Notes on Thermodynamic Systems

There are a number of definitions that are needed as one begins a discussion of thermodynamic systems. These defined quantities actually help establish the conceptual framework for our further studies in this area.

Microscopic Variable A variable pertaining to the individual atoms and molecules making up the system. Examples include the x component of a particle's velocity, the orientation of the axis of a diatomic molecule, the quantum number for a particular vibrational mode of a molecule, and the magnetic moment vector of a paramagnetic ion.

Macroscopic Variable A measurable quantity used to describe the gross state of the system. It depends collectively on the behavior of all the atoms and molecules. These are also referred to as thermodynamic variables.

Extensive Variables The system under consideration is often defined as encompassing some specific N molecules. Then extensive variables are those whose magnitude is proportional to N.

Intensive Variables Those macroscopic variables whose magnitude is independent of N.

Extensive	Intensive
V volume	P pressure
A area	$\mathcal{S}$ surface tension
L length	$\mathcal{F}$ tension
$\mathcal{P}$ polarization	$\mathcal{E}$ electric field
M magnetization	H magnetic field
$\ldots\ldots\ldots$	$\ldots\ldots\ldots$
	T temperature
U internal energy	

The variables above the line should be familiar from courses in mechanics and electricity and magnetism. Those below the line are new and will require further discussion.

Adiabatic Walls Partitions which provide complete isolation between two systems. Changes in one system do not influence the other in any way.

Diathermic Walls Partitions which separate two systems but do allow one to influence the other: heat may flow or work may be done across this type of wall.

Equilibrium A state reached by a system enclosed by adiabatic walls after any transient behavior has died away. The macroscopic variables are independent of time. The probability density for the microscopic variables is independent of time. Turbulence, temperature gradients, internal stresses, and "sloshing" motion have disappeared. The times necessary to achieve equilibrium vary: non-uniform concentrations in alloys and amorphous forms of crystalline solids can persist for long periods of time. The system is not static, however, in that there is still motion on the atomic scale. There are many microscopic states of the system that will correspond to the same macroscopic state.

Steady State The system is not isolated and not in thermal equilibrium, yet the macroscopic variables are not changing. Some external field is driving a current such as heat flow, electrical conduction, or mass motion.

Complete Specification of an equilibrium state. For each system there are a certain number of the macroscopic variables (designated the independent variables) which must be given in order to be able to determine all of the other macroscopic variables (referred to as the dependent variables). Although the *number* is fixed for a given system, there are usually many choices for the particular set of independent variables. Examples include

simple fluid (homogeneous gas or liquid): 2
P, V or T, P or U, V etc.

binary mixture : 3
$P, V, C_A \equiv N_A/(N_A + N_B)$, or T, V, C_B etc.

rigid lattice of magnetic dipoles : 2
T, H or U, M etc.

gas of electric dipoles : 3
$P, V, \mathcal{E}$ or $T, P, \mathcal{P}$ etc.

Equation of State A functional relationship giving some major dependent variable in terms of the independent ones. Or, since one often does not know which of the variables will be taken to be independent in a subsequent calculation, a functional relationship between major macroscopic variables. Examples include

ideal gas : $PV = NkT$

simple elastic solid : $V = V_0(1 + \alpha T - \mathcal{K}_T P)$

simple paramagnet : $M = cH/(T - T_0) \quad T > T_0$

In Equilibrium with Each Other Imagine that two isolated systems are brought together and placed in thermal contact (using a diathermal wall). Under most circumstances this will result in each system undergoing some change and eventually settling down in a new equilibrium state. It is conceivable, however, that macroscopic state of each system would *not* change. If the latter case is true, one says that the two systems before contact were in thermal equilibrium with each other. One can also turn this around and say that when two systems are in thermal equilibrium with each other, if they are brought into contact their thermodynamic states will not change.

Thermodynamics Thermodynamics is the study of the relationships between the macroscopic variables, the work that can be done by a given system, and the heat transfer between systems. It does not deal with the microscopic variables. It requires the equation of state (or equivalent information in a different form) as an input.

Statistical Mechanics Statistical mechanics starts with a microscopic description of the system, usually the Hamiltonian as a function of the microscopic variables. It has two separate and qualitatively different goals: to determine the probability densities for the microscopic variables, and to derive the equations of state relating the macroscopic variables.