

Topic: Thermodynamics

1.1 The Phase Rule

Writing extended definitions

- A. Read the following excerpt and using information from the text as well as from C above write an extended definition of Phase Rule (not more than 90 words). Remember to use your own words!**

Excerpt 1

The state of a pure homogeneous substance is fixed whenever two state functions are set at definite values. However, for more complex systems this number is not necessarily two. For example, a mixture of steam and liquid water in equilibrium at 1(atm) can exist only at 100(°C). It is impossible to change the temperature without also changing the pressure if vapor and liquid are to continue to exist in equilibrium; one cannot exercise independent control over these two variables for this system. There is a general rule which allows one to determine the number of independent variables that must be arbitrarily fixed so as to establish the intensive state of a system. This number is referred to as the degrees of freedom F of the system, and it is given by the celebrated phase rule of J. Willard Gibbs, who deduced it by theoretical reasoning in 1875. It is presented here without proof in the form applicable to non-reacting systems:

$$F = 2 - \pi + N \quad (2-12)$$

where

π = number of phases

N = number of chemical species

The intensive state of a system at equilibrium is established when its temperature, pressure, and the compositions of all the phases are fixed. These are therefore taken as the phase-rule variables, but they are not all independent. The phase rule gives the number of variables from this set which when arbitrarily specified will also establish the remaining variables at fixed values.

A phase is a homogeneous region of matter. A gas or a mixture of gases, a liquid or a liquid solution, and a solid crystal are examples of phases. It is not necessary that a phase be continuous. Examples of discontinuous phases are a gas dispersed as bubbles in a liquid, a liquid dispersed as droplets in another liquid with which it is immiscible, and a crystalline solid dispersed in either a gas or liquid. In each case there are a dispersed phase and a continuous phase. An abrupt change in properties always occurs at the boundary between phases.

Various phases can coexist, but they must be in equilibrium for the phase rule to apply. An example of a system at equilibrium which is made up of three phases is a boiling saturated solution of a salt in water with excess salt crystals present. The three phases are crystalline salt, the saturated aqueous solution, and the vapor generated by boiling.

It is to be emphasized that the phase rule relates to the intensive state of a system. Such a state is determined when the intensive properties of the individual phases are fixed. These properties are independent of the extent of the system and of the individual phases. Thus the phase rule gives the same information for a large system as for a small one, and regardless of the relative amounts of the various phases present. Moreover, the only compositions that are phase-rule variables are those of the individual phases. Overall or total compositions are not phase-rule variables when more than one phase is present.

The minimum number of degrees of freedom for any system is zero. When $F = 0$, the system is said to be invariant, and Eq. (2-12) becomes $\pi = 2 + N$. This value of π is the maximum number of phases which can coexist at equilibrium for a system containing N chemical species. When $N = 1$, this number is 3, and we have a triple point. For example, the triple point of water, where liquid, vapor, and the common form of ice exist together in equilibrium, occurs at 0.01(°C) and 0.00602(atm). Any change from these conditions will cause at least one phase to disappear (1, pp. 39-40).