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Thermodynamical Fundamental Concepts

Thermodynamics is that branch of physics which is concerned with the transformation of heat into mechanical work.

Thermodynamic system

A thermodynamic system refers to a definite quantity of metter bounded by some closed surface is called boundary.

Any thing outside the system which can exchange energy with it is called as its surrounding. System which can exchange both matter and energy with surrounding are known as open system.

System which can exchange only energy (not matter) with the surrounding is called closed system.

System which is not influenced in any way by its surrounding is called isolated. Thus, isolated system can exchange neither heat nor work with its surroundings.

Thermal and Thermodynamic equilibrium

If an isolated system is left to itself the pressure and temp. at given point approach to a steady value with the passage of time. when these quantities have attained a steady value, the system is said to be in a state of thermodynamic equilibrium. When a system is in thermodynamic equilibrium the temperature, pressure, density and other thermodynamic variables are same at all point of the system. For a system to be in thermal equilibrium, the following condition must be fulfilled

(I) Mechanical equilibrium

For a system to be in mechanical equilibrium there should be no unbalanced forces existing between different part of system or between the system and surrounding.

(II) Thermal equilibrium

For a system to be in thermal eq^n the temperature of all parts of a system must be same and should be identical with that of surroundings.

(III) Chemical equilibrium

For a system to be in chemical equilibrium the composition of system should remain fixed and definite.

Equation of state.

The equation relating the thermodynamic variables (P, V and T) and expressing the complete behaviour of thermodynamic system in equilibrium is called eqn. of state. For 1 mole of ideal gas, eqn. of state is

$$PV = RT$$

For n-mole, $PV = nRT$.

Thermodynamic processes:

a) Reversible and Irreversible process

If a process can be carried out in such a way that the effects produced by it on the system as well as the surrounding can be completely restored to their intial states and no changes are left in any of the systems taking part in the process or in the surroundings then a process is said to be a reversible process.

If a process does not satisfy these condition, it is called irreversible. Thus, the process which produce a permanent change in the thermodynamic state of the system and can not be retraced in the opposite order, are known as irreversible process.

b) Quasi-static process

The process in which there is small change or derivation in thermodynamic eq^{n} is known as quasi-static process. This process is only possible at slao rate. Eg. If the piston is ~~only~~ pushed very rapidly, the gas requires kinetic energy and can't establish thermodynamic equilibrium. But when the piston is pushed slowly, the system at all remains in thermodynamic equilibrium and the process can be considered qaasi-static.

(c) Isobaric process

The process in which the pressure remains constant is known as isobaric process. From 1st law of thermodynamics, if dq is total heat supplied. Then $dq = dv + dw$

$= MC_v dT + pdv$

$= C_v dT + pdv$ for unit mass

(d) Isochoric process:

It process in which the volume remains constant is known isochoric process.

So, from 1st law of thermodynamics,
$dq = C_v dT$ [$dv = 0$]

(e) Isothermal process

The process in which the temperature remains constant and the process is carried in a thermodynamic system consisting perfectly conducting cylinder.

(f) Adiabatic process

The process in which no exchange of heat takes place between the system ~~consisting perfectly~~ and surroundings is called adiabatic process. This process is carried in a perfectly insulating vessel.

(g) Reversible adiabatic process / Isentropic process

A process is reversible and adiabatic if and only if it has zero entropy change.

(h) Irreversible adiabatic process

If the pressure, volume and temperature at these points on expansion and on contraction are not same, then the process is irreversible process and it is adiabatic process.

(I) External and Internal workdone

The work that is done either by the system or on the system is called the external work.

The work that is done by one part of the system is called internal work.

Eg: Intermolecular force of attraction betn the gas

Relation between C_p and C_v:

$$C_p - C_v = R$$

Adiabatic eqn of a perfect gas:

From 1st law of thermodynamics,

$$dq = du + pdv \longrightarrow (1)$$

For adiabatic,

$dq = 0$, $du = C_v dT$ for one mole of gas

Then,

$$C_v dT + pdv = 0 \longrightarrow (2)$$

For a perfect gas

$$PV = RT$$

Diff. on both sides, we get

$$PdV + Vdp = RdT$$

or, $\frac{Pdv + Vdp}{R} = dT$

putting this value in equation (3) we get

$$C_v\left(\frac{Pdv + Vdp}{R}\right) + Pdv = 0$$

or, $C_vPdv + C_vVdp + RPdv = 0$

or, $(C_v + R)Pdv + C_vVdp = 0$

Since, $C_p - C_v = R$

or, $C_p = C_v + R$

$\therefore C_pPdv + C_vVdp = 0 \longrightarrow (3)$

Dividing both sides by C_vPV, we have

$$\frac{C_p}{C_v}\frac{dV}{V} + \frac{dP}{P} = 0$$

But $\frac{C_p}{C_v} = \gamma$

$$\therefore \gamma\frac{dV}{V} + \frac{dP}{P} = 0$$

Integrating

$$\gamma\int\frac{dV}{V} + \int\frac{dP}{P} = \text{constant } (K)$$

where K is constant of integration

$\gamma \log V + \log P = K$

or, $\log V^{\gamma} + \log P = K$

$pv^{\gamma} = e^{K}$ = a constant

pv^{γ} = constant $\longrightarrow$ (4)

Which is equation of state for adiabatic

If P_1, V_1 and P_2, V_2 are the values corresponding to intial and final states during an adiabatic process, then

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

In terms of temperature and volume

$P = \frac{RT}{V}$ Then, eqn (4) becomes

$TV^{\gamma-1}$ = constant

In general,

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

In terms of temp. and pressure

Use, $V = \frac{RT}{P}$

Then,

$T^{\gamma}p^{1-\gamma}$ = constant

Workdone during an adiabatic process

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

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

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

Then,

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

or, $W = \int_{V_1}^{V_2} K \frac{dV}{V^{\gamma}}$

or, $W = K\int_{V_1}^{V_2} V^{-\gamma} dV$

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

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

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

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

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

$$\text{or, } W = \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]$$

$$\text{or, } W = \frac{1}{1-\gamma}R\left[T_2 - T_1\right] \quad [\because PV = RT]$$

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

Workdone during isothermal process

we have,

$$\text{Workdone } (W) = \int_{V_1}^{V_2} p\,dV$$

But $PV = RT$

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

Then,

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

or, $W = RT (\ln V)_{V_1}^{V_2}$

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

For isothermal process

$P_1V_1 = P_2V_2 \Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_2}$

Then,

$$W = RT \ln \frac{P_1}{P_2}$$