But since $\sum_j n_{j,i} = N$ and $\sum_j n_{j,i}\varepsilon_j = U$ the equilibrium entropy can be written as

$$S_{eq}^{MB}(\beta,U,N,V) = k\beta U + Nk\,\ell n\,[Z(\beta,V)] \qquad \text{(IIIB-9)}$$

Now we turn our attention to the task of relating the remaining unknown multiplier, β, to a macroscopic property. This is accomplished by considering the process of thermal equilibration of an isolated system. The second law for such a process is $dS_{isol} \geq 0$. Consider a system composed of Boltzons and subdivided into regions A and B, Fig. IIIB-1. The wall that separates A from B is rigid and impermeable (there is no work or particle transfer; N_A, N_B, V_A and V_B are fixed). The wall allows energy transport as heat. Thus if the two regions are not initially in thermal equilibrium, a heat interaction, $dQ_A = -dQ_B$, will occur until equilibrium is achieved. As a result of this process the energy of each region will change subject to the isolation condition (viz., $dU = dU_A + dU_B = 0$ or $dU_A = -dU_B$). We wish to study the effect of this process on the system entropy. This can be done by determining the entropy change of regions A and B, since $S = S_A + S_B$. The determination of dS_A and dS_B is facilitated if we specialize our system so that each separate region remains in an extensive quilibrium state. Since our intent is the study of the effect of *an* equilibration process on the overall system, this limitation does not defeat our purpose. With this restriction, eqn. IIIB-9 is applicable; it allows us to relate the entropy change of each region to the equilibration causing energy transport. The coefficient that relates these parameters is the partial derivative of the entropy with respect to the energy.[12]

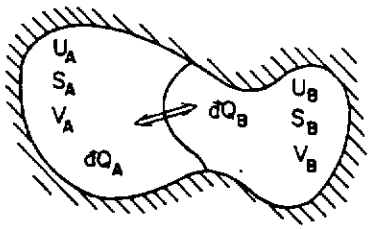

Fig. IIIB-1 Thermal Equilibration in an Isolated System

$$dS_A = \left(\frac{\partial S_A}{\partial U_A}\right)_{V_A,N_A} dU_A \quad \text{and} \quad dS_B = \left(\frac{\partial S_B}{\partial U_B}\right)_{V_B,N_B} dU_B$$

This coefficient is developed for Boltzons in the following example.

<u>Example 2</u>. Use eqn. IIIB-9 for Boltzons to derive the expression $(\partial S/\partial U)_{N,V} = k\beta$.

The equilibrium entropy of a Boltzon system is $S_{eq}^{MB} = k\beta U(\beta,V,N) + Nk\,\ell n\,[Z(\beta,V)]$. Therefore

$$\left(\frac{\partial S_{eq}^{MB}}{\partial U}\right)_{N,V} = \frac{\partial}{\partial U}\,[k\beta U(\beta,V,N) + Nk\,\ell n\,Z(\beta,V)]_{N,V}$$

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[12]Unit S2 presents the definition of a partial derivative and illustrates example determinations.