Thermodynamics

2nd Sem (General)

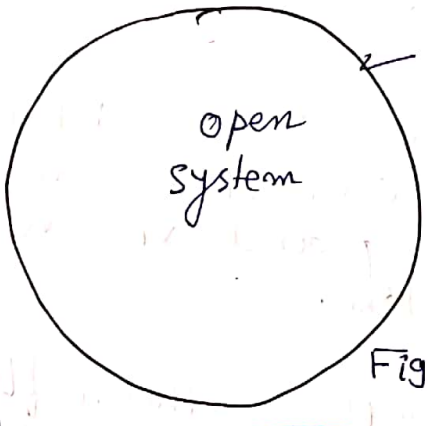
Thermodynamics deal with heat which transforms into work. In thermodynamics some basic parameters are definition are necessary.

System:— System means where work is performed.

Surrounding:— Surrounding means outside of the system where work cannot be performed.

Open system

When both matter and energy can exchange from system to surrounding and vice-versa it is called open system (Fig-1)



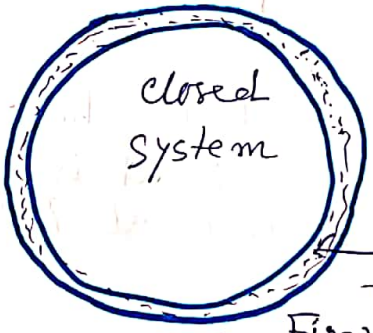
matter and energy can exchange from system to surrounding and vice-versa.

Surrounding

Fig-1

Example:—

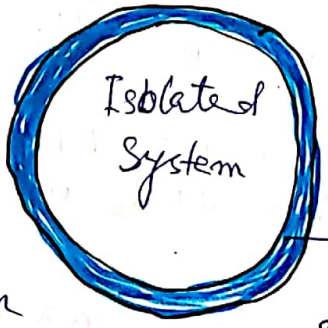
When a glass of hot milk is kept on the table, after sometimes the hot milk will be cooled. Here heat energy goes to surrounding. Again any foreign matter can fall in the milk or from milk some tiny particles may be go away by means of wind etc.



Surrounding

porous plug that can pass energy

Fig-2



Surrounding

insulator that does not allow to pass ~~neighe~~ neither heat energy nor matter.

Fig-3

Closed system :- When heat energy can exchange from system to surrounding and vice-versa but matter cannot exchange, it is said to be Closed System

example :- If hot milk contained in a glass covering with a plate is kept on the table then after sometimes milk will be cooled as heat goes to surrounding but no matter can exchange. [Fig - 2]

Isolated system: When both matter and energy can not exchange from system to surrounding and vice-versa, it is called Isolated system.

Example — Thermoflask.

Isothermal ~~Exothermic~~ system :- In a system if temperature remains constant it is called ~~exothermic system~~. ~~OR it is~~ isothermal system

Adiabatic system :- If heat remains constant, it is called adiabatic system

Isochoric system :- When volume of a system remains constant, it is called isochoric system.

Isobaric system :- When pressure of a system remains constant, it is called Isobaric system :-

N:B — here the system is also called process

1st law of thermodynamics: —

1st law of thermodynamics deals with laws of conservation of energy

Consider a system of having heat content q_1, internal energy E_1 is transferred to another system where heat content is q_2 and internal energy is E_2

Now change of heat content $= q_2 - q_1 = dq$

Change of internal energy $= E_2 - E_1 = dE$

To carry out the process from system 1 to system-2 suppose work is performed which is W

So first law will be as

$$\boxed{dq = dE + W} \quad \text{--- (1)}$$

In thermodynamics work is perfored by changing volume. If volume changes from V_1 to V_2 at constant pressure P then $W = P(V_2 - V_1)$ ...(2)

From equation (1) and (2) ⇒

$$dq = dE + P(V_2 - V_1)$$

or $$\boxed{dq = dE + PdV} \quad (V_2 - V_1 = dV) \quad \text{(3)}$$

This equation is known as 1st law of thermodynamics

NB $dq = dE + PdV$ says that total heat cannot be converted into work.

Heat Capacity Heat required by one mole of gas through 1°c temperature is known as heat capacity of gases

In thermodynamics heat capacity of gases referred at constant pressure and volume.

At constant P, $\boxed{C_p = \left(\frac{dH}{dT}\right)_p}$

ie change of enthalpy with respect to the change of temperature at constant pressure is known as heat capacity at constant pressure.

At constant volume, $\boxed{C_v = \left(\frac{dE}{dT}\right)_v}$

ie change of internal energy with respect to the change of temperature at constant volume is known as heat capacity at constant volume.

Show that for ideal gases $C_p - C_v = R$

Ans —— $C_p - C_v = \left(\frac{dH}{dT}\right)_p - \left(\frac{dE}{dT}\right)_v$ --- (1)

But $\boxed{H = E + PV}$

So, $C_p - C_v = \frac{d(E+PV)}{dT} - \left(\frac{dE}{dT}\right)_v$

$$= \left(\frac{dE + PdV}{dT}\right)_p - \left(\frac{dE}{dT}\right)_v$$

$$= \cancel{\left(\frac{dE}{dT}\right)} + \left(\frac{PdV}{dT}\right) - \cancel{\left(\frac{dE}{dT}\right)}$$

$$= P\left(\frac{dV}{dT}\right) \text{ ———— (2)}$$

For 1 mole of ideal gas $PV = RT$, $PdV = RdT$, $P = \frac{RdT}{dV}$

Substituting in eq^n (2)

$$C_p - C_v = R\left(\frac{dT}{dV}\right) \times \left(\frac{dV}{dT}\right)$$

$\therefore$ $\boxed{C_p - C_v = R}$ — proved

2nd Sem (General)

Workdone from 1st law of thermodynamics.

We have 1st law $\boxed{dq = dE + p\,dV}$ ... (1)

For ideal gases, there is no change of internal energy. i.e $dE = 0$, at constant temperature.

So equation (1) $dq = p\,dV$ ---- (2)

1 mole of gas shows $pV = RT$

$$p = \frac{RT}{V}$$

Substituting the value of p in equation (2)

$$\boxed{dq = \frac{RT}{V}\,dV} \quad \text{--------- (3)}$$

In equation total heat is converted into work, so

$$\therefore dq = dW$$

Thus $dW = \frac{RT}{V}\,dV$ --- (4)

Integrating eqn (4) =>

$$\int_1^2 dW = RT\int_1^2 \frac{1}{V}\,dV$$

$$W_2 - W_1 = RT \ln \frac{V_2}{V_1}$$

$$\therefore W = RT \ln \frac{V_2}{V_1}$$

$$\boxed{W = 2.303\,RT \log \frac{V_2}{V_1}}$$

or $\boxed{W = 2.303\,RT \log P_1/P_2}$ $[P_1V_1 = P_2V_2]$

Significance — In this equation it shows that total heat is converted into work, it is only possible for ideal gases. In case of real gas it is impossible to convert into work with hundred percent. The above system is called isothermal.

In adiabatic system :- In adiabatic system heat remains constant. When 1 mole of ideal gas is expanded through adiabatic system, $dq = 0$

1st law is $dq = dE + PdV$

$$\therefore \quad dE = -PdV \qquad (dq = 0)$$

$$C_v dT = -PdV \qquad \left[\because \left(\frac{dE}{dT}\right) = C_v\right]$$

$$C_v dT = -\frac{RT}{V} dV \qquad [PV = RT]$$

$$\frac{C_v dT}{T} = -R\frac{1}{V} dV$$

Integrating $\quad C_v \int_1^2 \frac{1}{T} dT = -R \int_1^2 \frac{1}{V} dV$

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

or $\ln \left[\frac{T_2}{T_1}\right] = -\ln \left[\frac{V_2}{V_1}\right]^{R/C_v}$

or $\left(\frac{T_2}{T_1}\right) = -\left(\frac{V_2}{V_1}\right)^{\frac{C_p - C_v}{C_v}} \qquad [C_p - C_v = R]$

or $\frac{T_2}{T_1} = -\frac{V_2}{V_1}^{\frac{C_p}{C_v} - 1}$

or $\frac{T_2}{T_1} = \left(\frac{-V_2}{V_1}\right)^{\gamma - 1} \qquad \left[\frac{C_p}{C_v} = \gamma\right]$

$$\frac{T_2}{T_1} = \left[\frac{V_1}{V_2}\right]^{\gamma - 1}$$

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$$

$$\boxed{T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}}$$

Second law of thermodynamics :-

Why second law of thermodynamics is needed —

Second law of thermodynamics is needed because

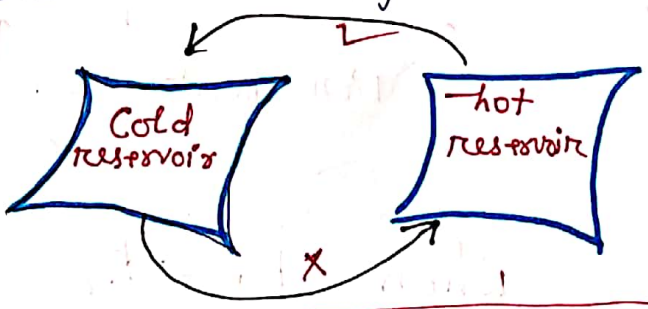
1. First law of thermodynamics deal with transformation of energy but it does not say about the direction of energy
2. 1st law fails to interprete the mechanism of engine etc.

So second law of thermodynamis is needed to mitigate the reality of heat energy into work.

Definition :— It is impossible to have any mechanism where heat flows from colder region to hotter region.

Kelvin says — It is impossible for a cyclic process to take heat from a cold reservoir and convert into work without at the same time transforming heat from a colder to hotter region.

Clausius says — It is impossible to construct a machine which is able to convey heat by a cyclic process from one reservoir at a lower temperature to another at a higher temperature unless work is done on the machine by some outside agency



It is impossible to flow heat from colder to hotter region.

Spontaneous and non spontaneous

Spontaneous —— It is irreversible process, all natural phenomenon are spontaneous.

Example ——

(i) River water flows from higher to lower level

(ii) Growth of trees.

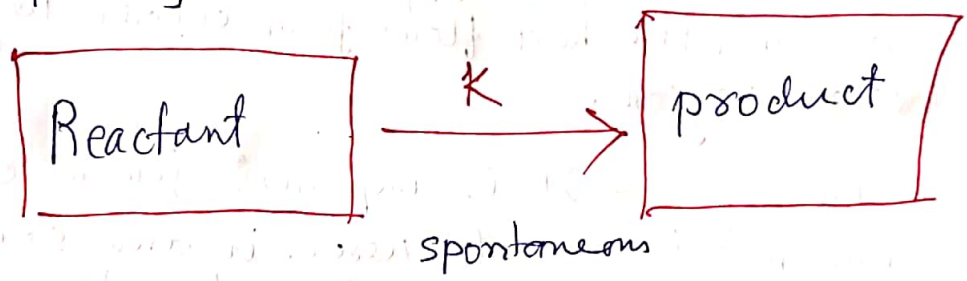
(iii) Flow of heat from hotter to colder

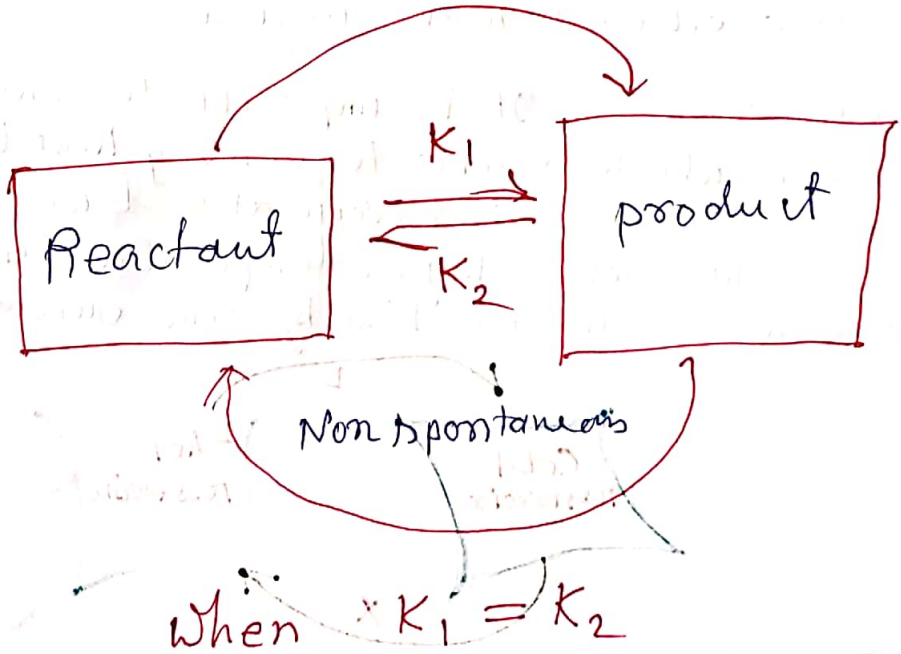
Non spontaneous — It is reverse to spontaneous

(i) Reversible reaction

(ii) Flow of current

(iii) Falling water etc.





When $K_1 = K_2$

equilibrium attained.

Carnot's cycle — In cyclic process the net change of internal energy becomes zero. i.e $dE = 0$

1 mole of gas is taken in the four stroke

Stroke-1 The gas is expanded reversibly and isothermally at chamber-1. here $dE = 0$

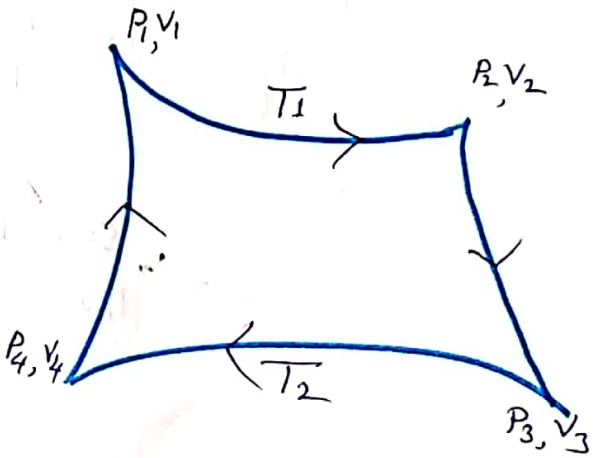
so $Q = W$ ie total heat is converted into work. The work done will be, $Q = 2.303 RT_1 \log \frac{V_2}{V_1}$

$$W_1 = 2.303 RT_1 \log \frac{V_2}{V_1} \quad \text{--- (1)}$$

here volume is expanded from volume V_1 to volume-2 at temperature T_1

Stroke-2 The gas is now transferred to stroke-2, the system is insulated so that heat cannot exchange, the gas is expanded adiabatically thus heat is absorbed by the system. The work done

$$W_2 = C_v (T_2 - T_1) \quad \text{here } dq = 0 \text{ --- (2)}$$



Stroke-3 — The gas again transferred to stroke-3, In this chamber the gas is Compressed isothermally from volume V_3 to V_4 at T_2 temperature, here ~~$dQ = 0$~~ $dE = 0$

work done $$-W_3 = 2.303 RT_2 \log \frac{V_4}{V_3} \quad \text{--- (3)}$$

here work is negative

Stroke-4 — At Last stage the gas is subjected to Compress adiabatically so that $dq = 0$

work done $W_4 = +C_v(T_1 - T_2)$

or $W_4 = -C_v(T_2 - T_1)$ ---- (4)

If total workdone $= W$ then

$$W = W_1 + W_2 + W_3 + W_4$$

$$= 2.303RT_1 \log\frac{V_2}{V_1} + C_v(T_2 - T_1) + 2.303RT_1 \log\frac{V_4}{V_3} - C_v(T_2 - T_1)$$

or $W = 2.303RT_1 \log\frac{V_2}{V_1} + \cancel{C_v(T_2 - T_1)} - 2.303RT_2 \log\frac{V_4}{V_1} - \cancel{C_v(T_2 - T_1)}$

$$= 2.303RT_1 \log\frac{V_2}{V_1} - 2.303RT_2 \log\frac{V_2}{V_1} \quad \left(\frac{V_4}{V_3} = \frac{V_2}{V_1}\right)$$

$$= 2.303R\log\frac{V_2}{V_1}(T_1 - T_2) \quad (5)$$

$$\eta = \frac{W}{Q} = \frac{2.303\cancel{R}\cancel{\log\frac{V_2}{V_1}}(T_1 - T_2)}{2.303\cancel{R}T_1\cancel{\log\frac{V_2}{V_1}}} = \frac{T_1 - T_2}{T_1}$$

$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$ where η is efficiency