

Statistical Thermodynamics

**B.Sc Chem (H) 5 th Semester
Physical Chemistry**

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➤ What is Statistical Thermodynamics?



Statistical World deals with
microscopic world while
Classical world deals with
macroscopic world



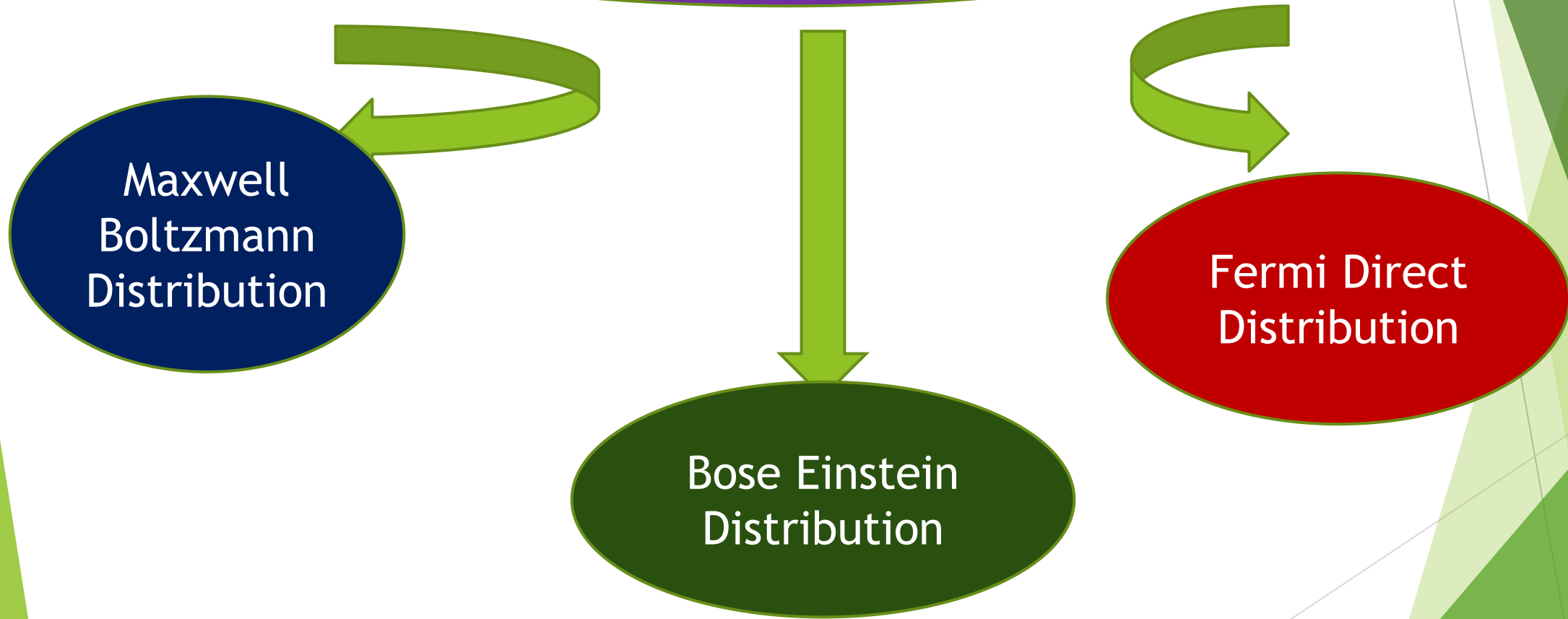
**Difference between
Classical and
Statistical
Thermodynamics**

Distribution of Particles in energy levels according to statistical thermodynamics

Maxwell Boltzmann Distribution

Bose Einstein Distribution

Fermi Direct Distribution



Maxwell Boltzmann Distribution

Assumptions-

1. Particles are distinguishable.
2. No restrictions are there i.e. any one of the particles can occupy any of the energy level.
3. The distribution is independent of internal structure of the particles.

Bose Einstein Distribution

Assumptions--

1. Particles are indistinguishable.
2. No restrictions are there i.e. any one of the particles can occupy any of the energy level.
3. Only those particles follow this distribution whose nuclear spins are in integral multiple e.g. 1,2,3.
These particles are called Boson particles.
4. Wave functions of boson particles are symmetric e.g. hydrogen, helium, nitrogen etc.

Fermi Direct Distribution

Assumptions--

1. Particles are indistinguishable.
2. Restrictions are there e.g. only one particle can occupy any of the energy level.
3. Only those particles follow this distribution whose nuclear spins are in half integral multiple e.g. $1/2, 3/2, 7/2$. These particles are called Fermions.
4. Wave functions of these particles are antisymmetric.

Ensembles

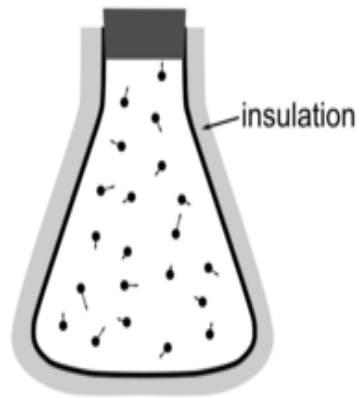
Large collection of identical units i.e,
molecules , particles and atoms

Ensembles

Probability densities in phase space cannot be computed by considering only a single system at a single instant in time. Such a system will be in some random microstate, but what we need is the statistics of such microstates. This problem was solved by Gibbs, who considered ensembles that consist of a very large number of identical systems in possibly different microstates. The microstates for a system with M molecules with f degrees of freedom each are points in $2fM$ dimensional phase space. If we have information on the probability density assigned to such points, we can use probability theory to compute thermodynamical state function.

CLASSIFICATION OF ENSEMBLES

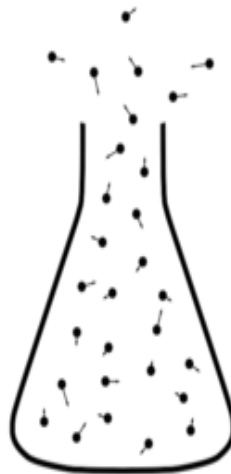
Statistical ensembles



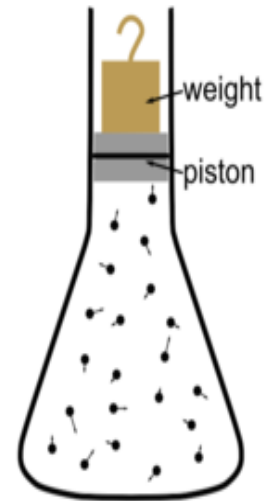
Microcanonical
(const. NVE)



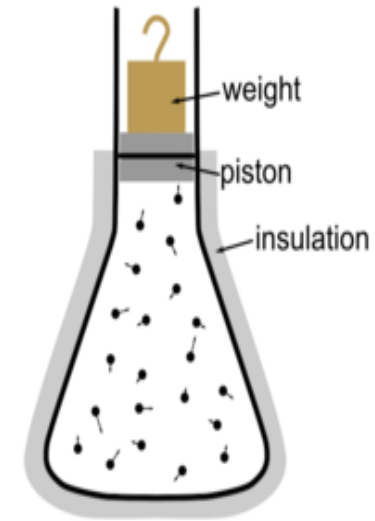
Canonical
(const. NVT)



Grand Canonical
(const. μVT)



Gibbs or
Isobaric-isothermal
(const. NPT)

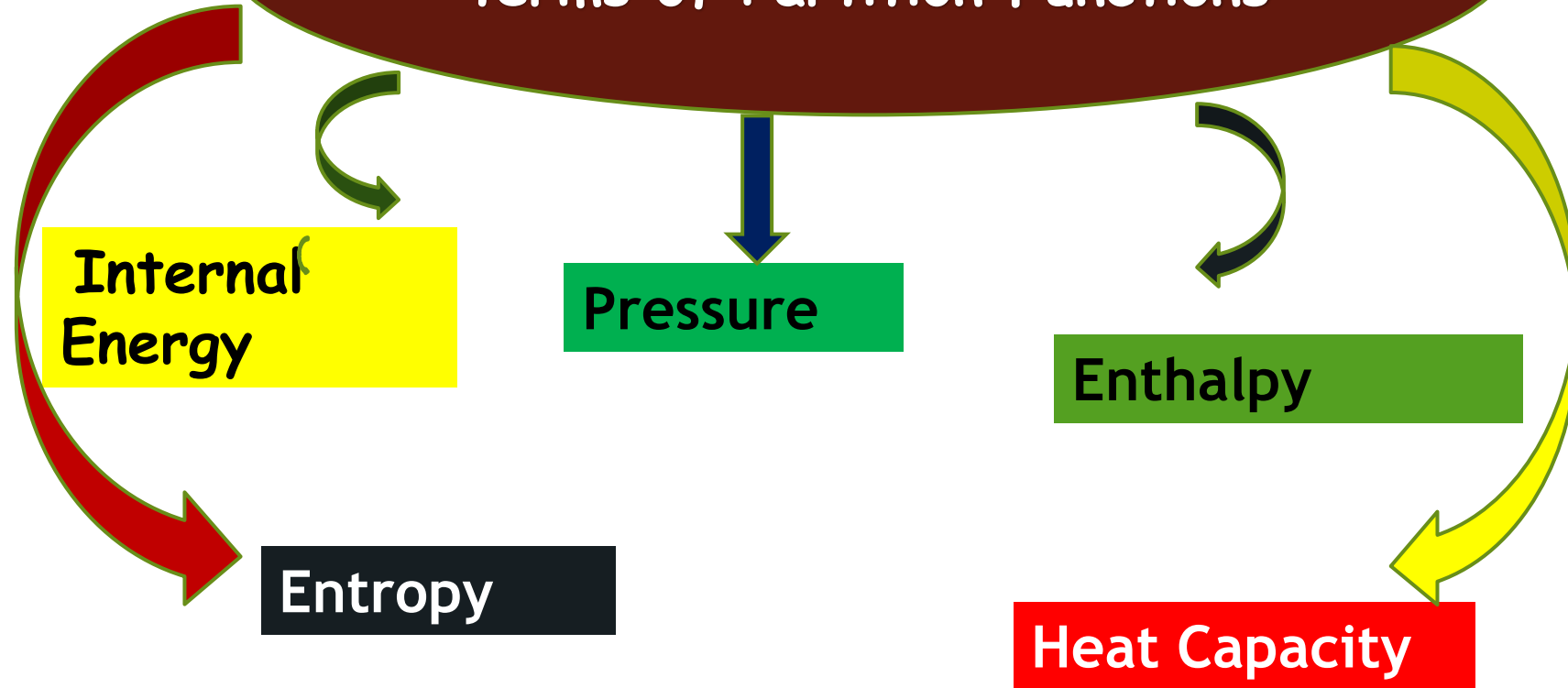


Enthalpy or
Isoenthalpic-isobaric
(const. NPH) $H=E+PV$

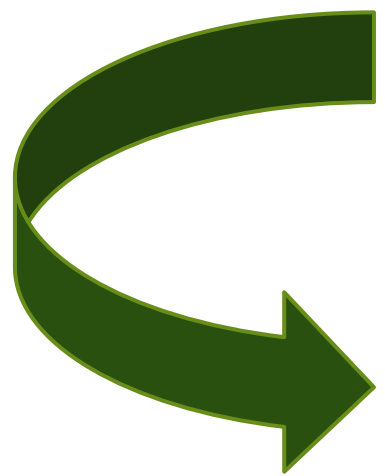


Discussions of problems on
fermions and Bosons

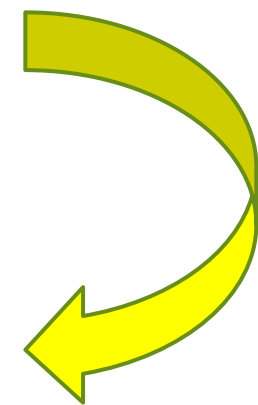
Thermodynamic properties in terms of Partition Functions



Partition Function



Concept



Properties

Numerical Problems

