$$dS_{univ} = dS_{sys} + dS_{surr} \geq 0 \qquad \Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0 \qquad \text{(IIIB-5)}$$

Eqn. IIIB-5 is so far only symbolic since W_i, and hence S_i and S, are to this point calculable only by trial and error. In Section II below, we develop the equilibrium distribution on an analytic, closed form basis that allows the macroscopic equilibrium thermodynamic properties, including entropy, to be determined from microscopic models. This procedure is used in application in Units IIIC, D, and E. And in Section III the equilibrium distribution provides the basis for the relation of entropy to other macroscopic properties.

Note to the Student. The following is a rationale of the objectives for this unit.

1. The material of Sections I and IV is important to all students for both conceptual and practical applications of the second law. Therefore, all students will be examined on its form, meaning, and application (Objectives 1-7).

2. Students who do not proceed to additional Units III will not be examined on Sections II and III. However, since Sections II and III develop the macroscopic relations of Section IV, at least a cursory reading of these sections is recommended.

3. The development in Sections II and III is the foundation for the remainder of Units III. Students who continue in this sequence will be examined on the objectives of this portion (Objectives 8 to 11), in addition to those of Sections I and IV.

II. EQUILIBRIUM DISTRIBUTION FUNCTIONS

The equilibrium properties of a real system are those of its equilibrium group macrostates. One of the equilibrium macrostates is the most probable. If we can find its distribution and its properties we will have found those of the system in equilibrium. It is advantageous to consider the most probable macrostate because its entropy is the greatest and therefore its distribution can be determined by means of the extremum principle. Specifically we wish to find the distribution, $n_{j,i}$, whose entropy is a maximum subject to the constraints imposed on the system by its energy, U, volume, V, and number of articles, N.[5] This problem is expressed in the mathematical form

$$dS = k\, d\,[\ln W_i(n_{j,i})] = 0 \qquad \text{(IIIB-6a)}$$

$$dN = d\left(\sum_j n_{j,i}\right) = \sum_j \delta n_{j,i} = 0; \qquad dU = d\left[\sum_j n_{j,i}\varepsilon_j(V)\right] = \sum_j \varepsilon_j(V)\delta n_{j,i} \qquad \text{(IIIB-6b,c)}^{6,7}$$

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[5]Recall that the development of Unit IIIA was, implicitly, for a simple compressible system, $\bar{X}_k = V$. The set (U,V,N) is an extensive set of 3 variables consistent with the State Postulate, Unit IB.

[6]The derivative of $n_{j,i}$ is written as $\delta n_{j,i}$ instead of $dn_{j,i}$ as a reminder that $n_{j,i}$ is a discrete variable (i.e., $n_{j,i} = 0, \pm 1, \pm 2, \ldots$).

[7]The derivative of $\varepsilon_j(V)$ is zero since the volume is fixed.