

Vapor/Liquid Equilibrium: Introduction

Preceding chapters have dealt largely with pure substances or with constant-composition mixtures. e.g., air. However, composition changes are the desired outcome, not only of chemical reactions, but of a number of industrially important mass-transfer operations. Thus composition becomes a primary variable in the remaining chapters of this text. Processes such as distillation, absorption, and extraction bring phases of different composition into contact, and when the phases are not in equilibrium, mass transfer between the phases alters their compositions. Both the extent of change and the rate of transfer depend on the departure of the system from equilibrium. Thus, for quantitative treatment of mass transfer the equilibrium T , P , and phase compositions must be known.

The most commonly encountered coexisting phases in industrial practice are vapour and liquid, although liquid/liquid, vapour/solid, and liquid/solid systems are also found.

The Nature Of Equilibrium

Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. This implies a balance of all potentials that may cause change. In engineering practice, the assumption of equilibrium is justified when it leads to results of satisfactory accuracy. For example, in the reboiler for a distillation column, equilibrium between vapour and liquid phases is commonly assumed. For finite vaporization rates this is an approximation, but it does not introduce significant error into engineering calculations. An isolated system consisting of liquid and vapour phases in intimate contact eventually reaches a final state wherein no tendency exists for change to occur within the

system. The temperature, pressure, and phase compositions reach final values which thereafter remain fixed. The system is in equilibrium.

Measures of Composition

The three most common measures of composition are mass fraction, mole fraction, and molar concentration. Mass or mole fraction is defined as the ratio of the mass or number of moles of a particular chemical species in a mixture or solution to the total mass or number of moles of the mixture or solution:

$$x_i \equiv \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}} \quad \text{OR} \quad x_i \equiv \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$$

Molar concentration is defined as the ratio of the mole fraction of a particular chemical species in a mixture or solution to its molar volume:

$$C_i \equiv \frac{x_i}{V}$$

This quantity has units of moles of *i* per unit volume. For flow processes convenience suggests its expression as a ratio of rates. Multiplying and dividing by molar flow rate \dot{n} gives:

$$C_i = \frac{\dot{n}_i}{q}$$

Where \dot{n}_i is molar flow rate of species *i*, and *q* is volumetric flow rate.

The molar mass of a mixture or solution is, by definition, the mole-fraction-weighted sum of the molar masses of all species present:

$$M \equiv \sum_i x_i M_i$$
