The branch of phys that studies the general properties of a substance connected to thermal motion in condition of equilibrium is called thermodynamics

Thermodynamics deals with the transformation of one from of energy into another during chemical and physical changes.

1. Partial derivative of a function:

If a function contains more than one independent variable then differentiation of the func. w.r.t any one of the variables is called partial derivative of the func.

If $f = f(x, y)$ be an explisive func. then $\left[\frac{\partial f}{\partial x}\right]_y$ & $\left[\frac{\partial f}{\partial y}\right]_x$ are the partial derivative of f w.r.t. x and y respectively.

the higher order derivetive are

$$f_{xy} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x = \frac{\partial^2 f}{\partial x \partial y}$$

$$f_{yx} = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y = \frac{\partial^2 f}{\partial y \partial x}$$

ii) <u>Total differentiation:</u>

Let $f = f(x, y, z)$ be a function of the variables x, y and z. Then the total differentiation of f is given by

$$df = \left(\frac{\partial f}{\partial x}\right)_{yz} dx + \left(\frac{\partial f}{\partial y}\right)_{xz} dy + \left(\frac{\partial f}{\partial z}\right)_{xy} dz$$

iii) <u>Cyclic rule:</u>

<u>Q.1</u> Proove that if $f(P, V, T) = 0$,

then $\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = -1$

<u>Ans</u> Since,

$$f(P, V, T) = 0$$

Then we can write.

$$P = f(V, T),\ V = f(T, P),$$

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \quad \text{---(i)}$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{---(ii)}$$

from (i) and (ii)

$$dP = \left(\frac{\partial P}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right] + \left(\frac{\partial P}{\partial T}\right)_V dT$$

$$= \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial P}{\partial T}\right)_V dT \qquad \text{(iii)}$$

eqn 3 is valid for all values of P, V, and T

Let us consider P and T as independent variables. so that dP and dT may have any values.

i) $dP \neq 0$ & $dT = 0$

then eqn (iii) becomes

$$1 = \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}$$

(ii) $dP = 0$ & $dT \neq 0$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial P}{\partial T}\right)_V = 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$= -\left\{\frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}\right.$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

* Exact differendiation

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

i.e, $$\frac{\partial^2 Z}{\partial y \partial x} = \frac{\partial^2 Z}{\partial x \partial y}$$

The eq^n of state of ideal gas is $PV = RT$

Q.2 ~~show~~ that

dT is a perfect exact differencial

$$PV = RT$$

$$\left(\frac{\partial T}{\partial V}\right)_P = P/R$$

$$\frac{\partial^2 T}{\partial P \partial V} = \frac{1}{R}$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R}$$

$$\left(\frac{\partial^2 T}{\partial V \partial P}\right) = \frac{1}{R}$$

so, $$\frac{\partial^2 T}{\partial P \partial V} = \frac{\partial^2 T}{\partial V \partial P}$$ so,

dT is perfect.

Q: what is mean by state function?

Ans The function is called state func. whose value depends only on parameter of the system but not on the path.

eg: internal energy (U), enthalpy (H), entropy (S)
but Q (Heat) and P (Pressure) are not the state func. because its value depends on way of transformation those are called path func.

* Thermodynamic equillibrium of a system :

a system is in thermodynamic equillibrium if it is in mechanical equillibrium, thermal and chemical equillibrium

(i) Mechanical equillibrium : It is established when there is no unbalansed force in the interior of the system and also between the system and surroundings

(ii) Thermal equillibrium : In thermal equillibrium all parts of the system are at the same temperature and this temperature is the same as that of the surrounding.

(iii) Chemical equillibrium: When the composition of the system remains fixed and defined the system is said to be in chemical equillibrium.

Eqn's of state

To define the state of eqn of a gasious system completely, we must know three parameters (P, V, T)

These parameters are linked by ~~s~~ some suitable relationship called the eqn of state, which may be represented as f(P,V,T)

$f(P,V,T) = \text{constant}.$

A simple form of the eqn of state is that for a perfect gas obtain from the combn of Charle's and Boyel's law,

$PV = RT.$

Q.1 ~~can~~ Is ~~u equal to~~ $u = \frac{3}{2}NKT$ be an eqn of state

An Here the eqn is $U = \frac{3}{2}NKT$, as these eqn is a func of u and T but not of P, V, and T, so

This not an eqⁿ of state.

Coefficient of thermal expansion (α)

It is defined as the rate of change of volume with temparature at constant pressure per unit volume of the substance. This is called also thermal expansivity.

$$\therefore \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Compressivity coefficient (β)

It is defined as the rate of change of volume with pressure at constant temperature per unit volume of the substance.

$$\therefore \beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Isothermal Bulk modulus (B)

The isothermal Bulk modulus which may be defined as the ratio of pressure change to the change volume per unit volume at constant temperature

$$\therefore B = -\left(\frac{\partial P}{\frac{\partial V}{V}}\right)_T$$

$$= -V\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\beta} \quad \therefore B = -\frac{1}{\beta}$$

* **What is process?** when 1 of more of the parameters of a system change, the state of the system also changes. It is said that the system is undergoing a process.

* **Reversable Process:**

A reversable process is ~~the~~ one which can be reversed in such a way that all chages taking place in the direct process are exactly repeted in the inverse order and ~~an~~ oppose same and no other chaanges are let in the external bodies.

In revesable proces the changes takes place slowly and ~~occour~~ occour in succesive stages of ~~infinites~~ ~~ici~~ of infinitecinal order. This reveseable changes is called Quasistatic process.

In the reversable process the follwing condn. should be satisfied.

(i) The dissipative effect must be absent.

(ii) The pressure and temp. of the system must never differ from it surroundings at any stage of the process. The process must take place very slowly such that the system must ~~mainta~~ maintain ~~virual~~ ~~virtual~~ thermodynamic equilibr. at all of the small steps.

~~Ex~~ ~~example~~ ex: Suppose in a process, heat is absorved by a substance to produce external work, if an equal quantity of external work is done on the substance at any stage, then it gives the same quantity of heat, the process is called to be reversable one.

If two bodies are at the same temp. and heat tranfer take place between them, then the process will be reversable one

* Irreversable process

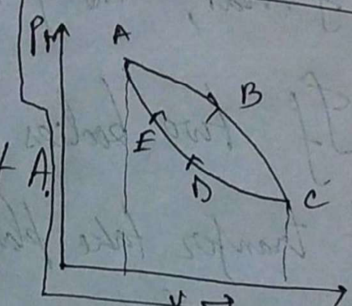
: The proces in which all changes are exactly ~~reapeted.~~ repeted in ~~are~~ the inverse order and in opposite sence, Then it is called irreversable process. In fact it will be seen that all natural process are irreversable process.

Heat produce by friction, Heat tranfer by conduction and radiation, heat produce by electric resistance, and diffusion of gas etc. are examples of irreversable process.

Cyclic process

Cyclic process is the process which brings the system to the same initial state after a series of operations (expansion and compression)

Let us consider a given mass of a gas its initial state be represented by a pt A in the P-V diagram. Now



first the gas expansions along the path ABC and then compresses along the path CDEA to come back to its initial state A. It is a cyclic process and the closed curve ABCDEA is called a cycle.

As the working substance comes back to its initial state, the change in internal energy

$\boxed{dU = 0}$ is zero.