ON ENANTIOTROPY AND MONOTROPY. I.

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It can be considered that any polymorphism, including the cases where the number of modifications exceeds two, is composed of pairs of dimorphisms. The behaviours of dimorphism, therefore, play the fundamental rôle in the study of polymorphism. O. Lehmann(1) was the first in classifying dimorphism into two distinct categories, enantiotropy and monotropy. He stated: "Die charakteristische Eigentümlichkeit enantiotroper Modifikationen besteht in der Umkehrbarkeit des Umwandlungsvorganges bei der *normalen* Umwandlungstemperatur. . . . . Ganz wesentlich verschieden hiervon verhalten sich die monotropen Modifikationen. . . . . , denn die Umwandlung ist nicht umkehrbar, irreversibel. Bei dieser Klasse von Körpern existiert also eine im festen Zustande stets stabile und eine stets labile Modifikation, von welchen sich unter allen Umständen nur die letztere in die erstere umwandelt und zwar unter Freiwerden von Wärme." Later some interpretations on this subject were made by Ostwald, Schaum, Roozeboom, Tammann and others, on the basis of the phase theory.(2) The definitions of the terms, enantiotropy and monotropy, however, have not been made which are consistent with the experimental cases. On this point, much ambiguities and incompleteness were found by the author. One of the chief objects of this paper is to make clear the definitions for them as well as the thermodynamic relations connected to them.

Definitions of Enantiotropy and Monotropy. The fundamental idea of O.Lehmann is to classify the behaviours of dimorphism, "under the atmospheric pressure" or "at the *normal* pressure", into two categories, enantiotropy and monotropy. We may, however, extend it more generally for the cases "at constant pressure." Some dimorphism which is enantiotropic or monotropic at one atmospheric pressure may change into the other by the effect of pressure.(3) It is, therefore, necessary to add the condition of pressure or the range of pressure when we express in such cases, the relations of stability in terms of enantiotropy and monotropy.

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(1) O. Lehmann, "Molekularphysik" (1888), I, p. 193.

(2) Wilh. Ostwald, *Z. physik. Chem.*, **22** (1897), 313; Schaum, *Lieb. Ann.* **300** (1897), 215; H.W.B. Roozeboom, "Die heterogenen Gleichgewichte" (1901), I, pp. 109, 159; G. Tammann, "Kristallisieren und Schmelzen" (1903), p. 101.

(3) O. Lehmann gave no remarks on the effects of pressure on the stability of dimorphism as is clear in the quotation given above.

Let us now interpret more closely the term, "transition." Two types of transition are probable. One is the case in which it occurs from the metastable to the stable⑴ modification, the other is the case in which it occurs from the metastable to the metastable modification. In general, the first case occurs in nature. And as the experimental fact, fairly smooth phase changes occur from the solid to the liquid or the gaseous phase. Hence, in the use of the terms enantiotropy and monotropy, it will be convenient to confine it only in such cases, in which the transition occurs from the metastable to the stable modification and the phase changes from the two modifications to any other phases are free from the effects of pseudequilibrium.

We may now define enantiotropy by the following two conditions at constant pressure:

(1) There should be (neutral) equilibrium temperature between the two modifications A and B in one component.⑵

(2) In the neighbourhood thereof, A should be stable above it, B being stable below it, or vice versa.

The dimorphism which does not satisfy the above conditions at constant pressure is defined to be monotropy, if only one of the two modifications is stable. With the above conditions in mind, we are able to consider that monotropy is included in the following cases:

(i) The dimorphism without any equilibrium temperature.⑶

(ii) The dimorphism with equilibrium temperature only in the unstable domain of A and B.

(iii) The dimorphism with equilibrium temperature, however, only A (or B) is stable except there.

By means of a few examples these definitions will be more clear. The schematically drawn *pT*-diagrams⑷ of sulphur, methylene iodide and phenol are shown in Fig. 1, Fig. 2 and Fig. 3 respectively. Fig. 1 is the case in which the enantiotropic dimorphism at one atmospheric pressure changes into the monotropic at high pressure. Fig. 2 is the case in which the monotropic dimorphism at low pressure changes into the enantiotropic at high pressure. In Fig. 3 we found one of the examples with two transition points at constant pressure.

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(1) The term "stable" will be used in the sense of "more stable than any other phases."

(2) When clear, the condition of "one component" will be omitted. And the two modifications will be considered to satisfiy the condition of "pure homogeneous phase".

(3) After the general customs of the study in this field, equilibrium temperature is considered even in the unstable domain. Monotropy (i) is the case in which such temperature cannot be considered both in the stable and unstable domains of the two modifications.

(4) G. Tammann, loc. cit. p. 270 (sulphur); p. 280 (methylene iodide): p. 310 (phenol). As for methylene iodide, cf., A.H.R. Müller, *Z. physik. Chem.*, **86** (1913), 237.

In our definitions, it is enantiotropic at P_2 in Fig. 1 and at P_3 in Fig. 2. At P_1 and P_2 in Fig. 3 we have the enantiotropy with two transition points. At P_1 one of the transition points lies in the unstable domain, the rest being in the stable domain. It may be mentioned here that it cannot always be monotropic even if one of the transition points lies in the unstable domain. At P_4 in Fig. 3 we have one of the examples for monotropy (i), and at P_3 in Fig. 1 and at P_2 in Fig. 2, monotropy (ii), and also at P_3 in Fig. 3, monotropy (iii). It is evident that we have always monotropy (iii) and (ii), at and below the pressure of the triple point among two solids and gas, as at P_1 in Fig. 1 and Fig. 2. And also we have monotropy (iii) at the pressure of the triple point among two solids and liquid in Fig. 1 and Fig. 2.

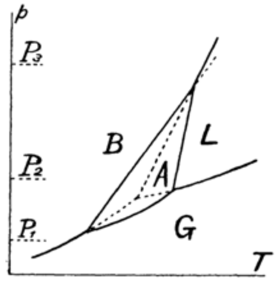

Fig. 1.

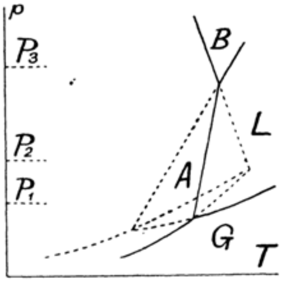

Fig. 2.

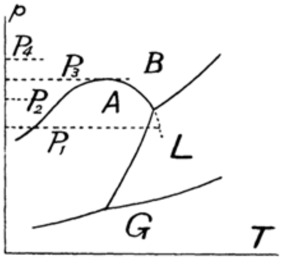

Fig. 3.

Criteria of Mutual Stability and Equilibrium. In the pT-diagram, the most convenient criteria for equilibrium and stability is the Gibbs' ζ-function. In order to know the mutual stability of the two modifications A and B at the point (pT), we have to consider the difference Z of the specific values of ζ-fuction for A and B.

$$Z=\zeta_{\mathrm{B}}-\zeta_{\mathrm{A}}, \quad \text{or} \quad Z=X-Q,$$

where X is the heat absorbed when the transition occurs naturally from A to B at constant temperature and pressure, or the calorimetric heat of transition; and Q is the heat absorbed when it is made in the reversible way at constant temperature.

A and B are in equilibrium when $Z=0$, or $X=Q$. It is clear that A is more stable than B when $Z>0$, or $X>Q$, for such a change cannot occur in nature in which the calorimetric heat is greater than that of the reversible change as before. And also B is more stable than A when $Z<0$, or $X<Q$.

At constant pressure, we have $Z=f(T)$, or Z varies only with the variation of temperature along the curve $f(T)$. If we let the equilibrium temperatures be $T_0\,T_0'$, ... etc., we have these as the roots of the equation $f(T)=0$, or $Z=0$. It is, therefore, necessary to investigate the nature of the equation $f(T)=0$, or the nature of the Z-curve, in order to find the equilibrium point as well as to know the relation of mutual stability in the given dimorphism at constant pressure.

We have monotropy (i) if there is no real root in the equation $Z=0$, and only one modification is stable. If there is one real and positive root T_0 in the equation $Z=0$, the behaviour of the Z-curve will be as in Fig. 4.

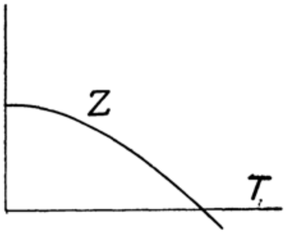

Fig. 4.

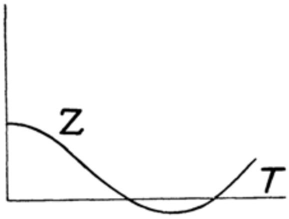

Fig. 5.

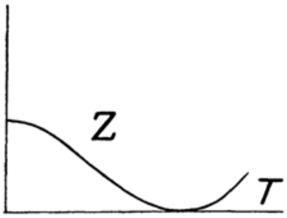

Fig. 6.

If there is only one melting point for each modification at constant pressure, we shall have monotropy (ii) when T_0 lies above the melting point; and also enantiotropy, when below. We shall next consider the cases with two real and positive roots in the equation $Z=0$, each modification having only one melting point. In these cases, we shall have in general enantiotropy or monotropy (ii) as before. The behaviour of the Z-curve is as in Fig. 5. However, if the two roots are equal, the Z-curve will be brought in contact with the T-axis as in Fig. 6, which is the case at P_3 in Fig. 3. In this case, the two modifications have an equilibrium point. However, if the transition is made to occur directly(1) at the pressure under considerations, it shall be limited in one direction as in monotropy (i) and (ii). It is not enantiotropic and may be ascribed to monotropy (iii).(2)

We may therefore consider enantiotropy,(2)on the basis of thermodynamics, as follows; It shall be enantiotropic when Z-curve cuts T-axis between the stable domain of the two modifications. In which case, the direct transition shall occur in two opposite directions above and below the transition point.

Besides above cases, we may be able to consider lots of special cases and the cases in which two melting points exist for each modification at constant pressure. However, these cases are omitted here, for the sake of brevity and owing to the lack of the experimental examples.

Some Theories hitherto Proposed on Enantiotropy and Monotropy and the Cases of Pseudequilibriums. It was first proposed by Ostwald(3) that

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(1) We have to add the condition, " directly ", or " without any intermediate states including ion." For instance, the red phosphorus changes into the white when heated and distilled. Whereas these modifications stand in the relation of monotropy under the atmospheric pressure.

(2) Monotropy (Gr. *monos*—single; *tropos, trepein*—to change) and enantiotropy (Gr. *enantios*—opposite; *tropos, trepein*—to change).

(3) Wilh. Ostwald, loc. cit.

it is enantiotropic or monotropic according as the transtion point lies below or above the melting point. It is implied in this statement that, under the atmospheric pressure, there is only one melting point for each modification, and one transition point between the two modifications, which is an experimental rule adopted by many authors. Our monotropy (i) and (iii) were not included here. The category of pseudomonotropy was proposed by Roozeboom,⁽¹⁾ in order to make more complete the Ostwald's theory on monotropy, in which following cases were included :

(a) The dimorphism with its transition point in the low temperature where the transition is retarded. In which cases, it may manifest itself like monotropic.

(b) The dimorphism with the equilibrium point at absolute zero.

In the foregoing paragraphs, such cases have been excluded in which the phase changes from the two modifications to any other phases are disturbed by the effects of pseudequilibrium. It is, however, probable that there are the cases in which the dimorphism appears like enantiotropic by such effects which may be called pseudenantiotropy. It is also probable that there are the cases which appear like monotropic and yet can not be classified in our monotropy. It may be called pseudomonotropy. In which the case of (a) in the pseudomonotropy of Roozeboom may be included although it is not necessary to distinguish it from enantiotropy from the thermodynamic standpoint. The case of (b) is nothing but the special case of our monotropy (iii). It may be added here that in the cases of pseudenantiotropy and pseudomonotropy the effects of pseudequilibrium or retardation are necessary.

In a later paper, it will be discussed how our *Z*-function varies with the temperature and pressure in conjunction with the measurable quantities, and some ambiguous or abstruse cases will be treated.

In conclusion, I would express my hearty thanks to Prof. J. Sameshima whose counsels have been constantly at my disposal.

Summary.

It is a well known fact that there are two distinct behaviours of dimorphism in which transitions are of reversible and irreversible natures. O. Lehmann was the first in classifying it by the two categories, enantiotropy and monotropy. Later it was interpreted by Ostwald and others on the basis of the phase theory. However, clear definitions have not been made so far, which are consistent with all the experimental cases in the wide range of *pT*-diagram. To make it more complete and concrete, some definitions are

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(1) H.W.B. Roozeboom, loc. cit., p. 177.

given for the terms enantiotropy and monotropy. These terms not only serve to express the absolute stability but also to express the mutual stability of the two modifications in one component. The thermodynamic relations connected to them are also described. The cases of pseudequilibrium are also spoken of. As the result of these considerations, various theories on enantiotropy and monotropy are brought into one conformity.

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