Macroscopic Definitions for Phase Studies

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The concepts necessary for a discussion of phases and phase transformations are defined and discussed. It is pointed out that common usage leads to a contradiction but that this contradiction is not inherent in the definitions. It is shown that phase relationships may be discussed in a precise and non-contradictory fashion by the use of the defined concepts.

In recent years studies at high temperatures have brought about an increased interest in non-stoichiometric condensed phases, and in the ordering which occurs in these phases at low temperatures. This interest has resulted in and been the result of studies of phase relationships in condensed systems. For example, studies on the disorder and order in solid solutions of oxygen in α-titanium, on the structures of the chromium sulfides, and on the vanadium oxides within the VO_{0.25}−VO_{1.5} region have been carried out and a study of the VS_{1−r} phases is in progress. Studies of phase relationships are most fruitfully carried out with a background of precise definitions. Such definitions enable the workers in the field to communicate precisely and to interpret results in a logically consistent framework. Only a portion of this framework has been available in the form of precise definitions, and this portion, due to its incomplete nature, has been largely overlooked. It is the purpose of this paper to present a logically consistent and complete set of definitions for the discussion of phases and phase transformations. The proposed set is not unique nor is each definition original. The set was constructed so that each definition would conform, as closely as is consistent with the above stated purpose, with general usage.

DEFINITIONS AND DISCUSSION

The concepts of phase and phase transformation are fundamental to considerations of heterogeneous equilibria. The concept of phase is explicitly defined in the literature while that of phase transformation is defined only impli-
licitly. The definition of phase which is adopted here is that which includes homogeneous regions with gradients, namely:

i. A phase is a region of matter within which all macroscopic properties vary continuously as functions of position.

This definition agrees with those given in Refs.\textsuperscript{7,8} A more restricted definition has been adopted elsewhere\textsuperscript{9–11} and is stated here as a special case:

ii. A uniform phase is a region of matter within which all properties are independent of position.

In order to determine the number of different phases in a system it is necessary to know when two phases are the same, hence:

iii. Two uniform phases are the same phase if their macroscopic properties are the same.

The concept of same phase is used frequently in the literature although not in conformity with the definition given by Gibbs which is, in essence, definition iii. For example, the chemist says, "the solid A phase" when referring to solid A with a given crystal structure, but with variable temperature, pressure, and composition. The justification for adopting definition iii is not only that it is in agreement with the original definition by Gibbs, but also that the common usage results in a contradiction.

This contradiction may be pointed out by a consideration of the phase changes which occur along the dashed lines on the four phase diagrams shown in Fig. 1. Along each of these paths there is a phase transformation between a and b. Thus it is said that a and b are "different phases". Consider the paths between a and b shown in Fig. 2. Along these lines there is no phase transformation, and thus the contradiction.

A second problem arises from the lack of an explicit definition of same phase. Consider, for example, a crystalline substance in which a change of composition results in a change in the long range order along one crystallographic direction and random (short range) changes in two other directions. As the composition is varied in such a substance there results a continuous
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transition between symmetry types. With no clear cut definition of same phase
the question of whether two phases so related are the same remains unansw-
ered. By iii it is clear that these substances are different phases (and would
be if the changes had been random in all directions). In fact each of the three
pairs: 1. NaCl(s) at $T_1$ and $T_2$; 2. EtOH in H$_2$O with $N_{\text{EtOH}} = 0.75$ and
$N_{\text{H}_2\text{O}} = 0.25$; 3. O$_2$(g) at $P_1$ and $P_2$, consists of two phases. The relationship
between the phases in these pairs is that the two members of each pair are in
the same one phase region.

iv. A one phase region is a volume in the space of the chosen independent
variables of a system within which all state points are points at which there
exists one uniform phase in the system.

v. If during any quasistatic change of state of a region of matter which is
initially a uniform phase there exists either a discontinuous change in $G$, $(\delta G/\delta T)_{P,N}$, $(\delta G/\delta P)_{T,N}$, $(\delta^2 G/\delta T^2)_{P,N}$, . . . . for the region of matter at
some state or a two phase mixture within the region of matter at some states,
then there exists a phase transformation at that state (those states).

Example: H$_2$O(l) = H$_2$O(s) at 0°C at 1 atm is a transformation between an
H$_2$O(l) phase and an H$_2$O(s) phase (not the H$_2$O(l) and the H$_2$O(s) phases).
Remark: It is useful to distinguish between transformations in which the two
phases in equilibrium at the transformation have the same composition and
those in which the two phases have different compositions. This may be accom-
plished by referring to the former as transitions.

Remark: If the discontinuity occurring at a transition state is in $G$ the
transition is zero order (non-equilibrium), if in $(\delta G/\delta T)_{P,N} = -S$ or
$(\delta G/\delta P)_{T,N} = V$ the transition is first order, if in $(\delta^2 G/\delta T^2) = -C_p/T$ then
the transition is second order.

vi. Two uniform phases are in the same one phase region if there exists a
quasistatic path such that the two regions of matter can be made to be the
same phase by a change in the macroscopic state of one of the regions along
that path and at no state along that path do two phases exist in the region
of matter.

Examples: 1. In the phase diagram examples given above (Figs. 1 and 2)
the phases at $a$ and $b$ are in the same one phase region. 2. $\beta$ and $\beta'$ brass are
connected through a second order transition and thus are in the same one
phase region. 3. LiCl(s) and LiBr(s) are in the same one phase region since
they are miscible in all proportions at, for example, 500°C.

Digression on second order transitions:

1. Transitions occurring along lines of varying temperature. If such a
transition is thought of as occurring between two phases then:

$$\Delta G \approx k(T_i - T)^2$$

in the neighbourhood of the transition temperature $T_i$. Thus the free energy
change for the transition has the same sign on both sides of the transition
point. Furthermore, for such transitions two phase mixtures do not result.
These facts are difficult to reconcile with the concept of a transition between
phases in different one phase regions.

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2. Transitions occurring along lines of varying quantity of one component in a binary system.

(a) The Gibbs-Konowalow theorem\textsuperscript{16} states for transformations in binary systems: If a transformation is first order and occurs between phases with the same composition then the transition occurs at a state at which the temperature-composition transformation line is at a maximum or a minimum. An equivalent statement of this theorem is: If an equilibrium transition occurs at a state other than that at which the temperature composition is at a maximum or a minimum then the transition is higher order than first, or: equilibrium transitions occurring along lines of varying composition are second order or higher.

(b) Consider a transition which occurs when \( n_i \) moles of component one have been added to component two. The free energies of the two phases (\( \alpha \) & \( \beta \)) may be expanded about \( n_1 = n_i \):

\[
G^\alpha = G^\alpha(n_i) + \mu_1^\alpha(n_i - n_1) + \frac{1}{2} \left( \frac{\delta^2 G^\alpha}{\delta n_1^2} \right)_{n=n_1} (n_i - n_1)^2 + \beta(n_i - n_1)^3
\]

\[
G^\beta = G^\beta(n_i) + \mu_1^\beta(n_i - n_1) + \frac{1}{2} \left( \frac{\delta^2 G^\beta}{\delta n_1^2} \right)_{n=n_1} (n_i - n_1)^2 + \beta(n_i - n_1)^3
\]

and thus:

\[
G^\beta - G^\alpha = \Delta G \cong k(n_i - n_1)^2
\]

and a similar anomaly to that mentioned above results.

Remark: Definition vi requires that there be no first order transitions along the path connecting two phases in the same one phase region. It was felt that the anomalies mentioned in the digression warranted limiting the stipulation to first order transitions.

The term phase boundary as used for lines on phase diagrams is not consistent with the above definitions. More appropriate terms might be transformation and transition lines, these lines being the loci of state points of phases undergoing transformations and transitions. Since second order transitions are of interest it might be worthwhile to devise a special line representing second order transitions on phase diagrams.

The definitions given above provide no means of distinguishing between liquid and vapor or of stating a definite relationship between \( a \) and \( b \) in Figs. 1 and 2. These means are provided by the following:

vi. Two uniform phases are connected through a transformation along a univariant path if the two phases can be made to be the same phase by a quasi-static change of one property of one of the regions of matter along that path and there exists a transformation along that path.

Conclusions. Thus the thermodynamic distinction between liquid and vapor may be stated: two phases are in the relationship of being the liquid and vapor of a substance if they are in the same one phase region and are connected through a (first order) transition along a path of varying temperature for all pressures below some critical pressure and greater than some triple point pressure.
All $a-b$ pairs described above are connected through transformations along univariant lines.

The question of the relationship between the crystalline phases related by unidirectional ordering is also answered. The two forms are different phases in the same one phase region ($\Delta V = 0$). The phases may be connected through a second order transition. Whether they are or not must be independently determined.

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