Phase Equilibria: Phase Behaviour at Low to Moderate pressure

Thermodynamics is an abstract subject,

it takes an abstract mind to understand it.

Prerequisite

- Introduction to Chemical Engineering Thermodynamics I
- MATLAB programming

Phase Equilibria: Phase Behaviour at Low to Moderate pressure

Let me begin this lecture with a brief overview of **Property**, **State** and **Process**, then followed by the definition of a **Phase**. Also, I will discuss some basic concepts (terms) that should be well understood about equilibrium and chemical equilibrium in particular before the main topic, phase equilibria.

Property, State and Process

To describe a system and predict its behaviour, the knowledge of its properties and how those properties are related is required.

- A **property** is a macroscopic characteristic of a system such as mass, volume, energy, pressure and temperature to which a numerical value can be assigned at a given time without the knowledge of the past history (behaviour) of the system. Many other properties are considered during the course of our study of chemical engineering thermodynamics. Thermodynamics also deals with quantities that are not properties, such as mass flow rate and energy transferred by work and heat.

Property, State and Process (2)

- **State** refers to the condition of a system as described by its properties. Since there are normally relations among the properties of a system, the state often can be specified by providing the values of a subset of the properties.

- When any of the properties of a system change, the state changes and the system is said to have undergone a process. A **process** is a transformation from one state to another. However, if a system exhibits the same values of its properties at two different times, it is in the same state at these times. A system is said to be at **steady state** if none of its properties changes with time.

Extensive and Intensive Properties

Thermodynamic properties can be placed in two general classes: extensive and intensive. A property is called extensive if its value for an overall system is the sum of its values for the parts into which the system is divided.

- **Extensive** properties depend on the size or extent of a system. The extensive properties of a system can change with time, and many thermodynamic analyses consist mainly of carefully accounting for changes in extensive properties such as mass and energy as a system interacts with its surroundings.

- **Intensive** properties are independent of the size or extent of a system and may vary from place to place within the system at any moment. Thus, intensive properties may be functions of both position and time, whereas extensive properties vary at most with time. Specific volume, pressure, and temperature are important intensive properties.

Phase and Pure Substance

- A **phase** is a quantity of matter that is homogeneous throughout in both chemical composition and physical structure. Homogeneity in physical structure means that the matter is all solid, or all liquid, or all gas (all vapour). A system can contain one or more phases. For example, a system of liquid water and water vapour (steam) contain two phases.

- When more than one phase is present, the phases are separated by phase boundaries. Note that gases for example, oxygen and nitrogen, can be mixed in any proportion to form a single gas phase. Certain liquids, such as alcohol and water, can be mixed to form a single liquid phase. But liquids such as oil and water are immiscible forming two liquid phases.

Phase and Pure Substance (2)

- A **pure substance** is one that is uniform and invariable in chemical composition. A pure substance can exist in more than one phases, but its chemical composition must be the same in each phase.
  - For example, if liquid water and water vapour form a system with two phases, the system can be regarded as a pure substance because each phase has the same composition.
- A uniform mixture of gases can be regarded as a pure substance provided it remains a gas and does not react chemically. A system consisting of air can be regarded as a pure substance as long as it is a mixture of gases; but if a liquid should form on cooling, the liquid would have a different composition from the gas phase, and the system would no longer be considered a pure substance.

Equilibrium

- Classical thermodynamics places primary emphasis on equilibrium states and changes from one equilibrium state to another from a macroscopic approach.
- Whereas statistical thermodynamics is concerned with the structure of matter.
- The objective of statistical thermodynamics is to characterize by statistical means the average behaviour of the particles making up a system of interest and relate this information to the observed macroscopic behaviour of the system. For applications involving lasers, plasmas, high-speed gas flows, chemical kinetics, very low temperatures (cryogenics), the methods of statistical thermodynamics are essential.

Equilibrium (2)

- In mechanics, equilibrium means a condition of balance maintained by an equality of opposing forces.
- In thermodynamics, equilibrium means not only maintaining a balance of forces but also a balance of other influences. Each kind of influence refers to a particular aspect of thermodynamic, or complete equilibrium.
- Several types of equilibrium must exist individually to fulfil the condition of complete equilibrium; among these are mechanical, thermal, phase and chemical equilibrium.

Equilibrium (3)

For now, we shall test to see if a system is in thermodynamic equilibrium by the following procedure:

- Isolate the system from its surrounding and check for changes in its observable properties. If there are no changes, we conclude that the system was in equilibrium at the moment it was isolated. The system can therefore be said to be at an equilibrium state.
- When a system is isolated, it does not interact with its surroundings; however, its state can change as a consequence of spontaneous events occurring internally as its intensive properties, such as temperature and pressure, tend toward uniform values. When all such changes cease, the system is in equilibrium.

Equilibrium (4)

- Hence, for a system to be in equilibrium it must be single phase or consist of a number of phases that have no tendency to change their conditions when the overall system is isolated from its surroundings.
- At equilibrium, **temperature** is uniform throughout the system. Also, **pressure** can be regarded as uniform throughout as long as the effect of gravity is not significant; otherwise a pressure variation can exist, as in a vertical column of liquid.
- 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 phases alters their compositions. 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, as we have defined earlier is a static condition in which no changes occur in the macroscopic properties of a system with time.
- 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 vapourization rates, this is an approximation, but it does not introduce significant error into engineering calculations.

The Nature of Equilibrium (2)

- An isolated system consisting of liquid and vapour phases in intimate contact eventually reaches 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.
- Nonetheless, at the microscopic level, conditions are not static. The molecules comprising a phase at a given instant are not the same molecules that later occupy the same phase. Molecules with sufficiently high velocities near the interface overcome surface forces and pass into the other phase. However, the average rate of passage of molecules is the same in both directions and no net interphase transfer of material occurs.

Measures of Composition

There are three most common measures of composition, which 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.
  Mathematically,

$$x_i = \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}} \tag{1}$$

$$x_i = \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}} \tag{2}$$

Measures of Composition (2)

Where:

i denote the number of chemical species $(1, 2, 3, 4, ...)$

x_i is the mass or mole fraction of chemical species

m_i is the mass of chemical species

m is the number of moles of chemical species

n_i is the total mass or number of moles of the system

- **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.

$$C_i = \frac{x_i}{V} \tag{3}$$

Measures of Composition (3)

- This quantity has units of moles of per unit volume. For flow rate process, it is expressed as a ratio of rates.

$$C_i = \frac{\dot{n}_i}{q} \tag{4}$$

Where:
$\dot{n}_i$ is the molar flow rate of species and is the volumetric flow rate.

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

$$M = \sum_i x_i M_i \tag{5}$$

The Phase Rule

It is impossible to change the temperature without also changing the pressure, if vapour and liquid are to continue to exist in equilibrium.

- The state of a pure homogeneous fluid is fixed whenever two intensive thermodynamic properties are set at definite values.

- In contrast, when two phases are in equilibrium, the state of the system is fixed when only a single property is specified. For example, a mixture of steam and liquid water in equilibrium at 101.33 kPa can only exist at 100 ^oC.

- The number of variables at equilibrium that may be independently fixed in a system at equilibrium is the difference between the total number of variables that characterize the intensive state of the system and the number of independent equations that can be written connecting the variables.

The Phase Rule (2)

- The intensive state of a PVT system containing N chemical species and π phases in equilibrium is characterized by the intensive variables, temperature T, pressure P, and $N-1$ $\left(\sum_i x_i = 1\right)$ mole fractions for each phase.
- These are the phase-rule variables, and their number is:

$$2 + (N-1)(\pi) \tag{6}$$

The masses of the phases are not phase-rule variable, because they have no influence on the intensive state of the system.

The Phase Rule (3)

- An independent phase-equilibrium equation may be written connecting intensive variables for each of the N species for each pair of the phases present. Thus, the number of independent phase-equilibrium equations is:

$$(\pi - 1)(N) \tag{7}$$

- The difference between the number of phase-rule variables and the number of independent equations connecting them **is the number of variables that must be fixed independently**. This is also called **degrees of freedom** of the system F,expressed as:

$$F = N_V - N_E \tag{8}$$

$$F = [2 + (N - 1)(\pi)] - [(\pi - 1)(N)] = 2 - \pi + N \tag{9}$$

Duhem's Theorem

- Duhem's theorem is another rule which is similar to the phase rule, but less celebrated. It applies to closed systems at equilibrium for which the extensive state as well as the intensive state of the system is fixed.

- The state of a closed system is said to be completely determined, and is characterized by both the $2 + (N - 1)(\pi)$ intensive phase-rule variables and by the π extensive variables represented by the masses (or mole numbers) of the phases. Thus, the total number of variables is:

$$2 + (N - 1)(\pi) + \pi = 2 + N\pi \tag{10}$$

Duhem's Theorem (2)

- For a closed system formed from specified amounts of chemical species present, then a material-balance equation can be written for each of the N chemical species. These in addition to the $(\pi - 1)(N)$ phase-equilibrium equations gives a total number of independent equations as:

$$(\pi - 1)(N) + N = N\pi \tag{11}$$

- The difference between the number of variables and the number of equations is:

$$(2 + N\pi) - (N\pi) = 2 \tag{12}$$

Duhem's Theorem (3)

- Duhem's theorem states that:
- **For any closed system formed initially from given masses of specified chemical species, the equilibrium state is completely determined when any two independent variables are fixed**.
- The two independent variables subject to specification may in general be either intensive or extensive. However, the number of independent intensive variables is given by the phase rule. Thus, when $F = 1$ at least one of the two variables must be extensive, and when $F = 0$ both must be extensive.