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Lee O. Case's "Elements of the Phase Rule", Chapter 1, One component systems

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I. SYNOPSIS

This is the first chapter, concerning one component systems. In each of the three chapters of this book, I've scanned the text (a major problem with a typewritten text which dates from 1960), corrected as much as possible, and added interpolations marked with (cwd). The text is unique, and therefore worth preserving in as close as possible to its original form. I hope you agree.

II. ONE COMPONENT SYSTEMS

For a one component system, the phase rule analysis furnishes the following immediate results:

P	$V(=3-P)$	U
1	2	$2(p,T)$
2	1	$2(p,T)$
3	0	$2(p,T)$

As indicated in the table, the only phase rule variables in this case at p and T, since each phase consists of the pure component, its mol fraction concentration for example being unity in every phase.

Any specific property of a single phase can accordingly he represented as a function of the two variables p and T, for example, the density, refractive index, specific heat conductivity, etc. If the chosen dependent variable is the volume of a fixed weight of the phase, the result when graphed is the familiar $p-V-T$ diagram for a pure substance.

The simplest case of heterogeneous equilibrium arises if $P=2$. The phase rule result, that $V=1$ for this case, signifies that there must exist a relation $p=f(T)$ for coëxistence of a pair of phases in a one component system. Concerning the form of this relation the phase rule, of course, gives no information; it merely predicts its existence. Experiment must be relied upon to furnish the necessary data to define the function $p=f(T)$ for a given pair of phases in a certain system. Naturally for the same system there will be a different relation between p and T for every possible pair of phases which may exist in equilibrium with one another. Since, however, all such functions involve the same pair of variables, they may be

represented graphically in the same coordinate system – for example, in terms of the rectangular coordinates p and T. The result is a "phase rule diagram". On a phase rule diagram for a one component system there will thus appear a set of $p-T$ curves, one for each possible pair of coëxisting phases.

For three-phase equilibrium the table shows that both p and T must posses definite values fixed by nature for the system in question. It will be instructive to show how such a situation arises as a direct consequence of the occurrence on the same diagram of the several curves characteristic of different two-phase equilibria. As a concrete example, reference will be made to the water system in the range of pressures and temperatures in which the phases solid, liquid and vapor are possible. The coëxistence of liquid and vapor is described by a function $p=f_1(T)$, that of solid and vapor by a different function $p=f_2(T)$, both shown on the same $p-T$ diagram in Figure 1 and Figure 2. If these two curves happen
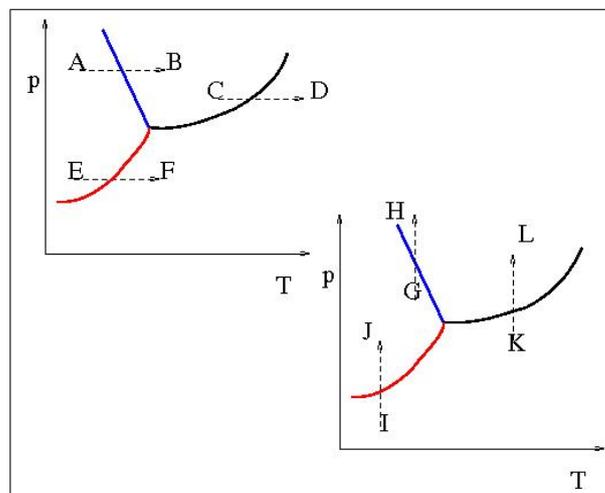

FIG. 1: A simple one-component phase diagram which shows only three phases. The area shared by A and E corresponds to solid, the area shared by B and C corresponds to liquid and the area shared by D and F corresponds to gas. Heating a sample initially at A makes solid disappear and liquid appear (B). Heating liquid (C) makes it disappear, and vapor (gas) appears (D). Transitions between phases are illustrated both with respect to heating (and of course, cooling) but also with respect to increasing or decreasing pressure isothermally.

to intersect, then the conditions for three-phase equilibrium are satisfied for, since the point of intersection lies

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on both curves, it must represent the conditions for equilibrium between liquid and vapor and also between solid and vapor, and hence Figure 2. For the coëxistence of
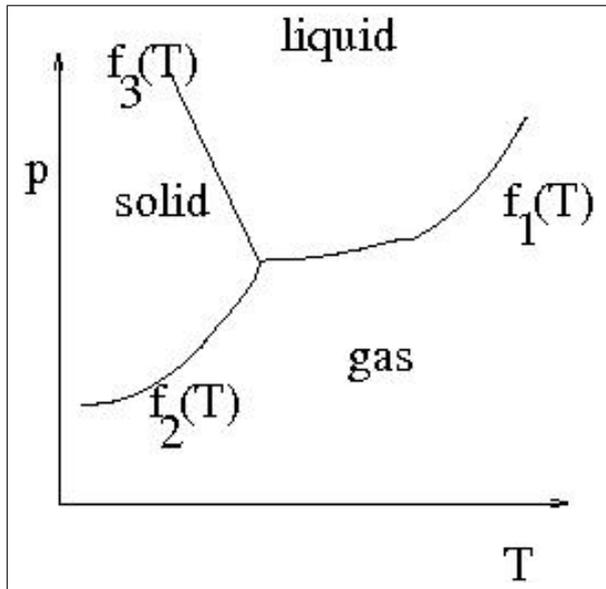

FIG. 2: A simple one-component phase diagram which shows only three phases. The coëxistence curves $f_1(T); g \rightleftharpoons \ell$ (evaporation), $f_2(T); s \rightleftharpoons g$ (sublimation), and $f_3(T); s \rightleftharpoons \ell$ (melting) are shown.

solid, liquid and vapor. (Such a point is a called a "triple point"). Furthermore the location of this point is fixed by nature for the system; its coördinates must satisfy $p = f_1(T) = f_2(T)$. In other words, the variance is zero for such equilibrium. But this is precisely the conclusion of the phase rule for, if $P = 3, V = 0$.

Another important result follows immediately from the fact of intersection of the two curves under consideration. Since at the point of intersection solid, liquid and vapor are in equilibrium, each possible pair of the three phases must be separately in equilibrium. But the possible pairs include not only solid-vapor and liquid-vapor (already considered) but the new pair solid-liquid; hence the triple point must also lie on a third curve, $p = f_3(T)$, representing the conditions for equilibrium between solid and liquid.

Now although these ideas have been developed with respect to the three phases solid, liquid and vapor, it is clear that the phase rule furnishes a generalization of the results for all possible types of equilibria for one component systems. Additional types will occur if the substance is capable of existing in the solid state in different crystal forms (allotropic modifications). (There can never be more than one liquid phase in a one component system, nor more than one gas phase regardless of the number of components.) The additional types may be symbolized $G - S_1 - S_2, \ell - S_1 - S_2, S_1 - S_2 - S_3 (S_1, S_2,$ and S_3 representing different solid forms): a given system

might involve a large number of examples of each type. Regardless of type the phase rule shows that

1. for each pair of phases capable of coëxistence there must be a curve on the $p - T$ diagram;

2. for each set of three phases in equilibrium there must be a point on the diagram from which radiate three curves, one for each pair of phases in equilibrium at that point.

The resulting curves, of course, mark off the surface of the $p - T$ plane into areas representing the conditions for existence of single phase.
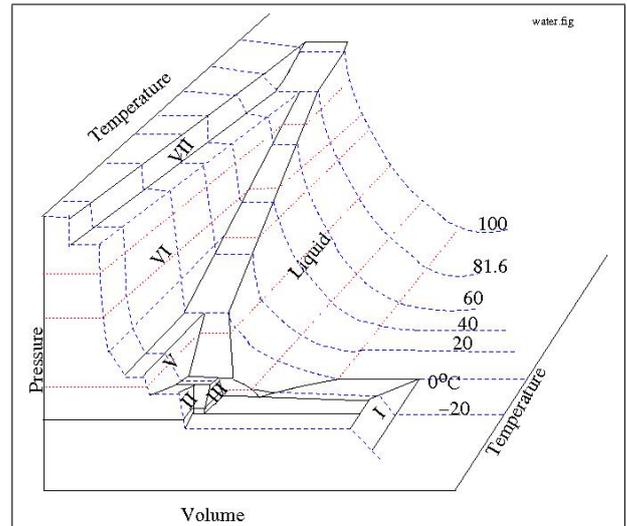

FIG. 3: The best (IMHO) water phase diagram ever published F. L. Verweibe, Am. J. Phys., 3, 179 (1935). One has to place his/her eye somewhere on the positive V axis and look back towards the "origin" to see the $p - T$ kind of diagrams illustrated here and in texts.

For a more detailed discussion of one component systems, two principles are of great value. The first of these is the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$$

which relates the slope of a two-phase curve to the absolute temperature T, the heat effect, ΔH, and the volume change, ΔV, accompanying the transformation of one phase into the other. Although this equation is early met with in the study of physical chemistry as applied to the equilibria solid-vapor, liquid-vapor, and solid-liquid, it is valid for any case of two-phase equilibrium in a one component system (or in general for a system involving any number of components C existing in $(C+1)$ phases.) This equation shows that ΔH and ΔV must have the same sign if $\frac{dp}{dT} > 0$, opposite signs if $\frac{dp}{dT} < 0$. As is well known, it may be integrated under certain reasonable assumptions for the cases of liquid-vapor and solid-vapor equilibria, furnishing in these cases the actual form of

the corresponding phase rule relations, which in other instances must be furnished entirely by experiment,

The second useful principle referred to is the Le Chatelier Rule, which a system in equilibrium reacts to changes in the conditions imposed upon it. Since in the usual discussion of the Phase rule, the external condition variables are restricted to pressure and temperature, the Le Chatelier principle need be applied only to these factors. The results are respectively that

1. increase of pressure (at constant temperature) favors the formation of the phase of smaller volume, i.e., greater density; and

2. increase of temperature (at constant pressure) favors that process which occurs with absorption of heat,

As an illustration of a more complicated diagram in which several different solid phases occur, the system water may again be used. Up to 5000 kg/cm^2 water is capable of existing in five different stable solid phases. The diagram is reproduced schematically in Figure 4, the
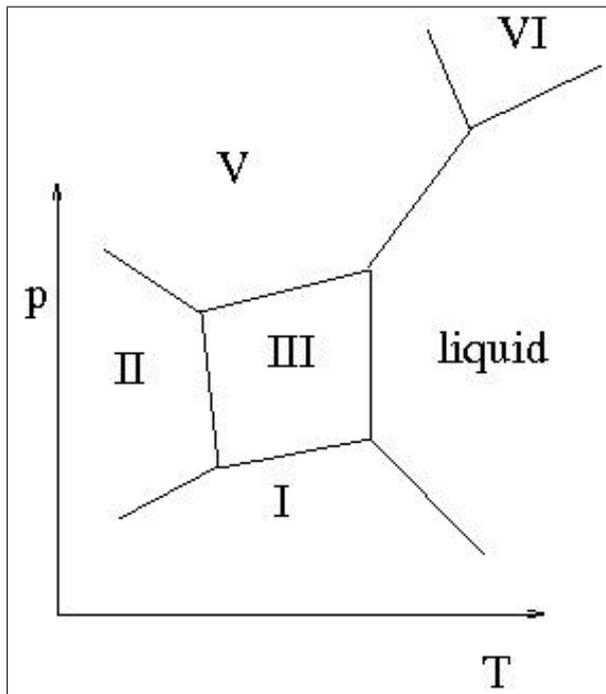

FIG. 4: Part of the water phase diagram (schematic) showing various allotropes of solid water (ices).

different solid forms being distinguished by Roman numerals (due to the small scale required for the pressure axis in comparison with that of Figure 2, the vapor region as well as the curves S-G and ℓ-G of Figure 4 are coincident with the T-axis) No detailed discussion of this diagram need be given, since no new principles are involved. It is interesting to note, however, that of the several forms of ice which can exist in equilibrium with

liquid, "common" ice (ice I) is the only one which shows the remarkable property of being less dense than its liquid.

A remark concerning the limitations of the phase rule may be made with reference to this diagram. It will be recalled that the phase rule gives no indication as to what particular equilibria are possible for a given system but only as to the conditions required for equilibria of various general types. Thus for the water system, in the $p-T$ region in which five stable solid phases are possible in addition to liquid and vapor (actually several additional metastable solid phases are known even in. this region), one might expect for the total of seven phases $\frac{7!}{P!(7-P)!}$ equilibria for each value of P. The results and the comparison with actual experience as shown by the diagram are shown in the following table:

	P = 1	2	3
Theoretical Equilibria	7	21	35
Actual Equilibria	7	12	6

The remaining types are either metastable or completely unstable. The probable locations for some of the missing metastable triple points may be estimated by prolonging a pair of equilibrium lines having a single phase in common. Only experiment can tell whether or not one of these equilibria can be realized.

Suitable methods for the experimental determination of a phase rule diagram may be outlined by reference to the diagram of Figure 5. Thus for a selected constant pressure a temperature-time curve must show halts of constant temperature corresponding to the transition of one phase into another. From the phase rule point of view this involves using up one degree of variance by arbitrary selection of the value of one variable; the remaining variance is then one for one–phase equilibria; zero for two-phase equilibria. Therefore, although the temperature of a single phase may be altered at constant pressure, for example by progressive removal of heat resulting in a so-called "cooling curve", if at some temperature in the series passed over a second phase makes its appearance the temperature must remain constant in spite of continued removal of heat so long as both phases are present. The physical mechanism provided for this maintenance of constant temperature is of course the liberation of the latent heat of transition which must occur at just the right rate to compensate for the heat removed from the system. The duration of the halt in temperature will naturally depend upon

1. the rate of removal of heat,

2. the magnitude of the heat of transition, and

3. the mass of the system.

The application of the experimental method of heating or cooling curves is limited in a practical sense to the lower pressures and will be met with again in connection with systems of more than one component. The
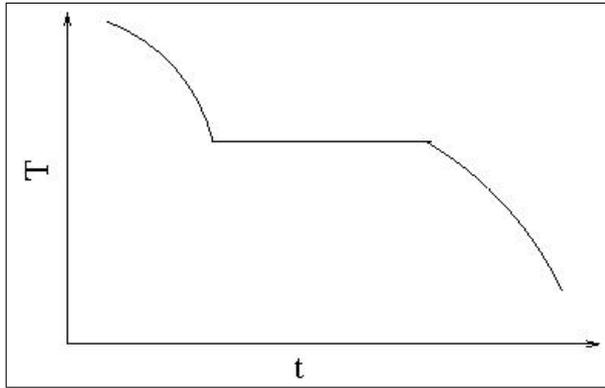
FIG. 5: Cooling curve for a phase change in a one component system. T(emparture)-t(ime) plots such as this are used to establish locations of invariant points in which sufficient phases are present so that neither temperature nor pressure (nor compositions in poly-component systems) remain variable. In this case starting on the left of the figure, we have cooling of a phase, then at the break (in slope) a two phase equilibrium. As time passes, the original phase disappears and the new phase appears, until the first phase is completely consumed, whereupon the new phase begins cooling, starting at the second discontinuity (cwd).

limitation of the method with respect to high pressures is due to the fact that for high pressure work somewhat massive apparatus is necessary to contain the sample and that as a result the heat capacity of the system is generally small in comparison with that of the container. It is evident, however, that a completely parallel method of procedure is available at constant temperature by following the changes of pressure required to alter the volume of the system. In this case the phase rule requires that the pressure of the system shall remain constant during the volume change accompanying the transition of one phase into another. This is the method actually employed in tracing phase rule diagrams for systems under high pressure.

In concluding this brief discussion of one component systems, an apparent conflict with experience should be resolved. The conflict referred to is that whereas the data for the one component system indicate that ice, water, and water vapor can coëxist only at $t = 0.0075^oC.$, $p = 4.6mm.$, it is a matter of common knowledge that under a pressure of one atmosphere at which the freezing- point of water is defined as 0.00^oC., water vapor is also present, a total of three phases. The fact is, of course, that under these conditions the system is no longer one of one component. In other words, on a phase diagram for a one component system, the p-coördinate must represent the pressure due to the component (and equal, for equilibrium, to the pressure upon the system). But due to the fact of complete mutual solubility of all gases, to which reference has already been made, a gas phase, while it may transmit pressure to solid and liquid phases, cannot do so with respect to another gas. Under the new conditions the system in question can be adequately treated by considering it to consist of two component- water and air (which, although a mixture, is of essentially constant composition). For coëxistence of the three phases - solid, liquid and gas - the variance is now $V = 2 + 2 - 3 = 1$. But if the total pressure is fixed at one atmosphere the degree of variance is assigned, whence the temperature for coëxistence of the three phases at constant pressure is fixed, in agreement with experience.