by heat transfer
- Work and heat are modes of energy transfer. The discussion related to their quality will be done later in the second law of thermodynamics.

2.2 Work

- The work is said to be done by a force when it acts on a body moving in the direction of force. This definition of work is more suitable from mechanics point of view.
- In thermodynamics, work transfer is considered occurring between the system and the surroundings. Work is said to be done by the system if the sole effect on the things external to the system can be converted into raising of weights, though the weight may not be actually raised.
- In Fig. 2.2 (a), a battery is connected to a motor which is in turn driving a fan. The system is doing work on the surroundings. When the fan is replaced by a pulley and a weight as shown in Fig. 2.2 (b), the sole effect on things external to the system is then the raising of a weight.

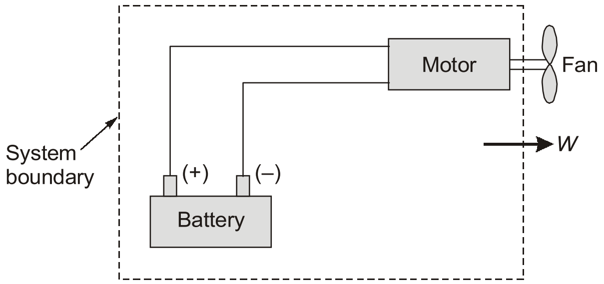


Figure 2.2 (a)

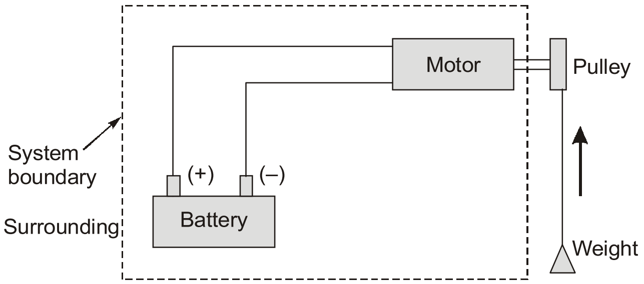


Figure 2.2 (b)

Remember : Force should act on the system boundary and it should cause some displacement in the surroundings. Hence this is also called boundary work.

Types of Work Interaction

(i) Expansion and compression work (Displacement work) – this has been dealt with in detail later.

(ii) Stretching of wire: If a wire is stretched by length dL due to force *F*, then work done on the system.

$$\delta W = Fdl$$

(iii) Electrical work: Electricity flowing in or out is always deemed to be work.

$$\delta W = VI\,dt$$

(iv) Work done in stretching of liquid film: If the soap film is stretched through an area dA.

then, $$\delta W = \sigma dA$$

where σ is the surface tension. Other examples include work of a reversible chemical cell; work of polarization and magnetization etc.

2.3 Closed System Analysis

2.3.1 pdV or Displacement Work

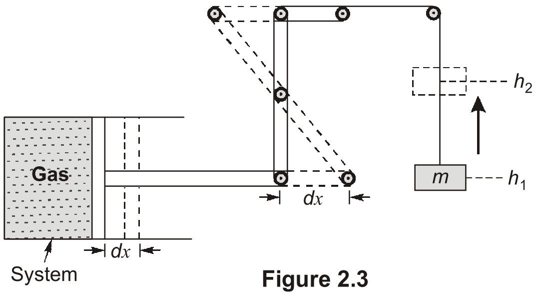


Figure 2.3

- Let us consider the raising of the mass m from an initial elevation h_1 to a final elevation h_2 against gravitational force. To raise this mass, the force acting on the mass is given by $F = mg$.

  Thus the work done on the body is $W = mg\,(h_2 - h_1)$.
- From fig 2.3, it can be seen that expansion of the gas gets reduced to raising of a mass against gravitational force.

$$\delta W = F\,dx$$
$$= PA\,dx$$

Now, $$dV = A\,dx \quad \{\text{small change in volume}\}$$

$\therefore$ $$\delta W = Pd\,V$$

Hence total work: $$W = \int \delta W = \int_1^2 PdV \qquad \text{...(i)}$$

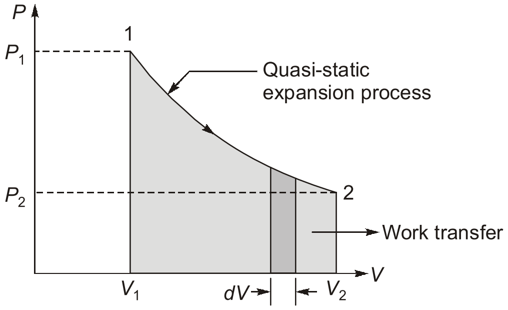


Figure 2.4

- Plotting the above process on a P-V diagram, assuming the process to be quasi-static Fig. 2.4.
- When the piston moves infinitely slowly, the process is reversible and we get a solid line on the P-V diagram. The integration $\int PdV$ gives the work which is actually the area enclosed under the curve on P-V diagram.

Remember : The equation (i), $W = \int PdV$ is applicable for **(a)** Closed system, **(b)** Quasi-static (reversible) process.

- **Sign convention:** The signs of work and heat transfer are arbitrarily chosen. The most followed sign convention for work transfer is:

  Work done by the system is +ve

  Work done on the system is –ve

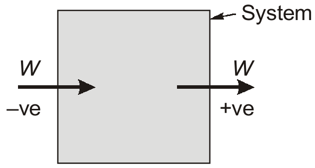


Figure 2.5

Remember : Work is done by a system to overcome some resistance, since vacuum does not offer any resistance there is no work transfer involves in free expansion.

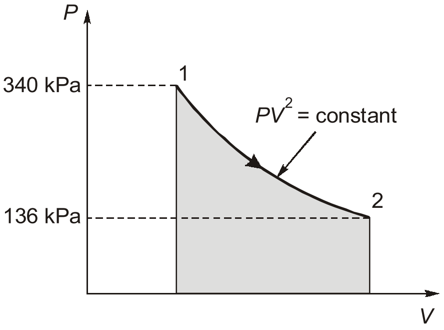
NOTE

- All left to right processes on the P-V diagram represent work done by the gas or the system hence are taken positive in nature and vice versa.
- Area enclosed by a cycle on P-V diagram represents net work interaction during the cycle.
- All clockwise cycles on P-V diagram are power producing cycles and vice versa.

Example 2.1 A gas expands from an initial state with P_1 = 340 kPa and V_1 = 0.0425 m^3 to a final state where P_2 = 136 kPa. If the pressure volume relationship during the process is PV^2 = constant, determine the work in kJ.

Solution :

Refer to figure



Given: $P_1 = 340\text{ kPa},\quad P_2 = 136\text{ kPa},\quad V_1 = 0.0425\text{ m}^3$

As $PV^2 = C$ {Polytropic process with $n = 2$}

$\therefore\ P_1V_1^2 = P_2V_2^2$ {Applying between (1) and (2)}

Assumption: (i) Gas is ideal gas (ii) Process is quasi-static

Putting values $340 \times 0.0425^2 = 136 \times V_2^2$

$\Rightarrow\ V_2 = 0.0672\text{ m}^3$

We know for a polytropic process,

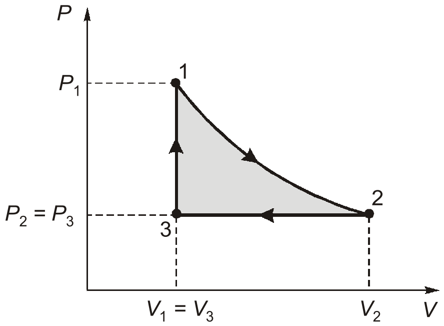
$$W = \frac{P_1V_1 - P_2V_2}{n-1}$$

$$= \frac{340 \times 0.0425 - 136 \times 0.0672}{2-1} = 5.311\text{ kJ}$$

Example 2.2 Unit mass of a fluid is contained in a cylinder at an initial pressure of 20 bar. The fluid is allowed to expand reversibly behind a piston according to law PV^2 = constant until the volume is doubled. The fluid is then cooled reversibly at constant pressure until the piston regains its original position; heat is then supplied reversibly with the piston firmly locked in position until the pressure rises to original value of 20 bar. Calculate the net work done by the fluid, for an initial volume of 0.05 m^3.

Solution :

The following P-V diagram is plotted with the help of processes given in the problem.



Process 1-2 → Polytropic

Process 2-3 → Isobaric

Process 3-1 → Isochoric

Assumption:

1. Fluid is ideal gas
2. Processes are quasi-static

Given: $P_1 = 20\text{ bar},\quad V_1 = 0.05\text{ m}^3$

and $PV^2 = C$ for process 1-2,

$V_2 = 2V_1 = 0.1\text{ m}^3$

$\therefore$ For process 1-2, $P_1V_1^2 = P_2V_2^2$

$$20 \times 0.05^2 = P_2 \times 0.1^2$$

$$P_2 = 5 \text{ bar}$$

$\therefore$ $$W_{1\text{-}2} = \frac{P_1V_1 - P_2V_2}{n-1} \qquad \{\text{Polytropic process work}\}$$

$\Rightarrow$ $$W_{1\text{-}2} = \frac{20 \times 0.05 - 5 \times 0.1}{2-1} \times 10^5 \text{ J} = 50 \text{ kJ}$$

For process 2-3, $V_3 = V_1 \quad P_2 = P_3$

$\therefore$ $$W_{2\text{-}3} = P_2(V_3 - V_2)$$

$$= 5(0.05 - 0.1) \times 100 \text{ kJ}$$

$$W_{2\text{-}3} = -25 \text{ kJ} \qquad \{\text{–ve sign implies work done on the fluid}\}$$

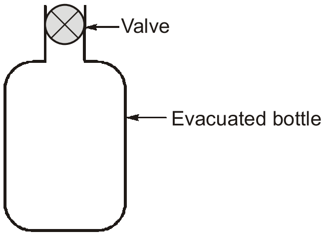
For process 3-1, $W_{3\text{-}1} = 0$ {Isochoric process}

$\therefore$ $$W_{net} = W_{1\text{-}2} + W_{2\text{-}3} + W_{3\text{-}1}$$

$$= 50 - 25 \text{ kJ} = \mathbf{25 \text{ kJ}}$$

NOTE : As W_{net} comes out to be positive, this implies that it is a work producing cycle.

Example 2.3 When the valve of the evacuated bottle as shown in figure is opened atmospheric air rushes into it. If the atmospheric pressure is 101.325 kPa and 0.6 m³ of air (measured at atmospheric condition) enters into the bottle, calculate the work done by air.



Solution :

If we take outside air as our system, then the displacement work done by the air

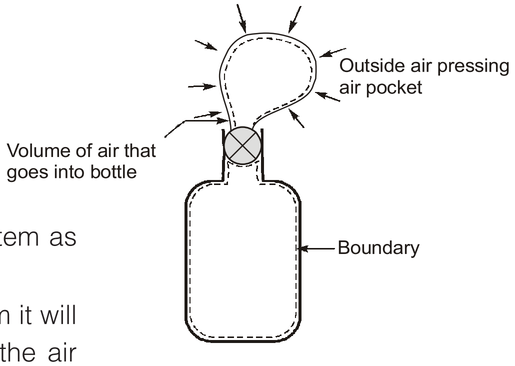
$$W = P_0 \Delta V$$

where P_0 = Atmosphere pressure

ΔV = Change in volume

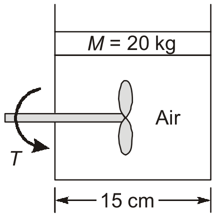
$\therefore$ $$W = 101.325 \times 0.6$$

$$W = \mathbf{60.8 \text{ kJ}}$$



- This work done is positive if we consider our system as surrounding air (as it pushes air into the bottle).
- If we consider air entering the bottle as our system it will be negative as that amount of work is done on the air entering to make it enter the bottle.

Example 2.4 A paddle wheel as shown in figure requires a torque of 25 Nm to rotate at 100 rpm. If it rotates for 20 seconds, calculate the net work done by the air if the frictionless piston rises by 1 m during this time [Assume P_{atm} = 101.325 kPa]



Solution :

Given: $T = 25$ Nm, $N = 100$ rpm, $t = 20$ s

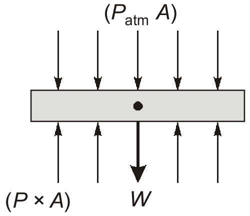
Displacement of piston, $x = 1$ m

The work input by paddle wheel, $W_{in} = -T\omega\Delta t$

{–ve assuming our system is air and work is done on it}

$$= -T \times \frac{2\pi N}{60} \times \Delta t = -25 \times \frac{2\pi \times 100}{60} \times 20$$

$$W_{in} = -5.236 \text{ kJ}$$



The work needed to raise the piston requires that the pressure of air be known. It is found as follows:

FBD of piston

$$\therefore \quad PA = P_{atm}A + W$$

$$\frac{P\pi(0.15)^2}{4} = 101.325 \times 10^3 \times \frac{\pi}{4}(0.15)^2 + 20 \times 9.81$$

$$P = 112.428 \text{ kPa}$$

The work done by the air to raise the piston is then

$$W_{op} = P\Delta V$$

$$= P \times A \times x = 112.428 \times \frac{\pi}{4}(0.15)^2 \times 1 = 1.987 \text{kJ}$$

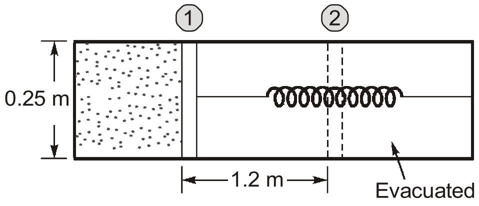
$$\therefore \quad W_{net} = W_{in} + W_{op} = -5.236 + 1.987 = \mathbf{-3.249 \text{ kJ}}$$

NOTE : The negative sign implies that overall work is being supplied to the system.

Example 2.5 A closed cylinder of 0.25 m diameter is fitted with a light frictionless piston. The piston is retained in position by a catch in the cylinder wall and the volume on one side of the piston contains air at pressure of 750 kN/m^2. The volume on the other side of piston is evacuated. A helical spring is mounted coaxially with the cylinder in this evacuated space to give a force of 120 N on the piston in this position. The catch is released and the piston travels along the cylinder until it comes to rest after a stroke of 1.2 m. The piston is then held in its position of maximum travel by a ratchet mechanisms. The spring force increases linearly with piston displacement to a final value of 5 kN. Calculate the work done by the compressed air on the piston.

Solution :

Refer to the following figure



Given: $F_1 = 120$ N,

$F_2 = 5000$ N,

$P_1 = 750$ kPa

The work done by the gas results in compression of the spring.

Method 1: By integration

Let the piston moves by a distance x.

Spring force at this position, $F_x = 120 + kx$

where k is the spring constant

when $\quad x = 1.2$ m,

$$F_x = 5000\text{ N}$$

i.e. $\quad 5000 = 120 + k \times 1.2$

$$k = 4066.67\text{ N/m}$$

$\therefore$ Work done by the gas = Workdone by the spring force on the spring

$$\Rightarrow \quad W = \int_0^x F_x dx = \int_0^{1.2} (120 + 4066.67x)\,dx$$

$$= \left[120x + 4066.67\frac{x^2}{2}\right]_0^{1.2} = 120 \times 1.2 + 4066.67 \times \frac{1.2^2}{2}$$

$$= 3072.24\text{ J} = \mathbf{3.072\text{ kJ}}$$

Example 2.6 A system of volumes V contains a mass m of gas at pressure P and temperature T. The macroscopic properties of the system obey the following relationship:

$$\left(P + \frac{a}{V^2}\right)(V - b) = mRT$$

where a, b and R are constants.

Obtain an expression for the displacement work done by the system during a constant-temperature expansion from volume V_1 to volume V_2. Calculate the work done by a system which contains 10 kg of this gas expanding from 1 m^3 to 10 m^3 at a temperature of 293 K. Use the values of $a = 15.7 \times 10^4$ Nm^4, $b = 1.07 \times 10^{-2}$ m^3 and $R = 0.287$ kJ/kgK.

Solution :

Assumption: The expansion process is quasistatic and the system is a closed system.

Given: Process is isothermal.

$$\therefore \quad \left(P + \frac{a}{V^2}\right)(V - b) = \text{mRT} = \text{constant }(k) \qquad \text{...(i)}$$

$$\text{Work done, } W = \int_1^2 PdV \qquad \text{...(ii)}$$

from equation (i), we get

$$P + \frac{a}{V^2} = \frac{mRT}{V - b}$$

or

$$P = \frac{mRT}{V - b} - \frac{a}{V^2}$$

Substituting this expression in equation (ii), we get

$$W = \int_1^2 \left(\frac{mRT}{V - b} - \frac{a}{V^2}\right)dV = \left[mRT\ \ln(V - b) + \frac{a}{V}\right]_1^2$$

$$W = mRT\ \ln\left(\frac{V_2 - b}{V_1 - b}\right) + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

Now, given: $\quad m = 10$ kg, $\quad T = 293$ K, $\quad R = 0.287$ kJ/kgK

$$a = 15.7 \times 10^4\text{ Nm}^4, \quad b = 1.07 \times 10^{-2}\text{ m}^3$$

$$V_2 = 10\text{ m}^3, \quad V_1 = 1\text{ m}^3$$

Substituting the values in the obtained expression.

we get

$$W = 10 \times 0.287 \times 293 \ln\left(\frac{10 - 1.07 \times 10^{-2}}{1 - 1.07 \times 10^{-2}}\right) + \frac{15.7 \times 10^4}{10^3}\left(\frac{1}{10} - \frac{1}{1}\right)$$

$$= 1803.11 \text{ kJ}$$

Remember : Carefully balance the units in big expressions to avoid silly mistakes.

2.3.4 Realization of Various Processes

- This section gives an idea of how the various processes mentioned in section 2.3.3 are actually realized.

1. Isochoric Process: This process is said to have occurred if it is carried out in a rigid container.
2. Isobaric Process: This process occurs when the piston is free to move and the external forces are not changing during the process.
3. Isothermal Process: If an isothermal process has to be carried out for a single phase of a substance then it must be carried out infinitely slowly (quasi-statically). If isothermal process is fast then it must be for the phase change of a substance.
4. Adiabatic Process: A quasistatic adiabatic process can be realized only with perfect insulation. However if an adiabatic process has to be realized without insulation then it must be carried out in a very fast manner.
5. Polytropic Process: (For $1 < n < \gamma$) In this process even though the heat transfer takes place but it is not isothermal since energy going out in the form of work exceeds the energy added in the form of heat.

   It is a process somewhere in between isothermal and adiabatic processes.

NOTE : The above situations are helpful in deciding the type of process followed by the system while solving problems.

2.4 Ideal Gas

- It is a hypothetical gas which obeys the law $PV = mRT$ at all pressures and temperature.

Remember : $PV = mRT$ is also called the equation of state.

- Real gases do not confirm to this equation of state with complete accuracy. As $P \to 0$ or $T \to \infty$; the real gas approaches the ideal gas behaviour.
- Two common assumptions made in order to consider real gases as ideal gas are:
  1. Inter-molecular forces are negligible.
  2. Volume occupied by the gas molecules is negligible compared to the container volume.
- Two favourable conditions for a real gas to behave closely as an ideal gas are:
  1. Low pressure
  2. High temperature

Objective Brain Teasers

Q.1 A 2 kW electric resistance heater in a room is turned on and kept on for 30 min. The amount of energy transferred to the room is

(a) 1800 kJ (b) 3600 kJ
(c) 7200 kJ (d) 900 kJ

Q.2 In a hot summer day, the air in a well sealed room is circulated by a 0.60 hp fan driven by a 70% efficient motor. The rate of energy supply from the fan motor assembly to the room is

(a) 0.981 kJ/s (b) 0.754 kJ/s
(c) 0.639 kJ/s (d) 0.4721 kJ/s

Q.3 Thermodynamic work is the product of

(a) two intensive properties
(b) two extensive properties
(c) an intensive property and change in an extensive property
(d) an extensive property and change in an intensive property

4. Match **List-I** (Parameter) with **List-II** (Property) and select the correct answer using the codes given below the lists:

List-I	List-II
A. Volume	1. Path function
B. Density	2. Intensive property
C. Pressure	3. Extensive property
D. Work	4. Point function

Codes:

	A	B	C	D
(a)	3	2	4	1
(b)	3	2	1	4
(c)	2	3	4	1
(d)	2	3	1	4

Q.5 A man is pulling a bucket of water up to the roof of a building of 6 m height. The total weight of the rope is 20 N and the weight of the bucket with water is 100 N. The work done by the man is

(a) 720 Nm (b) 660 Nm
(c) 420 Nm (d) 600 Nm

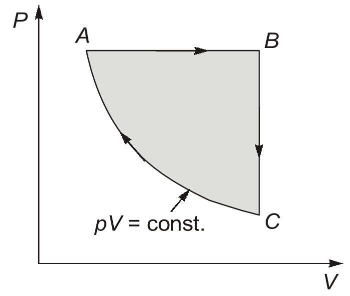
Q.6 One kg of a perfect gas is compressed from pressure P_1 to pressure P_2 by

1. Isothermal process
2. Adiabatic process
3. The law $PV^{1.1}$ = constant

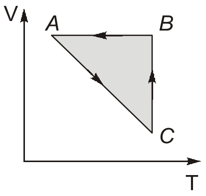
The correct sequence of there processes in increasing order of their slope on p-v diagram is:

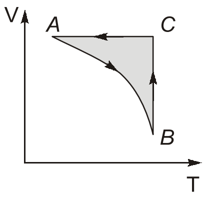
(a) 1, 2, 3 (b) 1, 3, 2
(c) 2, 3, 1 (d) 3, 1, 2

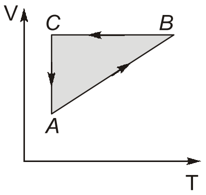
Q.7 A cyclic process *ABC* is shown on a *P-V* diagram

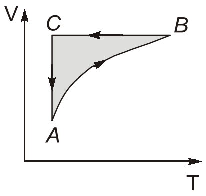


The same process on V-T diagram will be represented by

(a)


(b)


(c)


(d)


Q.8 Polytropic index *n* is given by

(a) $\dfrac{\mathrm{In}(P_2 / P_1)}{\mathrm{In}(V_1 / V_2)}$ (b) $\dfrac{\mathrm{In}(P_1 / P_2)}{\mathrm{In}(V_1 / V_2)}$

(c) $\dfrac{\mathrm{In}(V_1 / V_2)}{\mathrm{In}(P_2 / P_1)}$ (d) $\dfrac{\mathrm{In}(V_2 / V_1)}{\mathrm{In}(P_2 / P_1)}$

Q.9 Reversible adiabatic process may be expressed as $\frac{T_1}{T_2}$ equal to

(a) $(V_2/V_1)^{\gamma+1}$ (b) $(V_2/V_1)^{(\gamma+1)/\gamma}$
(c) $(P_1/P_2)^{(\gamma-1)/\gamma}$ (d) $(P_1/P_2)^{\gamma-1}$

Q.10 A gas is so expanded in a cylinder that its temperature remains constant. The resulting variation of pressure vs volume is

(a) A parabola (b) A hyperbola
(c) A straight line (d) None of these

Q.11 When air expands from initial pressure, P_1 and volume V_1 to final volume $5V_1$ following the law $pV^n = C$

(a) greater the value of n, greater the work obtained
(b) smaller the value of n, smaller the work obtained
(c) for $n = 0$, the work obtained is greatest
(d) for $n = 1.4$, the work obtained is greatest

Q.12 When the gas expands under adiabatic conditions, its temperature

(a) increase (b) decreases
(c) does not change (d) None of these

Q.13 What mass of steam at 100°C must be mixed with 150 g of ice at 0°C, in a thermally insulated container to produce liquid water at 50°C?

Take L_f of ice = 333 kJ/kg, L_V of water = 2256 kJ/kg and c of water = 4.19 kJ/kgK.

(a) 0.022 kg (b) 0.033 kg
(c) 0.044 kg (d) 0.055 kg

Linked Date Question Q.14 to Q.15

An aluminium electric kettle of mass 0.560 kg contours a 2.4 kW heating element. It is filled with 0.640 L of water at 12°C.

Given $c_{Al} = 0.9$ kJ/kgK, $c_{water} = 4.19$ kJ/kgK, L_V for water = 2256 kJ/kgK, $\rho_{water} = 998$ kg/m^3

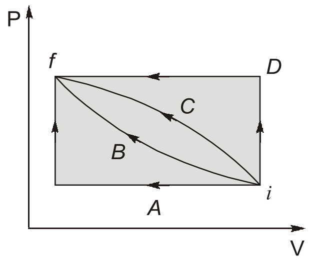
Q.14 How long will it take for the boiling to begin?

(a) 105 s (b) 110 s
(c) 117 s (d) 134 s

Q.15 Total time taken for the kettle to boil dry (Assume that the temperature of the kettle does not exceed 100°C at any time)

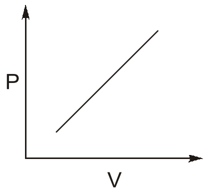
(a) 117 s (b) 600 s
(c) 483 s (d) 717 s

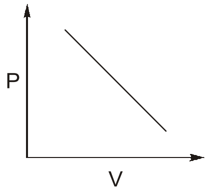
Q.16 In which of the paths between initial state i and final state f in the below figure is the work done on the gas, the greatest?

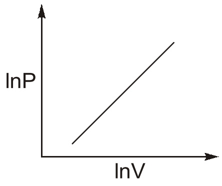


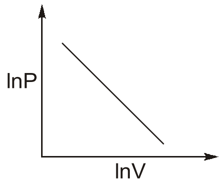
(a) A (b) B
(c) C (d) D

Q.17 In a closed system, the adiabatic reversible expansion of an ideal gas with constant specific heats is represented by

(a)


(b)


(c)


(d)


■ ANSWERS

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

Hints & Explanation

1. (b)

Given, $P = 2$ kW; $t = 30$ min

$\therefore$ Energy supplied to room

$= $ Energy used by heater

$= P \times t = 2 \times 30 \times 60$

$= 3600$ kJ

2. (c)

$$P_{\text{fan}} = 0.6 \text{ hp}; \qquad \eta_{\text{motor}} = 0.7$$

$$1 \text{ hp} = 746 \text{ W} = 0.746 \text{ kW}$$

$$\therefore \quad P_{\text{fan}} = 0.6 \times 0.746 \text{ kW}$$

$$P_{\text{supplied}} = \frac{P_{\text{fan}}}{\eta_{\text{motor}}} = \frac{0.6 \times 0.746}{0.7}$$

$$= 0.639 \text{ kJ/s}$$

3. (c)

We know by definition thermodynamic work

$W = $ displacement work

$$= \int p dv$$

here, $p = $ intensive property

and $V = $ extensive property

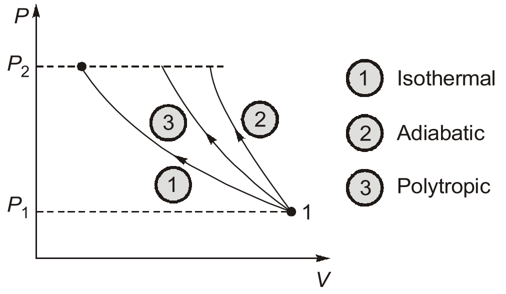
Hence option (c) is correct

5. (b)

$$\text{Work done} = 100 \times 6 + 20 \times \frac{6}{2}$$

$$= 660 \text{ N}$$

6. (b)



$\therefore$ The correct sequence of slope in increasing order is 1, 3, 2

7. (c)

Process $AB \rightarrow$ Constant pressure

Process $BC \rightarrow$ Constant volume

Process $CA \rightarrow$ isothermal ($pV = C$)

for A-B $\quad pV = mRT$

$\therefore \quad V \propto T \quad \Rightarrow \quad V = kT$

Straight line through origin

8. (a)

For a polytropic process $pV^n = C$

Taking $\log_e$ on both sides, we get

$$\ln P + n \ln V = C'$$

Now applying it in between (1) and (2)

$$\ln P_1 + n \ln V_1 = \ln P_2 + n \ln V_2$$

$$n(\ln V_1 - \ln V_2) = \ln P_2 - \ln P_1$$

$$n = \frac{\ln(P_2 / P_1)}{\ln(V_1 / V_2)}$$

9. (c)

For reversible adiabatic assuming ideal gas

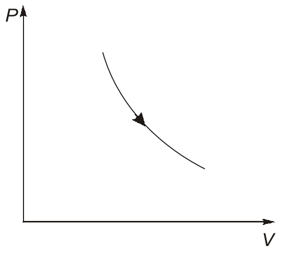
We know $$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

10. (b)

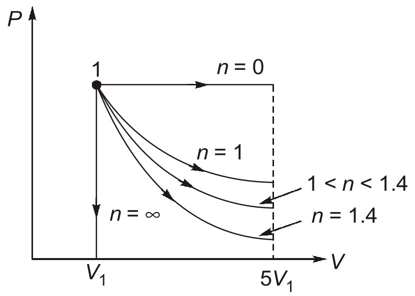
The process is isothermal i.e.

$$pV = \text{Constant}$$

Thus the nature of the curve is a hyperbola



11. (c)



As can be seen, area enclosed under the curve is maximum in case of

$$n = 0$$

$\therefore \quad W_{\max}$ for $n = 0$