Phase coexistence: Gibbs phase rule [tln27]

Consider a K-component fluid system in a state that allows P coexisting phases (a pure pVT system has $K = 1$).

Internal energy: $dU^{(i)} = TdS^{(i)} - pdV^{(i)} + \sum_{\ell=1}^{K} \mu_\ell^{(i)} dN_\ell^{(i)}, \quad i = 1, \ldots, P.$

Each $U^{(i)}$ is a function of $K + 2$ extensive variables.

Conditions of phase coexistence: $[(P-1)(K+2)$ relations$]$

- thermal equilibrium: $T^{(1)} = T^{(2)} = \cdots = T^{(P)}$,
- mechanical equilibrium: $p^{(1)} = p^{(2)} = \cdots = p^{(P)}$,
- chemical equilibrium: $\mu_\ell^{(1)} = \mu_\ell^{(2)} = \cdots = \mu_\ell^{(P)}, \ \ell = 1, \ldots, K.$

The number of independent *extensive* variables is independent of P:

$$P(K+2) - (P-1)(K+2) = K + 2.$$

Of this set, P extensive variables, e.g. $V_1, \ldots, V_P$, are necessary to specify the size of all coexisting phases. The remaining independent state variables can be chosen to be *intensive*.

The number of independent intensive state variables required to describe the thermodynamic state of P coexisting phases in a K-component system is

$$F = K + 2 - P \qquad \text{(Gibbs phase rule)}.$$

The maximum number of coexisting phases is $K + 2$, which is realized for $F = 0$. In this case, no intensive variables need to be specified. All are determined by the conditions of phase coexistence.

Example: 1-component fluid ($K = 1$)

- $P = 1$ (one phase): $F = 2$ means that both p and T must be specified to locate the thermodynamic state in the (p, T)-plane.
- $P = 2$ (two phases): $F = 1$ means that only p or T must be specified to locate the thermodynamic state in the (p, T)-plane. The state lies on a coexistence line.
- $P = 3$ (three phases): $F = 0$ means that the coexistence condition determines the values of p and T. The state is located at the triple point in the (p, T)-plane.