

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 $K = 1$).

$$\text{Internal energy: } dU^{(i)} = T^{(i)}dS^{(i)} - p^{(i)}dV^{(i)} + \sum_{\ell=1}^K \mu_{\ell}^{(i)}dN_{\ell}^{(i)}, \quad i = 1, \dots, P.$$

Each $U^{(i)}$ depends on $K + 2$ extensive variables for a total of $P(K + 2)$.

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

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

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, \dots, 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

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

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.