U_A, V_A, S_A \rightarrow U_B, V_B, S_B

Figure 3.13. Two systems that can exchange both energy and volume with each other. The total energy and total volume are fixed.

U_A and V_A, as shown in Figure 3.14. The equilibrium point is where $S_{total}$ attains its maximum value. At this point, its partial derivatives in both directions vanish:

$$\frac{\partial S_{total}}{\partial U_A} = 0, \quad \frac{\partial S_{total}}{\partial V_A} = 0. \quad (3.36)$$

We studied the first condition already in Section 3.1, where we concluded that this condition is equivalent to saying that the two systems are at the same temperature. Now let us study the second condition in the same way.

The manipulations are exactly analogous to those in Section 3.1:

$$0 = \frac{\partial S_{total}}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} \frac{\partial S_A}{\partial V_B} - \frac{\partial S_B}{\partial V_B} \frac{\partial S_A}{\partial V_A} \quad (3.37)$$

The last step uses the fact that the total volume is fixed, so $dV_A = -dV_B$ (any volume added to A must be subtracted from B). Therefore we can conclude

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \quad \text{at equilibrium.} \quad (3.38)$$