

12.2: Gibbs Phase Rule

In [chapter 1](#), we have already seen that the number of independent variables required to describe an ideal gas is two. This number was derived by counting the total number of variables ($3 : P, \bar{V}, T$), and reduce it by one because the ideal gas law constrains the value of one of them, once the other two are fixed. For a generic system potentially containing more than one chemical substance in several different phases, however, the number of independent variables can be different than two. For a system composed of c components (chemical substances) and p phases, the number of independent variables, f , is given by the Gibbs phase rule:

$$f = c - p + 2. \quad (12.2.1)$$

The Gibbs phase rule derives from the fact that different phases are in equilibrium with each other at some conditions, resulting in the reduction of the number of independent variables at those conditions. More rigorously, when two phases are in thermodynamic equilibrium, their chemical potentials are equal (see [Equation 12.1.4](#)). For each equality, the number of independent variables—also called the number of **degrees of freedom**—is reduced by one. For example, the chemical potentials of the liquid and its vapor depend on both T and P . But when these phases are in equilibrium with each other, their chemical potentials must be equal. If either the pressure or the temperature is fixed, the other variable will be uniquely determined by the equality relation. In other terms, when a liquid is in equilibrium with its vapor at a given pressure, the temperature is determined by the fact that the chemical potentials of the two phases is the same, and is denoted as the boiling temperature T_b . Similarly, at a given temperature, the pressure of the vapor is uniquely determined by the same equality relation and is denoted as the vapor pressure, P^* .

The Gibbs phase rule is obtained considering that the number of independent variables is given by the total number of variables minus the constraints. The total number of variables is given by temperature, pressure, plus all the variables required to describe each of the phases. The composition of each phase is determined by $(c - 1)$ variables.¹ The number of constraints is determined by the number of possible equilibrium relations, which is $c(p - 1)$ since the chemical potential of each component must be equal in all phases. The number of degrees of freedom f is then given by

$$\begin{aligned} f &= (c - 1)p + 2 - c(p - 1) \\ &= c - p + 2 \end{aligned}$$

which is the Gibbs phase rule, as in [Equation 12.2.1](#).

1. For a 1-component system $c - 1 = 1 - 1 = 0$, and no additional variable is required to determine the composition of each phase. For a 2-component system, however, each phase will contain both components, hence $c - 1 = 2 - 1 = 1$ additional variable will be required to describe it—the mole fraction.

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