

## Criteria for Thermodynamic equilibrium

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Thermodynamic equilibrium is an internal state of a single thermodynamic system. For a completely isolated system  $S$  is maximum for thermodynamic equilibrium. For a system with controlled constant temp. and volume,  $A$  is minimum at thermodynamic equilibrium. For a system with controlled constant temp. and pressure,  $G$  is minimum at thermodynamic equilibrium. The various types of equilibrium are achieved as follows:—

- 1) Two systems ~~are~~ are in thermal equilibrium when their temp. are the same.
- 2) Two systems are in thermal equilibrium when their pressure are the same.
- 3) Two systems are in diffusive equilibrium when their chemical potential are the same.
- 4) All forces are balanced and there is no significant external driving force.

The second law of thermodynamics states that when a body of materials starts from an equilibrium state in which portions of it are held at different states by more or less permeable or impermeable partitions and a thermodynamic operation removes or makes the partitions more permeable and it is isolated then it spontaneously reaches its own new state of internal thermodynamic equilibrium and this is accompanied by an increase in the sum of the entropies of the portions.

Classical thermodynamics deals with states of dynamic equilibrium. The state of a system at thermodynamic equilibrium is the one for which some thermodynamic potential is minimised or for which the entropy ( $S$ ) is maximised for specified conditions. One such potential is the Helmholtz free energy ( $A$ ), for a system with surroundings at constant temperature and volume.

$$A = U - TS$$

Another potential, the Gibbs free energy ( $G$ ) is minimised at thermodynamic equilibrium in

System with surroundings at controlled constant temperature and pressure.

$$G = U - TS + PV$$

Where  $T$  denotes the absolute thermodynamic temperature,  $P$  the pressure,  $S$  the entropy,  $V$  the volume and  $U$  the internal energy of the system.

Thermodynamic equilibrium is the unique stable stationary state that is approached or eventually reached as the system interacts with its surroundings over a long time. The above mentioned potentials are mathematically constructed to be the thermodynamic quantities that are minimised under the particular conditions in the specified surroundings.

A system in thermodynamic equilibrium may move with uniform acceleration through space but must not change its shape or size while doing so. Thus it is defined by a rigid volume in space. It may lie within external fields of force. The system can be in thermodynamic equilibrium

only if the external force & fields are uniform and are determining its uniform acceleration or if it lies in a non-uniform force field but is held stationary there by local forces such as mechanical pressure on its surface.

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