4.3 Equilibrium conditions for pure substances and second law

The general condition for equilibrium is $(dS)_{U,V,n} = 0$, i.e. S at maximum. We have

$$dU(S,V,n) = -p\,dV + T\,dS + \sum_i \mu_i\,dn_i \Rightarrow dS(U,V,n) = \frac{dU}{T} + \frac{p}{T}\,dV - \frac{1}{T}\sum_i \mu_i\,dn_i \tag{4.2}$$

Assuming two phases of a pure substance (α, β) inside an ISOLATED system (const. U, V, n) we get

$$\begin{aligned}
\Rightarrow dS(U,V,n) =&\ dS^\alpha + dS^\beta = 0 \\
=&\ \frac{dU^\alpha}{T^\alpha} + \frac{p^\alpha}{T^\alpha}\,dV^\alpha - \frac{\mu^\alpha}{T^\alpha}\,dn^\alpha + \frac{dU^\beta}{T^\beta} + \frac{p^\beta}{T^\beta}\,dV^\beta - \frac{\mu^\beta}{T^\beta}\,dn^\beta \\
&\ U = U^\alpha + U^\beta = const. \Rightarrow dU^\alpha = -dU^\beta; \quad dV^\alpha = -dV^\beta; \quad dn^\alpha = -dn^\beta \\
\Rightarrow&\ \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta}\right) dU^\alpha + \left(\frac{p^\alpha}{T^\alpha} - \frac{p^\beta}{T^\beta}\right) dV^\alpha - \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta}\right) dn^\alpha = 0 \\
\Rightarrow&\ T^\alpha = T^\beta \quad \text{and} \quad p^\alpha = p^\beta \quad \text{and} \quad \mu^\alpha = \mu^\beta
\end{aligned} \tag{4.3}$$

which means that 1) thermal equilibrium, 2) mechanical equilibrium, and 3) chemical/phase equilibrium holds.