SEMESTER I
(PHYSICAL CHEMISTRY HONOURS)

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STATE OF A SYSTEM:
EXACT AND INEXACT DIFFERENTIAL

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State of a system

- ✓ The ***state of the system*** is the condition in which the state is present when the macroscopic properties have a definite value.
- ✓ The state of as ystem can be defined only when the system has reached *thermodynamic equilibrium*.
- ✓ The state can be defined or specified in terms of some measurable properties (pressure , temperature, elasticity, heat capacity , volume, etc) of the system. For example, for an ideal gas system, the state can be defined by specifying the pressure, temp., volume if the gas is kept in a closed container.These measurable properties are called ***state variables***.
- ✓ For a closed system , when composition is fixed , ***n*** or ***mass*** is not a state variable.
- ✓ **State function** is the property of the system which depends only on the state of the system and independent of the path by which the state is reached.
- ✓ The **cyclic process** is one where the system reaches the same state after a series of changes.

Exact differentials and state functions

Thermodynamic functions like pressure, volume, temperature are state functions. The change in the values of these quantities does not depend on how the change is carried out but depends only on the initial and final states of the system.

If **Z** is any thermodynamic property of a homogeneous system of constant composition, then its value is completely determined by the three thermodynamic variables, pressure, volume and temperature. They are related to one another by an equation of state . Any two of three variables is sufficient to define any thermodynamic property.

We can write

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

Where Z may be energy, enthalpy, volume, entropy etc . Any change in Z resulting from changes in the values of P and T is given by:

- **$\Delta Z = Z_{\text{final state}} - Z_{\text{initial state}}$**

Using the property of calculus , the total differential for an infinitesimal change dZ in the **state property Z** as

$$dZ = \left(\frac{\partial Z}{\partial P}\right)_T dP + \left(\frac{\partial Z}{\partial T}\right)_P dT \quad \text{(dZ is called a complete or exact differentia)}$$

$$dZ = L(P,T)\,dP + \mathrm{M(P,T)}\,dT$$

$$L(P,T) \equiv L = \left(\frac{\partial Z}{\partial P}\right)_T ; \left(\frac{\partial L}{\partial T}\right)_P = \frac{\partial^2 Z}{\partial T \partial P}$$

$$M(P,T) \equiv M = \left(\frac{\partial Z}{\partial T}\right)_P ; \left(\frac{\partial M}{\partial P}\right)_T = \frac{\partial^2 Z}{\partial P \partial T}$$

- ***For a state function $\frac{\partial^2 Z}{\partial T \partial P} = \frac{\partial^2 Z}{\partial P \partial T}$ (a state function does not depend on path taken ; i.e, the sequence of steps during a transformation)***

  i. e, $\left(\frac{\partial L}{\partial T}\right)_P = \left(\frac{\partial M}{\partial P}\right)_T$ (This is known as Euler's theorem of exactness)
- ***For an exact differential, its value for cyclic transformation is zero.***

$$\oint dZ = 0$$

$$\oint \quad = cyclic\ integral$$

- ***d Z between two s pacified states is independent of path of transformation***
- ***Z is single valued depending entirely on the values of temperature and pressure***
- ***Prove that P is an exact differential taking the ideal gas equation for one mole of gas***

Soln .

P = f (T,V)

For dP to be an exact differential, we have

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

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

Using ideal gas equation

$$PV = RT$$

$$\boldsymbol{P = \frac{RT}{V}}; \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}\left(\frac{\partial T}{\partial T}\right) = \frac{R}{V}; \qquad \frac{\partial^2 P}{\partial V \partial T} = -\frac{R}{V^2} \qquad \textbf{(1)}$$

$$\text{and} \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} \quad ; \quad \frac{\partial^2 P}{\partial T \partial V} = -\frac{R}{V^2} \qquad \textbf{(2)}$$

From (1) and (2) , we have, $\frac{\partial^2 P}{\partial V \partial T} = \frac{\partial^2 P}{\partial T \partial V} = -\frac{R}{V^2}$

Hence dP is an exact differential.

Assignment :

Similarly,

- *Prove V is an exact differential using equation :*

$PV = RT$

- *Prove P is an exact differential using equation:*

$\left(P + \frac{a}{V^2}\right)V = RT$ *(Hint : $P = \frac{RT}{V} - \frac{a}{V^2}$)*

- *Find out which of these:*
  PdV, Vdp, PdV +VdP are state functions or not

Cyclic Rule:

Considering any thermodynamic function Z as a function of Volume V and temperature T, we can write

$$Z = f(T, V)$$

$$dZ = \left(\frac{\partial Z}{\partial V}\right)_T dV + \left(\frac{\partial Z}{\partial T}\right)_v dT$$

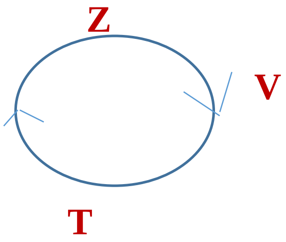
$If\ dZ = 0;$

$$\left(\frac{\partial Z}{\partial V}\right)_T dV = -\left(\frac{\partial Z}{\partial T}\right)_V dT$$

$$\left(\frac{\partial Z}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_Z = -\left(\frac{\partial Z}{\partial T}\right)_v$$

Rearranging we get,

$$\left(\frac{\partial Z}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_Z \left(\frac{\partial T}{\partial Z}\right)_v = -1$$



- **Prove that w is an inexact differential also written as** Type equation here.

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

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

$$d\omega = PdV = P\left(\frac{\partial V}{\partial P}\right)_T dP + P\left(\frac{\partial V}{\partial T}\right)_V dT \qquad \text{(i)}$$

$$w = f(P,T)$$

$$dw = \left(\frac{\partial w}{\partial P}\right)_T dP + \left(\frac{\partial w}{\partial T}\right)_P dT \qquad \text{(ii)}$$

Comparing the coefficients in (i)and(ii)

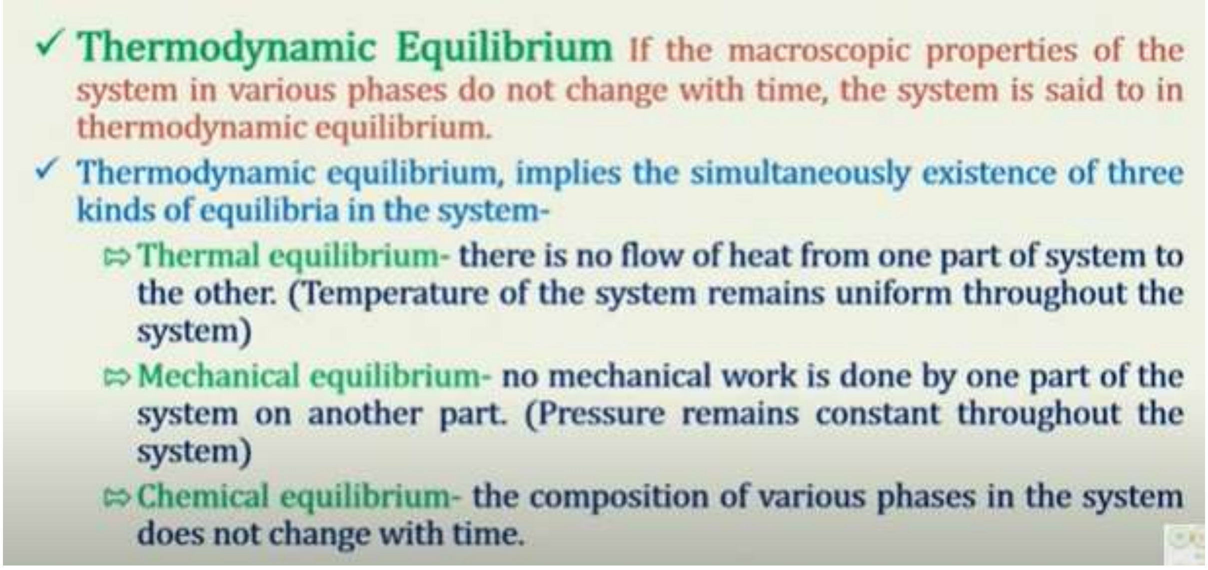
- $(a)\left(\frac{\partial \omega}{\partial P}\right)_T = P\left(\frac{\partial V}{\partial P}\right)_T$

  Or, $\frac{\partial^2 \omega}{\partial T \partial P} = P\left(\frac{\partial^2 V}{\partial T \partial P}\right)$

- And (b) $\left(\frac{\partial \omega}{\partial T}\right)_P = P\left(\frac{\partial V}{\partial T}\right)_P$

  Or, $\frac{\partial^2 w}{\partial P \partial T} = \left(\frac{\partial V}{\partial T}\right)_P + P \cdot \frac{\partial^2 V}{\partial P \cdot \partial T}$

$$\frac{\partial^2 \omega}{\partial T \partial P} \neq \frac{\partial^2 w}{\partial P \partial T}$$



- ✓ **Thermodynamic Equilibrium** If the macroscopic properties of the system in various phases do not change with time, the system is said to in thermodynamic equilibrium.
- ✓ Thermodynamic equilibrium, implies the simultaneously existence of three kinds of equilibria in the system-
  - ⇨ Thermal equilibrium- there is no flow of heat from one part of system to the other. (Temperature of the system remains uniform throughout the system)
  - ⇨ Mechanical equilibrium- no mechanical work is done by one part of the system on another part. (Pressure remains constant throughout the system)
  - ⇨ Chemical equilibrium- the composition of various phases in the system does not change with time.