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Thermodynamic Equilibrium.

Promita Ghosh,
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Abstract:

This article is about equilibrium in a thermodynamic sense.

An absence of unbalanced force in the interior of a system, or between the system and the surroundings, implies mechanical equilibrium. Non fulfillment of this condition causes changes, both in the system and in the surroundings in general, which cease only when the mechanical equilibrium is restored.

The absence of any spontaneous change of internal structure by way of diffusion or chemical reaction or by both in a system in mechanical equilibrium implies chemical equilibrium.

For a system in mechanical and chemical equilibrium, thermal equilibrium is said to be attained when there is no spontaneous change in the coordinates of the system when separated from the surroundings by diathermic wall. It is obvious that in thermal equilibrium the temperature is the same all throughout the system and is identical with that of the surroundings.

When all the conditions stated above are fulfilled by a system, it is said to be in thermodynamics equilibrium and there will be no proneness of either the system or the surroundings to any change of state. The state of thermodynamic equilibrium is specified in terms of macroscopic coordinates which we may designate as thermodynamics variables or coordinates.

For systems undergoing rate process, thermodynamical description of the same is not possible. The system in the event of failing to fulfill the conditions of any of the three types of equilibrium is said to be in non equilibrium state. This may be due to an unbalanced force in the interior of a system, or between the system and the surroundings. Phenomena like turbulence, acceleration etc. drift the system to states where pressure cannot be defined for the system as a whole and subsequently temperature and density vary from point to point. The states traversed by the system cannot be represented by thermodynamic coordinates. Under such circumstances, the system is divided into a large number of subsystems which are considered to be in local thermodynamic equilibrium. The formalism of non-equilibrium thermodynamics is distinct from that of the equilibrium thermodynamics. The thermodynamic coordinates (X, Y, Z) specifying an equilibrium state are related among each other by an equation of the form f(X,Y,Z) = 0 , and is known as the equation of state for the system.

For a gas confined in a volume V it takes the form f(p,V,T) =0. For an ideal gas , pV = nRT.

Equation of State for some Physical Systems:

System	Thermodynamic variables	Equation of state (parametric form)
1. Chemical or hydrostatic	p, V, T	$f(p, V, T) = 0$
2. Stretched wire (elastic system)	L, F, T	$f(L, F, T) = 0$
3. Magnetic system	M, B, T	$f(M, B, T) = 0$
4. Electric cell	Z, E, T	$f(Z, E, T) = 0$
5. Surface film	A, S, T	$f(A, S, T) = 0$

Reference:

Thermal physics —A.B. Gupta , H.P. Roy.