

The phase rule (Atkins, de Paula, Physical Chemistry, 9th ed., WH Freeman and Co.)

The following is a scanned copy of (part of) Atkins' discussion of the phase rule and, in particular, its derivation.

$$F = C - P + 2 \quad \boxed{\text{The phase rule}} \quad (4.1)$$

A **component** is a *chemically independent* constituent of a system. The number of components, C , in a system is the minimum number of types of independent species (ions or molecules) necessary to define the composition of all the phases present in the system. In this chapter we deal only with one-component systems ($C = 1$). By a **constituent** of a system we mean a chemical species that is present. Thus, a mixture of ethanol and water has two constituents. A solution of sodium chloride has three constituents—water, Na^+ ions, and Cl^- ions—but only two components because the numbers of Na^+ and Cl^- ions are constrained to be equal by the requirement of charge neutrality. The **variance** (or *number of degrees of freedom*), F , of a system is the number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium.

In a single-component, single-phase system ($C = 1, P = 1$), the pressure and temperature may be changed independently without changing the number of phases, so $F = 2$. We say that such a system is **bivariant**, or that it has two **degrees of freedom**. On the other hand, if two phases are in equilibrium (a liquid and its vapour, for instance) in a single-component system ($C = 1, P = 2$), the temperature (or the pressure) can be changed at will, but the change in temperature (or pressure) demands an accompanying change in pressure (or temperature) to preserve the number of phases in equilibrium. That is, the variance of the system has fallen to 1.

Justification 4.1 *The phase rule*

Consider first the special case of a one-component system for which the phase rule is $F = 3 - P$. For two phases α and β in equilibrium ($P = 2, F = 1$) at a given pressure and temperature, we can write

$$\mu(\alpha; p, T) = \mu(\beta; p, T)$$

(For instance, when ice and water are in equilibrium, we have $\mu(s; p, T) = \mu(l; p, T)$ for H_2O .) This is an equation relating p and T , so only one of these variables is independent (just as the equation $x + y = xy$ is a relation for y in terms of x : $y = x/(x - 1)$). That conclusion is consistent with $F = 1$. For three phases of a one-component system in mutual equilibrium ($P = 3, F = 0$),

$$\mu(\alpha; p, T) = \mu(\beta; p, T) = \mu(\gamma; p, T)$$

This relation is actually two equations for two unknowns, $\mu(\alpha; p, T) = \mu(\beta; p, T)$ and $\mu(\beta; p, T) = \mu(\gamma; p, T)$, and therefore has a solution only for a single value of p and T (just as the pair of equations $x + y = xy$ and $3x - y = xy$ has the single solution $x = 2$ and $y = 2$). That conclusion is consistent with $F = 0$. Four phases cannot be in mutual equilibrium in a one-component system because the three equalities

$$\mu(\alpha; p, T) = \mu(\beta; p, T) \quad \mu(\beta; p, T) = \mu(\gamma; p, T) \quad \mu(\gamma; p, T) = \mu(\delta; p, T)$$

are three equations for two unknowns (p and T) and are not consistent (just as $x + y = xy$, $3x - y = xy$, and $x + y = 2xy^2$ have no solution).

Now consider the general case. We begin by counting the total number of intensive variables. The pressure, p , and temperature, T , count as 2. We can specify the composition of a phase by giving the mole fractions of $C - 1$ components. We need specify only $C - 1$ and not all C mole fractions because $x_1 + x_2 + \cdots + x_C = 1$, and all mole fractions are known if all except one are specified. Because there are P phases, the total number of composition variables is $P(C - 1)$. At this stage, the total number of intensive variables is $P(C - 1) + 2$.

At equilibrium, the chemical potential of a component J must be the same in every phase (Section 4.4):

$$\mu(\alpha; p, T) = \mu(\beta; p, T) = \dots \text{ for } P \text{ phases}$$

That is, there are $P - 1$ equations of this kind to be satisfied for each component J . As there are C components, the total number of equations is $C(P - 1)$. Each equation reduces our freedom to vary one of the $P(C - 1) + 2$ intensive variables. It follows that the total number of degrees of freedom is

$$F = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

which is eqn 4.1.