proaches equilibrium), yet is additive over the subdivisions of a system. This property, called entropy (S) is defined for any macrostate (i) as[2]

$$S_i = k \ln W_i \qquad \text{(IIIB-1)}$$

where k is the Boltzmann constant defined in Unit IA.[3] Thus, as a system approaches equilibrium, $W_i \to W_{eq}$, and the entropy of the system increases monotonically, $S_i \to S_{eq}$. Furthermore, if two systems are combined,

$$S_i = k \ln W_i = k \ln (W_{A,i} \cdot W_{B,i}) = k \ln W_{A,i} + k \ln W_{B,i} = S_{A,i} + S_{B,i}$$

Entropy like all other properties has an ensemble average value, as defined by eqn. IIIA-11

$$\hat{S} = \sum_{i=1}^{I^*} p_i S_i = \sum_{i=1}^{I^*} p_i k \ln W_i \qquad \text{(IIIB-2)}$$

Using the perception developed in Unit IIIA, for real systems

$$S_{eq} \to \hat{S} = k \ln W_{eq}$$

In Unit IIIA, we used trial-and-error procedures to determine the distributions, $n_{j,i}$. (W_i is analytically determinable once the $n_{j,i}$ are known.) The recognition that trial-and-error techniques are operationally impossible for real systems makes the development of the concept of equilibrium an extremely significant result of Unit IIIA. Since equilibrium macrostates have properties that are indistinguishable from the ensemble average, we need only determine the properties of this group to obtain average system properties. Furthermore, the properties of any member of this group are virtually the same so we can choose the one most amenable to analysis. This is the *most probable macrostate* characterized by W_{mp}. Its distribution and properties can be determined without trial and error using analytical procedures developed below. With this choice the equilibrium condition in terms of the property, entropy, is

$$\hat{S} = S_{eq} \simeq S_{mp} = k \ln W_{mp} \qquad \text{(IIIB-3)}$$

This is Boltzmann's equation.

With the knowledge that entropy of an isolated system is maximized in equilibrium, we can write the *Second Law of Thermodynamics as*

$$dS_{isol} \geq 0 \qquad \text{(IIIB-4)}$$

If the system was in equilibrium when isolated the equality holds, otherwise the entropy of the system increases until equilibrium is attained.

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[2]Reference 1, pg. 147, establishes this form with an argument of functional analysis.

[3]The rationale for the introduction of Boltzmann's constant is explained later.