THERMODYNAMICS

Thermodynamics is a branch of physics that deals with the concepts of heat and temperature and the inter conversion of heat and other forms of energy. Thermodynamics is a macroscopic science.

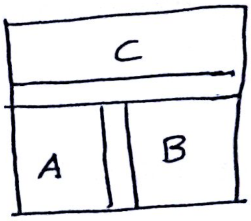
Thermal equilibrium

The state of a system is said to be an equilibrium state, if the macroscopic variables that characterise the system do not change with time.

adiabatic wall :- An insulating wall that does not allow the flow of energy

diathermic wall :- A conducting wall that allows energy flow (heat) from one to another.

Zeroth law of thermodynamics



Two systems in thermal equilibrium with a third system seperately are in thermal equilibrium with each other

$$T_A = T_C \text{ \& } T_B = T_C$$

$$\therefore T_A = T_B$$

When two systems A and B are in thermal equilibrium there must be a physical quantity that has the same value for both. This thermodynamic variable whose value is equal for two systems in thermal equilibrium is called temperature.

Heat, internal energy and work

Internal energy is the sum of kinetic energies and potential energies of the molecules. Internal energy depends only on the state of the system

Heat and work are two distinct modes of energy transfer to a system that results in change in its internal energy

(a) Heat is energy transfer due to temperature difference between the system and the surroundings

(b) Work is energy transfer brought about by means that do not involve such a temperature difference.

First law of thermodynamics

The total energy given to a system is equal to the sum of its increase in internal energy and the workdone by the system on the surroundings

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

$$\Delta Q - \Delta W = \Delta U$$

But $\Delta W = P\Delta V$

IF $\Delta U = 0$

$\therefore \Delta Q = \Delta U + P\Delta V$

$$\Delta Q = \Delta W$$

Specific heat Capacity

Heat capacity $S = \frac{\Delta Q}{\Delta T}$

Specific heat capacity $s = \frac{1}{m}\frac{\Delta Q}{\Delta T}$

Molar specific heat capacity $C = \frac{1}{n}\frac{\Delta Q}{\Delta T}$

Consider 1 mol of an ideal gas

$$\Delta Q = \Delta U + P\Delta V \quad \text{--- (1)}$$

At Constant Volume, $\Delta V = 0$

$$\therefore \quad \Delta Q = \Delta U$$

$$C_v = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} \quad \text{--- (2)}$$

At Constant Pressure,

eqn (1) becomes

$$C_p = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} + P\frac{\Delta V}{\Delta T} \quad \text{--- (3)}$$

From ideal gas eqn

$$PV = RT$$

$$P\Delta V = R\Delta T$$

$$P\frac{\Delta V}{\Delta T} = R$$

$\therefore$ Eqn (3) becomes

$$C_p = \frac{\Delta U}{\Delta T} + R \quad \text{--- (4)}$$

From (2) & (4), We get $C_p = C_v + R$

or $\underline{C_p - C_v = R}$

Thermodynamic state variables and equation of state.

The quantities that describe equilibrium states of a system are called thermodynamic state variables. The connection between the state variables is called the equation of state

$$PV = nRT$$

Thermodynamic state variables are of two types

(1) Extensive – These variables indicate the 'size' of the system
Eg: mass, volume, internal energy etc

(ii) Intensive – Variables that do not indicate the 'size' are are called intensive
Eg: pressure, Temperature, density etc.

Thermodynamic Processes

(1) Quasi-static – The process in which the temperature & pressure of a system changes by an infinitesimally small amount is called quasi-static

(2) Iso thermal – Temperature remains constant

(3) Iso baric – Pressure remains constant

(4) Iso choric – Volume remains constant

(5) Adiabatic – No heat flow between the system and the surroundings.

Isothermal Process

The thermodynamic process in which the temperature of the system remains constant is called an isothermal process.

∴ The ideal gas equation becoms

$$PV = a \text{ constant}$$

We have $\Delta W = P \Delta V$

$$\lim_{\Delta t \to 0} \frac{\Delta W}{\Delta t} = \lim_{\Delta t \to 0} P \frac{\Delta V}{\Delta t}$$

$$dW = P\,dv$$

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

But $P\cancel{V} = \mu RT$

$$P = \frac{\mu RT}{V}$$

$$= \frac{\mu RT}{V} \int_{V_1}^{V_2} dV$$

$$= \mu RT \int_{V_1}^{V_2} \frac{dV}{V}$$

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

Case 1, $V_2 > V_1$

The work done is positive. ie in an isothermal expansion, gas absorbs heat and does work

Case 2, $V_2 < V_1$

The workdone is −ve. ie work is done on the gas by the environment and heat is released.

Adiabatic Process

In an adiabatic process, the system is insulated from the sorroundings and heat absorbed or released is zero.

In an adiabatic process of an ideal gas

$PV^{\gamma} =$ a Constant, Where $\gamma = \frac{C_p}{C_p}$

$P_1V_1^{\gamma} = P_2V_2^{\gamma} =$ a constant — (1)

~~dw =~~

$$dW = Pdv$$

$$PV^{\gamma} = K$$

$$P = \frac{K}{V^{\gamma}}$$

$$\int dW = \int_{V_1}^{V_2} Pdv$$

$$= K \int_{V_1}^{V_2} \frac{dv}{V^{\gamma}}$$

$$= K \int_{V_1}^{V_2} V^{-\gamma} dv$$

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

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

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

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

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

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

$$= \frac{\mu R (T_2 - T_1)}{1-\gamma}$$

$$\boxed{W = \frac{\mu R (T_1 - T_2)}{\gamma - 1}}$$

If work is done by the system, w is positive

$T_1 > T_2$

If work is done on the system, w is -ve

$T_1 < T_2$, temperature increases.

Isochoric Process

In an Isochoric process, V is constant. No work is done on or by the gas.

Isobaric Process

P is fixed.

$w = P(V_2 - V_1)$

$w = \mu R(T_2 - T_1)$

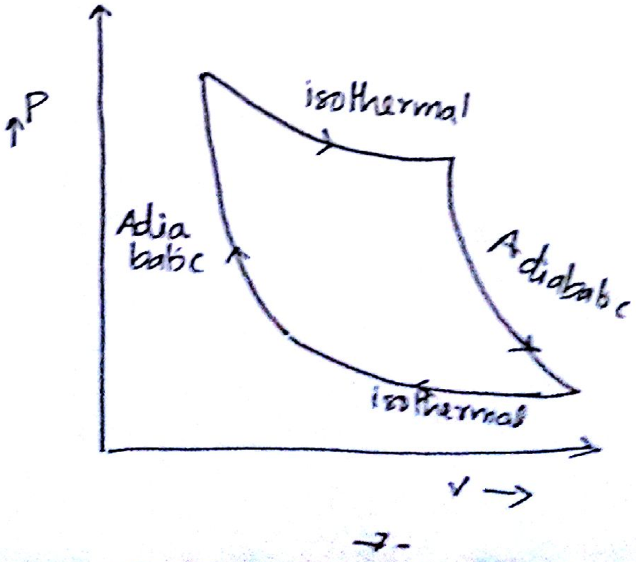
Cyclic Process.

In a cyclic process, the system returns to its initial state. Since Internal energy is a state variable, $\Delta U = 0$.

∴ Total heat absorbed = work done by the system.

~~Isothermal Process~~

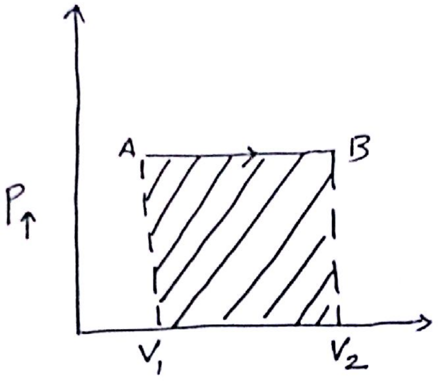
PV curves for isothermal and adiabatic processes of an ideal gas



PV- diagram – Graphical representation of work

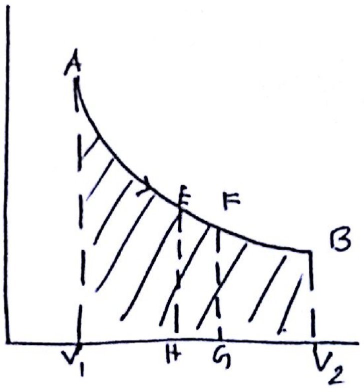
A graph drawn by taking Pressure along Y-axis and Volume along X-axis is called the PV diagram. Area under PV diagram is equal to the workdone.

(i) At constant Pressure.



$W = P(V_2 - V_1)$

(ii) Variable Pressure.



$$W = \int_{V_1}^{V_2} P\,dV$$

Heat engine

A heat engine is a thermodynamic device used to convert heat supplied to it into mechanical work continuously.

Parts of a heat engine

(1) The source – a body at a constant high temperature and of infinite thermal capacity so that any amount of heat drawn from it does not affect its temperature.

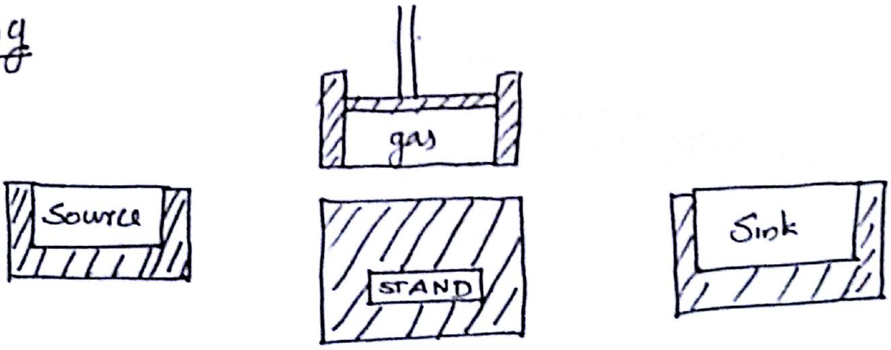
(2) Working substance

Eg: ideal gas (Carnot engine)
air (Petrol and diesel engine)

3) Insulating stand

4) The sink – a body at a constant low temperature, to which heat is rejected. This also has infinite thermal capacity.

Working



The working substance absorbs heat from source, part of which is converted in to ~~heat~~ Work and the remaining part is given to the sink. The working substance comes back to the original condition This process is repeated and continuous work is obtained.

Thermal efficiency.

It is defined as the ratio of external work done to the heat absorbed by the working substance from the source.

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

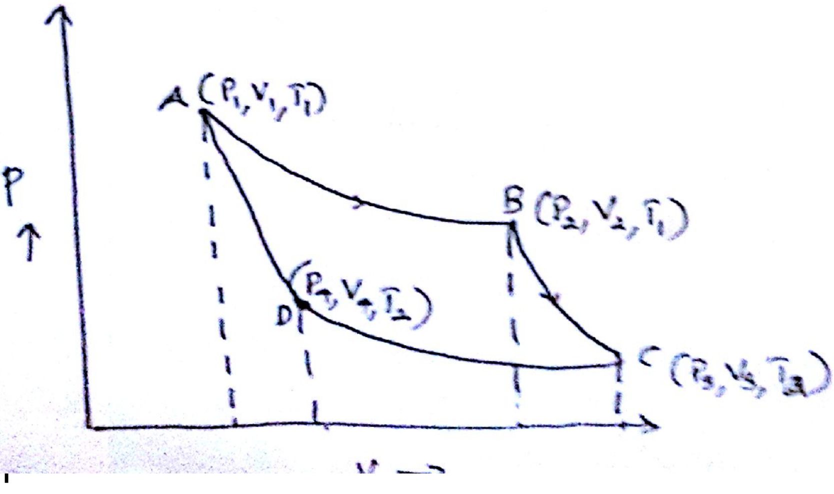
Carnot's Cycle – The ideal Heat engine

① Isothermal Expansion – The cylinder is placed on the source mainted at temperature T_1K and the gas is allowed to expand isothermally.

(ii) Adiabatic Expansion – The cylinder is next placed on the stand. The gas is allowed to expand adiabatically.

(iii) Isothermal compression – The cylinder is now placed on the cold reservior at temp T_2 and the gas is made to undergo isothermal compression.

(iv) Adiabatic compression – Finally the cylinder is placed back on the stand and the cycle is completed by adiabatic compression.



Expression for efficiency.

Let the heat absorbed from the source is Q_1 at T_1 and the heat rejected to the sink is Q_2 at T_2. After a cycle, the working substance comes back to its original state. So change in internal energy is zero.

Hence the net workdone on the cycle is $W = Q_1 - Q_2$

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

$$\eta = 1 - \frac{Q_2}{Q_1} \quad \text{——— (1)}$$

During isothermal expansion,

$$Q_1 = RT_1 \log_e \frac{V_2}{V_1}$$

During isothermal compression

$$Q_2 = RT_2 \log_e \frac{V_3}{V_4}$$

$$\therefore \quad \eta = 1 - \frac{RT_2 \log_e \frac{V_3}{V_4}}{RT_1 \log_e \frac{V_2}{V_1}} \quad \text{——— (2)}$$

But during adiabatic expansion

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad \text{——— (3)}$$

during adiabatic compression

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1} \quad \text{——— (4)}$$

$$\frac{(3)}{(4)} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

∴ Eqn (2) becomes

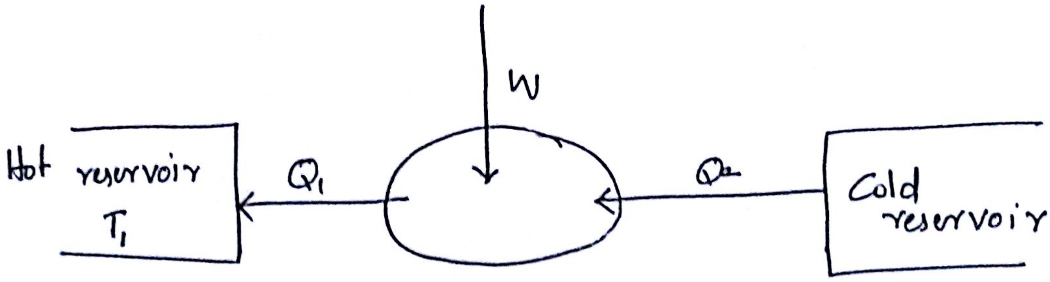
$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$

The efficiency depends up on the temperature of the source T_1 and the temperature of the sink T_2 and does not depend upon the nature of the working substance.

T_2 is always less than T_1. Hence η is always less than one.

Refrigerators & heat Pump

A refregerator is the reverse of heat engine. Here the working substance extracts heat Q_2 from the cold reservoir at temperature T_2, Some external work is done on it and heat Q_1 is released to the hot reservoir at temperature T_1



Coefficient of performance

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

Second law of thermodynamics

① Kelvin – Planck Statement

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

② Clausius statement

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