Lecture 4

Learning Objectives:

- Meanings of words “phase” and “Equilibrium”
- The phase rule and its application to specific situations.

We have seen, in everyday life, that the same substance can exist in different forms, depending on the conditions involved. Water can exist as ice or liquid water or steam, depending on the temperature and pressure at which it exists. If you drop a chunk of ice in a glass of water, the ice begins to melt and the water temperature decreases. Once the water temperature has reaches near zero degrees Celsius, the melting of ice slows down. If the glass was perfectly insulated so that no heat was entering the system, the melting of ice will stop at the temperature of zero degrees Celsius. Thus water and ice can coexist at zero degree forever. It shows that under some conditions of temperature and pressure it is possible for the same substance to exist in more than one phase simultaneously.

When two or more phases of a substance or mixture of substances continue to coexist for a long period of time, we call the system to be under equilibrium. Before examining the issue any further, let us first define what is meant by the words "phase" and "equilibrium."

Phase:

A phase at equilibrium conditions is defined as a completely homogeneous and uniform state of matter.

- Homogenous and uniform state means that the properties like density, chemical composition and crystalline structure are same everywhere within the phase.
- Ice and water have same chemical composition, but their density and molecular arrangement are different, so they are different phases.

Equilibrium:

Equilibrium means the system has reached a perfect balance between all the forces of change that were acting on it so that there is no further change in temperature, velocity, composition or structure of the system.

4.3 The Phase Rule

The number of different phases that can coexist at equilibrium at any given conditions is dictated by the so-called phase rule. It states that

$F + P = C + 2$

Where,
P = # of phases present at equilibrium
C = # of components
F = Degrees of freedom, which means the number of intensive variables that can be independently specified while retaining P number of phases.

The intensive variables mean variables that do not depend on the size of the system, for example: temperature, pressure or mole fractions.

4.3.1 The Number of Phases, P

- There can only be one gas phase in any system, regardless of whether it is a pure substance or a multicomponent mixture.
- Only one liquid phase can exist in case of a pure substance.
- A multicomponent mixture may produce two or more liquid phases.
- Two or more solid phases can coexist for mixtures as well as for pure substances.

To decide how many phases are present in a system, you have to remember what is meant by the word "phase." The main criterion is that a phase must be homogeneous on a scale larger than the molecular dimensions. Distinct phases must also be separated by distinct boundary surfaces. However, sometimes the application of these rules is not straightforward. For example, the phase may exist as disconnected droplets or particles that are separated from one another by distinct boundaries. However, since they all have the same molecular arrangement and same composition, they belong to the same phase. You need differences in crystalline structure or composition to have distinct phases. Let us consider a few examples.

- **A spoonful of sugar crystals** -- all crystals have the same structure and same composition, therefore, they all belong to the same phase. The boundaries between the crystals notwithstanding.
- **A mixture of salt and sugar crystals** -- Now two distinct compositions and crystal structures are present, so you have two phases.
- **A blend of oil and water in which the oil is emulsified in the form of small droplets dispersed in water**. There are two phases, the small droplets of oil have different composition from the continuous water and form a different phase. However, all droplets of the oil belong to the same phase.
- **A blend of water and ethanol** – it is a single-phase mixture.

- **Milk** is a two-phase system since it contains animal fat emulsified in water.

4.3.2 The Number of Independent Components, C

To understand c, we consider two different types of systems separately.

1. No chemical reactions involved (non-reactive systems)
2. Chemical reactions may be involved (reactive)

Non-reactive Systems:

In non-reactive systems, the number of components is equal to the number of distinct chemical species present.

- **Sugar solution in water** -- two components; sugar and water.
- **NaOH dissolved in water** -- also two components; NaOH and water. However, if ionic equilibrium between Na+ and OH- is being considered then it becomes more complicated but then it is no longer a non-reactive system.

Thus, the number of components in a non-reactive system is easy to figure out, just count the number of distinct species involved.

Reactive Systems:

The number of independent components in a reactive system is a little more difficult to determine. It is defined as the number of chemical species required for making all the components present in the system. Thus it makes a distinction between the independent components and components that can be produced by reactions of the independent components.

C= Number of distinct chemical species needed to make all components present in the system.

Another way to look at this situation is by defining the number of components in a reactive system as:

C = Total number of components present - number of independent chemical reactions involved.

For example, consider a system containing H_2, O_2 and H_2O

The number of distinct chemical species needed to make all of the species present = 2, since H_2O can be made from the reaction between H_2 and O_2. An alternate way of looking at the situation would be as follows.

We know that it is a reactive system and involves the following reaction.

$$H_2 + O_2 ==> H_2O$$

Number of distinct chemical species present = 3; H_2, O_2, H_2O
Number of chemical reactions = 1.

Therefore, number of independent components = 3-1 = 2.

Consider a system containing elemental sulfur. We know that it can form S2, S4, S8 and other molecules. However, since only elemental S is needed to form all of these, it only has one component.

4.3.3 Degrees of Freedom, F

Degrees-of-freedom is equal to the number of intensive variables that can be independently varied without changing the number of phases present in the system.

Recall that intensive variables are those variables that do not depend on the size of the phases. Density of a phase is an intensive variable, but the mass of the phase and its volume are not intensive-variables.

The most often encountered intensive variables for application in the phase rule are:

- Temperature
- Pressure
- Density
- Mole fractions or mass fractions in different phases

- However, you can also use viscosity, refractive index, thermal conductivity or electrical conductivity etc. as intensive variables.
- Any intensive property that depends on the temperature, pressure and composition of the phase can be used as the specified intensive variable.

Although, a large number of intensive variables can be used to describe the system, these are not all independent of one another. You only need to specify a certain number of variables, the number that is given by the phase rule, before the state of *the system is completely fixed and all other variables become dependent on the already specified conditions. This is what degrees-of-freedom is all about, that is the number of variable that you are free to choose for the system containing the specified number of components and phases.*

Let us look at a few examples.

Let us take pure water and specify that only one phase is present.

$F = C + 2 - P = 1 + 2 - 1 = 2.$

The phase rule tells us that the degrees of freedom are two. You must specify two intensive variables to fix the state of the system. These could be temperature and pressure. Once the temperature and pressure are fixed, all other intensive variables are also fixed. You cannot say that the temperature is $20^{o}C$; pressure 100 kPa and the density should be 1050 kg/m^3. The density is already fixed at the specified temperature and pressure and is no longer free to be specified independently.

Now let us change the system a little and say we have dissolved NaCl present in the system, i.e. we have increased the number of components to two. Now when we apply the phase rule we see that the degrees of freedom is:

$F = C + 2 - P = 2 + 2 - 1 = 3.$

Therefore, after specifying the temperature and pressure, we still have one more variable that can be specified independently.
It can be the mass fraction of NaCl or it could very well be the density of the solution.

If we want the density to be 1050 kg/m^3, we need to have a little more than 7 mass percent of salt present. Note again that once this variable is specified, the system is fully defined; you cannot specify any other intensive variable arbitrarily. Of course, you could have used some other intensive variable in the place of density, for example refractive index.

Now let us see what happens when two phases are present. Considering the same example of NaCl and water and consider the situation in which we have added so much salt that some of it remains un-dissolved in the form of suspended crystals. The phase rule tells us that an increase in the number of phases will result in corresponding decrease in the degrees of freedom. Applying the phase rule now gives

$F = C + 2 - P = 2 + 2 - 2 = 2.$

We have only two degrees of freedom. The temperature and pressure can be varied but that will completely fix the state of the system, that is, it will fix the values of all other intensive variables.
But we can add more salt, you say, to change the overall composition.
The overall composition is not an intensive variable; it is the composition of phases that can be considered to be intensive variables.
The overall composition depends on the relative amount of different phases present. By adding more salt you will increase the mass of the solid phase present, but its composition will still be 100% salt. The liquid phase composition will remain that of the saturated solution.

Example Problem

How many degrees of freedom are there in a system containing an unsaturated sodium chloride solution in equilibrium with ice?

Solution

There are two phases and two components. Therefore, by applying the phase rule we determine the degrees of freedom to be:

$F=C+2-P=2+2-2=2$

When the temperature and pressure are specified, the concentration of the salt solution is fixed.