

### 3.B. Coexistence of Phases: Gibbs Phase Rule

Read Reichl's §3.A.

Most substances can exist in a number of different (equilibrium) **phases**, each exhibiting noticeably different physical characteristics. For a given set of values for the system variables, the particular phase a system assumes must be a global minimum for the thermodynamic potential appropriate for the boundary conditions. Quite often, for a certain range of values for the system variables, the thermodynamic potential possesses multiple global minima. In which case, multiple phases can **coexist** in equilibrium with each other.

Coexistence of two phases of different concentrations in a binary mixture was already demonstrated in Ex.2.9 of §2.H.2 [ further discussion of the case can be found in Ex.3.6 of §3.E.2 ].

Now, in order to establish thermal and mechanical equilibria, the coexisting phases must have the same  $T$  and  $Y$  [ see §2.H ]. Hence, the natural thermodynamic potential for the problem is the Gibbs energy  $G(T, Y, \{n_j^\alpha\})$ , where  $n_j^\alpha$  is the number of moles of type  $j$  molecules in the phase  $\alpha$ . Thus,

$$j = 1, \dots, l \quad \alpha = 1, \dots, r$$

where  $l$  is the number of molecular species and  $r$  the number of phases.

In each pure phase  $\alpha$ , the Gibbs energy takes the form

$$G^\alpha(T, Y, \{n_1^\alpha, \dots, n_l^\alpha\}) = n^\alpha \mu^\alpha(T, Y, \{x_1^\alpha, \dots, x_{l-1}^\alpha\}) \quad (3.1a)$$

where  $\mu^\alpha$  is the chemical potential for phase  $\alpha$  and

$$x_j^\alpha = \frac{n_j^\alpha}{n^\alpha} = \text{concentration of type } j \text{ molecules in phase } \alpha.$$

(3.1a) shows that  $\mu^\alpha$  depends only on  $2 + (l - 1) = l + 1$  independent, intensive, variables. In equilibrium,  $(T, Y)$  are the same in all coexisting phases. Therefore, the number of independent variables among the chemical potentials in  $r$  coexisting phases is

$$N_{\text{var}} = 2 + r(l - 1) \quad (3.1b)$$

Now, chemical (here means particle transfer) equilibrium requires  $\mu_j^\alpha$  to be the same in all coexisting phases for each  $j$ , i.e.,

$$\mu_j^1 = \mu_j^2 = \dots = \mu_j^r \quad \forall j = 1, \dots, l \quad (3.1c)$$

The number of independent equations in (3.1c) is

$$N_{\text{eqn}} = l(r - 1) \quad (3.1d)$$

The degree of freedom  $F$  is defined as

$$\begin{aligned} F &\equiv \text{number of free variables} \\ &= N_{\text{var}} - N_{\text{eqn}} \\ &= 2 - r + l \end{aligned} \quad (3.1e)$$

which is known as **Gibbs phase rule**.

Consider now a pure  $YXT$  substance so that we can dispense with the label  $j$ . (3.1e) becomes

$$F = 3 - r \quad (3.1f)$$

Thus, in a pure phase,  $F = 2$ , which means the system point can be anywhere in the  $T$ - $Y$  plane.

For the coexistence of two phases I & II,  $F = 1$  so that the system point is restricted to a curve ( called the **coexistent curve** )

$$Y = Y(T) \quad (3.2)$$

that is the solution to the coexistence condition

$$\mu^I(T, Y) = \mu^{II}(T, Y) \quad (3.1)$$

For the coexistence of 3 phases I, II & III,  $F = 0$  so that the system point is restricted to a point ( called the **triple point** ) that is the solution to the coexistence conditions

$$\mu^I(T, Y) = \mu^{II}(T, Y) = \mu^{III}(T, Y) \quad (3.3)$$

For the coexistence of  $r > 3$  phases,  $F < 0$  so that there is no solution.