Conditions for thermal equilibrium [tln19]

Consider a fluid system in a rigid and isolated container that is divided into two compartments A and B by a fictitious partition.

Conserved extensive quantities:
$U = U_A + U_B = \text{const}, \quad V = V_A + V_B = \text{const}, \quad N = N_A + N_B = \text{const}.$

Fluctuations in internal energy: $\Delta U_A = -\Delta U_B$
Fluctuations in volume: $\Delta V_A = -\Delta V_B$
Fluctuations in number of particles: $\Delta N_A = -\Delta N_B$

Entropy: $S(U, V, N), \quad dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN$

$$\begin{aligned}
\Delta S &= \sum_{\alpha=A,B} \left[\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha N_\alpha} \Delta U_\alpha + \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha N_\alpha} \Delta V_\alpha + \left(\frac{\partial S_\alpha}{\partial N_\alpha}\right)_{U_\alpha V_\alpha} \Delta N_\alpha \right] \\
&= \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \Delta U_A + \left(\frac{p_A}{T_A} - \frac{p_B}{T_B}\right) \Delta V_A + \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) \Delta N_A
\end{aligned}$$

At thermal equilibrium, the entropy is a maximum. Hence the entropy change due to fluctuations in U, V, N must vanish.

$\Rightarrow \; T_A = T_B, \quad p_A = p_B, \quad \mu_A = \mu_B$

If the fictitious wall is replaced by a real, mobile, conducting wall, then particle fluctuations in the two compartments are suppressed: $\Delta N_A = 0$. In this case, $\mu_A \neq \mu_B$ is possible at equilibrium.

If the mobile, conducting wall is replaced by a rigid, conducting wall, then volume fluctuations in the two compartments are also suppressed: $\Delta V_A = 0$. In this case, also $p_A \neq p_B$ is possible at equilibrium.

If the conducting wall is replaced by an insulating wall, then energy fluctuations in the two compartments are also suppressed: $\Delta U_A = 0$. In this case, also $T_A \neq T_B$ is possible at equilibrium.