

Thermodynamics

Basic definitions:

Heat: The energy transferred between two or more systems or surroundings as a result of temperature difference only, is called heat

Unit : joule in SI, Calorie in CGS system.

Temperature: Temperature is defined as the thermal condition of a body which determines its ability to describe the relative hotness or coldness of a body.

Unit: Kelvin(K) in absolute scale.

System: The region ay contains a collection of large number of atoms or molecule with in a real or imaginary surroundings

Ex: A gas enclosed in a cylinder having movable piston.

Surroundings: The medium or matter or vacuum that surrounds the system which may participate in the process of exchange of matter or energy or both with the system.

Types of systems: There are three types of systems viz.,

- a) Closed System
- b) Open System
- c) Isolated system.

Closed System: The closed system is the one which exchange only energy with its surroundings, but no exchange of matter with the surroundings.

Ex: Cylinder fitter with a movable piston.

Open System: An open system is the one which can exchange energy as well as matter with the surroundings.

Ex: An open vessel / Air compressor.

Isolated system: An isolated system is one which cannot exchange energy or matter with its surroundings.

Ex: The fluid contained by a thermos flask..

Thermodynamic equilibrium: If a system is simultaneously in a state of mechanical equilibrium, chemical equilibrium and thermal equilibrium, then the system is said to be in thermodynamic equilibrium.

Internal energy of a system (u): The internal energy of a system is defined as the sum of all the energies contained in the system.

The internal energy of a gas is sum of kinetic energy and intermolecular potential energies of the gas.

Internal energy of the gas

$$U = \Sigma PE + \Sigma KE$$

ΣPE arises due to the intermolecular forces of attraction/repulsion among the molecules.

ΣKE arises due to the translation, vibration and rotational kinetic energies of the molecules of the gas.

First law of thermodynamics

Statement: If the quantity of heat supplied to a system is capable of doing work, then the quantity of heat absorbed by the system is equal to the sum of the increase in the internal energy and the external work done by it.

$$dQ = dU + dW$$

→(1)

Where dQ → The quantity of heat energy supplied to the system.

dU → The increase in internal energy.

dW → The external work done by the system.

Sign convention:

- (1) If the heat energy dQ is added to the system is taken as positive.
- (2) If the heat energy dQ is released from the system is taken as negative
- (3) The increase in internal energy dU is taken as positive.
- (4) The decrease in internal energy dU is taken as negative.
- (5) The work is done dW by the system is taken as positive.
- (6) The work is done dW on the system is taken as negative.

Significance:

- (1) This law verifies the law of conservation of energy in thermodynamics.
- (2) This law introduces the concept of internal energy.
- (3) This law is applicable for all the states and natural process.

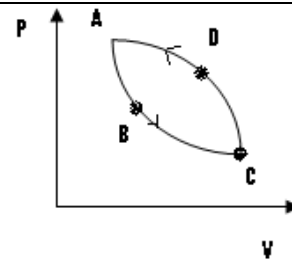
Limitations:

- (1) This law fails to explain the direction of heat flow.
- (2) This law fails to explain the concept of entropy.

Thermodynamic processes:**Path:**

The locus of the series of points representing the states through which the system passes is called path.

Consider a system undergoes a change of state from state A to State C as shown in figure passing through intermediate state by absorbing different amount of heat along ABC is the path for the system from state A to State C.

**Process:**

The complete description of change of state along with the path is called a process.

It is observed that a system undergoes a process along the path represented by the graph ABC by absorbing some amount of heat. If the system is made to undergo another change of state again from CAD by radiating some amount of heat and that the complete description of the change of state is called process.

Reversible process:

A reversible process is that which can be retraced in the opposite direction i.e. if a small change is made in the forward direction, the process is reversed completely and the working substance passes through exactly the same directions as it does in the direct process.

Example: -Consider the conversion of water at 0°C into ice at 0°C by removing certain quantity of heat. If the same quantity of heat is supplied to 0°C ice it will melt and will be converted to its original state of water.

Irreversible process:

A process in which reversal does not take place is called as irreversible process.

Example:-The conduction of heat from hot body to a cold body is an example of irreversible process.

Isothermal process:-

A process in which a system undergoes physical changes in such a way that the temperature remains constant by the exchange of heat energy with the surroundings is known as isothermal process.

- (i) In this process Temperature remains constant hence $\Delta T = 0$
- (ii) $P \propto 1/V$ or $PV = \text{constant}$ i.e. P-V graph is a rectangular hyperbola with $P_1V_1 = P_2V_2$
- (iii) Since $\Delta T = 0$, hence $\Delta U = 0$ for an ideal gas where U is internal energy is a function of temperature.

Work done during Isothermal process:

Consider one mole of an ideal gas enclosed in an isothermal chamber i.e. the walls of chamber; base and piston are good conductors. Now the gas expands at constant temperature isothermally from volume V_1 to V_2 . Let the corresponding pressure be P_1 and P_2

At any instant let “P” be the pressure of the gas, the motion of the piston through an elementary change dx , area of the piston is “A” then the work-done is given by

$$dW = \text{Force} \times dx = PAdx = PdV$$

Where dV is the infinitesimally small increase in volume of the gas at that pressure.

$$W = \int dW = \int_{V_1}^{V_2} P \cdot dV$$

But from gas equation $P = RT/V$

$$\therefore W = \int_{V_1}^{V_2} \frac{RT}{V} \cdot dV$$

Or $W = RT \log_e \left[\frac{V_2}{V_1} \right]$

Or $W = 2.303 RT \log_{10} \left[\frac{V_2}{V_1} \right]$

The expression for “n” moles the work done is

$$W = 2.303nRT \log_{10} \left[\frac{V_2}{V_1} \right]$$

Adiabatic Process:

A process in which a system undergoes physical changes in such a way that the total heat energy remains constant hence heat energy neither allowed to enter the system from the surrounding nor allowed to leave the system to the surroundings is called an adiabatic process.

- (i) In adiabatic process, the total heat energy remains constant hence $\Delta Q = 0$
- (ii) From the first law of thermodynamics $dU + dW = 0$ or $dU = -dW$.
- (iii) In this process $PV^\gamma = \text{constant}$ (or) $TV^{\gamma-1} = \text{constant}$ (or) $P^{1-\gamma} T^\gamma = \text{constant}$

Work done during adiabatic process:

Consider one mole of an ideal gas enclosed in an adiabatic chamber i.e. the walls of chamber; base and piston are bad conductors. Now the gas expands at constant heat energy from volume V_1 to V_2 . Let the corresponding pressure be P_1 and P_2

At any instant let "P" be the pressure of the gas, the motion of the piston through an elementary change dx , area of the piston is "A" then the work-done is given by

$$dW = \text{Force} \times dx = PAdx = PdV$$

Where dV is the infinitesimally small increase in volume of the gas at that pressure.

$$W = \int dW = \int_{V_1}^{V_2} P \cdot dV$$

For an adiabatic change

$$PV^\gamma = K \text{ (constant)} \quad \therefore P = K/V^\gamma$$

$$\therefore W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} \cdot dV = K \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2}$$

$$\therefore W = \frac{K}{1-\gamma} [V_2^{1-\gamma} - V_1^{1-\gamma}]$$

$$\text{(Or)} W = \frac{1}{1-\gamma} [KV_2^{1-\gamma} - KV_1^{1-\gamma}]$$

$$\text{But } P_1 V_1^\gamma = P_2 V_2^\gamma = K$$

$$\therefore W = \frac{1}{1-\gamma} [P_2 V_2^\gamma V_2^{1-\gamma} - P_1 V_1^\gamma V_1^{1-\gamma}]$$

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

$$\therefore W = \frac{1}{1-\gamma} [RT_2 - RT_1]$$

$$\therefore W = \frac{R}{1-\gamma} [T_2 - T_1]$$

$$\therefore W = \frac{R}{\gamma-1} [T_1 - T_2]$$

This expression gives the work-done for a 1 mole of gas.

For 'n' moles of gas

$$\therefore W = \frac{nR}{\gamma-1} [T_1 - T_2]$$

Isobaric process:-

The process in which a system undergoes a change in volume and temperature at constant pressure by the exchange of heat energy with the surroundings is called isobaric process

In this process the pressure remains constant.

Isochoric process:-

The process in which a system undergoes a change in pressure and temperature at constant volume by the exchange of heat energy with the surroundings is called isochoric process

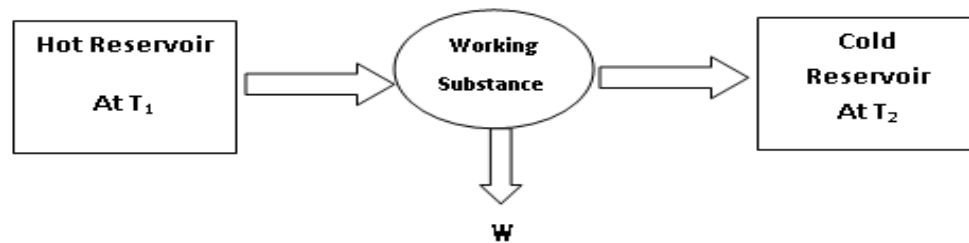
In this process the volume remains constant.

Heat Engine

The heat engine is a device used to convert heat energy into mechanical work through a medium, called working substance which is normally in the form of a vapour or gas.

A heat engine consists of the following parts

1. **Source:** It is a hot reservoir or a body which is at higher temperature T_1 and can extract any quantity of heat Q_1 without any change in its temperature.
2. **Sink:** It is a cold reservoir or body at lower temperature T_2 which can take any amount of heat Q_2 rejected by the working substance without any change in its temperature.
3. **Working substance:** It is substance depends on the engine which absorbs certain amount of heat from the source, converts a part of it into work and rejects the remaining heat to the sink.



Note: The efficiency of an engine is the ratio between work done (W) by the engine and the amount of heat absorbed (Q_1) by the engine

Efficiency of heat engine

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

Carnot's engine and Carnot's cycle:-

Carnot devised an ideal engine which is based on a reversible cycle called Carnot's cycle.

A reversible heat engine operating between two temperatures is called a Carnot's engine.

Carnot's engine consists of

- (i) A cylinder of perfectly non-conducting wall and perfectly conducting bottom. On the top of the cylinder is covered with piston made with adiabatic material and the movement is frictionless. The working substance in the cylinder is assumed to be air which is supposed to behave like a perfect gas.
- (ii) A source of heat to supply heat at constant temperature say T_1
- (iii) A sink or cold body to receive the rejected heat at a constant temperature say T_2
- (iv) An insulating stand which is connected to the bottom of the cylinder.



Working:

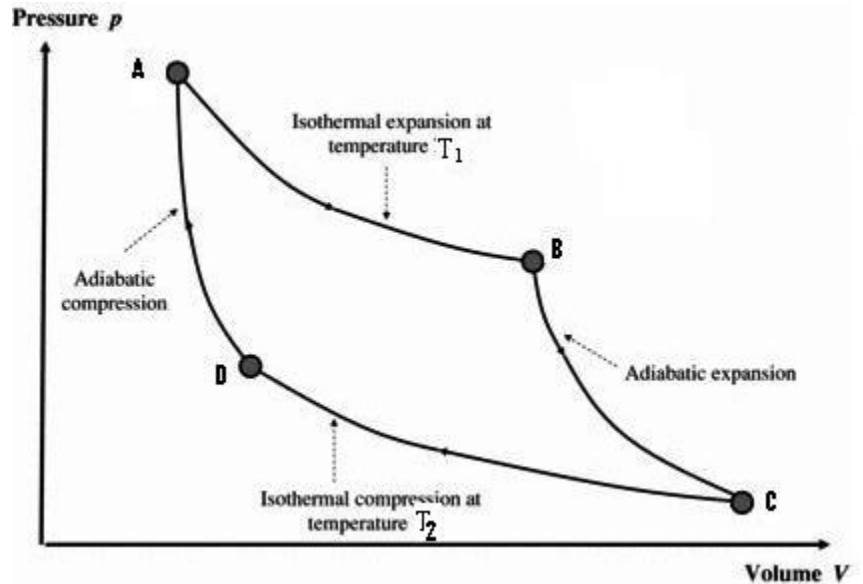
The working substance in a Carnot's engine is taken through a reversible cycle consisting of the following operations in succession

- a) Isothermal Expansion b) Adiabatic Expansion c) Isothermal Compression
d) Adiabatic Compression

Isothermal expansion: The working substance containing "n" moles of ideal gas placed on source and the gas is allowed to expand slowly at constant temperature T_1 absorbing heat Q_1 . This isothermal expansion is represented by the curve AB in the indicator diagram.

The state of gas at $A(P_1, V_1, T_1)$ changes to $B(P_2, V_2, T_1)$. The heat energy absorbed Q_1 equal to work done by the gas

$$Q_1 = W_1 = nRT_1 \log(V_2/V_1) \rightarrow (1)$$



Adiabatic expansion: The working substance is then placed on the insulating stand and the gas is allowed to expand adiabatically till the temperature falls from T_1 to T_2 , as shown in curve along BC

The state of gas changes from $B(P_2, V_2, T_1)$ to $C(P_3, V_3, T_2)$ the work done by the gas is

$$W_2 = \frac{nR(T_2 - T_1)}{1 - \gamma} \rightarrow (2)$$

Isothermal compression: The working is now placed on the sink and the gas is compressed at constant temperature T_2 along the path CD by transferring a certain quantity of heat Q_2 to the sink

The state of gas changes from $C(P_3, V_3, T_2)$ to $D(P_4, V_4, T_2)$ the work done by the gas is

$$W_3 = nRT_2 \log(V_4/V_3) \rightarrow (3)$$

Adiabatic compression: The working substance finally placed on the insulating stand and the compression along the curve DA

The state of gas changes from $D(P_4, V_4, T_2)$ to $A(P_1, V_1, T_1)$ the work done by the gas is

$$W_4 = \frac{nR(T_1 - T_2)}{1 - \gamma} \rightarrow (4)$$

The total work-done by the by the gas $W = W_1 + W_2 + W_3 + W_4$

$$W = nRT_1 \log(V_2/V_1) + \frac{nR(T_2 - T_1)}{1-\gamma} + nRT_2 \log(V_4/V_3) + \frac{nR(T_1 - T_2)}{1-\gamma} \rightarrow (5)$$

Hence

$$W = nRT_1 \log(V_2/V_1) + nRT_2 \log(V_4/V_3) \rightarrow (6)$$

But from adiabatic relations $TV^{\gamma-1} = \text{constant}$

$$\text{Along BC } T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \rightarrow (7)$$

$$\text{Along DA } T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1} \rightarrow (8)$$

By dividing above equations

$$V_2/V_1 = V_3/V_4 \rightarrow (9)$$

Hence equation (6) transform to

$$W = nR \log(V_2/V_1) (T_1 - T_2)$$

The efficiency of Carnot's engine is given by the relation

$$\eta = W/Q_1 = \frac{nR \log\left(\frac{V_2}{V_1}\right) (T_1 - T_2)}{nR \log\left(\frac{V_2}{V_1}\right) T_1} \rightarrow (10)$$

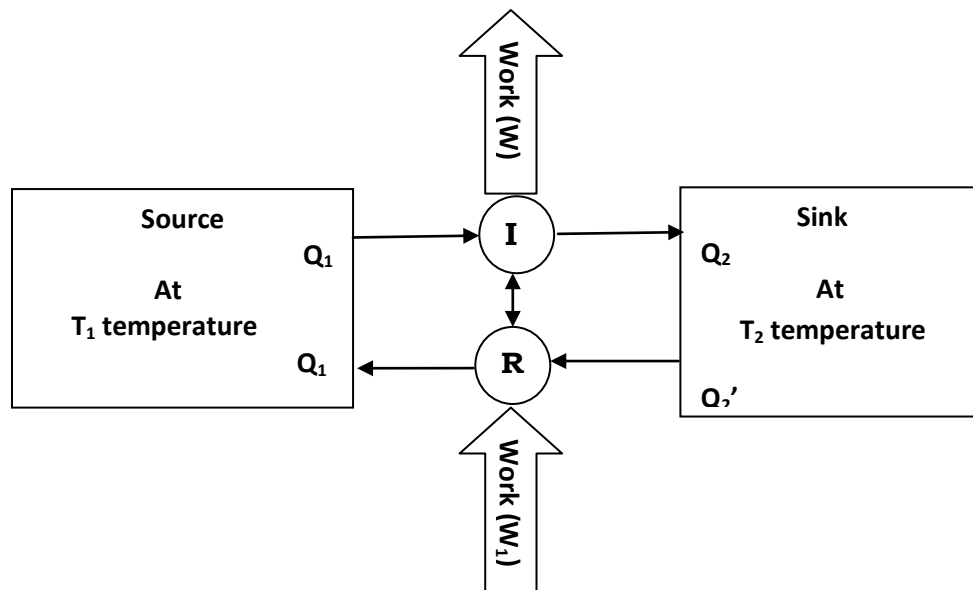
$$\therefore \eta = 1 - (Q_2/Q_1) = 1 - (T_2/T_1)$$

Carnot's Theorem:***Statement:***

No heat engine can have more efficiency than the reversible engine operating between the same source (T_1) and sink (T_2) and the efficiency of Carnot engine is independent of the nature of the working substance.

Proof:

Consider an irreversible engine (I) and a reversible engine (R) working between same source and sink as shown in figure



Let the engine I extracts Q_1 heat from source at T_1 and releases Q_2 heat to sink at T_2

The work done by the engine $W = Q_1 - Q_2$

Heat given to the sink $Q_2 = Q_1 - W \rightarrow (1)$

The efficiency $\eta_I = W/Q_1 \rightarrow (2)$

Now the reversible engine R works as refrigerator

This extracts Q_2' from sink at T_2 and releases Q_1 heat to the source at T_1 by absorbing work W_1 from surroundings

The work done on the system $W_1 = Q_1 - Q_2'$

Heat absorbed from sink $Q_2' = Q_1 - W_1 \rightarrow (3)$

The efficiency $\eta_R = W_1/Q_1 \rightarrow (4)$

Let the efficiency of I > the efficiency of R

$$\therefore \eta_I > \eta_R \Rightarrow W/Q_1 > W_1/Q_1 \Rightarrow W > W_1$$

By coupling these two engines such that work done by the Irreversible engine can be given to Reversible engine such that the compound engine extracts Q_2' from the sink and releases Q_2 to sink and given by

$$Q_2' - Q_2 = (Q_1 - W_1) - (Q_1 - W) = W - W_1 > 0 \therefore W > W_1$$

Hence the net heat taken from the sink is positive. But this is impossible for self acting machine extracts heat from cold body without aid of external agency.

\therefore Our assumption that the irreversible engine is more efficient than the reversible engine is wrong.

Thus no heat engine working between a Source and sink can be more efficient than a reversible engine.

Since efficiency of engine is given by $\eta = 1 - T_2/T_1$ which is independent of nature of working substance.

Let us consider two reversible engines A and B working between the same source and sink then A cannot be more efficient than B and B cannot be more efficient than A so two heat engines are equally efficient.

Second law of thermodynamics:

Second law of thermodynamics is a fundamental law of nature which explains that heat can flow only from hot body to cold body by itself. There are several statements of this law. Two are the most significant viz.,

(a) ***Kelvin- Planck statement:***

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

It is impossible to get a continuous supply of work from a body by cooling it to a temperature lower than that of the surroundings.

(b) ***Clausius statement:***

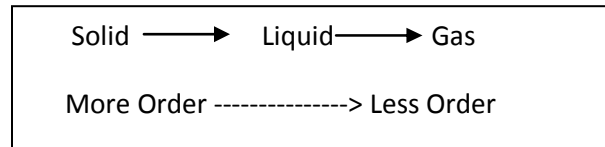
No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

It is impossible for self acting machine to transfer heat from colder body to hotter body without an aid of external agency.

Concept of entropy:

The concept of entropy refers to state of order represented by S

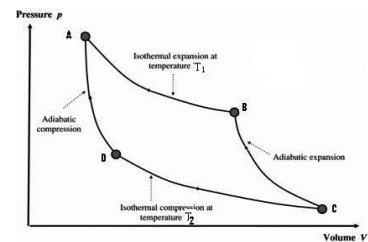
A change in order is a change in the number of ways of arranging the particles, and it is a key factor in determining the direction of any process



The increase in entropy is given by $dS = \frac{dQ}{T}$

Change in Entropy in a reversible and irreversible process:

Consider a reversible process such as Carnot cycle ABCDA as shown in the fig., during isothermal expansion from A→B, the temperature constant but the heat energy increases by Q_1 , hence the entropy of the working substance from A→B will be increases as Q_1/T_1

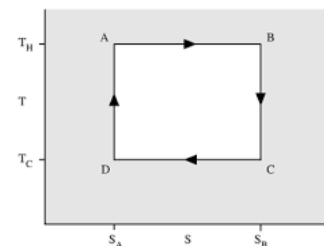


Since B→C and D→A are adiabatic processes hence there is no change in entropy. Along C→D the working substance rejects heat energy Q_2 , hence the loss in entropy is Q_2/T_2 .

Hence the net gain in entropy of the working substance in one complete cycle ABCDA is

$$= Q_1/T_1 - Q_2/T_2$$

Since in a Carnot cycle $Q_1/T_1=Q_2/T_2$ hence the change in entropy in a reversible process is zero. i.e., in a reversible process the entropy remains same.



Now consider an irreversible process such as conduction or radiation in which heat is lost by a body at higher temperature T_1 and gained by the body at lower temperature $T_2(T_1>T_2)$ with the change in heat energy is given by Q

∴ Gain in entropy of the cold body = Q/T_2

Loss in entropy of the hot body = Q/T_1

Hence the net change in entropy of the system = $Q/T_2 - Q/T_1$

As $T_1 > T_2$ the change in the entropy is +ve quantity, hence entropy increases in irreversible process.

Entropy and second law of thermodynamics

If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

Entropy and Third law of thermodynamics:

As the temperature tends to absolute zero, the entropy also tends to zero and the molecules of a substance or a system are in perfect order is called third law of thermodynamics.

Example: The molecules in a gaseous state are more free as compared to liquid state, hence entropy is more in case of gas than liquid state i.e., as temperature increases degree of disorderness increases.

Entropy and probability:

According to Boltzmann theory the entropy(S) of particular macrostate and multiplicity/ number of microstates(w) are related by a logarithmic function given by

$$S = k \ln w \quad \text{Where } k = \text{Boltzmann constant}$$

The multiplicity defines the probability of occurrence of the different systems by the molecules.

Example if N no. of molecules in a system can be distributed in two systems such that n_1 molecules in state 1 and n_2 molecules in state 2 then their multiplicity is given by

$$w = \frac{N!}{n_1! \times n_2!}$$

An example: Imagine a gas consisting of just 2 molecules. We want to consider whether the molecules are in the left or right half of the container. There are 3 macrostates: both molecules on the left, both on the right, and one on each side. There are 4 microstates: LL, RR, LR, RL.

Then the multiplicity is given by

$$1 \text{ macro state and } 3 \text{ macro state } w = \frac{2!}{2! \times 0!} = 1 \text{ then } S = 0 \therefore \ln w = 0$$

$$2 \text{ macro state } w = \frac{2!}{1! \times 1!} = 2 \text{ then } S = 9.5 \times 10^{-24} \text{ J/K}$$

Since the total entropy of two systems is the sum of their separate entropies, however the probability of two independent systems is the product of their separate probability.