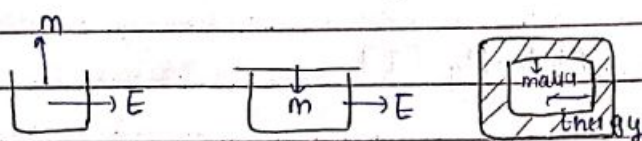


5 Feb 2022

THERMODYNAMICS

Science which deals with study of different forms of energy with quantitative relationship.

System and Surrounding - universe



Open system

Closed system

Isolated system

State function and path functions -

State function

- Those properties of system that depend only on initial and final state of system but it does not depend on path.

ex - enthalpy (H), entropy (S), gibbs free energy (G), Internal energy (U) etc.

Path function

- Those properties of system that depend on path.
- ex - work, heat

Extensive and Intensive property -

Extensive - Those properties which depend on size of matter present in the system

m_1	m_2
V_1	V_2
T	T
P	P
d	d

ex - mass, volume, all type of Energy, mole etc.

Intensive - does not depend on size of matter

ex - pH, molarity, Temp, Pressure, density, all type of constants etc.

Note The ratio of 2 extensive properties is equal to intensive property.

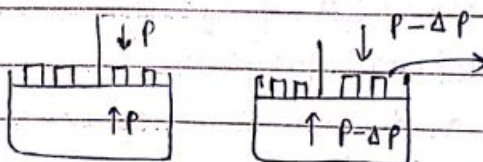
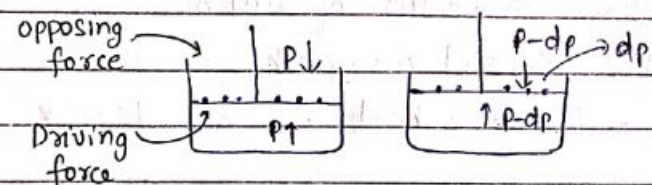
$$\frac{\text{mole [E]}}{\text{Volume [E]}} = \text{Molarity [I]}$$

$$\frac{\text{mass (E)}}{\text{Volume (E)}} = \text{density (I)}$$

Reversible and Irreversible Thermodynamic Process -

Reversible

Irreversible



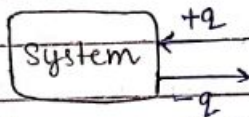
- It is carried out in multistep
- It takes infinite time for completion (very slow)
- Each step is in equilibrium with previous step.
- This is ideal process
- Driving force is slightly large than opposing force
- Driving force > opposing force

- It is carried out in single step
- It is immediately completed (fast process)
- Equilibrium exist only with initial and final state not in b/w
- This is real process
- Driving force is very very large than opposing force
- Driving force >>> opposing force.

Heat

- * It is denoted by q .
- * It is a form of energy which is exchange between system and surrounding. due to diff. of temp.

- * q is +ve when heat is transfer from surrounding to system while q is -ve, which means heat is transfer from system to surrounding.



unit - J, erg, calorie, atm lit

$$1 \text{ J} = 10^7 \text{ erg}$$

$$1 \text{ J} = \frac{1}{4.182} \text{ cal.}$$

$$1 \text{ cal} = 4.182 \text{ J}$$

→ Specific heat capacity (c):-

Amount of heat req. to rise the temp. of 1g of a gas by 1°C or 1K

$c = \frac{q}{m\Delta T}$
OR $q = c \cdot m\Delta T$

for Isothermal process,

$$\Delta T = 0 \text{ so } c = \infty$$

for Adiabatic process,

$$q = 0 \text{ so } c = 0$$

So, we can say that specific heat capacity value can be from zero to infinite.

Specific heat capacity at constant vol. and constant pressure should be written as c_v and c_p respectively.

$$c_v = \frac{q}{m \cdot \Delta T} \quad (\text{s.H.c at constant } v)$$

$$c_p = \frac{q}{m \cdot \Delta T} \quad (\text{s.H.c at constant pressure})$$

Molar specific heat capacity :-

• denoted by (C)

$$C = \frac{q}{n \Delta T}$$

$$C_v = \frac{q}{n \Delta T}$$

$$C_p = \frac{q}{n \Delta T}$$

→ Relation between c_v and c_p -

$$c_p - c_v = R \quad (\text{Mayer eq.}) \quad \text{--- (i)}$$

Here R = Universal Gas constant

$$R = 1.98 \text{ Calorie/mole } K \quad \text{or} \quad 8.31 \text{ Joule/mole } K$$

→ Poisson's ratio (Adiabatic Index)

$$\frac{c_p}{c_v} = \gamma \quad (\text{gamma}) \quad \text{--- (ii)}$$

Some different Relation or formulas —

$$C_p = \gamma C_v \quad \text{--- (3)}$$

③ in ①

$$\gamma C_v - C_v = R$$

$$C_v(\gamma - 1) = R$$

$$C_v = \frac{R}{\gamma - 1} \quad \text{--- (4)}$$

Relation between degree of freedom (F) and Molar heat Capacity —

Molar heat capacity of diff. gases depends on degree of freedom (DOF) for monoatomic gas the value of DOF is 3, for diatomic gas is 5 and triatomic or polyatomic it should be 6

$$C_v = \frac{F}{2} \cdot R \quad \text{--- (5)} \quad C_p = R \left(1 + \frac{F}{2}\right) \quad \text{--- (6)}$$

	C_v $\left(\frac{F}{2} R\right)$	C_p $\left(R \left(1 + \frac{F}{2}\right)\right)$	γ $\frac{C_p}{C_v}$
Monoatomic gas	$\frac{3}{2} R$	$\frac{5}{2} R$	$\frac{5}{3} = 1.66$
Diatomic gas	$\frac{5}{2} R$	$\frac{7}{2} R$	$\frac{7}{5} = 1.4$
Polyatomic gas	$3R$	$4R$	$\frac{4}{3} = 1.33$

Decreasing order of poisson ratio for different gases should be
 $\gamma_{\text{Monoatomic}} > \gamma_{\text{diatomic}} > \gamma_{\text{polyatomic}}$
 1.66 1.40 1.33

Que calculate the C_v and C_p value in calorie for oxygen gas.

$$C_v = \frac{f}{2} \times R = \frac{5}{2} \times 2 = 5 \text{ calorie}$$

$$C_p = 2 \left(1 + \frac{5}{2}\right) = \frac{2+5}{2} \times 2 = 7 \text{ calorie}$$

Que calculate the C_p value in J for CO_2 gas

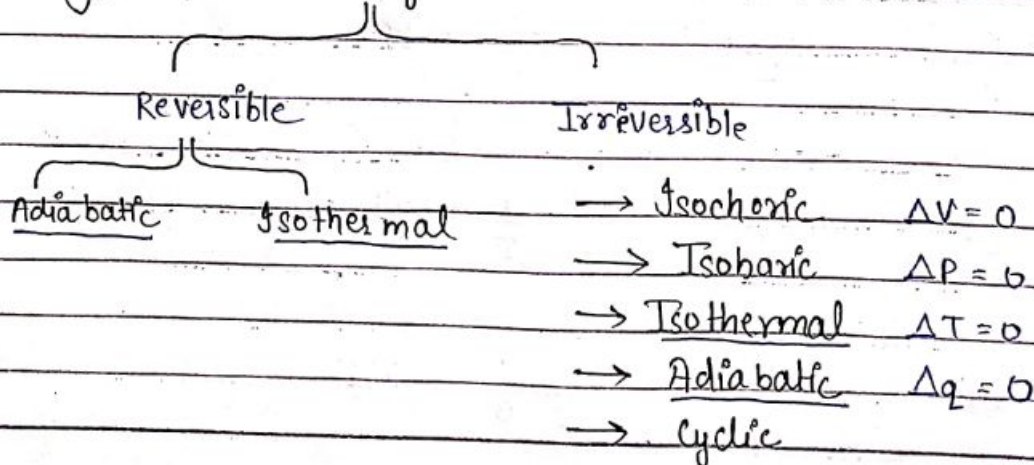
$$C_p = R \left(1 + \frac{f}{2}\right) = \left(1 + \frac{6}{2}\right) \times 8.31$$

$$4 \times 8.31 = 33.24 \text{ J}$$

* The value γ also calculated by

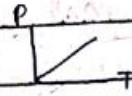
$$\gamma = 1 + \frac{2}{f}$$

→ Type of Thermodynamic Process —



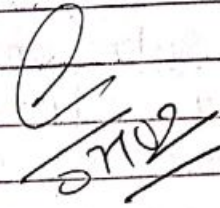
1) Isochoric Process -

- change in volume $\Delta V = 0$
- Pressure and Temperature is variable
- Work done is equal to $-P_{ext} \Delta V = 0$
- It is applicable for closed system (irreversible process)



2) Isobaric Process -

- Pressure is constant
- Carried out in open system
- Volume and temperature are variable
- Work done should be equal to $-P_{ext} \Delta V$
- It is always irreversible process.



Isothermal and Adiabatic Process -

$\Delta T = 0$
conductive system
very slow process

$\Delta q = 0$
insulated system
very fast process

$PV = \text{constant}$
 $P_1 V_1 = \text{constant}$
 $P_2 V_2 = \text{constant}$

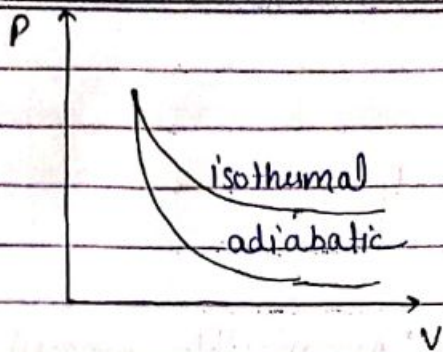
$PV^r = \text{constant}$
 $P_1 V_1^r = \text{const.}$
 $P_2 V_2^r = \text{const.}$

P and V variable
follow Boyle's law
property

P & V should be variable
follow Boyle's law but not
proper hold

$$\Delta V = 0$$

$$\Delta S = 0$$



Cyclic process -

When a system undergoes a no. of diff pathway process and finally returned to its initial state.

It is termed as cyclic process

In cyclic process, all change in state fun. will be zero.

Example of Adiabatic process -

Brusting of tyre and shaking thermos

