

2.H.1. Conditions for Local Equilibrium in a PVT System

According to the 2nd law [see (2.49) of §2.D.3], the condition for an equilibrium (or stable) state in an isolated system is that its entropy S must be a maximum. Hence,

$$\Delta S = 0 \quad \text{for 1st order changes in the state variables} \quad (2.156a)$$

$$\Delta S < 0 \quad \text{for 2nd order changes in the state variables} \quad (2.156b)$$

Consider now a mixture of l types of particles in an isolated box of volume V . The box is divided into two parts A & B using a conducting, porous, and mobile wall. Hence, heat, matter, and work can be exchanged freely between A & B . To simplify matters, no chemical reactions are allowed.

By the definition of extensive variables, we have

$$U = \sum_{\alpha=A,B} U_{\alpha} \quad (2.156)$$

$$V = \sum_{\alpha=A,B} V_{\alpha} \quad (2.157)$$

$$N_j = \sum_{\alpha=A,B} N_{j,\alpha} \quad (2.158)$$

$$S = \sum_{\alpha=A,B} S_{\alpha} \quad (2.159)$$

Since the system is isolated, any fluctuation must satisfy

$$\Delta U = \Delta V = \Delta N_j = 0 \quad (2.160)$$

so that

$$\Delta U_A = -\Delta U_B \quad \Delta V_A = -\Delta V_B \quad \Delta N_{jA} = -\Delta N_{jB} \quad \Delta S_A = -\Delta S_B \quad (2.160a)$$

Now,

$$U = U(S, V, \{N_j\}) \quad \rightarrow \quad S = S(U, V, \{N_j\})$$

so that, for small fluctuations, we can write

$$\Delta S = \sum_{\alpha=A,B} \left[\left(\frac{\partial S}{\partial U_{\alpha}} \right)_{\{V_{\beta}, \{N_{j\beta}\}} \right} \Delta U_{\alpha} + \left(\frac{\partial S}{\partial V_{\alpha}} \right)_{U, \{V_{\beta \neq \alpha}\}, \{N_{j\beta}\}} \Delta V_{\alpha} \right] \quad (2.161)$$

$$+ \sum_{j=1}^l \left(\frac{\partial S}{\partial N_{j\alpha}} \right)_{U, \{V_{\beta}\}, \{N_{k \neq j, \beta \neq \alpha}\}} \Delta N_{j\alpha} \Bigg]$$

$$= \sum_{\alpha=A,B} \left(\frac{1}{T_{\alpha}} \Delta U_{\alpha} + \frac{P_{\alpha}}{T_{\alpha}} \Delta V_{\alpha} - \sum_{j=1}^l \frac{\mu_{j\alpha}'}{T_{\alpha}} \Delta N_{j\alpha} \right) \quad [(2.58-60) \text{ used. }]$$

$$= \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right) \Delta V_A - \sum_{j=1}^l \left(\frac{\mu_{jA}'}{T_A} - \frac{\mu_{jB}'}{T_B} \right) \Delta N_{jA} \quad [(2.160a) \text{ used. }] \quad (2.162)$$

Since (2.162) is 1st order in the fluctuations of the state variables, the stability condition (2.156a) applies, i.e.,

$$\Delta S = 0 \quad (2.162a)$$

Now, the values of ΔU_A , ΔV_A & ΔN_{jA} are arbitrary. Therefore, (2.162a) can be satisfied only if the coefficients in (2.162) all vanish, giving

$$T_A = T_B \quad [\text{For thermal equilibrium.}] \quad (2.163)$$

$$P_A = P_B \quad [\text{For mechanical equilibrium.}] \quad (2.164)$$

$$\mu_{jA} = \mu_{jB} \quad j = 1, \dots, l \quad [\text{For "chemical" equilibrium.}] \quad (2.165)$$

where we have used the short-hand "chemical equilibrium" to denote the state of zero average particle transfer for all species of particles.

Thus, a specific type of equilibrium is established if and only if the corresponding generalized forces are equalized.

If (2.163-5) are all satisfied, the system is in thermodynamic equilibrium and S of the system is at a global maximum. Indeed, the presence of the partition becomes immaterial.

However, by using a partition that can block specific type(s) of exchange between the chambers, the system can be in equilibrium even if one or more of the conditions (2.163-5) are violated. For example, the system can be in equilibrium with $T_A \neq T_B$ if the partition does not conduct heat. S of the system is then at a local maximum.

Obviously, (2.163-5) can be generalized to the case where the system is partitioned into an arbitrary number M of cells. If these cells are macroscopically small enough to be treated as mathematical points, but microscopically large enough to be treated as a thermodynamic system in local equilibrium, we enter the domain of statistical mechanics.