

GIBBS' PHASE RULE REVISITED

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Gibbs' phase rule and related properties of phase diagrams are obtained using the simple combinatorial methods of associating a graph to each thermodynamic system. We think this approach allows a deeper understanding of the geometric roots of this rule.

1. Introduction

Gibbs' phase rule [1] is a result which was obtained from very general properties of the fundamental equation and equilibrium conditions of a thermodynamic system. Its deduction in modern thermodynamic textbooks (see, e.g., [2]) could be phrased as follows. Given a system with r components and M coexistent phases, there are $r + 2$ intensive parameters, $T, P, \mu_1, \dots, \mu_r$, each of which being constant from phase to phase. In each of the M phases, there is a Gibbs–Duhem relation among these variables. These M equations reduce the number of independent parameters to $(r + 2) - M$ and the degree of freedom f is then

$$f = r - M + 2.$$

The above equation is proved by solving a system of equations and using the relation between the number of equations and variables, as is usually done in linear algebra.² However, because we are dealing with thermodynamic surfaces (and not only planes), the above argument cannot be considered a rigorous proof. In fact, there are several papers that emphasize this point, although their approach is different from ours (see [3] and the references therein).

The objective of this paper is to discuss Gibbs' phase rule from a different viewpoint, based on the fact that Gibbs' phase rule is not a consequence of analytic properties of the fundamental equation, but of the combinatorial properties of phases and their coexistence.

2. Gibbs' phase rule for substances with r components

In classical thermodynamics, the state of a substance with r components is characterized by the fundamental equation $U = U(S, V, N_1, \dots, N_r)$. The Legendre transform with respect to certain variables leads us to different thermodynamic potentials. The stability conditions constrain these potentials such that they are convex functions of their extensive variables and concave functions of their intensive variables.

In particular, if we apply the complete Legendre transform to $U = U(S, V, N_1, \dots, N_r)$, we obtain the thermodynamic potential $U = U[T, P, \mu_1, \dots, \mu_r]$. Using the Gibbs–Duhem relation, this is equivalent to an $r + 1$ -variable potential $\mu_r = \mu_r[T, P, \mu_1, \dots, \mu_{r-1}]$, which can be represented by a hypersurface that exists in $r + 2$ dimensions³.

The thermodynamic equilibrium conditions between systems I and II are given by the thermal equilibrium $T^I = T^{II}$, the mechanical equilibrium $P^I = P^{II}$, and the equilibrium with respect to material flow, $\mu^I = \mu^{II}$. In the case of a substance with different phases, the system can be considered to be composed of simple thermodynamic subsystems separated by nonrestrictive walls. Thus, each different phase has an associated

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²Using this method, it is proved that two planes intersect in a line, three planes at a point, and so on.

³It is not difficult to realize that this hypersurface is concave, even though this condition is not needed in our reasoning.

thermodynamic potential, and the coexistence of these phases can be treated in the same way as the balance among thermodynamic systems.

For each of these different phases i of the substance, there is a different equation μ_r^i . These different phases coexist if and only if they have the same values for each of their $r + 1$ intensive variables T, P , and μ_1, \dots, μ_{r-1} .

In this form, the condition for the coexistence of M phases for a substance of r components can be reduced to the two following axioms:

Axiom 1. *If the phases f_1, \dots, f_M coexist, then each pair f_i, f_j coexists for a hypersurface of dimension less than the dimension of the hypersurface which represents the phase.*

Axiom 2. *If two phases f_i, f_j coincide in an entire region of the same dimension, then $f_i = f_j$.*

3. The phase graph of the system

Here, we associate a graph to each of the r components (to review graph definitions, see [4]), called the *phase graph* $G(r)$, in the following way:

To each phase f_i , we associate a vertex v_i .

To each border between f_i and f_j (the hypersurface where f_i, f_j coexist), if it exists, we associate the edge (v_i, v_j) that connects vertices v_i and v_j .

Phase graphs have the following simple properties.

Property 1. Each graph $G(r)$ is composed of complete subgraphs K_j , $j \in \{1, \dots, n\}$, whose maximum number of vertices j is $n = r + 2$ and corresponds to the number of vertices of the simplex [5] in $(r + 1)$ dimensions⁴.

Property 2. For each of these complete subgraphs K_j of $G(r)$, let us define

$$\deg fr(K_j) = (r + 1) - dg(K_j),$$

where $dg(K_j) = j - 1$ is the common degree of the vertices of K_j . Then $\deg fr$ represents the dimension of the hypersurface where $f_{i_1} \dots f_{i_j}$ coexist (this follows immediately from Axioms 1, 2, and Property 1).

A number of physical consequences can be deduced from $G(r)$. We give some of them here and illustrate them with two examples.

1. From Property 1, the maximum number of phases that can coexist in a system with r components is $r + 2$. In this case, $\deg fr(K_{r+2}) = 0$, that is, the $r + 2$ phases coexist at a single point called the " $(r + 2)$ -point."
2. In general, where M phases coexist (the case K_M), using the fact that $dg(K_M) = M - 1$, we have

$$\deg fr(K_M) = r - M + 2,$$

which is nothing less than Gibbs' phase rule for a pure substance where $\deg fr(K_M)$ represents the thermodynamic *degree of freedom*.

3. Each complete subgraph K_n of $G(r)$ corresponds to a different physical condition of the system. Thus, it can be the case that the system has many $(r + 2)$ -points, $(r + 1)$ -points, etc.

Examples:

(a) In particular, let us consider the case of water. It is a substance with one component ($r = 1$). The associated graph $G(1)$ is shown in Fig. 1. It is composed of the complete subgraphs K_1, K_2, K_3 , which correspond to the coexistence of one, two, or three phases, respectively. There are 7 triple points (the seven

⁴In a hypersurface of dimension l , the simplex has $l + 1$ vertices.

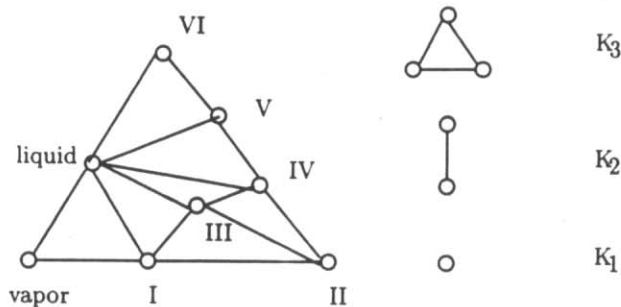


Fig. 1. The graph of H_2O .

K_3 's in Fig. 1), 14 cases of the coexistence of two phases (the fourteen K_2 's) and 8 phases (the eight K_1 's or vertices).

(b) For a substance with two components, let us assume that there are four phases in equilibrium among themselves. Then we can say that there can be 4 different triples of coexisting phases with 1 degree of freedom, 6 pairs of coexisting phases with 2 degrees of freedom, and 4 different phases with 3 degrees of freedom. In general, this corresponds to considering a simplex of M vertices and counting the number of hyperplanes of lower dimensions that it has. It is known (see, e.g., [5]) that this number is given by

$$f_k(T^d) = \binom{d+1}{k+1},$$

where d is the dimension of the hyperplane and k is the number of faces, with $k < d$. In the previous example, the dimension of the hyperplane is $d = 3$, so we obtain the different values from $f_k(T^3)$.

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