Thermodynamics

THERMODYNAMIC SYSTEM

A thermodynamic system refers to a certain portion of universe selected for investigation.

Surroundings

Everything outside the system that can influence its behaviour is known as the surroundings of the system.

Boundary

The envelope which encloses a system and separates it from its surroundings is known as boundary of the system.

* In isolated system neither the energy nor the matter can be exchanged between the system and the surroundings.
* In closed system, only the energy not the matter can be exchanged between the system and surroundings.
* In open system, both the energy as well as matter can be exchanged between the system and the surroundings.

Thermal Equilibrium

A thermodynamical system is said to be in thermodynamical equilibrium when macro variables (like pressure, volume, temperature, mass, composition etc). of the system do not change with time.

ZEROTH LAW OF THERMODYNAMICS

It states that if two systems are in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

HEAT

Heat is the energy transfer arising due to temperature difference between the system, and the surroundings.

○ It is a scalar quantity. Its S.L unit is joule.
○ Calorie is the old unit of heat. 1 calorie is the amount of heat required to raise the temperature of 1 g of water from $14.5°C$ to $15.5°C$.
● 1 cal = 4.186 J.
○ It is path dependent.
○ Heat absorbed by a system is taken as positive while the heat lost by the system is taken as negative.

WORK

Work is the energy transfer brought about by other means such as moving the piston of a cylinder containing the gas, by raising or lowering some weight connected to it.

○ It is a scalar quantity. Its SI unit is joule.
○ It is path dependent.
○ Work done by a system is taken as positive while the work done on a system is taken as negative.
○ In P-V diagram (also called indicator diagram) the area under PV curve represents work done.
○ In a cyclic process work done is equal to the area under the cycle and is positive if the cycle is clockwise and negative if the cycle is anticlockwise.

INTERNAL ENERGY

Internal energy of a system is the sum of kinetic energy and potential energy of the molecular constituents of the system.

* Change in internal energy is path independent and depends only on the initial and final states of the system.
* Change in internal energy in a cyclic process is always zero.
* The increase in internal energy of a system is taken as positive while decrease in internal energy is taken as negative.

THERMODYNAMIC VARIABLES

These are macroscopic physical quantities like pressure (P), volume (V) and temperature (T) etc. which are used to describe the state of the system. The relation between these variables is called equation of state. Heat and work are not thermodynamic variables.

* Thermodynamic variables are of two kinds.
  (i) Extensive   (ii) Intensive
* Internal energy U, volume V, total mass M are extensive variables. Pressure P, temperature T and density ρ are intensive variables.

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is the general law of conservation of energy applied to any system in which energy transfer from or to the surroundings (through

heat and work) is taken into account. It states that

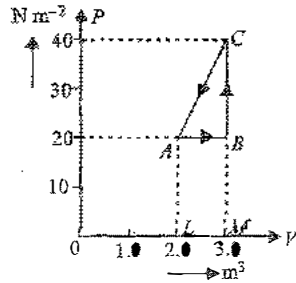$$\Delta Q = \Delta U + \Delta W$$

where ΔQ is the heat supplied to the system, ΔW is the work done by the system and ΔU is the change in internal energy of the system.

Illustration 1

Calculate the workdone.

(a) Along path AB
(b) Along path BC
(c) Along path CA
(d) For the whole cycle.

The indicator diagram, between P and V, is as shown.

Soln.: Workdone is positive when gas expands and negative when gas contracts.

In P-V diagram, P is represented along y-axis and V is taken along x-axis. Workdone is positive if the cycle is clockwise and workdone is negative if cycle is anticlockwise.

(a) Workdone $= P \times$ change in volume ΔV

$W_{AB} = 20 \times (3 - 2) = 20 \times 1 = 20$ J

(b) $W_{BC} =$ Pressure $\times (3 - 3) =$ zero.

= zero, as there is no change of volume.

(c) $W_{CA} =$ It is negative because volume decreases.

$= -$ Area of $CALMC = -$ Area of $(ABC + ABML)$

$$= -\left(\frac{1}{2} \times 1 \times 20 + AB \times BM\right)$$
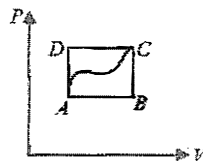
$= -(10 + 1 \times 20) = -30$ J

(d) For whole cycle,

workdone $= -$ area of $\triangle ABC = -\dfrac{1 \times 20}{2}$

∴ workdone for whole cycle $= -10$ J

Note : For whole cycle, we may consider $W_{AB} + W_{BC} + W_{CA}$ also. Result is the same

Illustration 2

In the indicator diagram, we have

(a) Change in internal energy along ABC is 10 J.

(b) Workdone along path $AB = 20$ J

(c) $U_C = 5$ J

(d) Heat absorbed by the system along path AD is 5 J.

Calculate

(a) Change in internal energy along the path CDA

(b) Heat given to the system along path ABC.

(c) Value of U_A.

(d) Change in internal energy along AD.

Soln.: (a) $U_C - U_A = 10$ J

∴ $U_A - U_C = -10$ J

(b) $\Delta Q = \Delta U + \Delta W = (U_C - U_A) + \Delta W$

or $\Delta Q = 10 + 20 = 30$ J

(c) $\Delta Q = (U_C - U_A) + \Delta W$

or $U_A = U_C + \Delta W - \Delta Q = 5 + 20 - 30 = -5$ J

or $U_A = -5$ J

(d) $U_D - U_A = \Delta Q_{(AD)} - \Delta W_{AD} = 5 - 0 = 5$ J.

Illustration 3

A certain mass of gas is carried from A to B, along three paths via ACB, ADB and AEB. Indicate the path along which the work done is
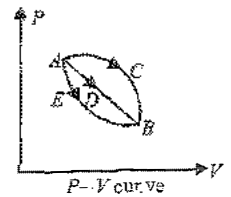
(a) Maximum
(b) Minimum.

P-V curve

Soln.: Workdone by a gas depends on the area enclosed between the P-V curve and the volume axis.

(a) The area enclosed by curve ACB is maximum. Hence workdone is maximum along path ACB.

(b) The area enclosed by curve AEB is minimum. Hence workdone is minimum along path AEB.

Illustration 4

The P-V curves in two cases are shown, as a smaller circle x and a bigger circle y, in the figure. Indicate whether the net workdone is positive or negative.
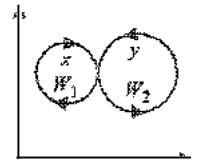
Sol. The cyclic process x is clockwise. Hence the workdone W_1 is positive. The cyclic process y is anticlockwise. Hence the workdone W_2 is negative.

∵ Area of $y >$ Area of x

∴ $W_2 > W_1$

∴ Net workdone will be negative.

Illustration 5

If heat given to a system is 6 kcal and workdone is 6 kJ, then calculate the change in internal energy.

Soln. : $\Delta Q = \Delta U + \Delta W$

∴ $\Delta U = \Delta Q - \Delta W = (6 \times 1000 \times 4.2) - (6 \times 1000)$

$= 6000 (4.2 - 1) = 6000 \times 3.2$

$= 19.2 \times 1000 = 19.2$ kJ.

THERMODYNAMIC PROCESSES

Quasi-static Process

An infinitely slow process in which the system remains in thermal and mechanical equilibrium with the surroundings.

Isothermal Process

A thermodynamic process in which the temperature remains constant.

Equation of isothermal process $PV = $ constant.
Work done during isothermal process,

$$W = \mu RT \ln\left(\frac{V_2}{V_1}\right); \; W = \mu RT \ln\left(\frac{P_1}{P_2}\right)$$

- The slope of isothermal curve on a P-V diagram at any point on the curve is given by

$$\frac{\Delta P}{\Delta V} = -\frac{P}{V}$$

Illustration 6

Two gram-moles of a gas are compressed isothermally at 273 K from 10 m^3 to 1 m^3. Calculate the workdone during compression.

Soln.: Workdone in an isothermal change $= 2.3nRT$

$$\log_{10}\left(\frac{V_2}{V_1}\right)$$

$\therefore$ $W = 2.3 \times 2 \times 8.4 \times 273 \times \log_{10}\left(\frac{1.0}{10}\right)$

or $W = 2.3 \times 2 \times 8.4 \times 273 \times [\log_{10} 1 - \log_{10} 10]$

or $W = -2.3 \times 2 \times 8.4 \times 273$

or $W = -10548$ J.

Here work is done on the gas. The energy will be absorbed during compression. This is the indication of negative work in an isothermal change.

Illustration 7

Which of the following is correct for the case of isothermal expansion of an ideal gas?
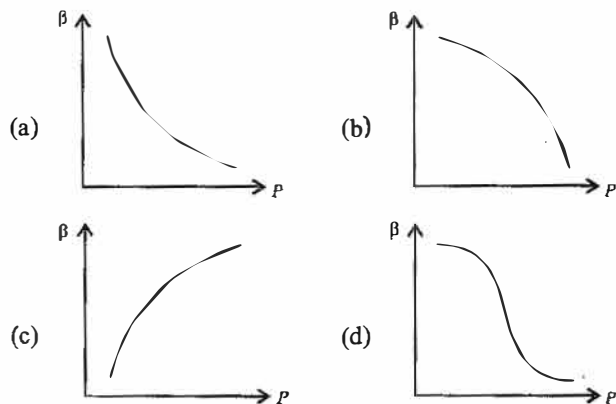
(a) $Q = 0$ (b) $W = 0$
(c) $\Delta U = 0$ (d) $\Delta U \neq 0$

Soln. (c) : For isothermal process, $\Delta T = 0$

$\Rightarrow$ $\Delta U = nC_V \Delta T = 0$.

Illustration 8

Which of the following graphs correctly represents the variation of $\beta = -\left(\frac{dV}{dP}\right)\frac{1}{V}$ with P for an ideal gas at constant temperature?

β ↑
(a)
→ P

β ↑
(b)
→ P

β ↑
(c)
→ P

β ↑
(d)
→ P

Soln. (a) : For an ideal gas, the differential form of gas law is

$VdP + PdV = nRdT$

At constant temperature $dT = 0$

$\Rightarrow VdP + PdV = 0$

$PdV = -VdP$

$\frac{-dV}{dP} = \left(\frac{V}{P}\right)$ or $-\left(\frac{dV}{dP}\right)\frac{1}{V} = \frac{1}{P} \Rightarrow \beta = \frac{1}{P}$

$\beta P = $ constant

Hence the graph could be a rectangular hyperbola as shown in (a).

Adiabatic Process

A thermodynamic process in which no heat flow between the system and the surroundings.

○ Equation of adiabatic process, $PV^\gamma = $ constant where $\gamma = C_P/C_V$.
Other equations of adiabatic process are
○ $P^{1-\gamma} T^\gamma = $ constant
○ $TV^{\gamma-1} = $ constant
○ Work done during adiabatic process,

$$W = \frac{(P_1 V_1 - P_2 V_2)}{(\gamma - 1)}; \; W = \frac{\mu R(T_1 - T_2)}{\gamma - 1}$$

- The slope of adiabatic curve on a P-V diagram at any point on the curve is given by

$$\frac{\Delta P}{\Delta V} = -\gamma\left(\frac{P}{V}\right)$$

- In adiabatic expansion, temperature decreases while in adiabatic compression, temperature increases.

Isochoric (Isometric) Process

A thermodynamic process in which volume remains constant.

○ Equation of isochoric process : $\frac{P}{T} = $ constant.
○ No work done by the gas in an isochoric process.
○ The slope of the isochoric curve on a P-V diagram is infinite.

Isobaric Process

A thermodynamic process in which pressure remains constant.

○ Equation of isobaric process,
○ Work done during isobaric process,
$W = P(V_2 - V_1) = \mu R(T_2 - T_1)$.
○ The slope of the isobaric curve on a P-V diagram is zero.

Illustration 9

The pressure P_1 and density d_1 of a diatomic gas ($\gamma = 7/5$) change to P_2 and d_2 during an adiabatic operation. If $\frac{d_2}{d_1} = 32$, find $\frac{P_2}{P_1}$.

Soln.: In an adiabatic operation, $P_1 V_1^\gamma = P_2 V_2^\gamma$

$\therefore$ $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma = \left(\frac{m}{d_1} \times \frac{d_2}{m}\right)^\gamma = \left(\frac{d_2}{d_1}\right)^\gamma$

$$\therefore \quad \frac{P_2}{P_1} = (32)^{7/5} = (2^5)^{7/5} = 2^7 = 128 \quad \therefore \frac{P_2}{P_1} = 128.$$

Illustration 10

The volume of air increases by 2% in its adiabatic expansion. Calculate the percentage decrease in pressure.

Sol. For an adiabatic change,

$$PV^\gamma = \text{constant} \qquad \qquad ...(i)$$

Here $\gamma = \dfrac{C_P}{C_V} = 1.4$ for air

Take log and differentiate, equation (i)
i.e., $\log P + \gamma \log V = \log \text{(constant)}$

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

$$\text{or} \quad \frac{dP}{P} = -\gamma \frac{dV}{V} = -1.4 \times \frac{2}{100} = -\frac{2.8}{100}$$

$$\text{or} \quad \frac{dP}{P} \times 100 = -2.8.$$

[Minus sign shows decrease in pressure.]
$\therefore$ Percentage decrease in pressure = 2.8%.

Illustration 11

Two moles of an ideal monoatomic gas occupy a volume V at 27°C. The gas expands adiabatically to a volume $8V$. Find the change in internal energy of the system.

$$\left[\text{Given } C_V = \frac{3R}{2} \text{ J mol}^{-1} \, ^\circ\text{C}^{-1} \right]$$

Soln.: For an adiabatic change, $TV^{\gamma-1} = \text{constant}$

$$\therefore \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} = \left(\frac{V}{8V} \right)^{\frac{5}{3}-1} = \left(\frac{1}{8} \right)^{2/3}$$

Here, $\gamma = \dfrac{5}{3}$ for monoatomic gas

$$= \left(\frac{1}{2^3} \right)^{2/3} = \left(\frac{1}{2} \right)^2 = \frac{1}{4}$$

$$\text{or} \quad T_2 = \frac{T_1}{4} = \frac{(273+27)}{4} = \frac{300}{4} = 75 \text{ K}$$

Now, $\Delta U = nC_V \, dT$

$$\text{or} \quad \Delta U = 2 \times \frac{3R}{2} \times (75 - 300) = 3 \times 8.3 \times (-225)$$

$$= 5602.5 \text{ J}$$

Illustration 12

Ten moles of N_2, contained at constant pressure, is heated from 27°C to 527°C. Calculate the amount of heat required. $R = 2$ cal/(mol × °C).

Sol. For N_2, $C_P = \dfrac{7R}{2} = \dfrac{7 \times 2}{2} = 7 \dfrac{\text{cal}}{\text{mol} \times {}^\circ\text{C}}$

Amount of heat required $= nC_P \, dT = 10 \times 7 \times 500$ cal
$= 35000$ cal $= 35000 \times 4.2$ J $= 147000$ J
$= 1.47 \times 10^5$ J.

Illustration 13

The pressure of a gas, during an adiabatic operation, is found to be proportional to the cube of its absolute temperature. Calculate the ratio of specific heats of the gas.

Soln.: In an adiabatic operation, $P \propto T^{\frac{\gamma}{\gamma-1}}$

Given: $P \propto T^3$

$$\therefore \quad \frac{\gamma}{\gamma-1} = 3 \Rightarrow 3\gamma - 3 = \gamma \Rightarrow \gamma = \frac{3}{2} \quad \therefore \frac{C_P}{C_V} = \frac{3}{2}.$$

Illustration 14

A monatomic 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 the gas column, before and after expansion respectively,

then $\dfrac{T_1}{T_2}$ is given by

(a) $\left(\dfrac{L_1}{L_2} \right)^{2/3}$ (b) $\left(\dfrac{L_2}{L_1} \right)^{2/3}$

(c) L_1/L_2 (d) L_2/L_1.

Soln. (b) : For monatomic gas, $\gamma = 5/3$

For adiabatic process, $TV^{\gamma-1} = \text{constant}$

$$\therefore \quad T_1(L_1 A)^{2/3} = T_2(L_2 A)^{2/3}$$

$$\therefore \quad \frac{T_1}{T_2} = \left(\frac{L_2}{L_1} \right)^{2/3}.$$

SECOND LAW OF THERMODYNAMICS

Kelvin-Planck Statement

No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

Clausius Statement

No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process

* A reversible process is one which can be retraced in the opposite direction.
* A quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is an example of a reversible process.

Irreversible Process

* An irreversible process is one which cannot be retraced back in the opposite direction.
* All spontaneous processes of nature are irreversible processes. e.g. transfer of heat from a hot body to a cold body, diffusion of gases, etc. are all irreversible processes.

HEAT ENGINE

* It is a device which converts heat energy into the mechanical energy.

- Every heat engine basically consists of three parts:
  - a hot reservoir called source
  - a working substance
  - a cold reservoir called sink
- The schematic diagram of a heat engine is shown below:
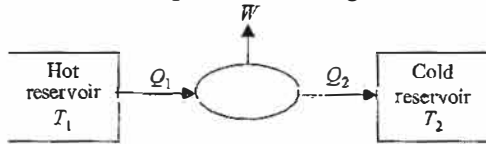
- The efficiency of a heat engine is given by

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

CARNOT ENGINE

- Carnot engine is a reversible heat engine operating between two temperatures T_1 (source) and T_2 (sink).

Carnot Cycle

- Carnot engine works in series of operations. The operations consist of an isothermal expansion and then adiabatic expansion. Further operations are isothermal compression and adiabatic compression so that the working substance is back at the initial state at the end of each cycle. This cycle of operations is called Carnot cycle.
- The efficiency of a Carnot engine is given by

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

- The efficiency of Carnot engine depends on the temperature of source (T_1) and temperature of the sink (T_2), but does not depend upon the nature of the working substance.

Carnot Theorem

- No heat engine operating between two given temperatures can be more efficient than a Carnot engine operating between the same two temperatures.

Illustration 15

A Carnot engine maintains constant efficiency between 27 K and 527 K and between T Kelvin and 1054 K. Determine the unknown temperature.

Soln.: Efficiency of Carnot's engine $(\eta) = 1 - \frac{T_2}{T_1}$

$\therefore \quad 1 - \frac{27}{527} = 1 - \frac{T}{1054}$

or $\quad T = \frac{27 \times 1054}{527} = 27 \times 2 = 54$ K

$\therefore$ Unknown temperature = 54 K.

Illustration 16

A Carnot's engine extracts 1.5×10^3 kilocalorie of heat from a reservoir at 627°C and exhausts it to a sink maintained at 27°C. How much work is performed by the engine?

Soln.: Efficiency of Carnot engine $\eta = 1 - \frac{T_2}{T_1}$

Work performed = ηQ

$\therefore$ Work performed by engine $= \left(1 - \frac{T_2}{T_1}\right) Q$

$\therefore \quad W = \left(1 - \frac{300}{900}\right) \times (1.5 \times 10^3 \times 10^3)$ cal

or $\quad W = \frac{2}{3} \times 1.5 \times 10^6 \times 4.2$ J $= 4.2 \times 10^6$ J

$\therefore \quad W = 4.2 \times 10^6$ J.

Illustration 17

A reversible heat engine converts one-sixth of heat, which it extracts from source, into work. When the temperature of the sink is reduced by 40°C, its efficiency is doubled. Find the temperature of source.

Soln.: Efficiency $\eta = \frac{W}{Q_1} = \frac{1}{6}$

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

or $\quad \frac{1}{6} = 1 - \frac{T_2}{T_1} \Rightarrow T_2 = \frac{5T_1}{6}$ ...(i)

Finally, efficiency $= 2\eta = \frac{2 \times 1}{6} = \frac{1}{3}$

$\therefore \quad \frac{1}{3} = 1 - \frac{T_2 - 40}{T_1}$ or $\frac{T_2 - 40}{T_1} = \left(1 - \frac{1}{3}\right) = \frac{2}{3}$

or $2T_1 = 3T_2 - 120$.

Put $T_2 = \frac{5T_1}{6}$ from (i)

or $2T_1 = \left(3 \times \frac{5T_1}{6}\right) - 120$ or $2.5T_1 - 2T_1 = 120$

or $T_1 = \frac{120}{0.5} = 240$ K.

Illustration 18

Four engines are working between
(a) 100 K and 80 K   (b) 40 K and 20 K
(c) 60 K and 40 K   (d) 120 K and 100 K.
Which one has maximum efficiency?

Sol. Efficiency $\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$
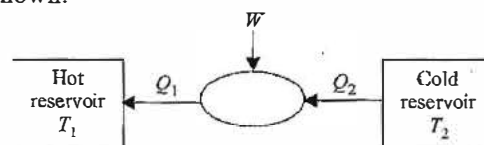In all the four cases, given above,
$\qquad T_1 - T_2 = 20$ K.
$\therefore \quad \eta$ is highest when T_1 is lowest.
$\therefore \quad$ At option (b), 40 K and 20 K, has maximum efficiency.

REFRIGERATOR OR HEAT PUMP

- A refrigerator or heat pump is basically a heat engine run in reverse direction.
- The schematic diagram of a refrigerator or heat pump is shown.

• The coefficient of performance of a refrigerator is given by

$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

Illustration 19

A refrigerator whose coefficient of performance is 5 extracts heat from the cooling compartment at the rate of 250 J per cycle. How much electric energy is spent per cycle? How much heat per cycle is discharged to the room?

Soln.: $\beta = \dfrac{Q_2}{W}$

$\therefore \quad W = \dfrac{Q_2}{\beta} = \dfrac{250}{5} = 50$ J

$\therefore$ Electric energy spent per cycle = 50 J
Again, $Q_1 = Q_2 + W$
or $Q_1 = 250 + 50$ or $Q_1 = 300$ J
$\therefore$ Heat energy discharged per cycle to room = 300 J.

Illustration 20

Find the coefficient of performance of a refrigerator working between 10°C and 20°C.

Soln.: $T_1 = 273 + 20 = 293$ K
$T_2 = 273 + 10 = 283$ K

$\therefore \quad \beta = \dfrac{T_2}{T_1 - T_2} = \dfrac{283}{293 - 283} = \dfrac{283}{10} = 28.3.$