CHAPTER – 12

THERMODYNAMICS

Thermodynamics means heat flow. Thermodynamics deals with the conversion of heat into work and work into heat.

Thermal equilibrium

Two systems are said to be in thermal equilibrium, if their temperatures are the same. Then there will not be any heat flow from one system to another.

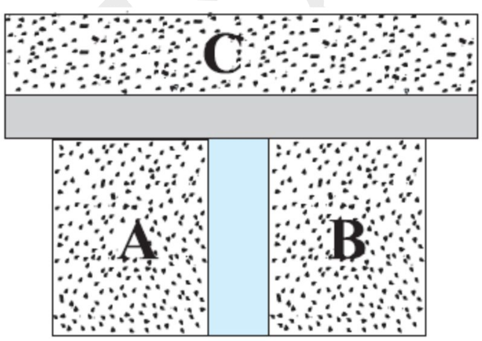
Internal energy

It is the sum of all kinetic energies and potential energies of the molecules of the system.

Zeroth Law of thermodynamics

This law was formulated by **R.H. Fowler**.

The law states that "two systems which are in thermal equilibrium with a third system separately are in thermal equilibrium with each other."



First Law of thermodynamics

The first law of thermodynamics is a statement of law of conservation of energy.

The law states that "If an amount of heat is given to a system, a part of the heat is used to increase the internal energy and other part is used to do the external work"

$$\boxed{\Delta Q = \Delta U + \Delta W}$$

ΔQ = Heat supplied to the system.

ΔU = change in internal energy

ΔW = workdone by the system

But $\Delta W = P\Delta V$

$$\therefore \boxed{\Delta Q = \Delta U + P\Delta V}$$

Thermodynamic state variables

The physical quantities which characterise a system are known as state variables.

Eg: - Pressure, volume, temperature, mass, density, internal energy, heat capacity, specific heat capacity etc.

Thermodynamic state variables are of two types:

i) Intensive state variables

They are the state variables which do not depend on the size of the system.

Eg: - Pressure, temperature, density, specific heat capacity etc.

ii) Extensive sate variables

They are the state variables which depend on the size of the system.

Eg: -volume, mass, heat capacity, internal energy etc.

Note: - Heat and work are not state variables.

Thermodynamic Processes

(i) **Quasi - static Process**

A quasi-static process is an infinitely slow process such that the system remains in thermal and mechanical equilibrium with the surroundings throughout the process.

(ii) **Isobaric Process**

In an isobaric process, **pressure is constant** throughout the process.
If heat is applied, the piston moves up. A part of heat supplied is used increase the internal energy and the other part are used to do the work.

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

$\Delta Q = nC_P \Delta T$

$C_P \rightarrow$ Molar specific heat capacity at constant pressure.

(iii) **Isochoric Process**

In an isochoric process, **volume is constant** throughout the process.

$\Delta V = 0$

$\Delta W = P\Delta V = 0$

$\therefore \Delta Q = \Delta U$

The heat supplied is completely used to increase the internal energy.

$\Delta Q = nC_V \Delta T$

$C_V \rightarrow$ molar specific heat capacity at constant volume.

(iv) **Isothermal process**

It is a process taking place at **constant temperature**.
Equation for isothermal process is $\boxed{PV = \text{Constant}}$ [Boyle's law]
(Here the constant is μRT)

Conditions for isothermal process

i. The process must be slow
ii. There should be a perfect conducting wall (diathermic wall) between the system and surroundings.

Eg: - The expansion of a gas in a metallic cylinder placed in a large reservoir of fixed temperature is an example of isothermal process.
Melting of ice at its normal melting point, vaporization of a liquid at its normal boiling point etc. are other examples.

Work done during an isothermal process

Suppose a system of gas is expanding from an initial volume V_1 to a final volume V_2 during an isothermal process.
The work done for the small change in volume '**dV**' is given by

$dW = PdV$

$\therefore$ The total workdone,

$$W = \int_{V_1}^{V_2} dW$$

$$= \int_{V_1}^{V_2} PdV, \quad \text{But } PV = nRT$$

$$\Rightarrow P = \frac{nRT}{V}$$

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$= nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$= nRT \left[\log V\right]_{V_1}^{V_2}$$

$$= nRT \left[\log V_2 - \log V_1\right]$$

But we have, $\log A - \log B = \log \frac{A}{B}$

$$\therefore W = nRT \log\left(\frac{V_2}{V_1}\right)$$

$$\boxed{W = nRT \log\left(\frac{V_2}{V_1}\right)}$$

Adiabatic Process

During an adiabatic process, no heat enters or leaves the system. In an adiabatic process all of the quantities P, V and T changes.

Equations for Adiabatic Process

$$PV^{\gamma} = \text{Constant}, \quad \gamma = \frac{C_p}{C_v}$$

$$\text{or} \quad TV^{\gamma-1} = \text{Constant}$$

$$\text{or} \quad P^{\gamma}V^{1-\gamma} = \text{Constant}$$

Eg: - Sudden burst of an inflated balloon or a tyre tube, propagation of sound through air.

[During a sudden expansion no intake of heat takes place. So the work for the expansion is done using the internal energy of the system. So the internal energy of the system decreases and hence temperature decreases. Thus during an adiabatic expansion cooling is produced.]

Work done during an adiabatic process

The work done during an adiabatic change of an ideal gas from the state (P_1, V_1, T_1) to the stateP_2,V_2, T_2) is given by,

$$W = \int_{V_1}^{V_2} dW$$

$$= \int_{V_1}^{V_2} PdV$$

We have, $PV^{\gamma} = k$

$$\Rightarrow P = \frac{k}{V^{\gamma}}$$

$$\therefore W = \int_{V_1}^{V_2} \frac{k}{V^{\gamma}} dV$$

$$= k\int_{V_1}^{V_2} V^{-\gamma} dV$$

We have, $\int x^n dx = \frac{x^{n+1}}{n+1}$

$$\therefore W = k\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$= \frac{k}{1-\gamma}\left[V^{1-\gamma}\right]_{V_1}^{V_2}$$

$$= \frac{k}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$$= \frac{1}{1-\gamma}\left[kV_2^{1-\gamma} - kV_1^{1-\gamma}\right]$$

But $k = P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$$\therefore W = \frac{1}{1-\gamma}\left[P_2V_2^{\gamma}.V_2^{1-\gamma} - P_1V_1^{\gamma}.V_1^{1-\gamma}\right]$$

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]$$

but $P_1V_1 = nRT_1$ and $P_2V_2 = nRT_2$

$$\therefore W = \frac{1}{1-\gamma}\left[nRT_2 - nRT_1\right]$$

$$= \frac{nR}{1-\gamma}\left[T_2 - T_1\right]$$

$$= \frac{nR}{\gamma-1}\left[T_1 - T_2\right]$$

$$\boxed{W = \frac{nR}{\gamma-1}\left[T_1 - T_2\right]}$$

Problem1: Three moles of an ideal gas kept at a constant temperature of 300 K are compressed from the volume of 10 litres to 5 litres. Calculate the work done to compress this gas.

Ans:

Problem2: Draw indicator diagrams for isothermal and adiabatic processes.

Ans:

Problem3: If a gas is compressed to half its volume first rapidly and then slowly, in which case the work done will be greater?

Ans:

Problem4: A thermos flask contains coffee. It is violently shaken. Considering the coffee as a system answer the following:

a) Does the temperature rise?
b) Has heat been added to it?
c) Has internal energy changed?

Ans:

Problem5: Isothermal, isobaric, isochoric and adiabatic processes are some special thermodynamic processes. In which of these processes, the work done is maximum when the gas expands from V_1 to V_2?

Ans:

Problem6: A gas expands adiabatically so that **50 J** of work is obtained. What is the change in temperature in the above process if the working substance is a monoatomic gas? (R=8.314J/molK)

Ans:

Problem7: A thermodynamic system performs work without taking heat from an external source.

a) Which process is involved in this case?
b) What is the source of energy for this work?
c) By what factor does the pressure of the system decrease if the volume is doubled (γ=1.4).

Cyclic Process

In a cyclic process, the system returns to its initial state.

$\therefore \Delta U = 0$, for a cyclic process.

Then $\Delta Q = \Delta W$

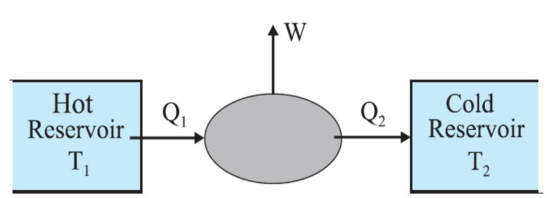
Heat Engines:

Heat engine is a device to convert heat energy in to mechanical energy.

It consist of:

i. A very hot body of large specific heat capacity called the **source**.
ii. A **working substance**. **Eg**: a mixture of fuel vapour and air in a petrol or diesel engine or steam in a steam engine.
iii. **An insulating stand**
iv. A cold body of large specific heat capacity called **sink**.

Schematic representation of a heat engine is given below.



Working substance absorbs heat of amount $\mathbf{Q_1}$ from the source; a part of the heat is converted into useful work

W and other part Q_2 is given to the sink.

Efficiency of a heat engine (η)

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

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

For $Q_2 = 0$, $\eta = 1$

i.e., 100% efficiency for heat engine, which is never possible.

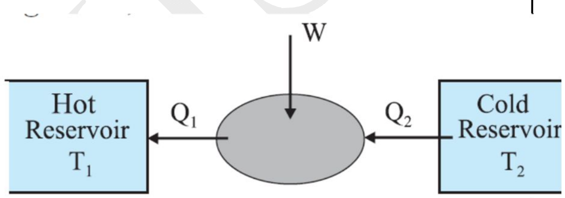
Types of heat engines:

1. **External combustion engine** – in which heat is produced by burning fuel outside the cylinder. Eg: **steam engine**
2. **Internal combustion engine** – in such engines heat is produced by burning fuel inside the cylinder. Eg. Petrol and diesel engines.

Refrigerators and heat Pumps:

A refrigerator works in the reverse order of a heat engine.

The working substance for both refrigerator and heat pump is **Freon**.



Here the working substance absorbs heat Q_2 from the sink, some work **W** is done on the working substance by an external agency and the working substance liberates a large amount of heat Q_1 to the source.

$$Q_1 = Q_2 + W$$

$$\text{or } W = Q_1 - Q_2$$

The coefficient of performance of a refrigerator

$$\boxed{\alpha = \frac{Q_2}{W}} = \frac{Q_2}{Q_1 - Q_2}$$

A heat pump is a device to pump heat into a portion of space (room).

Coefficient of performance of a heat pump

$$\boxed{\alpha = \frac{Q_1}{W}} = \frac{Q_1}{Q_1 - Q_2}$$

[In a refrigerator, sink is the cooling chamber. Source is the room in which the refrigerator is placed. The work (W) is the work done by the compressor by consuming electricity.]

[In a heat pump, sink is the environment outside the room. Source is the room which is to be heated.]

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 heat into work.

Explanation: - This statement says that the complete heat Q_1 cannot be converted into work. Thus the efficiency of a heat engine cannot be 100%.

Clausius Statement: **No process is possible whose sole result is the transfer of heat from a cold reservoir to a hot reservoir.**

Explanation: - This statement says that the transfer of heat from a cold object to a hot object will not takes place if no work is supplied. Thus the coefficient of performance cannot be infinite.

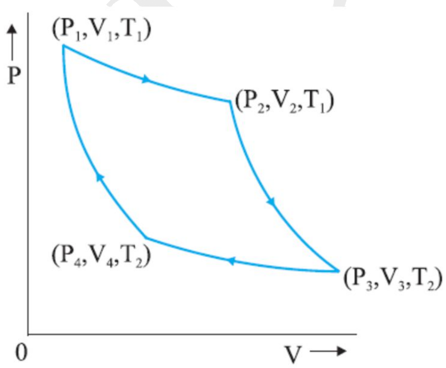
Reversible and irreversible processes

A process is reversible if it can be reversed such that both the system and surroundings return to their initial states, with no other change anywhere else in the universe.

Spontaneous processes of nature are irreversible. The idealised reversible process is a quasi –static process with no dissipative factors such as friction, viscosity etc.

Carnot engine

A reversible heat engine operating between two temperatures is called a Carnot engine. **Nicolas Sadi Carnot** introduced this ideal heat engine whose cycle of operation is called Carnot cycle.



The operation of the engine is completed in four stages:

Step 1→2: Isothermal expansion of the gas from the state (P_1, V_1, T_1) to (P_2, V_2, T_1) by absorbing a heat Q_1 from the source at T_1 K. The work done by the gas during this process.

Step $2 \to 3$: Adiabatic expansion of the gas from (P_2, V_2, T_2) to (P_3, V_3, T_1). Work done bythe gas during this process,

$$W_{2\to3} = \frac{nR}{\gamma-1}[T_1 - T_2]$$

Step $3 \to 4$: Isothermal compression of the gas from (P_3, V_3, T_2) to (P_4, V_4, T_2). Heat released (Q_2) by the gas during this compression is equal to the work done on the system.

$$W_{3\to4} = nRT_2 \log\left(\frac{V_4}{V_3}\right) = Q_2$$

Step $4 \to 1$: Adiabatic compression of the gas from (P_4, V_4, T_2) to (P_1, V_1, T_1). Work done on the gas

$$W_{3\to4} = \frac{nR}{\gamma-1}[T_2 - T_1]$$

$\therefore$ The total work done by the gas in one complete cycle,

$$W = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

$$W = nRT_1 \log\left(\frac{V_2}{V_1}\right) + \frac{nR}{\gamma-1}[T_1 - T_2]$$

$$+ nRT_2 \log\left(\frac{V_4}{V_3}\right) + \frac{nR}{\gamma-1}[T_2 - T_1]$$

$$= nRT_1 \log\left(\frac{V_2}{V_1}\right) + \frac{nR}{\gamma-1}[T_1 - T_2]$$

$$- nRT_2 \log\left(\frac{V_3}{V_4}\right) - \frac{nR}{\gamma-1}[T_1 - T_2]$$

$$W = nRT_1 \log\left(\frac{V_2}{V_1}\right) - nRT_2 \log\left(\frac{V_3}{V_4}\right)$$

The efficiency (η) of the carnot engine

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

$$= 1 - \frac{nRT_2 \log\left(\frac{V_3}{V_4}\right)}{nRT_1 \log\left(\frac{V_2}{V_1}\right)} \ldots\ldots\ldots\ldots\ldots (1)$$

Since step $2 \rightarrow 3$ is an adiabatic process,

$$\therefore T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \Rightarrow \frac{T_2}{T_1} = \frac{V_2^{\gamma-1}}{V_3^{\gamma-1}}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

$$\Rightarrow \frac{V_2}{V_3} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} \ldots\ldots\ldots\ldots (2)$$

Similarly step $4 \rightarrow 1$ is an adiabatic process,

$$\therefore T_2 V_4^{\gamma-1} = T_1 V_1^{\gamma-1} \Rightarrow \frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_4^{\gamma-1}}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$$

$$\Rightarrow \frac{V_1}{V_4} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} \ldots\ldots\ldots\ldots\ldots (3)$$

From (2) and (3)

$$\frac{V_1}{V_4} = \frac{V_2}{V_3} \text{ or } \frac{V_3}{V_4} = \frac{V_2}{V_1} \ldots\ldots\ldots\ldots\ldots (4)$$

Substituting (4) in (1)

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

Carnot's Theorem: -

i) Working between two given temperatures T_1 and T_2 of the hot and cold reservoirs respectively, no engine can have efficiency more than that of the Carnot engine.

ii) The efficiency of the Carnot engine is independent of the nature of the working substance.

Problem8: a) Which law of thermodynamics is used to explain the working of a heat engine?

b) What are the sink, source and working substance of a domestic refrigerator?

Ans:

Problem9: (a) What is the working substance of an ideal heat engine?

(b) Calculate the maximum efficiency of a heat engine working between steam point and ice point. Can you design an engine of 100% efficiency?

Ans:

<u>Problem10:</u> An ideal heat engine utilizes a perfect gas. The source is at **450 K** and sink is at **320 K**. If the engine takes **3600J** per cycle from the source, calculate the efficiency of the engine.

Ans:

<u>Problem 11:</u> a) Which thermodynamic process is called an iso-entropic process?

b) The efficiency of a Carnot engine is 1/6. If on reducing the temperature of the sink by 65^0C, its efficiency becomes 1/3, find the temperature of the sink and source.

Problem12: A Carnot engine working between 527^0C and 127^0C has a work output of 800J per cycle. How much heat is supplied to the engine from the source per cycle?

Ans: