PHY 3513 K. Ingersent

Callen's Thermodynamic Postulates

The postulates below assume an understanding of

- the distinctions between *macroscopic* and *microscopic* variables, and between *extensive* and *intensive* macroscopic variables;
- the concept of a *system* surrounded by *boundaries* that restrict (hold constant) some or all of the extensive variables of the system;
- the definitions of *internal energy* and *work,* and the concept of *heat* defined through the First Law of Thermodynamics: $đQ = đU - đW$ (W being the work done *on* a system).

For convenience, Callen formulates the postulates only for *simple systems*, defined as systems that are macroscopically homogeneous, isotropic and uncharged, that are large enough that surface effects can be neglected, and that are not acted on by electric, magnetic, or gravitational fields. (Extension to more general systems is straightforward.)

Postulate I. *There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U, the volume V, and the mole numbers N_1, N_2, ..., N_r of the chemical components.*

(1) The *chemical composition* refers to the number of each type of particle considered to be important to the system (molecules, electrons, quarks, photons, ...).
(2) A *composite system* can be formed from multiple subsystems α, each of which has equilibrium states that are characterized by their own values $U^{(\alpha)}$, $V^{(\alpha)}$, $N_1^{(\alpha)}$, ..., $N_r^{(\alpha)}$. The composite system is *closed* if its total energy $U = \sum_\alpha U^{(\alpha)}$, its total volume $V = \sum_\alpha V^{(\alpha)}$, and its total mole numbers $N_r = \sum_\alpha N_r^{(\alpha)}$ are all restricted. *Internal constraints* may prevent free flow of energy, volume, or matter between the subsystems.

Postulate II. *There exists a function (called the entropy S) of the extensive variables of any [closed,] composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those which maximize the entropy over the manifold of constrained equilibrium states.*

(1) This key postulate is equivalent to part of the Second Law of Thermodynamics.
(2) The theory has nothing to say nothing about nonequilibrium states.

Postulate III. *The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.*

(1) The first sentence implies that the entropy is extensive.
(2) The differentiability condition requires the existence of the first partial derivative $(\partial S/\partial X)$ with respect to each extensive parameter X upon which the entropy depends. It will be shown later that thermodynamic stability also requires that $(\partial^2 S/\partial X^2) \leq 0$ for each X.
(3) The second sentence implies that U is a well-behaved function of S, V, and N_1, ..., N_r. Exception: A few artificial systems (not covered in this course) violate the monotonicity condition and have no unique $U(S, V, N_1, \ldots, N_r)$.

Postulate IV. *The entropy of any system [is non-negative and] vanishes in the state for which $(\partial U/\partial S)_{V,N_1,N_2,\ldots,N_r} = 0$ (that is, at the zero of temperature).*

(1) This is a restatement of the Third Law of Thermodynamics or the "Nernst postulate."
(2) It is the least important postulate because we generally look at entropy differences.