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THE STATES OF AGGREGATION

THE CHANGES IN THE STATE OF MATTER IN THEIR DEPENDENCE UPON PRESSURE AND TEMPERATURE

BY

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Authorized Translation from the Second German Edition

BY

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TRANSLATOR'S PREFACE

PROFESSOR TAMMANN'S name is so well known in scientific circles that no apology need be made in offering an English translation to the public. The present work is a very complete outline of the equilibria in one-component systems, and includes the work for which Professor Tammann is so well known, namely, the experimental and theoretical work upon crystallization and melting at ordinary and also at high pressures.

No attempt has been made to amplify the original text in any way; it is presented as given in the German with only the remodeling necessary to smooth translation.

Acknowledgment is made to Dr. Donald P. Smith of Princeton University for help very kindly rendered during the preparation of the manuscript.

ROBERT F. MEHL.

CAMBRIDGE, MASS.

PREFACE TO THE SECOND GERMAN EDITION

In comparison to the original work, *Kristallisieren und Schmelzen* (*Crystallization and Melting*), the first edition of *Aggregatzustände* (*The States of Aggregation*) was disposed of with surprising rapidity. In the two years between the first and second editions of the later work there have been no noteworthy advances in this field, and the second edition, therefore, shows only slight changes in comparison with the first.

THE AUTHOR.

GÖTTINGEN.

PREFACE TO THE FIRST GERMAN EDITION

The relations between the liquid and the gaseous states of aggregation were the subjects of a great deal of investigation during the course of the last century. REGNAULT determined the vapor pressure curves of many substances, the critical phenomena were clearly explained by ANDREWS, and the application of the mechanical theory of heat to vaporization placed this subject upon a rational foundation.

The relations among the other states of matter, however, were only partly understood, and but little was known of the relations of the vitreous amorphous state to the liquid and to the crystalline states, and of the two latter to each other. Only the directions of a few melting curves at a pressure of 1 kg. per sq. cm. were known and it was thought that the course of the melting curve could be treated as completely analogous to that of the vapor pressure curve.

In 1896 the author began a theoretical and experimental study of this subject. The results of this period of work were published in *Kristallisieren und Schmelzen.* Leipzig, Joh. Ambr. Barth, 1903. This first period of work was supplemented by a second, extending from 1909 to 1914, during which the various theoretical considerations were further developed, and the conception of thermodynamic potential was applied. These investigations are to be found under the title *Zur Thermodynamik der Einstoffsysteme* (*The Thermodynamics of One-Component Systems*) in the *Ann. d. Physik,* Volumes 36–40. This period differs from the first also in the fact that greater regard was had to the molecular theory which served to develop the relations of the molecular structure of liquids to the species of heteromorphous crystals formed from them. At the same time a series of experimental studies were published by the author's co-workers.

P. W. BRIDGMAN of Harvard University has contributed greatly to the advance in this field by extending the experimenta

investigation of the phase diagrams to very high pressures. Equilibrium curves were followed up to 12,000 kg./cm.^{2}, and in one case to 20,000 kg. In the present work, besides the discussion of the equilibria of the states of aggregation with one another, the origin of these states from preceding unstable states is exhaustively treated.

Emphasis is placed upon the presentation of experimental results, though the book is not intended to serve as a work of reference, but chiefly as a review of the subject in its present state for the interested reader, assumed to have some knowledge of physical chemistry. Derivations are accordingly given elementary treatment. In addition to the elementary theory, the application of the thermodynamic potential to the chief problems in the study of equilibrium in one-component systems is made in Chapter IV, 6–9, and Chapter VII, 1, 4, and 5. The knowledge of this theory is not assumed and is therefore developed in sections *a* and *b* of Chapter IV, 6.

THE AUTHOR.

GÖTTINGEN.

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THE STATES OF AGGREGATION

I. THE STATES OF AGGREGATION

Text books on physics and chemistry commonly state that matter can assume three states: the solid, the liquid, and the gaseous. This enumeration of the states of aggregation, however, is neither complete nor unequivocal, for one and the same substance can exist in several solid forms, namely, in several crystalline forms and as a glass. The association of these states under the simple designation of "solid" cannot be recommended from the thermodynamic point of view, nor from the atomistic. It is true that these "solid" states have in common the property of resisting deformation, in which respect they differ from the liquid and the gaseous states, but this distinction does not have the fundamental significance of the following two.

1. A vitreous solid is fundamentally different from a crystalline solid. In a crystalline solid at least several of the properties are dependent upon direction; in a glass, as in a liquid or a vapor, all of the properties are independent of direction provided that the glass be made free from inner strain by prolonged cooling. The properties dependent upon direction are designated as vector properties, those independent of direction as scalar. Therefore, crystals are differentiated from gases, liquids, and vapors by the fact that at least a portion of their properties are vector whereas the properties of glasses, liquids, and vapors are scalar throughout.

2. Some states of matter are interconvertible in such a way that the properties of the substance change continuously during the change in state; other states are convertible into each other with a discontinuous change in properties. Only in a very exceptional kind of change in state (pT-lines) can a

continuous change in one property take place while the other properties simultaneously change in a discontinuous way. The states intertransformable in a continuous way are designated as isotropic, whereas the anisotropic are states continuously transformable neither into each other nor into the isotropic state.

In this way, upon the basis of the dependence of properties on direction, or upon the basis of the continuity of property changes during transformation from one state into another, the states of aggregation may be divided into two chief classes: the isotropic and the anisotropic. The isotropic includes three different states, and the anisotropic includes the various crystal forms, the number of which depends upon the nature of the substance.

Isotropic	*Anisotropic*
States	
Gas; liquid; glass.	Different crystal forms, I, II, etc.

This division is supported by atomistics. From the atomistic point of view substances differ according to structure in that the space lattice is peculiar to anisotropic substances and a random distribution of atoms in space peculiar to isotropic substances. In summary we may compare these two classes:

The Isotropic	*The Anisotropic*
No ordered arrangement of atoms in space.	Atoms arranged in space lattices.
All properties are scalar.	Properties are partly scalar, partly vector.
Continuous change from one isotropic state to another isotropic state is feasible.	Continuous change between different anisotropic states is not feasible, nor is such a transformation possible between an isotropic and an anisotropic state.

The objection may be made to this division that glasses or liquids can be compelled by external or internal forces to show vectorial properties. Double refraction can be introduced into an isotropic glass by means of pressure; but this double refraction disappears when the pressure is released. A chilling of small masses of glass may likewise bring about double refraction, and in fact large masses of slowly cooled glass ordinarily exhibit a weak and unevenly distributed double refraction. By warming to

about 500° every trace of this double refraction may be removed and thereafter the glass must be cooled with great caution in order to prevent the reproduction of the condition causing the double refraction. Similarly, liquid layers moving over each other with different velocities are doubly refracting, according to the experiments of A. KUNDT.[1] This double refraction in truly isotropic media disappears with the removal of the condition of stress that causes it, and in this way it differs essentially from the double refraction characteristic of a crystal. Accordingly, our classification relates to substances in their natural states.

Finally, objection may be raised to the above classification on the basis that liquid crystals are not considered. This objection can be given weight only by the elucidation of the nature of the liquid crystals. This will be discussed in the last chapter.

The behavior of any one substance, such as water, may be used to test the division of the states of aggregation into the gaseous, the liquid, and the solid. In the case of water, experiment has shown that at high pressures several crystal forms of ice exist, so that the short designation "solid" would not suffice completely to describe the behavior of this substance.

3. The amount of inner friction (viscosity) is likewise often taken as a basis for the distinction between the term "solid"—the word so often used to designate condition—and the term "liquid." If the viscosity have a small value the substance is called liquid; if a very great value, the substance is designated as solid. But viscosity cannot be taken as a basis for a comprehensive division of the states of aggregation, as may be seen from the following examples.

The viscosity of a liquid increases with increasing undercooling, and in a rather narrow temperature interval it increases very rapidly to values characteristic of solid crystals. A brittle glass is thus formed from an easily mobile liquid. This change in viscosity does not correspond to the behavior of the other properties, which in this temperature interval change relatively only slightly. The change in viscosity is a continuous one and no temperature can be chosen as the freezing-point, the point at which the liquid becomes solid. *Glasses are undercooled liquids.*

4. The melting of crystals of different substances produces liquids of different internal friction (viscosity) and the magnitude

[1] *Wied. Ann.* **13**, 110 (1881).

of the viscosity of the molten product can be of the same order as that of the crystal, as shown by silica and the acid silicates. In such cases the crystalline body does not become liquid on melting; and consequently the methods for the determination of the melting point founded upon the great decrease in viscosity that ordinarily occurs cannot be used. Splinters of albite or orthoclase placed upon the edge of a small platinum crucible and heated to a temperature higher than that of incipient melting, even though partly melted and therefore partly isotropic, will be but little deformed by their own weight. If such pieces be pressed, a sagging will take place; but this is common to both isotropic and anisotropic masses.[1]

5. On the other hand, crystals can be so weak that their surface tension can influence, and even determine, their crystalline form. Crystallites of pure metals, or of metal compounds formed by precipitation from melts of two metals, are frequently of spheroidal shape.[2] Copper crystallizing above 800° from melts of copper-bismuth forms crystals which are rounded, though under 800° the usual polyhedral crystals are formed.[3] Above 800° the crystal forces are so weak that the surface tension is able to overcome them, whereas under 800° the crystal forces are sufficiently great to be able to determine the form of the crystal in opposition to the surface tension. Similarly, silver iodide[4] and several other salts are very soft in the neighborhood of their melting points, and the same is true of many carbon compounds, such as camphene and the ester[5] formed by active amyl alcohol and anisalaminocinnamic acid or cyanbenzalaminocinnamic acid, which besides their softness are distinguished by a very strong rotation of the plane of polarized light.

The difference in viscosity between crystal and melt at the melting point is usually very great and quite evident to the eye. It can be very small, however, due either to a strong decrease in the viscosity of the crystal upon approach to the melting point, or to a strong increase in the viscosity of the liquid which then approaches the viscosity of the crystal.

[1] A. L. Day and E. T. Allen. *Z. phys. Chem.* **54**, 32 (1906).

[2] *Nachrichten d. Ges. d. Wiss. zu Göttingen*, (1912), page 557.

[3] Tammann. *Lehrbuch d. Metallographie*, Leipzig, 1921, page 17, Figs. 8*a* and 8*b*.

[4] O. Lehmann. *Molekularphysik*, and also *Z. phys. Chem.*, **5**, 89 (1890).

[5] D. Vorländer. *Berl. Ber.*, **41**, 2033 (1908).

The fact that the difference between the viscosity of the crystal and its melt may be very small is of no consequence in the differentiation and classification of the different states of aggregation; the magnitude of the property change effected by transformation from one state into another is unimportant, it is rather the kind and the manner of the change, whether it is continuous or discontinuous.

II. THE EQUILIBRIA OF THE STATES OF AGGREGATION

If a chemically homogeneous substance at constant temperature and constant pressure be permanently divided into two or three states, the states are said to be in equilibrium with one another. This equilibrium is given by *Gibb's*[1] *Phase Rule,* in which the states of aggregation are called *phases.* In the algebraic expression of the rule, F is the degree of freedom, n is the number of substances (components), and r is the number of phases:

$$F = n + 2 - r.$$

An investigation of the equilibrium conditions for a single substance discloses the fact that the highest number of phases (states of aggregation) that can exist in equilibrium with each other is three. In this case $F = 0$, that is, such an equilibrium between three states of aggregation can exist at one temperature, T, and one pressure, p, at a triple-point. If either T or p be changed, one of the three phases will disappear, and the substance will leave the equilibrium point for an equilibrium curve, upon which it is divided into two states of aggregation. This system has one degree of freedom, since p and T cannot change upon it independently of each other in case the substance retain the property of existing in two phases, but only as determined by the equilibrium curve. If p and T be changed in a way other than that defined by the equilibrium curve, one of the two phases will disappear, and the system will acquire two degrees of freedom, since p and T under these conditions can be changed within wide limits without the appearance of a second phase.

In order to represent the course of the equilibrium curves and their positions relative to one another, the *equilibrium diagram* is employed. The measured coordinates of the equilibrium curves are introduced into a coordinate system with the axes p and T, and the equilibrium curves are drawn.

[1] *Scientific Papers,* I, 96, London, 1906.

1. The Triple-Point

Figure 1 represents the course of the equilibrium curves in the neighborhood of the triple-point, at which the three states of aggregation, vapor, liquid, and crystal, are in equilibrium with one another. The three equilibrium curves are the limits of the three fields of stable states: the vapor, *v*, the liquid, *l*, and the crystalline, *c*. Upon each of the equilibrium curves those states exist in equilibrium the fields of stability of which are limited by the equilibrium curve.

The vapor pressure curve of the liquid, *vl*, runs through the triple-point more steeply than *vc*, the vapor pressure curve of the crystal, *c*. The angle at which these vapor pressure curves intersect at the triple-point is often very small, and is smaller the lower the pressure of the triple-point.

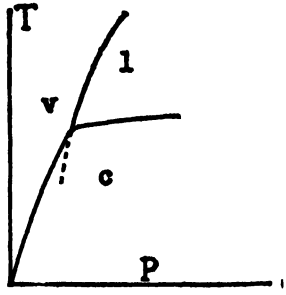


Fig. 1.

The melting curve, *lc*, ordinarily rises with increasing pressure to high temperatures. Since the influence of the pressure upon the equilibrium temperatures between crystal and melt (along *lc*) is very much smaller than upon both of the other equilibrium curves (*vl* and *vc*), the melting curve is much flatter than the other two curves.

If the triple-point *vlc* lie at very low pressures, on heating the crystalline substance at ordinary atmospheric pressure the line of the change in state for the substance, a perpendicular to the *p*-axis, will intersect the melting curve *lc*, because the pressure of the triple-point is much lower than atmospheric pressure. In this case the substance first melts and then boils; this is the usual behavior of substances. If, however, the triple-point lie at a pressure higher than atmospheric, the perpendicular to the *p*-axis describing the change in state of the substance upon heating does not intersect the melting curve, but intersects only the vapor pressure curve, *vc*, of the crystalline substance; the substance therefore vaporizes without melting. Thus carbon dioxide snow does not melt upon warming at atmospheric pressure because the triple-point lies at $-56.7°$ and 5.1 atmospheres. If, however,

carbon dioxide snow be introduced into a cooled vessel through a wide glass stopcock, which is subsequently closed, the pressure over the carbon dioxide snow will increase on warming according to the vapor pressure curve and when the temperature of the triple-point is reached, the substance will begin to melt.

Substances possessing more than one crystalline form will display one or more additional triple-points. Such a case is represented by Fig. 2, in which two crystalline forms c_1 and c_2 are in equilibrium with vapor and with each other. At the triple-point at the lower temperature both crystalline phases are in equilibrium with the vapor. In Fig. 3 two other crystalline phases, c_1 and c_2, are in equilibrium with the melt. In this

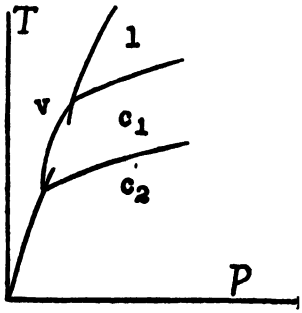


FIG. 2.

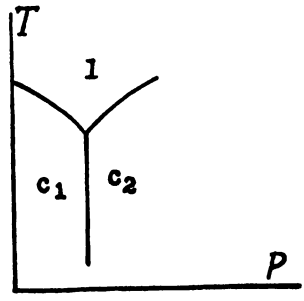


FIG. 3.

diagram the enumeration of the pressure units first begins at pressures at which the vapor has long since been condensed.

The relative positions of the equilibrium curves at the triple-point are given by the following rule: The prolongation of each equilibrium curve into the field of a phase that does not take part in the equilibrium described by the curve, falls between the other two equilibrium curves. For only in this position of the equilibrium curve is there no disagreement with the indicated limits of the phase field. This important law can easily be derived from the surfaces of the thermodynamic potential.

There is also the possibility that the crystal c' may be less stable than the crystal c throughout the whole phase field. In this case there is no equilbrium curve upon which both crystal forms are in equilibrium. Each of the two forms, however, may come into equilibrium with its melt and its vapor at a triple-

point (Fig. 4). Since the unstable form has the higher vapor pressure at any given temperature, the triple-point of the unstable form must necessarily lie at a lower temperature than that of the stable form. Furthermore, since the melting curves of the forms c and c' cannot intersect without a reversal of the stability of the two forms, at the same pressure the form possessing the higher vapor pressure, the unstable form, must melt at a lower temperature than the stable. The order of the melting points thus gives the order of the stability of the different forms of the same substance.

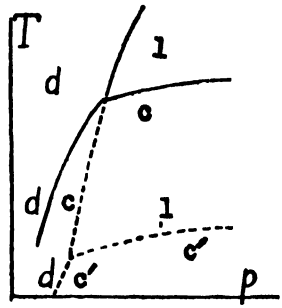


FIG. 4.

2. THE EQUATION OF CLAUSIUS-CLAPEYRON

The equation of *Clausius-Clapeyron* gives the relation of the direction of the equilibrium curves to the volume change, Δv in cm.^{3}/gm., and to the heat of transformation at constant pressure, R_p, per unit of mass of the substance. $R_p = 42.7 \cdot r_p$, where r_p represents the heat of transformation measured in calories per one gram, and since 1 cal. = 42.7 kg. cm., R_p is given in kg.cm. per one gram.

$$\frac{dT}{dp} = \frac{\Delta v T}{R_p}.$$

Let us suppose that the angle which any tangent to the equilibrium curve ab makes with the p-axis be α. Then $tan\,\alpha = dT/dp$, where dT is the change in the equilibrium temperature with unit increase in pressure. The direction of the equilibrium curve is determined at every point by the value of $\Delta v T/R_p$, and if Δv and R_p per one gram be known, the direction of the equilibrium curve may be determined for the temperature to which the inserted values refer. Since the equilibrium pressure p is not contained in the equation, not the equilibrium curve itself but only its direction is given by the equation of *Clausius-Clapeyron*. The equation, therefore, defines a bundle of parallel curves. If the p-value corresponding to a given T-value be known, it will be possible to pick from this bundle the curve

representing the equilibrium curve of the substance, and this curve, of course, will pass through the pT-point in question.

The derivation of this important equation rests upon the first two laws of thermodynamics. For a *Carnot* cyclic process the external work done, A, is equal to the heat absorbed, Q, multiplied by the difference of the temperatures between which the cyclic process takes place, divided by the original temperature T. Algebraically:

$$A = \frac{Q\Delta T}{T}.$$

The cyclic process is as follows: A large mass of substance occurs at a point pT upon an equilibrium curve and is divided into two states of aggregation. The volume of the whole system is increased by the amount Δv_1; one gram of the substance is then transformed from the first into the second state of aggregation and the work $A_1 = \Delta v_1 \cdot p$ is furnished by the substance (Fig. 5). The temperature of the substance is lowered by ΔT, whereby the pressure decreases Δp upon the equilibrium curve. The volume is then diminished to Δv_2, causing one gram of the substance to be transformed from the second to the first state of aggregation, and the work $A_2 = \Delta v_2(p - dp)$ to be expended. The mixture is warmed ΔT, and the initial pressure p restored. The smaller the values of Δp and ΔT, the more closely will Δv_1 and Δv_2 approximate each other, and their difference will disappear, as well as work terms of higher orders, upon passing to the limits dp and dT. Then the work obtained in the cyclic process, A, will be equal to the area of the parallelogram (Fig. 5) $\Delta v \cdot dp$, or $A = \Delta v \cdot dp$. If this value for A be introduced into the equation for the second law of thermodynamics and if R_p replace Q as the latent heat of vaporization or fusion per one gram, then,

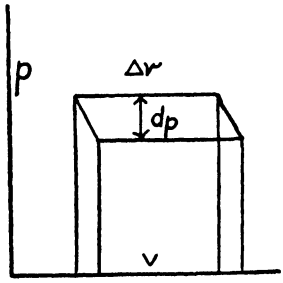


FIG. 5.

$$\frac{dT}{dp} = \frac{\Delta vT}{R_p}.$$

The heat quantity R_p therefore also contains the quantity of heat equivalent to the external work $\Delta v \cdot p$, and in specific cases represents the heat of vaporization, sublimation, fusion, or transition, plus the external work. Knowing Δv and R_p as functions of p and T, it is possible to determine the direction of the various equilibrium curves.

III. EQUILIBRIA BETWEEN VAPOR AND LIQUID

In order to determine whether or not the vapor pressure curve has a terminus it is necessary to know the dependence of Δv and R_p upon the vapor pressure curve. With increasing pressure and rising temperature the volume of a liquid increases upon the vapor pressure curve because the effect of temperature preponderates over the effect of pressure. The volume of the saturated vapor decreases with increasing pressure because in this case the effect of pressure overbalances that of temperature. Δv therefore decreases upon the vapor pressure curve and finally becomes equal to zero at P_c. Figure 6 is a representation of the volume surface over the vapor pressure curve; $a'c'$ is the vapor pressure curve in the pT-plane. The curves drawn on the volume surface give the dependence of the volume upon the pressure at constant temperature (the isotherms), and upon the temperature at constant pressure (the isobars). The discontinuous changes of these two groups of curves over the vapor pressure curve $a'c'$ are invested in the non-plane curve a_1ca_2.

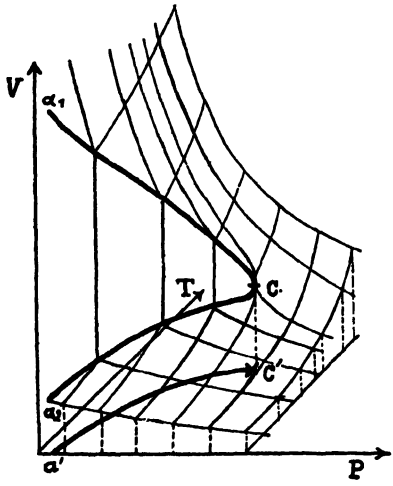


FIG. 6.

The heat of vaporization likewise decreases upon the vapor pressure curve with rising pressure.[1] In general, R_p varies along a curve, but it is essential that Δv and R_p assume zero values at the same point. If the values corresponding to the point p_cT_c, $\Delta v = 0$ and $R_p = 0$, be introduced into the CLAUSIUS-CLAPEYRON

[1] Mathias. *Ann. chem. phys.* (6), 21, 69 (1890).

equation, which gives the direction of the tangent to the equilibrium curve, we obtain

$$\frac{dT}{dp} = \frac{0}{0'}$$

dT/dp at the point $p_c T_c$ therefore has an indeterminate value, or the vapor pressure curve has a terminus. At pressures greater than p_c vaporization will not take place under conditions sufficient to produce it at pressures below p_c, that is, the original substance will not separate into two layers, and the formation of a meniscus will not be observed. The same considerations obtain for the compression of a gas at a temperature greater than T_c.

Before the existence of the end-point upon the vapor pressure curve was realized, futile attempts were made to liquefy the "permanent" gases O_2, H_2, and N_2 by compression at $t = 0°$. Naturally, these attempts were unsuccessful, because the temperature of the experiments lay above the critical temperatures of O_2, H_2, and N_2. Vaporization or liquefaction can set in only when the vapor pressure curve is intersected with the change of p or T, or of both. If the course of the change in state does not intersect the vapor pressure curve, no discontinuous change in properties will occur, and in this way liquids can be transformed into dilute gases, and vice versa, without a discontinuous change in properties.

The atomistic explanation for the existence of the critical-point, at which both liquid and vapor phases become identical, is the following. In the gaseous as well as in the liquid state the molecules are distributed at random in space. This distribution varies from moment to moment but retains its random nature. With a very small number of molecules, as, for instance, about a dozen, an essentially different structure of the small molecular complex would be presented from moment to moment. On the other hand, in the case of a large number of molecules (6.10^{23} per one mole), two equal masses might be divided into a series of smaller masses, each having equal molecular distribution, the number of such smaller masses being the same in each case; both masses would possess equal distribution of their molecules in space, and since this would be true at any one time, the two masses would permanently possess equal distribution of molecules.

The properties of an aggregate of molecules are determined

not only by the molecular distribution but also by the powerful forces of molecular translation and rotation. In a large aggregate these will likewise vary greatly though both masses will permit a division into a series of systems, for the equality of these magnitudes exists in both aggregates of molecules. The conclusion is therefore reached that with the molecular structure depicted and with equal specific volumes, two aggregates of molecules are identical.

Inasmuch as the specific volumes of a liquid and its vapor at the critical point are identical, the molecules of the same kind in large equal masses of the two states of aggregation at this point must be identical. The identity of all properties of these two states of aggregation therefore follows from the equality of the specific volumes.

The critical temperature has sometimes been comprehended as a limiting temperature, in the sense that below this temperature both vapor and liquid can exist, but that above it only vapor. This conception, however, is misleading, for through the critical point, the end of the vapor pressure curve, no limiting line passes dividing the region above this point from the region below. The difference between the two states, liquid and gaseous, is lost at the critical temperature and critical pressure in the sense that at temperatures or pressures greater than the critical, condensation or vaporization phenomena associated with the formation of two phases no longer appear. These states may be designated the hypercritical or the " fluid " states, though the latter designation is not applicable to all hypercritical states, for with increase in pressure viscosity also increases; and at very high pressures above the critical temperature the substance may become viscous, and the viscosity in fact may approach that of solid bodies. The domain of the isotropic states is a very wide one, for it extends from the most dilute to the most concentrated conditions of matter, and it has therefore been found expedient to give special names to certain sections of it.

1. The Pressure-Volume Diagram of Andrews[1]

The isotherms given in Fig. 7 may be determined by introducing carbon dioxide into a glass tube connected with a manometer,

[1] *Phil. Trans.* R. S. L., **159**, 575 (1869); **166**, 421 (1876). *Pogg. Ann.* Vol. V, **65**, (1871).

and determining the volume V in dependence upon the pressure p at constant temperature. Beginning at 13.1° the volume of the carbon dioxide may be diminished by small pressure increases, and it will be found that p and T vary along an hyperbolic curve. After the appearance of the first mist (drops of liquid) the pressure becomes independent of the volume and remains so, providing the carbon dioxide contain no impurity, until the last trace of the gaseous carbon dioxide disappears. Beyond this point, small volume diminutions will be brought about only by very great increases in pressure. The liquid carbon dioxide is only very slightly compressible; its mixture with vapor in absence of impurities, however, is infinitely compressible. The volume change with condensation per one gram carbon dioxide, Δv, decreases with rising temperature and disappears at the critical temperature. Upon the isotherm of the critical temperature there is a point of inflection, the tangent to which is parallel to the v-axis. The coordinates of this point give the critical pressure, p_c, and the critical volume, v_c, Δv having disappeared at this point. The isotherms at higher temperatures at first show a region of high compressibility, but this has already disappeared in the case of carbon dioxide at 48.1° C.

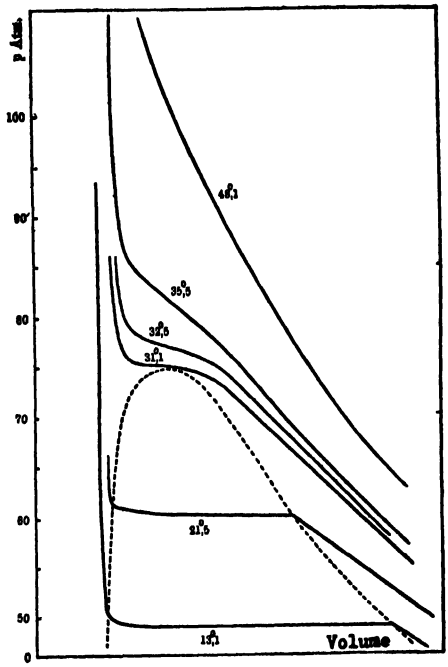


FIG. 7.

The dotted curve passing through the points of inflection on the isotherms defines the region of heterogeneous condition, the region in which the substance exists in two phases: vapor and liquid. At relatively high pressures and small volumes the sub-

stance is liquid, at relatively low pressures and large volumes the substance is gaseous. There is no limit between these states. A change in pressure causing the point that represents the condition of the system not to enter into the heterogeneous region will cause the liquid continuously to be transformed into its vapor, and the reverse, that is, the transformation takes place without the formation of a separating surface, a meniscus, and without the other condensation or vaporization phenomena making themselves evident. Such phenomena occur only when the boundary between the homogeneous and the heterogeneous field is trespassed.

If the pressure-volume diagram be drawn to represent a unit of mass of the substance the intersections of the limiting curve with a line parallel to the v-axis will give the specific volumes of the liquid v' and the vapor v'' for the corresponding values of T and p. For each specific volume, v, of the heterogeneous mass the relation of the masses of the two phases can be read from the diagram. Since the fraction x of the total mass 1 in the form of vapor amounts to $x = \frac{v - v'}{v'' - v'}$, and the fraction in the form of liquid $1 - x = \frac{v'' - v'}{v'' - v'}$, then $\frac{x}{1 - x} = \frac{v - v'}{v'' - v}$.

2. The Determination of the Critical Coordinates

The behavior of a substance for other prescribed changes of state may be derived from the diagram of isotherms.

For example, the variation of v and p during an increase in temperature with a constant fraction of the total mass present as vapor may be desired. The condition is that $x = \frac{v - v'}{v'' - v'} =$ a constant. For a given value of x the sections of the horizontal portions of the isotherms (Fig. 7) through which the path of the prescribed change in state must pass can be easily determined. Figure 8 represents such a construction for different x-values. In order to effect such a change it is necessary that all three variables, p, v, and T, change during the change in state.

Note.—The line $x = 0.1$ in diagram, Fig. 8, should intersect point C.—Translator.

By heating a liquid with its vapor in a tight glass vessel (at

constant volume) it is easy to determine which of the two phases, the liquid or the vapor, will disappear with the given volume, and at what pressure the disappearance occurs. The temperature corresponding to v and p is obtained from the diagram of the volume isotherms. If the volume of the glass tube, v, and the mass of the substance be known, in order to find the pressure it is necessary merely to erect a perpendicular upon the v-axis at the value of v/m and to determine the point at which it intersects the boundary curve.

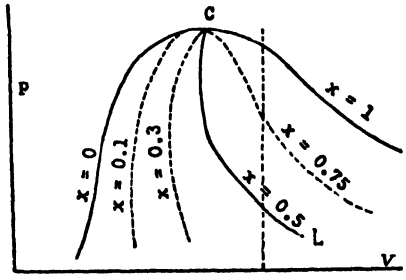


Fig. 8.

If the volume of the mixture of vapor and liquid be smaller than the critical volume, v_c, the vapor will disappear on heating, the meniscus will move towards the upper part of the tube; if the volume of the two phases be greater than the critical volume, the liquid will disappear, the meniscus will move towards the lower part of the tube. A consideration of the x-curves in Fig. 8 will make this clear.

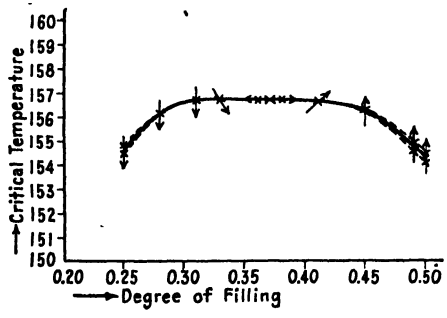


Fig. 9.

The boundary line between the heterogeneous field and the homogeneous may be determined in the following way. Different quantities of the liquid, the critical temperature and the critical volume of which are to be determined, are placed in small glass tubes of equal volumes, and the temperature at which the meniscus disappears noted. The curve determined in this way will have a maximum in dependence upon v/m since the curve defined by the volume-isotherms has one [1] (Fig. 9). The temperature of this maximum is the critical temperature. Figure 9 gives

[1] A. Stoletow, *Journ. russ. phys. Chem. Ges.*, **25**, 303 (1893); **26**, 26 (1894).

the results of a determination of the critical temperature of sulphur dioxide.[1] The arrow on each point of observation indicates the direction in which the meniscus moved at the time of its disappearance; at the maximal temperature the meniscus disappeared in the middle of the tube. In case of two points, the upper one refers to the temperature of the disappearance of the meniscus, the lower one to the temperature of its reappearance. The critical temperature of sulphur dioxide as obtained by this method is $157.26° \pm 0.2$. The determination of the critical volume in this way is less accurate since the maximum of the curve in Fig. 9 is a very flat one. The presence of admixtures in the substance investigated causes the limiting curve ordinarily not to show a maximum.

a. The Rule of Rectilinear Diameters

CAILLETET and MATHIAS [2] have found that the curve of the densities of a liquid and its saturated vapor has a linear diameter upon which lies the value of the critical density. If δ'' and δ' refer to the density of the saturated vapor and that of the liquid in equilibrium with each other, and Δv represent the critical density, then

$$\frac{\delta'' + \delta'}{2} = \Delta + \alpha(t_k - t).$$

This rule may be experimentally confirmed in the following way. A series of tubes containing different quantities of the liquid to be investigated are heated and the temperatures of the disappearance of one phase determined. These temperatures are plotted in dependence upon the density of the contents of the tube and the points obtained represent the density of one phase at the temperature of the disappearance of the other. Figure 10 represents such a series of determinations for methyl alcohol. If a curve be drawn through these points and the mean of the density of the saturated vapor and of the liquid plotted in dependence upon temperature, a straight line will be obtained, the rectilinear diameter, which passes through the critical point.

[1] M. Centnerszwer, *Z. phys. Chem.*, **46**, 473 (1903).

[2] *Compt. rend.*, **102**, 1202 (1886) and E. Mathias, *Le Point critique des corps purs.*, Paris, 1904.

The critical temperature for methyl alcohol as thus obtained is 240.2° ± 0.2 and the critical density 0.275.[1]

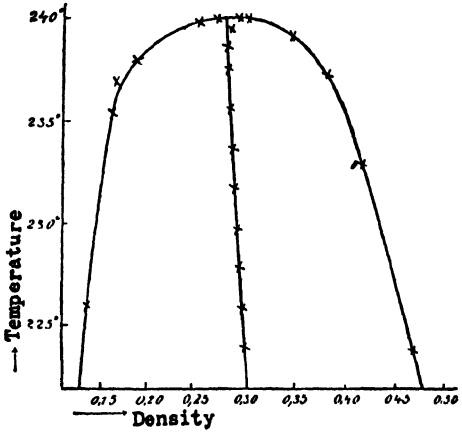


FIG. 10.

b. Determination of the Critical Pressure and the Critical Temperature

The vapor pressure of a liquid heated in contact with its vapor at constant volume will be given by the vapor pressure curve as long as both phases are present. However, if one of the two phases disappear, the pressure will no longer be determined by the vapor pressure curve, but will change either more rapidly or more slowly. In case the liquid alone remains, the pressure will change more quickly than demanded by the vapor pressure curve; in case the vapor alone remains the pressure will change more slowly. Which of the two phases will disappear depends upon the quotient of the constant volume by the mass of the substance. When this quotient is equal to the critical volume, v_c, the pressure follows the vapor pressure curve throughout its course and leaves it only at the critical point. When the quotient is less than v_c the vapor will disappear before reaching the critical temperature and the pressure will no longer rise along the vapor pressure curve AC (Fig. 11), but will follow the isometric line of the liquid DE. When the quotient is greater than v_c, the liquid will disappear

[1] Centnerszwer, *Z. phys. Chem.*, **49**, 204 (1904).

and the pressure will leave line AC and follow the isometric line of the vapor BII. If the quotients are so selected for two determinations that one is slightly smaller than v_c and the other slightly larger, the pressure upon heating will change along the lines CF and CG, and the intersection of these lines will approach the critical point C, the coordinates of which are p_c and t_c.

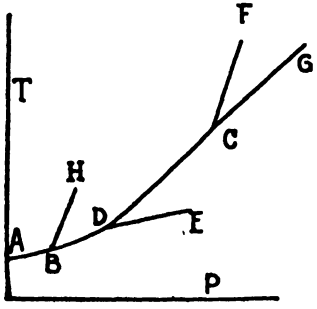


Fig. 11.

Using this method Cailletet and Colardeau[1] determined the critical temperature and critical pressure for water in steel tubes, and found t_c to be 366° and p_c to be 202 atm. In order to keep the volume enclosing the water nearly constant the mercury used in the steel tube communicated through a steel capillary to a second steel tube. Through the wall of this second steel tube passed an insulated wire the contact of which with the mercury column was evenly maintained during the change of p and T.

The following method for the determination of the critical pressure also gives good results when it is possible to carry out the determination in glass tubes. The temperature of a glass tube containing the substance to be investigated is lowered over a range that includes the critical pressure, and the pressure in the meantime is maintained higher than the critical. Under these conditions no bubbles of vapor appear in the tube. However, when the pressure is beneath the critical pressure, bubbles of vapor will appear. By successive trials the pressure at which bubbles last appear may be determined and the limiting pressure, the critical point, approached very closely.

c. *Adiabatic Volume Increase at Temperatures Slightly above the Critical*

FCD in Fig. 12 represents the boundary curve of the heterogeneous region and *BB* represents an hypercritical isotherm. A rapid adiabatic pressure diminution will cause the substance to leave the state represented by point *B* and to enter the hetero-

[1] *Journ. de Phys.*, II, 10, 333 (1891).

geneous region, as represented by the line from B to E. Upon this change a portion of the vapor condenses, and the liquid condensing upon the warmer walls of the vessel during the pressure diminution boils vigorously. The smaller the original pressure upon the isotherm BB_1, the smaller will be the amount of liquid formed by condensation. Beyond point B_1 upon the isotherm no liquid will form on adiabatic pressure diminution, because the adiabatic curves starting from such points do not intersect the boundary curve, but run only into the homogeneous field. An adiabatic entering the heterogeneous field to the right of C will be accompanied at the point of entry by the formation of liquid, the quantity of which, as we have seen, may vary greatly. A thermometric apparatus of low heat capacity introduced into the condensation vessel will indicate a rising temperature during the boiling of the condensed liquid, which is highest at the critical point C. Using this method the critical temperatures of O_2, N_2, and H_2 have been determined.

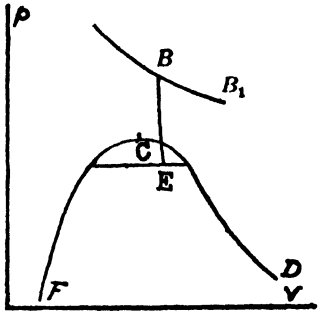


FIG. 12.

d. Linde's Process for the Liquefaction of Gases

JOULE and THOMSON have shown that a gas streaming through a porous plug from a pressure p_1 to a pressure p_2, and from a volume v_1 to a volume v_2, ordinarily experiences a fall in temperature from T_1 to T_2; only in the case of hydrogen has the opposite effect been observed, and the increase in temperature observed in this case is in fact very small. VAN DER WAALS[1] later showed that the change in temperature can be calculated from his equation of state,

$$\left(p + \frac{a}{v_2}\right)(v - b) = RT.$$

From this equation the following expression may be obtained:

$$c_p(T_1 - T_2) = \left(\frac{2a}{RT_1} - b\right)(p_1 - p_2).$$

[1] *Kontinuität des gasförmig und flüssigen Zustandes.* Leipzig, 1881.

Generally $2a/RT_1$ is greater than b and therefore T_1 is greater than T_2, hence a cooling is generally obtained. In the case of hydrogen alone the reverse relation is true. Since, however, $2a/RT_1$ is inversely proportional to T whereas b is independent of T, at sufficiently low temperatures hydrogen likewise should show a heating effect, and this has been observed at $-80°$. This behavior of gases has been employed by LINDE [1] in his work on liquefaction. In the machine used for the production of low temperatures a stream of gas is compressed in a helix-shaped tube contained in a larger tube. The compressed gas escapes through a nozzle at the end of the helix and there expands, whereupon its temperature sinks. The cooled gas is then made to circulate in the outer tube and therefore to cool the compressed gas in the inner tube. This arrangement causes a progressive lowering of the temperature, until finally the gas is liquefied.

In the derivation of the equation for $T_1 - T_2$ the assumption is made that p_1 has a small value, and as a consequence b may be disregarded as compared to v. At larger values of p this quantity cannot be neglected, and for the temperature T_1, at which $T_1 - T_2$ changes its sign,

$$T_1 = \frac{2a(v-b)^2}{Rbv^2}.$$

Thus T_1 depends upon v and therefore also upon p; T_1 varies with p_1 along a curve which for air, according to A. SCHULZE, [2] runs from $t_1 = 350°$ at $p = 1$ atm., to $t_2 = 30°$ at 370 atm., and then reverses so that at $p = 1$ atm., $t_1 = -140°$. Within the phase field enclosed by this pT-curve, cooling occurs upon expansion, outside of it warming occurs. The LINDE process worked under an external pressure of 400 atm. would produce a heating effect in the counter-current instead of the desired cooling effect.

e. The Surface Tension of a Liquid in Contact with its Saturated Vapor

It is to be expected that the rise in a capillary tube of a liquid in contact with its saturated vapor would be zero at the critical temperature. Generally, however, this is not the case, because

[1] *Wied. Ann.*, **57**, 328 (1896).
[2] *Ann. d. Phys.* **49**, 585 (1916).

within the capillary tube stirring by convection currents is much less efficient than it is in the surrounding liquid, and consequently a density gradient ordinarily occurs. RAMSAY and SHIELDS attempted to avoid this difficulty by making the capillary movable. Before making a determination the capillary was moved up and down by an electromagnetic stirrer in order to eliminate density differences. The substitution of two parallel glass plates for the capillary tube presents a simpler experimental arrangement more favorable to mixing, and using this method, G. GUOY [1] has shown convincingly that the rise of the liquid between the two glass plates does in fact disappear at the critical temperature.

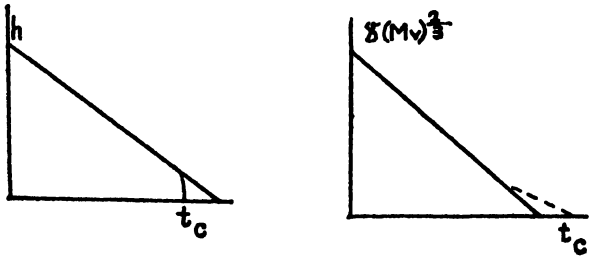


FIG. 13.

The rise in height of normal liquids in a capillary tube decreases linearly with increase in temperature, but the curve does not pass through the critical temperature, but cuts the temperature axis at a point from 6° to 15° higher. Therefore, near the critical temperature the capillary rise decreases more quickly with rising temperature than it does at lower temperatures.[2] Accordingly, the product of the molecular surface $(Mv)^{\frac{2}{3}}$ and the surface tension γ, which according to RAMSAY and SHIELDS [3] with normal liquids varies linearly with the temperature, in the neighborhood of the critical temperature decreases more rapidly than demanded by the linear relation. These deviations of the values for h and $\gamma(Mv)^{\frac{2}{3}}$ correspond to the very great change in the specific volume of the vapor and the liquid in the neighborhood of the critical temperature.

[1] G. Guoy. *Journ. de Phys.*, III, **6**, 479 (1897).
[2] de Vries. *Comm. Phys. Lab. Leiden*, No. **6**, 18, 32.
[3] *Z. phys. Chem.*, **12**, 433 (1893).

f. The Opalescence at the Critical Temperature

Intimately connected with the identity of the liquid and the vapor at the critical temperature is an optical phenomenon which has been described especially by TRAVERS and USHER.[1] Shortly before the disappearance of the meniscus in the middle of the tube a uniform opalescence appears throughout the tube which disappears soon after the disappearance of the meniscus. In transmitted light the contents of the tube appear brown, and in reflected light white, though outside of the critical pressure-temperature range the contents of the tube are colorless. If in disappearing the meniscus migrate towards the upper part or towards the lower part of the tube, only the part towards which the meniscus migrates becomes opalescent. When the temperature is caused to rise slowly, however, the meniscus wandering slowly towards either the top or bottom of the tube, the whole contents of the tube becomes opalescent. Electromagnetic stirring of the contents of the tube causes the opalescence to appear simultaneously throughout the tube shortly before the disappearance of the meniscus, the opalescence disappearing soon after the meniscus disappears. The cooling of the substance from a point in the hypercritical state produces a milky turbidity. In the case of sulphur dioxide the temperature interval is only 0.2°, and with ethyl ether it is 2.0°.

M. VON SMOLUCHOWSKI[2] has attempted to explain these phenomena by the random molecular distribution in space characteristic of liquids and vapors. This is supposed to cause from moment to moment the transient association of molecules in relatively large masses, which would not differ from the liquid at the critical point with respect to density, but which at the same time would not represent actual drops. The continual appearance and disappearance of these aggregates of molecules causes the opalescence, which in other causes has been showed to be due to the presence of many small particles. A. EINSTEIN[3] has theoretically investigated the color and intensity of the light dispersed by this opalescence.

[1] Travers, *Z. phys. Chem.*, **57**, 365 (1907)
[2] *Ann. d. Physik.*, **25**, 205 (1907).
[3] *Ann. d. Physik.*, **33**, 1275 (1910).

Similar phenomena have been observed in the neighborhood of the critical solubility of two partially miscible liquids.

J. FRIEDLÄNDER[1] has shown that cataphoresis cannot be brought about in such turbid media, and this indicates that the opalescence is not caused by actual drops, since these would show cataphoresis.

g. Abnormal Phenomena

It has been asserted by several authors that the equilibrium pressure of a vapor over a liquid is not independent of the mass relation of the two phases, and that this deviation from the normal behavior of a one-component system, especially noticeable near the critical point, is caused by the differences between the molecules of the liquid and those of the vapor and by their slow interconvertibility.

On the other hand KAMERLINGH ONNES,[2] RAMSAY,[3] and KUENEN[4] have been able to show that at least a portion of the supposed deviations from normal behavior were caused by admixtures more than anything else. KUENEN[5] especially has studied the critical phenomena in two component systems, following the work of VAN DER WAALS. Some of the deviations were also caused by slow equalization of the density and concentration differences; KUENEN was able to avoid this difficulty by the help of an electromagnetic stirrer.

As a result of these investigations it appears that the substances so far investigated behave normally as one-component systems, provided that the condition of complete chemical homogeneity be fulfilled, that is, the equilibrium pressure is independent of the quantities of both phases and of the time; the more closely the stipulation of chemical homogeneity is fulfilled the more nórmal is the behavior of the liquids.

This, of course, does not deny the existence of liquids, as yet uninvestigated, that under investigation would prove to be abnormal, for if a vapor and its liquid under the same conditions

[1] *Z. phys. Chem.*, **38**, 385 (1901).
[2] *Comm. Phys. Lab. Leiden*, No. **68** (1901).
[3] *Z. phys. Chem.*, **14**, 486 (1894).
[4] *Comm. Phys. Lab. Leiden*, No. 17 (1091).
[5] J. P. Kuenen. *Theorie der Verdampfung und Verflüssigung von Gemischen*, Leipzig, 1906.

of pressure and temperature have different molecular constitution, and if one of the varieties of liquid molecules transform into one or more other kinds, the observed system will then behave as a two-component system, and abnormal phenomena will appear. However, associated liquids, mixtures of several kinds of molecules, show no strikingly abnormal phenomena, and it is therefore to be concluded that the transformations of different molecules into one another at the critical temperature ordinarily takes place much more quickly upon sudden vaporization or condensation than is necessary for the heat set free from the transformation to produce the original temperature, and the values of pressure and volume dependent upon it.

It is well known that VAN DER WALLS has been able to derive the coordinates of the critical point from the deviations of the gases concerned from that of the ideal gas. Making use of these coordinates, the law of corresponding states has been derived. These studies are given in NERNST's textbook on physical chemistry, and more exhaustively in an excellent monograph by KUENEN.[1]

[1] J. P. Kuenen. *Die Zustandsgleichung der Gase und Flüssigkeiten und die Kontinuitätstheorie.* Viewig & Son. 1907.

IV. THE EQUILIBRIUM CURVES

The vapor pressure curve has a terminus which is the critical point. Because of this it is possible to change a liquid into a vapor in a continuous way, that is, without the occurrence of any point at which the transformation may be said to take place abruptly and completely. In order to accomplish this continuous transformation it is necessary merely to vary p and T in such a way that the path upon the pT-plane does not intersect the vapor pressure curve. Such a continuous change from liquid to vapor, or the reverse, is possible because of the nature of the molecular structure of liquids and vapors. In both of these states the molecules have random distribution, and in aggregate will therefore be identical when the specific volumes are made equal.

The relations between a crystal and its melt, however, are essentially different. In a crystal the molecules are oriented upon a space lattice, whereas in a melt the molecules are random in their distribution in space. Accordingly, these two states will not become identical when their specific volumes are made equal, as in the case of gases and liquids at the critical point. From this point of view a terminus to the melting curve analogous to the critical point on the vapor pressure curve is not to be expected. The same reasoning holds good for the equilibrium curve between two anisotropic phases. Inasmuch as continuous transformation of a crystal into its melt is not conceivable with the molecular structure of each, the phase field of a crystal must be separated from that of its melt in such a way as to make a continuous transformation of crystal into melt impossible. This requirement will be fulfilled by each of the following possibilities:

(1) The melting curve runs to infinitely high temperatures; (2) it asymptotically approaches a maximal melting temperature; (3) it has a maximum and finally intersects the pressure axis, (4) or intersects the sublimation curve for the second time.

Each of these four possibilities satisfies the requirement that it should not permit continuous transformation of liquid into melt, or *vice versa.*

Upon the basis of ordinary atomic considerations no decision can be made among the four possible forms of the melting curve, and in order to reach a decision, definite knowledge of the behavior of a crystal and its melt is necessary. If the dependence of the volume difference of a crystal and its melt upon p and T were known, and in addition, the like dependence of the heat of fusion, it would be possible to estimate the course of the melting curve from the equation of CLAUSIUS-CLAPEYRON.

1. THE NEUTRAL CURVES

When the specific volume of a crystal at low pressures is greater than that of its melt, $v' > v''$, and the same relation holds for the compressibility,

$$\frac{d_T v'}{dp} > \frac{d_T v''}{dp},$$

the volume isotherms of the two phases will intersect, as shown in Fig. 14.

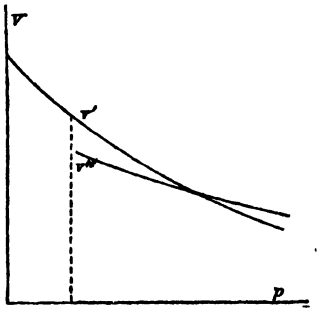


FIG. 14.

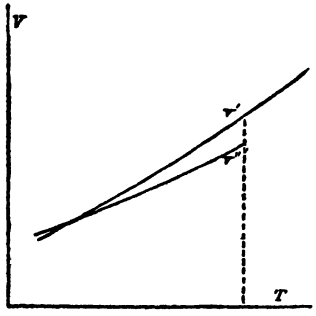


FIG. 15.

Furthermore, since it is likewise true of the heat of expansion of crystal and melt, that that of the crystal is smaller than that of the melt,

$$\frac{d_p v'}{dT} > \frac{d_p v''}{dT},$$

with decreasing temperature the volume isobars of a crystal and its melt will converge (Fig. 15), and will intersect if the temperature axis be not limited at low temperatures by the absolute zero.

In the case of some substances, such a strontium borate, sodium metaphosphate, and arsenic trioxide, the point of intersection at $p = 1$ kg./cm.^{2} appears to lie at realizable temperatures.

Completing our picture by conceiving to be constructed over the pT-plane the volume surfaces of the crystal and its melt, we will obtain two surfaces which intersect in a non-plane curve. The projection of this curve upon the pT-plane, AB, Fig. 16, will divide the phase field into two parts. In one of these parts $v' > v''$ and crystallization is accompanied by a volume diminution; in the other part $v' > v''$ and crystallization is accompanied by a volume increase. This curve upon the pT-plane we will name *the neutral curve of the specific volume*. For the changes in volume at constant temperature with pressure, or those at constant pressure with temperature, the following differences will be retained upon the neutral curve:

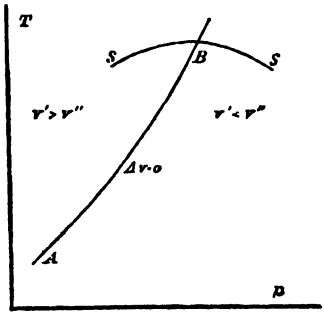


Fig. 16.

$$\frac{d_T v'}{dp} - \frac{d_T v''}{dp} \quad \text{and} \quad \frac{d_p v'}{dT} - \frac{d_p v''}{dT},$$

which follows from the geometrical significance of the neutral curve.

The validity of the inequality

$$\frac{d_T v'}{dp} > \frac{d_T v''}{dp},$$

was assumed on the basis of the following experience. Measurements of the volume isotherms of liquids show that the compressibility $\frac{d_T v'}{dp}$ decreases with increasing pressure. A decrease in volume upon crystallization can be referred to an increase in the inner pressure upon crystallization. In this case, however, it is to be expected that the above inequality will be valid for every equilibrium point. Extensive research in this field subsequently showed this to be true.

The properties of a crystal can be divided into two classes: the scalar, which are independent of the direction of measurement in the crystal, such as the specific volume and the heat content; and the vector, which depend upon the direction of measurement, as the linear crystallization velocity, the linear solution velocity (etch figures), the elastic properties, and the conductivity for heat, light, and electricity. The vector properties are not dependent upon direction in all crystals, for in regular (cubic) crystals the velocity of the propagation of light is independent of the direction of measurement. The properties of chemically homogeneous liquids are always scalar, those of a crystal are partly vector and partly scalar, and for some properties it depends upon the nature of the crystal as to whether the property be scalar or vector in nature.

A twofold change in properties is introduced upon crystallization. The scalar properties of the liquid are altered though remaining scalar in nature, or the scalar properties of the liquid change into vector properties in the crystal. In the first case a neutral curve exists, but in the second case a series of neutral curves exists, in the pT-values of which no change in the concerned values occurs. The position of the neutral curve upon the pT-plane for each property is unique, for if the neutral curve of all properties were to fall together, all of the properties of the crystal and its melt upon this single neutral curve would be equal, or the crystal and its melt would be identical. This, however, is in contradiction to our experience as well as with the original conception regarding structure of crystals and melts.

To summarize we may state that upon crystallization of a melt on its equilibrium curve with the crystal, the properties [1] ordinarily change discontinuously except upon the neutral curve. Moreover, a portion of the scalar properties of the melt become vector properties in the crystal.

The neutral curves of a crystal and its melt, or of two crystal species, are also of importance with respect to the course of the equilibrium curve. If the melting curve intersect the neutral curve of the specific volume, the point of intersection will be a

[1] Properties are excluded here that are equal to each other when equilibrium obtains between crystal and melt, such as the vapor pressure, the solubility, and the thermodynamic potential.

maximum upon the melting curve. If, then, in the equation

$$\frac{dT}{dp} = \frac{\Delta v T}{R_p},$$

Δv be equal to zero, dT/dp then equals zero, since R_p must have a finite value in accordance with the stipulation that the neutral curves of the specific volume and the heat content cannot coincide. However, when $dT/dp = 0$, as in the point of intersection of the melting curve SS with the neutral curve AB, Fig. 16, this point must be a maximum upon the melting curve since dT/dp at this point changes its sign.

Let us now picture the surfaces of the heat content of a unit of mass of a substance as constructed over the pT-plane (by heat content is meant the quantity of heat absorbed by a unit of mass in being heated from $T = 0$ to T). The difference of the two ordinates at the same point is equal to R_p, the total heat of fusion (which includes the external work $p \cdot \Delta v$).

The neutral curve of the surfaces of the heat content ordinarily runs to high pressures since R_p at low pressures and also at $T = 0$ has an appreciable positive value. Figure 17 represents the course of the neutral curve upon which $R_p = 0$. At the point of intersection of the equilibrium curve SS with the neutral curve CD, $dT/dp = \infty$, since $\Delta v/T$ has a finite value while $R_p = 0$. At this point of intersection the tangent to the equilibrium curve is therefore perpendicular to the p-axis, and since at this point R_p changes from positive through zero to negative while $\Delta v T$ maintains a constant positive value, at the point of intersection dT/dp jumps from the value of $+\infty$ to the value of $-\infty$ and the equilibrium curve at this point is retrograde.

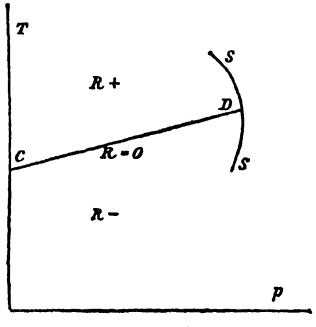


FIG. 17.

2. THE FORMS OF THE EQUILIBRIUM CURVES

The positions of the neutral curves $\Delta v = 0$ and $R_p = 0$, and of the triple point: vapor, liquid, crystal, determine the form of

the equilibrium curves. Not every conceivable position of the two neutral curves is admissible. If the neutral curve $R_p = 0$ for the equilibrium between crystal and melt on the pT-plane be above the neutral curve $\Delta v = 0$, the melting curve will run to higher temperatures with increasing pressure. But this cannot easily be reconciled with the molecular-kinetic conception of the melting process, in the light of which it is to be expected that the oscillatory motion of the molecules about their lattice points with sufficient increase in temperature would overcome the forces maintaining the lattice. The same difficulty would be encountered if neutral curve $R_p = 0$ ran more steeply than the neutral curve $\Delta v = 0$.

Consequently, the following cases alone are left: the neutral curve $\Delta v = 0$ lies over the neutral curve R_p, and if they intersect, the neutral curve $\Delta v = 0$ must run more steeply than that upon which $R_p = 0$. If the two neutral curves intersect upon the pT-plane at positive values of T, then a completely developed form of equilibrium curve, closed upon itself, is possible. Whether or not these completely closed equilibrium curves occur with actual substances is another question, which subsequently will be discussed in more detail.

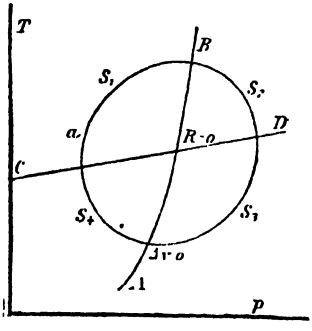


FIG. 18.

The intersection of the two neutral curves $\Delta v = 0$ and $R_p = 0$ over the pT-plane would make possible the closed form of the equilibrium curve, whether of melting or of transition (Fig. 18). At the point of intersection Δv as well as R_p equals zero. If the two phases at this pT-point were to have similar arrangements of molecules they would have to be identical; if the molecules differ in their distribution in space, identity of course is impossible. Upon the vapor pressure curve a critical point occurs corresponding to the disappearance of Δv and R_p, but in the case of the melting curve such a terminus does not occur, and when completely developed the melting curve simply turns around.

The sign of the heat of transformation or of fusion, R_p, the sign of the volume difference Δv, and the signs of dT/dp and

d^2T/dp^2 dependent upon the first named values as required by the equation of CLAUSIUS-CLAPEYRON, are collected in the following table. By quadrants are meant the sections of the equilibrium curve marked off by the two neutral curves.

Quadrant	Heat of Melting R_p	Change in Volume Δv	$\frac{dT}{dp}$	$\frac{d^2T}{dp^2}$
1	+	+	+	−
2	+	−	−	−
3	−	−	+	+
4	−	+	−	+

The equation of CLAUSIUS-CLAPEYRON thus permits a closed form of the equilibrium curve, though of course not requiring that it should exist with actual substances. If in reality there be no forms of this type, nevertheless the curve will be of great value if the real equilibrium curves may be regarded as pieces of this closed curve, or if by displacement of the coordinate axes p and T towards the stationary closed curve, the actual equilibrium curves of all the real forms may be derived.

The heat of fusion R_p is equal to the sum of the energy difference of the two phases plus the external work performed during the transformation

$$R_p = \Delta E + p \cdot \Delta v.$$

For substances stable in the crystalline state at small pressures, R_p at the absolute zero has a positive value as far as can be ascertained at the present time. Therefore the energy content E of the isotropic phase is greater than that of the anisotropic at all temperatures; ΔE is therefore always positive, and since the external work engendered during the transformation into the isotropic phase, $p \cdot \Delta v$, is negligible at small pressures, it is therefore necessary to add heat to effect the transformation from an anisotropic to an isotropic phase, R_p is therefore positive. At high pressures, after crossing the neutral curve upon which $\Delta v = 0$, Δv becomes negative and therefore at sufficiently high pressures R_p must change its sign.

As regards the position of the neutral curve upon which $R_p = 0$, it appears that at $T = 0$ and at a positive value for ΔE, the neutral curve $R_p = 0$ must cut the p-axis at a pressure higher than that for the neutral curve upon which $\Delta v = 0$. In this case

a form of the melting curve would obtain as represented in Fig. 19. In this representation the vapor pressure curve coincides with the T-axis. The substance is in a glassy state in the whole field bounded by the melting curve and the coordinate axes, and is therefore unstable, the field of its stable state lying at very high pressures. Between this state and the liquid state there is no equilibrium curve. The viscosity increases with increasing pressure as well as with decreasing temperature, and it is accordingly possible with sufficient pressure increase as well as with sufficient undercooling to change a substance into a viscous mass and then into a glassy mass. The substance must of course remain in the field of the isotropic state if devitrification is to be avoided. The dotted curve gives the p- and T-values at which the liquid is very viscous.

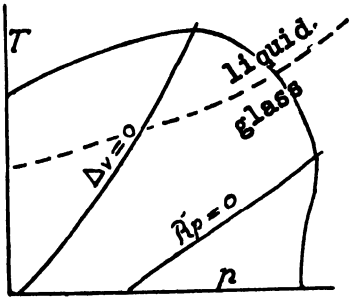


FIG. 19.

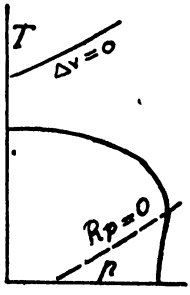


FIG. 20.

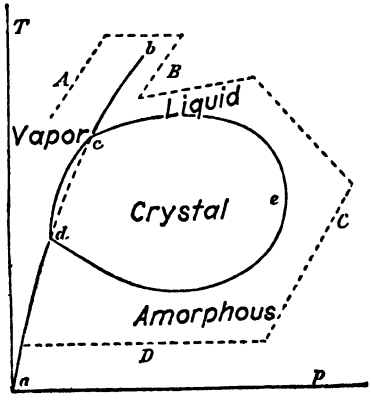


FIG. 21.

Substances melting at small pressures with volume diminution, when the neutral curve $\Delta v = 0$ falls into the region in which the anisotropic state is not realizable, will possess melting curves similar to the one represented in Fig. 20.

For actual substances investigated to the present time the melting curve does not appear to be so widely retrograde that it returns at small pressures and again intersects the vapor pressure curve, since R_p at small pressures down to $T = 0$ does not change its sign. Only when R_p changes its sign can a second triple-point: vapor, liquid, and crystal occur at low pressures. In Fig. 21 a fractional power of p is plotted along the p-axis in order to bring the vapor pressure curve and the melting curve into the same diagram. The vapor pressure curve of the isotropic state is indicated by a dotted line in the field of the crystal. At the triple-point c the crystal melts upon the addition of heat; at the triple-

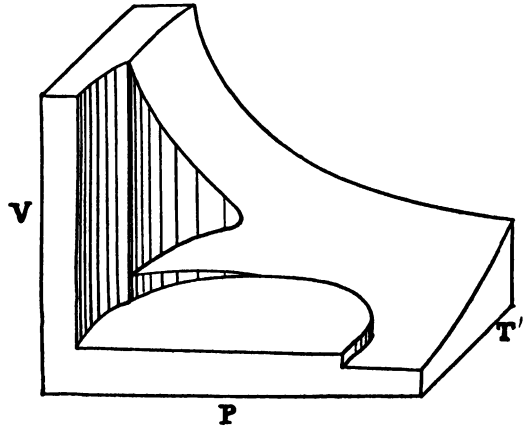


FIG. 21*a*.

point d the glass crystallizes upon the addition of heat. The dotted curve indicates a path upon which it is possible continuously to change a vapor into a glass stable at low pressures.

What we have said about melting curves might also be said about transition curves, the equilibrium curves between two anisotropic states, though the possibility of a completely developed equilibrium curve is less in this case than for melting curves, since many transition curves intersect the melting curve and are thereby terminated. The transition curves end in triple-points or intersect the pressure axis in harmony with the general law that the fields of the anisotropic phases are limited and that no critical point obtains upon a curve representing an equilibrium in which at least one anisotropic state takes part.

The points of intersection of the equilibrum curves with the neutral curves, the maximal equilibrium temperature at which $\Delta v = 0$ and the maximal equilibrium pressure at which $R_p = 0$, have both been observed and accurately investigated. Such points are the maximal equilibrium temperature for the melting curve of Glauber's salt, for the transition curve of red into yellow HgI_2, the maximal equilibrium pressure for the transition curve of Ice I into Ice III, and for the equilibrium curves of the two forms of benzene, I, and II. Reference to the respective phase diagrams will make this clear.

Figure 21*a* represents the volume surfaces over the pT-plane. In this figure may be seen the discontinuous volume change upon the sublimation curve as well as upon the vapor pressure curve, which disappears at the critical point, and the volume change upon melting which changes its sign at the maximal melting point.

3. The Change in Properties Resulting from a Change in the State of Aggregation

Properties may be divided into two classes according to the way in which they change during a change in the state of aggregation.

The properties of the first group: volume, heat content, electrical conductivity, magnetic susceptibility, and the solubility for foreign substances, ordinarily change discontinuously with a change in the state of aggregation. The change in these properties is discontinuous at all points upon the equilibrium curves except those defined by the intersection of the neutral lines with the equilibrium curve, at which points the change is continuous.

The properties of the second group: the vapor pressure, the thermodynamic potential, the solubility of the substance in another substance, and the electromotive force of the transition elements, never change discontinuously with a change in the state of aggregation.

Although no discontinuity occurs in the properties of the first group at the point of intersection of the equilibrium curve with the neutral curve, a discontinuous change appears in the differential quotient of these properties with respect to p and T, the property isotherms or isobars intersecting at the equilibrium

point at a larger or smaller angle. The same is true for the like differential quotients of the properties of the second group.

For the practical determination of transition points the following rules are of value:

1. The measurement of the properties of the first group for the purpose of finding transition points place fewer demands upon the accuracy of the measurement than those of the second class.

2. When the isobars or isotherms of a property of the first group show no discontinuity during a change in the state of aggregation, a discontinuity will appear upon the curve of the first differential of the property in dependence upon the pressure or temperature.

In order to represent any one property of a substance over the whole pT-plane it is customary to erect perpendiculars over the pT-plane and to lay off upon them lengths that are proportional to the values of the property concerned at the particular pT-points. Through the ends of these perpendiculars a plane is conceived which represents the property surface. Discontinuities will accordingly appear upon the planes of the properties of the first group, and the projections of these discontinuities upon the pT-plane for the properties of this group will coincide. These curves upon the pT-plane are the equilibrium curves.

A similar representation for the properties of the second group will show no discontinuities as shown by the properties of the first group. In place of the discontinuities there are edges formed by the intersection of the property surfaces of the different states. The projection of these edges upon the pT-plane for the various properties in this group coincide, as they do for the properties in the first group, and are likewise identical with the equilibrium curves.

4. Is it Necessary that the Vapor Pressure, the Sublimation, and the Melting Curves Intersect?

It is formally possible that some substances cannot exist in the liquid or the crystalline state.

1. (*a*) There may be substances that do not transform into the crystalline state. Such substances would possess only one vapor pressure curve.

(*b*) In case a substance is stable in the crystalline state only at

high pressures the melting curve will not intersect the vapor pressure curve.

These two cases may be mutually distinguished only if for case 1 (*b*) proof be furnished that the equilibrium curves for isotropic and anisotropic states at high pressures have such directions that the vapor pressure curve cannot be intersected.

2. If a substance be stable only as vapor and crystal, not existing as a liquid, its equilibrium diagram will lack a vapor pressure curve.

Inasmuch as the methods for the separation of different substances from one another are based mostly upon the process of crystallization, our knowledge of substances that do not crystallize at ordinary pressures is very limited; it is very seldom that a substance is encountered that does not crystallize and can be claimed as chemically homogeneous. One substance alone appears to belong to this class, the anhydride of boric acid, B_2O_3. It is prepared from the crystallized hydrate H_3BO_3 by the elimination of water.

In order to investigate the crystallization tendency of this unique substance, five grams of B_2O_3 were first fused in a platinum boat 8 cm. long, and a temperature gradient of 800°–20° maintained upon it. After eight days it was found that the glass has remained absolutely clear during this treatment. Between 800° and 20°, therefore, the number of crystallization centers in the liquid, the viscous, and the hard B_2O_3 is negligibly small. And in addition to this experiment, confirmatory evidence is to be had from industrial practice, which has disclosed no crystallized B_2O_3, though B_2O_3 is made in fair-sized quantities.

Furthermore, in one experiment 100 grams of B_2O_3 in pieces were compressed and heated under machine oil to a pressure of 300 kg. and a temperature of 150°, left there ten hours, and the temperature then slowly brought to atmospheric. No noticeable change had taken place under this treatment, and the pieces of B_2O_3 retained their characteristic transparent appearance at the conclusion of the experiment. It is possible, therefore, that only a vapor pressure curve is present in the phase diagram of B_2O_3, or that the melting curve runs to such high pressures that it does not intersect the vapor pressure curve.

The opposite case is presented when the tendency towards crystallization is so great that the substance is not stable in the

liquid state. In this case the phase diagram is without a vapor pressure curve and a melting curve. The sublimation curve runs steeply at small pressures to high temperatures and with increasing vapor density becomes flatter and flatter, and finally assumes the direction of a melting curve.

In answering the second question, as to whether there is any substance that does not exist in the liquid condition, it is necessary first of all to agree upon what is meant by the designation liquid. It is difficult to be strict in the use of ordinary terms here, for the phase field of the liquid is only partly limited by the vapor pressure curve, and it is consequently dependent upon the course

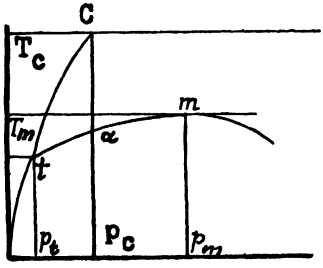


FIG. 22.

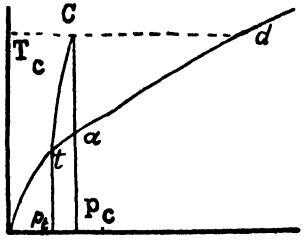


FIG. 23.

of the change in state as to whether condensation phenomena will be observed.

Upon isothermal change in state in a vapor, condensation phenomena will be observed during the crossing of the vapor pressure curve, the substance passing into the liquid field. These phenomena do not occur above the critical temperature T_c. Accordingly, the state of a substance can be designated as liquid in the strip between T_c and T_m (Fig. 22) extending to high pressures when the critical temperature lies higher than the maximal point T_m; when T_m lies higher than T_c the section CdT alone may be designated as liquid (Fig. 23).

There is, of course, no basis for distinguishing between isothermal and isobaric changes of state. Condensation phenomena occur upon isobaric change of state only when the pressure lies between p_t and p_c; at pressures greater than p_c no condensation phenomena occur. Since the critical point lies at comparatively low pressures, often between 100 and 200 kg./cm.^{2}, and since the absolute temperature of the triple-point T_t frequently lies at

$\frac{2}{3}$ of the critical, the field *tca* has a very limited extension. To use terms carefully in the light of our considerations it is not permissible to speak of the equilibrium of a crystal and a liquid at pressures higher than p_c, greater than 100–200 kg./cm.^{2} Our sole observation must be that the ordinary terms are not sufficient to describe the multiplicity of the changes in state, and that geometrical methods are very necessary in order clearly to express our ideas concerning these changes.

To return to our original question regarding the existence of a substance possessing no liquid state: Generally the absolute temperature of the triple-point is $\frac{1}{3}$ to $\frac{1}{2}$ that of the critical point. With substances that strongly dissociate upon vaporization the triple-point approaches the critical temperature and moves towards higher pressures. To this class of substances belong the ammonium and phosphonium salts. The equilibrium curves have been determined for phosphonium chloride, and are reproduced in Fig. 24. The vapor pressure curve extends over a temperature interval of only 20°; the melting curve has been followed to 102.4° and 3050 kg./cm.^{2}, the maximal melting point thus lying much higher than the critical point found to be at 50.1°. It is to be noticed that the angle at which the melting curve and the sublimation curve intersect is a very small one, though in general this angle ordinarily approaches a right angle. If the vapor pressure curve were to be lacking, the sublimation and the melting curves would merge into each other without a point of inflection, and the only equilibrium curve would be that between crystal and vapor. The richer the vapor in the products of dissociation of the crystalline compounds, the less probable is the condensation of the gaseous mixture to a liquid when the dissociation products occur in the hypercritical region. It is possible that the molecules of the compound alone manifest them-

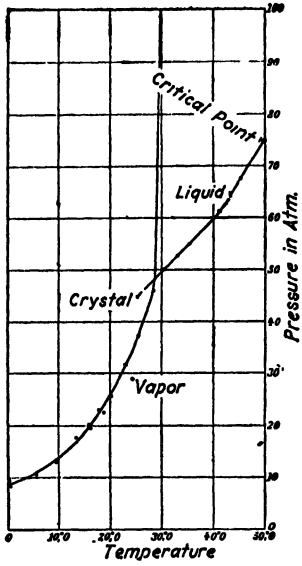


FIG. 24.

selves in the building of crystals. And in this case a vapor pressure curve is not to be expected.

5. Further Fundamental Differences between the Equilibria of Two Isotropic Phases and of Those at Least One of which is Anisotropic

a. The Course of the Volume Isotherm in the Region of Unstable Condition

Upon the transformation of a gas to a liquid without a division into two phases, were this possible, the volume would change upon the isotherm *caegfbd* in Fig. 25. It is well known that the continuity theory of the liquid and gaseous states as expressed in the equation of van der Waals $\left(p + \frac{a}{v^2}\right)(v - b) = RT$ requires either one or three real values of v for each pressure, since it is an equation of the third degree. The case of one value for v occurs with an isotherm in the hypercritical region, three values with isotherms beneath the critical region. The portion *acgfb* of the isotherm in Fig. 25 must have such a form that *aeg* is equal to *gfb*. The portions *ae* and *bf* can be actually determined since the pressure upon the vapor can be raised somewhat above the equilibrium pressure without the appearance of condensation, and since the pressure upon the liquid can be lowered below the vapor pressure without the formation of a vapor. But the piece *egf* upon which the pressure increases is unrealizable.

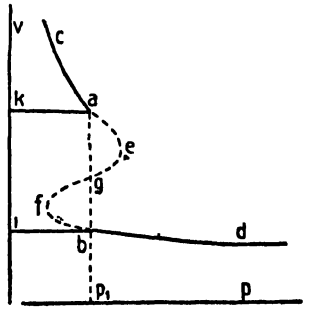


Fig. 25.

Since liquids can be subjected to powerful tensions without decomposition setting in, the point *f* of the piece of the equilibrium curve *gfb* must be conceived as removed far into the region of negative pressure.

J. Meyer [1] has followed the branch *bf* for water to the tension

[1] J. Meyer, *Zur Kenntnis negativer Drucke in Flüssigkeiten. Abhandb. d. Bunsenges.* Vol. III, 1911.

of about 30 kg./cm.^{2} and for ether to 78 kg./cm.^{2} and has shown that the branches *bf* as thus determined are continuations of the isotherm of the liquid at positive pressures.

A wholly different problem is presented by the volume isotherms in the liquid and the crystalline state. If the tendency towards spontaneous crystallization be low, the isotherm of the liquid can be followed to high pressures, but in the case of a crystal, the temperature can be lowered without the formation of a liquid phase only to the point at which the equilibrium pressure is reached. This statement is founded upon the general experience that pressure diminution upon a completely crystallized substance invariably causes immediate melting on the crossing of the melting curve, whereas an increase in pressure upon a completely liquid mass does not necessarily cause crystallization upon the crossing of the melting curve, and an excess pressure of a hundred or a thousand atmospheres may be attained if the tendency towards spontaneous crystallization be sufficiently low.

These facts are of significance in judging the question of whether it is permissible to represent a continuous transformation from an isotropic to an anisotropic phase of the kind partially realized in the transformation from a liquid into a solid, as represented by the isotherm *dbfgeac* in Fig. 25.

Disregarding the fact that the isotherm of the liquid runs to infinitely high pressures, if it be desired to represent the dependence of the volume of a crystal and its melt by an equation of the third degree similar to VAN DER WAALS' (to construct a loop similar to *aegfb* in Fig. 25), the loop *bgka* (Fig. 26) might be constructed, giving three volumes at one pressure; though in this case there is also a fourth volume at the pressure p_x upon the disregarded branch of the isotherm of the melt, isotherm 2. In a definite pressure interval with this kind of construction there will always be a fourth volume connected with a rather doubtful forking of the isotherm, and therefore any equation of the third degree including the anisotropic condition can be avoided only by a construction of the loop as given in Fig. 26, *abcd*. The curve *cd* must asymptotically approach the isotherm of the melt, and the area *cba* must be equal to the area of *cf* ∞ which lies between the isotherm 2 and the curve *cd* prolonged to ∞. The difficulty of the fourth volume may be avoided in this way, but only in hypothesis, for the loop *abcd* cannot be realized for a crystal beneath the melting

pressure, and no observations afford any likelihood to the assumption of the volumes corresponding to the curve *cd*.

Whereas it is possible to overheat a liquid, especially in small quantities suspended in another liquid (and in this state the volume and the other properties of the superheated liquid are clearly determined by p and T), it is impossible to overheat a crystal in the same sense. Upon reaching the melting point, the equilibrium temperature between crystal and melt, a crystal invariably and immediately melts. If the maximal linear crystallization velocity be great the crystal will melt rapidly, the quantity melting will correspond to the amount of heat coming to the crystal, and the melting point will not be overstepped. On the other hand, if the maximal linear crystallization velocity be

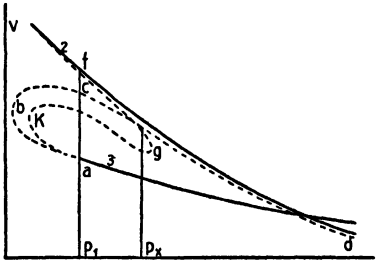


FIG. 26.

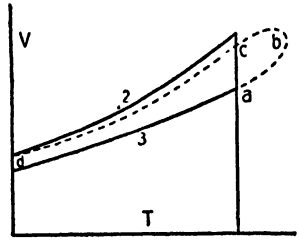


FIG. 27.

small, the melting velocity will likewise be small, and it should be possible by strong heating to exceed the temperature of the melting point. The crystal, however, does not remain in a static condition, similar in behavior to a superheated liquid, but melts steadily, and this melting velocity is in fact proportional to the degree of overheating (see also the chapter on the overheating of crystals). It would therefore be in contradiction to experimental knowledge to construct a loop *abcd* attached to the isobar of the crystal (Fig. 27, curve 3) in such a way that the branch *cd* meets the isobar of the isotropic phase at $T = 0$. There is in addition no experimental data in support of this construction; no volumes have been observed corresponding to the curve *dc*.

The process of crystallization, analogous in many ways to the condensation of a vapor, has no similarity to the process of condensation as regards a continuously changing intermediate state, a constantly varying single phase. There is no experimental support

to such an hypothesis and the whole conception is contrary to the consequences of the atomistic point of view.

b. Isothermal Cyclic Processes between Two Equilibrium Pressures

For a system consisting of a vapor and a liquid the equilibrium curve of which ends in a critical point it is possible to conceive an hypothetical cyclic process taking place below the critical temperature isotherm. Such cyclic processes lead to the equation of MAXWELL. Systems the equilibrium curves of which twice cut lines parallel to the p-axis because the curves do not end in a critical point, likewise permit the execution of isothermal cyclic processes, but these, in contradistinction to that of MAXWELL, are realizable and furnish an equation different from that of MAXWELL.

In the cyclic process of MAXWELL, the volume of the liquid at the point b (Fig. 25) is conceived to change upon the curve *bfgea*, causing the liquid to be transformed into a vapor in a continuous way. The work obtained is equal to the surface $bfgeaki = \int_{v_a}^{v_b} pdv$. The vapor in contact with its liquid can be led back along the straight line ba and be completely transformed into liquid. The work furnished in this process is equal to the rectangle $abik = -p_1(v_a - v_b)$. Since in an isothermal cyclic process the sum of the work terms is equal to zero, the following equation is obtained:

$$p_1(v_b - v_a) = \int_{v_a}^{v_b} pdv_2.$$

Systems possessing two equilibrium pressures at the same temperature permit the performance of the following realizable cyclic process. Figure 28 represents a section at constant temperature of the volume surfaces of phases 2 and 3. The volume of phase 2 is caused to change from the point a at the equilibrium pressure p_1 upon the volume isotherm ad to the pressure of point p_2. The process is realizable when the tendency towards spontaneous transformation of phase 2 into phase 3 is negligibly small. The work is equal to the surface $adhe = \int_{v_{2p_1}}^{v_{2p_2}} pdv_2$. The contact

of an infinitely small quantity of phase 3 with phase 2 will effect the transformation of 2 into 3, which is completed at the equilibrium pressure by an increase in volume to the point c. If the volume change be represented by $(v_2 - v_3)_{p_2}$ the work will be equal to $-p_2(v_2 - v_3)_{p_2}$. A decrease in the pressure upon the phase 3 from p_2 to p_1 will result in a change in volume upon the curve cb, and the accompanying work is equal to area $cbfg = -\int_{v_3p_1}^{v_3p_2} pdv_3$. Finally, an increase in the volume of phase 3 at the equilibrium pressure p_1 from b to a, which causes 3 to be transformed into 2, and will afford the work $-p(v_2 - v_3)_{p_1}$.

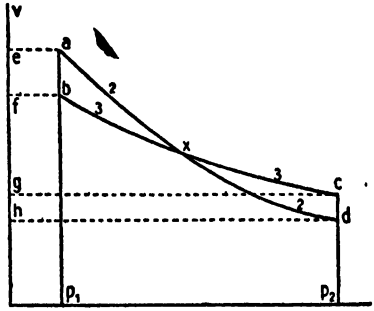


FIG. 28.

Since the sum of the work terms in an isothermal cyclic process is equal to zero,

$$\int_{v_2p_1}^{v_1p_2} pdv_2 = \int_{v_3p_1}^{v_3p_2} pdv_3 + p_1 \cdot (v_2 - v_3)_{p_1} + p_2 \cdot (v_3 - v_2)_{p_2}. \quad (1)$$

To express these work terms in areas, from Fig. 28,

$$adhe = bcgf + abfe + cdhg$$

or, collecting the areas on the right-hand side,

$$adhe = abcdhe.$$

Figure 28 also shows that

$$adhe = abxdhe + abx$$

and

$$abcdhe = abxdhe + cdx$$

so that

$$abx = cdx$$

or

$$\int_{p_1}^{p_x} v_2 dp - \int_{p_1}^{p_x} v_3 dp = \int_{p_x}^{p} v_2 dp - \int_{p_x}^{p_2} v_3 dp.$$

If $abx = cdx$, the following areas will be equal to each other,

$$axdp_2p_1 = bxcp_2p_1$$

or

$$\int_{p_1}^{p_2} v_2 dp = \int_{p_1}^{p_2} v_3 dp \quad \text{or} \quad \int_{p_1}^{p_2} (v_2 - v_3) dp = 0.$$

Not only the sum of the work terms is equal to zero in an isothermal cyclic process, but also the sum of the quantities of heat evolved and absorbed by the system. Therefore

$$- Q_{2_{p_2p_1}} + Q_{3_{p_2p_1}} + R_{p_1} - R_{p_2} = 0, \quad . \quad . \quad . \quad (2)$$

where $Q_{2_{p_2p_1}}$ represent the heats of compression of phases 2 and 3 between the pressures p_1 and p_2, and R_{p_1} and R_{p_2} represent the heats of transformation at the equilibrium pressures p_1 and p_2.

Since according to equation (1) the difference of the work terms of compression is equal to the sum of the external work terms of transformation, the same relation will hold for the work quantities measured in heat units:

$$- Q_{2_{p_2p_1}} + Q_{3_{p_2p_1}} = p_1 \cdot (v_2 - v_3)_{p_1} + p_2 \cdot (v_3 - v_2)_{p_2}.$$

If this equation be combined with equation (2) we obtain

$$p_1(v_2 - v_3)_{p_1} + R_{p_1} = p_2(v_2 - v_3)_{p_2} + R_{p_2}.$$

It is therefore possible to obtain R_{p_2} when the value of R_{p_1} and the equations of state are known.

The principal fact is that for an equilibrium including at least one anisotropic phase a relation may be obtained differing essentially from the MAXWELL equation for an isothermal cyclic process between two isotropic phases.

6. THE THERMODYNAMIC POTENTIAL

So far we have made use of only the simplest thermodynamic methods. But the results obtained can be reached in other ways, and especially by the use of the conception of the thermodynamic potential. Since this method is not very generally used, a brief introduction to its application will be given. The method was conceived by J. W. GIBBS, though he personally made no applications of it to the problems in which we are interested. An extensive presentation of its application to the problems of one-com-

ponent system is given in two papers by the present author: *Zur Thermodynamik der Gleichgewichte in Einstoffsystemen* (*The Thermodynamics of the Equilibria in One-Component Systems*).[1]

a. Heat, Energy, and Work

A quantity of heat dQ added to the unit of mass of a substance will cause the temperature to be raised dT; the absorbed heat is used to increase the energy content by dE and to furnish the external work $dA = pdv$. Thus

$$dQ = dE + dA = dE + pdv.$$

The quantities E and A differ essentially from each other with reference to their dependence upon the quantities that change during heating: p, v, and T. E is dependent upon only the initial and final conditions of the body; there is a completely defined function $E = f(pT)$, or $E = \phi(vT)$, corresponding to definite surfaces over the pT-plane or vT-plane, and accordingly dE is a complete differential. E behaves with reference to its dependence upon p and T as does the volume, which is likewise clearly determined by the initial and final values of p and T, and does not depend upon the path by which these end-values are reached.

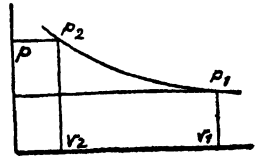


FIG. 29.

But the work A behaves in a wholly different manner. The curve in Fig. 29 represents the interdependence of p and v at contant temperature, and the work furnished with increase in volume from v_1 to v_2 is equal to the area $v_1p_1p_2v_2$, and $A = \int_{v_1}^{v_2} pdv$. Any variation in the curve passing through the points p_1 and p_2 results in a change in the content of the area $v_1p_1p_2v_2$, and A is therefore dependent upon the course taken during the change of p and v during warming. Consequently there is not one fixed work-area for a unit of mass, since $A = f(pT)$ or $A = \phi(vT)$ has a fixed value only when the change in v with p during warming is fixed. Inasmuch as this change can be arbitrarily influenced, as, for example, p or v can be held constant during warming,

[1] *Ann. d. Phys.*, **36**, 1027 (1911) and **40**, 297 (1913).

there are many work-areas for a unit of mass of one substance which may not be immediately evident. And since the value of the work can be determin[illegible] only when the change in p and v during warming is known, the same must be true of the quantity of heat Q; dQ therefore is not a complete differential.

However, a factor can be introduced into such functions as Q, causing the differential otherwise incomplete to become complete, causing the function of many significations to become definite. The second law of thermodynamics fixes this function at $1/T$. Although $\int_{T_1}^{T_2} dQ$ is indeterminate, $\int_{T_1}^{T_2} \frac{dQ}{T}$ can be determined, and for this sum there is a definite surface over the vT-plane. Since this is the case, the beginning value must be equal to the final value of Q_2/T_2 for a cyclic process in which a unit of mass of any substance is concerned, for in this cyclic process the initial and final value must be equal, as in case of other determinate functions. It is therefore to be shown that ordinarily

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This demonstration has been carried on by R. CLAUSIUS by the help of the CARNOT cyclic process as follows.

Upon isothermal expansion at T_1 the quantity of heat Q is absorbed, the work $ABGE$ (Fig. 30) is furnished, and the energy content of the substance changes from E_1 to E_2. According to equation (1),

$$Q_1 = a \times ABGE + E_2 - E_1.$$

Upon adiabatic expansion of the substance, the temperature sinking from T_1 to T_2, no heat is evolved or absorbed; the energy content alone changes, and work is afforded,

$$Q = 0 = a \times BCHG + E_3 - E_2.$$

An isothermal volume diminution at T_2 now follows, and for this we have

$$Q_2 = a \times DCHF + E_3 - E_4.$$

Finally the system is adiabatically compressed to the original volume:

$$Q = 0 = a \cdot ADFE + E_4 - E_3.$$

By trial it is always possible so to arrange conditions that the cycle is closed. a is a factor that changes the numerical value of the work expressed in work units to a value expressed in heat units. If the first two equations be added and the last two subtracted we get

$$Q_1 - Q_2 = a \cdot ABCD.$$

The relation of the quantity of heat transformed into work, $Q_1 - Q_2$, to the quantity of heat Q_1 furnished the isothermal process at the beginning, is known as the efficiency of the cyclic process. This efficiency must be independent of the nature of the substance with which the cyclic process is performed, for otherwise by means of two machines using two different substances and working in opposition to one another, cyclic processes could be executed between the same temperatures with equal heat absorption and evolution, and work could be obtained without heat transfer from the higher to the lower temperature.

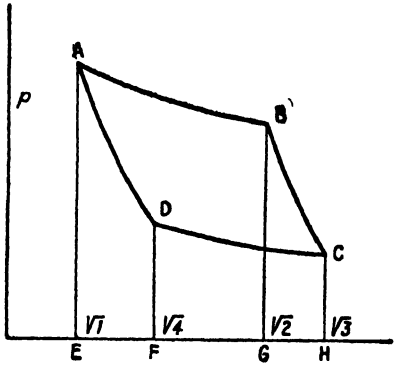


FIG. 30.

The efficiency of an ideal gas can thus be given, and since the efficiency is independent of the nature of the gas, the expression will be generally applicable.

For the adiabatic curves of an ideal gas $Tv^{k-1} = \text{a constant}$, and therefore for the adiabatic AD, $T_1 v_1^{k-1} = T_2 v_4^{k-1}$ and for the adiabatic BC, $T_1 v_2^{k-1} = T_2 v_3^{k-1}$. By the division of these two equations,

$$\frac{v_2}{v_1} = \frac{v_3}{v_4}.$$

For an ideal gas, the work resulting from the isothermal volume change is equal to the work taken in or given out.

$$Q_1 = aRT_1 \ln\frac{v_2}{v_1} \quad \text{and} \quad Q_2 = aRT_2 \ln\frac{v_3}{v_4} = aRT_2 \ln\frac{v_2}{v_1}.$$

If these values be introduced into the value for the efficiency of the cyclic process, then

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \cdot \frac{\ln \frac{v_2}{v_1}}{\ln \frac{v_2}{v_1}} = \frac{T_1 - T_2}{T_1},$$

or

$$\underline{\frac{Q_2}{Q_1} = \frac{T_2}{T_1}}, \quad \text{or} \quad \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0.$$

It is therefore evident that $1/T$ is the integrating factor of dQ, and since $(Q_1 - Q_2)/Q_1$ is independent of the nature of the substance, the last equation is generally applicable. There is also another function, the entropy η, the complete differential of which is

$$d\eta = \frac{dQ}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The CARNOT cycle can be carried out in two different directions. If the volume of an ideal gas be increased isothermally at a higher temperature T_2, the gas will furnish work for the cyclic process, and Q_1 goes from T_1 to T_2, and Q_2 goes from T_2 to T_1. With the reverse direction of the cyclic process the path upon the pT-plane will run in the reverse direction, but work is likewise furnished by the gas, and Q_2 is taken on at T_2 and Q_1 given off at T_1. In the first case work results from the heat while $Q_1 - Q_2$ sinks from higher to lower temperatures, in the second case by the work furnished $Q_1 - Q_2$ heat is raised from the lower to the higher temperature. CLAUSIUS has summarized these results in a few words: *Heat cannot of itself pass from a colder to a warmer body.* Upon the basis of this law he has shown further that the efficiency $(Q_1 - Q_2)/Q_1$ is independent of the nature of the substance. CARNOT arrived at the same conclusion by assuming the impossibility of perpetual motion. If perpetual motion be indeed impossible the efficiency must be independent of the nature of the substance, for otherwise by the use of two different substances it would be possible to construct a perpetual-motion machine.

Any cyclic process the track of which upon the vp-plane represents a closed curve can be analyzed into a number of CARNOT

cyclic processes. The sum of the entropies of these partial processes must be equal to zero if the process involved be cyclic, and

$$\int_{v_0p_0}^{vp} \frac{dQ}{T} = 0 \quad \text{or} \quad \int_{v_0p_0}^{vp} \frac{dQ}{T} = \eta_{vp} - \eta_{v_0p_0}.$$

For a given substance there is, therefore, over the vp-plane a definite entropy surface.

b. The Transformations of the Equations of the First Two Laws

A combination of equations (1) and (3) representing the first two laws gives us

$$dE = Td\eta - pdv, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is the differential of the energy surface with respect to the variables η and v. This surface has come into use as a result of the work of J. W. GIBBS.[1]

The energy surface above the η, v-plane must assume higher E-values with constant η and increasing v, and furthermore, it must be bent convexly to the η, v-plane in both sections.

Accordingly, from equation (4) we get

$$\left(\frac{dE}{d\eta}\right)_v = T \qquad \left(\frac{d^2E}{d\eta^2}\right)_v = \frac{T}{C_v}, ^2 \quad . \quad . \quad . \quad (5a \text{ and } b)$$

In Fig. 31 at a point on the surface $E = f(\eta, v)$ two tangents are laid in two planes parallel respectively to the E, η-plane and the E, v-plane. The tangent in the plane parallel to the E, η-plane forms the angle α with a parallel to the η-axis, so that $\tan \alpha \doteq T$; and the tangent in the plane parallel to the E, v-plane forms an angle β with a parallel to the v-axis, so that $\tan \beta = -p$. In both sections the E-surface is curved convexly to the η, v-plane.

[1] *Scientific Papers.* London, 1906, page 2.

[2] Since $\left(\frac{dE}{d\eta}\right)_v = \left(\frac{dT}{d\eta}\right)_v$, and $\left(\frac{dT}{d\eta}\right)_v = T\left(\frac{dT}{dQ}\right) = \frac{T}{c_v}$, equations 5*b* will follow.

$$\left(\frac{dE}{dv}\right)_\eta = -p \qquad \left(\frac{d^2E}{dv^2}\right)_\eta = -\left(\frac{dp}{dv}\right)_\eta . \quad . \quad (6a \text{ and } b)$$

The segment ab of the first tangent is equal to $E - T\eta$, the segment cd of the second tangent is $E + pv$, and the segment of the tangential plane upon the E-axis of is equal to $E - T\eta + pv$. Three such segments belong to each point upon the E-surface and the above named tangents defined by the values of T and $-p$ at this point. For these segments GIBBS has given the following relations:

	Independent variables.
$E - T\eta = \psi$	v and T
$E - T\eta + pv = \zeta$	p and T
$E + pv = \chi$	v and p.

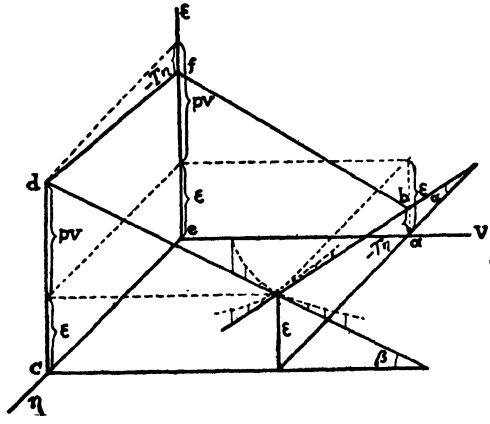


FIG. 31.

The two variables p and T are more suitable for observation than the two independent variables of the E-surface, η and v. It is therefore desirable to transform the E-surface into terms of p and T, or v and T. This may be done in the following way.

$dE = Td\eta - pdv$ is given, and the function corresponding to the surface is to be found in T and v, or as $f(T, v)$. In this transformation there is concerned merely a displacement of the otherwise stationary sections through the E-surface, perpendicular to the v-axis. Then $dE = Td\eta - pdv$ will become $df(T, v) = (\quad)dT - pdv$, in which the quantity in the parenthesis is still to be determined.

If $df(T, v)$ should be a complete differential and if both equations should be fulfilled the unknown member will be determined,

as $-\eta dT$; for this quantity alone makes $df(T, v)$ a complete differential upon the union of the two equations. Then we have

$$df(T, v) = dE - (Td\eta + \eta dT) = dE - d(T\eta).$$

This differential equation corresponds to the investigated form

$$f(T, v) = E - T\eta = \psi.$$

If the E-surface be transformed into one of the corresponding surfaces above the p, T-plane, we have

$$df_2(T, p) = dE - d(\eta T) + d(pv),$$

or the integrated form

$$f_1(T, p) = E - \eta T + pv = \zeta.$$

Finally the transformation of the E-surface into a surface over the p, v-plane leads to a function

$$E + pv = \chi.$$

These three transformations lead to very simple and clear results, which cannot be said of the seven transformations still possible. These three functions are therefore called the characteristic functions. As we will see, there is a special geometric significance corresponding to each.

For our purpose the ζ-function will be given the preference since its geometric interpretation is simplest. It permits us to obtain all the results desired, as is likewise true of the ψ- and E-functions.

c. The Thermodynamic Potential

A transformation of mass, such as vaporization, melting, etc., in a one-component system is accompanied by a change in the energy of the system. This change in energy is measured by the product of the quantity of matter changed, dm, and a function μ, the thermodynamic potential.

In a purely mechanical system the work brought about by a displacement of mass is equal to the mass times the difference in its potential before and after the displacement. The potential

energy of the system changes by this amount of work. In analogy with mechanical systems, the function by which the transformed mass is to be multiplied in order to obtain the corresponding change in energy, is called the thermodynamic potential.

Therefore, in the case in which the one-component system is heterogeneous, equation (4) obtains an addition member, μdm:

$$dE = Td\eta - pdv + \mu dm. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

And from this it follows that $\mu = \left(\frac{dE}{dm}\right)_{\eta, v}$. If we choose T and p for independent variables the value of μ assumes another form, since it then is expressed by the ζ-function. Differentiation of $\zeta = E - T\eta + pv$ gives us

$$d\zeta = dE - Td\eta - \eta dT + pdv + vdp,$$

which combined with (7) gives us

$$d\zeta = -\eta dT + vdp + \mu dm,$$

from which a value for μ is obtained

$$\mu = \left(\frac{d\zeta}{dm}\right)_{T, p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The condition for the equilibrium of two phases is that the values of p and T be the same for both phases, and that the values of the potentials likewise be identical,

$$\mu_1 = \mu_2 \quad \text{or} \quad \left(\frac{d\zeta_1}{dm}\right)_{T, p} = \left(\frac{d\zeta_2}{dm}\right)_{T, p}. \quad . \quad . \quad . \quad (9)$$

The differential quotients $(d\zeta/dm)_{T, p}$ are those derived from the ζ-isobars referring to a unit of mass, and by ζ-values are always understood these specific values, so that the condition of equilibrium can be written

$$\zeta_1 = \zeta_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

If the ζ-surfaces of two phases intersect, the p- and T-values of the projection of the non-plane curve of intersection upon the pT-plane will define the course of the equilibrium curve. With the crossing of the equilibrium curve there is a change in the relative magnitudes of the ζ-values corresponding to the change in stability. At any one pT-point the unstable phase has the greater ζ-value.

Since the quantities of the two phases in a one-component system have no effect upon the equilibrium, the equilibrium conditions are very simple as regards the ζ-isotherms. For a two-component system, in which a third independent variable is added, the equilibrium conditions become more complex; the same is true of a one-component system represented by the function ψ or E, for in this case an exchange of mass is of influence upon the independent variables of ψ, T, and v, and of E, η, and v.

d. The Form of the ζ-surfaces

Differentiation of the equation

$$\zeta = E - T\eta + pv$$

furnishes an equation which when combined with (4) gives us.

$$d\zeta = -\eta dT + vdp.$$

From this may be obtained the directions and curvatures of ζ-isotherms and the ζ-isobars,

$$\left(\frac{d\zeta}{dp}\right)_T = v, \quad \ldots\ldots\ldots \quad (11)$$

$$\left(\frac{d^2\zeta}{dp^2}\right)_T = \left(\frac{dv}{dp}\right)_T, \quad \ldots\ldots \quad (12)$$

$$\left(\frac{d\zeta}{dT}\right)_p = -\eta, \quad \ldots\ldots\ldots \quad (13)$$

$$\left(\frac{d^2\zeta}{dT^2}\right)_p = -\frac{c_p}{T}, \quad \ldots\ldots \quad (14)$$

The ζ-isotherms rise with increasing pressure since v is positive for all phases, and curve concavely to the p-axis since $(dv/dp)_T$ is always negative for realizable states.

The ζ-isobars fall with rising temperature and curve concavely to the T-axis.

The equation of CLAUSIUS-CLAPEYRON, derived on page 9 on the basis of a reversible cyclic process, now follows in a very simple manner. If the ζ-surfaces of the phases 1 and 2 intersect,

$$_1\left(\frac{d\eta}{dT}\right)_p - \frac{1}{T}\left(\frac{dQ}{dT}\right) = \frac{c_p}{T}.$$

the values of ζ_1 and ζ_2 upon the curve of intersection are equal to one another, and the same is true of their change with p and T. Since

$$d\zeta_1 = -\eta_1 dT + v_1 dp$$

$$d\zeta_2 = -\eta_2 dT + v_2 dp,$$

it follows that

$$\frac{dT}{dp} = \frac{v_1 - v_2}{(\eta_1 - \eta_2)} = \frac{\Delta v T}{R_p},$$

when $v_1 - v_2 = v$ and $(\eta_1 - \eta_2) = R_p/T$.

With respect to the position of the three equilibrium curves at the triple-point we have the rule that the prolongation of each equilibrium curve beyond the triple-point which corresponds to unstable equilibrium, falls between the two other equilibrium curves. The ζ-surfaces of the three phases in equilibrium intersect in three non-plane curves which in turn at the triple-point intersect in a point, corresponding to the triple-point. The prolongation of each of these non-plane curves beyond the point of intersection extends into a space between two cylindrical surfaces formed by the movement of a perpendicular to the pT-plane along the two non-plane curves. The rule must therefore hold good for the projection of these three non-plane curves upon the pT-plane; that the prolongation of an equilibrium curve into a field of instability always falls between the two other equilibrium curves (Fig. 32).

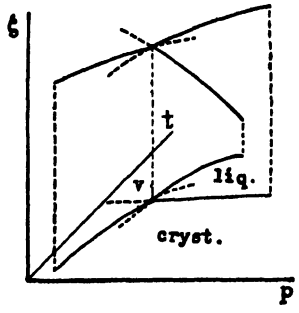


FIG. 32.

e. The Conditions for the Occurrence of Two Equilibrium Pressures at the Same Temperature

If the ζ-isotherms of phases 2 and 3, at least one of which is anisotropic, twice intersect, each of the pressures at which the ζ_2- and ζ_3-values are equal is an equilibrium pressure. If two equilibrium pressures exist at the same temperature, the equilibrium curve must have a maximum.

As regards the course of the two ζ-isotherms there are two cases to be distinguished: At the triple-point, where the crystal is in equilibrium with its vapor and melt, two relations can obtain, viz., $v_2 \gtrless v_3$.

1. If $v_2 > v_3$, the ζ-curves will intersect not only at p but also at a higher pressure p_2 (Fig. 33), and the preliminary condition that

$$\frac{d_T{}^2\zeta_2}{dp^2} < \frac{d_T{}^2\zeta_3}{dp^2} \quad \text{or} \quad \frac{d_T v_2}{dp} > \frac{d_T v_3}{dp}$$

must be fulfilled; if these conditions be not fulfilled the two isotherms diverging at the equilibrium pressure p_1 by the angle $v_2 - v_3$ upon rising temperature will diverge to an increasingly greater extent, since the ζ-isotherm will be curved more steeply towards the p-axis than the ζ_2-isotherm.

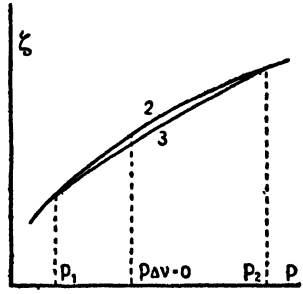


FIG. 33.

However, upon the fulfillment of these conditions, the divergence of the two ζ-isotherms, which is the difference

$$\frac{d\zeta_2}{dp} - \frac{d\zeta_3}{dp} = v_2 - v_3,$$

will decrease upon increasing pressure and a second equilibrium pressure will be possible.

If the compressibility of a crystal and its melt approach a zero value with increasing pressure, the curvature of the two ζ-isotherms will decrease and with increasing pressure will become more nearly linear. In order that the two ζ-isotherms shall not diverge to infinitely high pressures it is necessary that the condition be fulfilled that the difference

$$\frac{d\zeta_2}{dp} - \frac{d\zeta_3}{dp} = v_2 - v_3,$$

reach a zero value at a finite pressure. The fulfillment of this condition is likewise met when the two ζ-isotherms again intersect, the second time at the pressure p_2 (Fig. 33), and when the anisotropic phase becomes less stable than the isotropic at pressures higher than p_2.

When the isotherms of a crystal and its melt do not intersect until $p = \infty$, the melting curve asymptotically approaches a maximal melting pressure at the pressure $p = \infty$. This limiting form of the melting curve likewise prohibits a continuous transaction of the anisotropic into the isotropic state. It is the limiting case of a melting curve with a maximal melting temperature, in which the maximum lies at infinitely high pressures.

For the existence of two melting pressures at one temperature, that is, for the existence of a maximum upon the melting curve, two conditions must be fulfilled: The preliminary condition that the compressibility of the crystal be greater than that of its melt, and the chief condition that the volume difference of the melt and the crystal pass through a zero value at a finite pressure.

The preliminary condition is satisfied with all substances, as far as we know. With respect to the chief condition, for the present it can be said only that by the help of extrapolation it appears to be fulfilled.

2. If $v_3 > v_2$ and if also

$$\frac{d_T v_2}{dp} > \frac{d_T v_3}{dp},$$

the ζ-isotherms of the crystal 3 and its melt 2 intersecting the ζ-isotherm of the vapor 1 upon rising pressure (Fig. 34) themselves will intersect only once, since at pressures above the point of intersection p_1 the ζ_2-curve will curve more strongly towards the p-axis than ζ_3-curve, making a second intersection of the ζ_2- and the ζ_3-curves impossible.

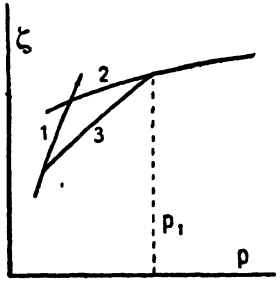


FIG. 34.

In Section 5*b*, page 44, we derived the second equilibrium pressure p_2 upon the basis of an isothermal cyclic process. The areas *abx* and *cdx* enclosed by the volume isotherms of the two phases are necessarily equal. The same conclusion may be reached by the help of the ζ-function.

For this purpose we have the following equations:

$$\zeta_{2p_2} = \zeta_{2p_1} + \int_{p_1}^{p_2} \frac{d_T \zeta_2}{dp} dp$$

$$\zeta_{3p_2} = \zeta_{3p_1} + \int_{p_1}^{p_2} \frac{d_T\zeta_3}{dp} dp,$$

and since $\zeta_{2p_2} = \zeta_{3p_2}$ and $\zeta_{2p_1} = \zeta_{3p_1}$,

$$\int_{p_1}^{p_2} \frac{d_T\zeta_2}{dp} dp = \int_{p_1}^{p_2} \frac{d_T\zeta_3}{dp} dp \quad \text{or} \quad \int_{p_1}^{p_2} (v_2 - v_3) dp = 0.$$

f. The Conditions for the Occurrence of Two Equilibrium Temperatures at the Same Pressure

If at a certain pressure phase 3 be more stable than phase 2 within the temperature interval $T_1 - T_2$, and if at the limits of this temperature interval a change in stability occur, the positions of the two ζ-isobars will be that given in Fig. 35. At T_1, then, we will have

$$\left(\frac{d\zeta_2}{dT}\right)_p > \left(\frac{d\zeta_3}{dT}\right)_p \quad \text{or} \quad -\eta_2 > -\eta_3,$$

and accordingly heat is absorbed in the transformation of phase 3 into phase 2. At T_2 we will have $\left(\frac{d\zeta_2}{dT}\right)_p > \left(\frac{d\zeta_3}{dT}\right)_p$ or $-\eta_2 > \eta_3$, and in this case, with the transformation of phase 3 into phase 2, heat will be absorbed. From this follows the condition for the occurrence of a second equilibrium temperature T_2: the heat of transformation must change its sign. When this is the case, a second equilibrium temperature is possible. If no such change occur down to $T = 0$, phase 2 will remain less stable than phase 3. In order, therefore, that $\eta_2 - \eta_3$ pass through a zero value it is necessary that the isobar ζ_2 be curved more steeply than the isobar ζ_3, that therefore $c_{2p} > c_{3p}$.

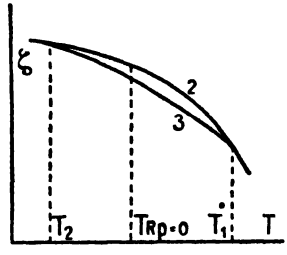


FIG. 35.

This condition relating to the specific heats of the anisotropic and the isotropic states is ordinarily fulfilled, but with decreasing temperature the difference $c_{2p} - c_{3p}$ generally decreases, and in the case of the silicates is vanishingly small even at ordinary temperatures.

When the equilibrium temperature T_1 is known, the second equilibrium temperature may be obtained from the following equation,

$$\int_{T_1}^{T_2} \frac{d_p\zeta_2}{dT} dT = \int_{T_1}^{T_2} \frac{d_p\zeta_3}{dT} dT. \quad . \quad . \quad . \quad . \quad (15)$$

And in addition,

$$\zeta_2 - \zeta_3 = E_2 - E_3 - (\eta_2 - \eta_3)T + (v_2 - v_3)p. \quad . \quad (16)$$

The relations at low temperatures as obtained for substances affording information with respect to the heat of fusion and the difference of the specific heats of the crystal and its melt in dependence upon temperature, are given in Fig. 36.

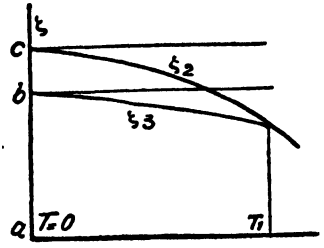


Fig. 36.

At $T = 0$, $ac = E_2$ and $ab = E_3$ since at small pressures $v_2 \cdot p$ and $v_3 \cdot p$ have negligible values, and ζ_2 as well as ζ_3 at $T = 0$ according to Nernst are likewise negligible. The tangents to the two ζ-curves at $T = 0$ are accordingly perpendicular to the ζ-axis. Because the difference $E_2 - E_3$ at $T = 0$ is so considerable a second equilibrium temperature cannot here exist, though the ζ_2-curve is curved more steeply than the ζ_3-curve. As long as $v_2 > v_3$ a second point of intersection of the two ζ-curves at $T = 0$ with increasing pressure cannot occur, since the value $(v_2 - v_3)_p$ increases the difference $\zeta_3 - \zeta_3$. After $v_2 - v_3$ has changed its sign this possibility exists since in this case $E_2 - E_3$ is compensated by $-(v_2 - v_3)_p$ at $T = 0$, and at higher pressures can be considerably exceeded. In this case a second point of intersection of the two ζ-isobars at $T = 0$ occurs, which with increasing pressure moves towards higher temperatures.

The question of the occurrence of a second equilibrium temperature may be approached from another angle. Equation (15) may be written in this form

$$\int_{T_1}^{T_2} (\eta_2 - \eta_3) dT = 0. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

And since at small pressures $(v_2 - v_3)_p$ is negligible, in place of (16) we may write

$$\zeta_2 - \zeta_3 = E_2 - E_3 - (\eta_2 - \eta_3)T. \quad . \quad . \quad . \quad . \quad (18)$$

For the equilibrium temperature T_1, $\zeta_2 - \zeta_3 = 0$ and therefore

$$E_2 - E_3 = (\eta_2 - \eta_3)T_1 = R_p. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

For other temperatures

$$\zeta_2 - \zeta_3 = -\int_{T_1}^{T} (\eta_2 - \eta_3)dT.$$

If this value be introduced into (18).

$$E_2 - E_2 = -\int_{T_1}^{T} (\eta_2 - \eta_3)dT + (\eta_2 - \eta_3)T. \quad . \quad (20)$$

In Fig. 37 the values of η_2 and η_3 are represented in dependence upon T. At $T = 0$, η_2 and $\eta_3 = 0$ in correspondence to the heat theorem of NERNST. In this diagram the values of $E_2 - E_3$

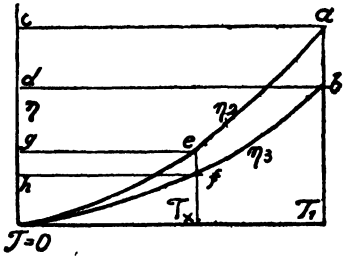


FIG. 37.

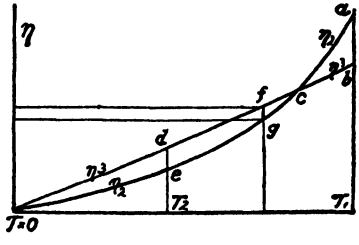


FIG. 38.

correspond to surfaces and the same is true for the values of $\zeta_2 - \zeta_3$ and $(\eta_2 - \eta_3)T$.

At the equilibrium temperature T_1, $(E_2 - E_3) = (\eta_2 - \eta_3)T = R_p$, which equals the areas of the rectangle *abcd*; and at temperatures T_x, $E_2 - E_3$ is equal to the surface between the two curves η_2 and η_3 from $T = 0$ to T_x plus the rectangle *efgh*. At $T \neq 0$, $E_2 - E_3$ equals the surface between the two η-curves from $T = 0$ to T_1. The case represented in Fig. 37 is similar to that in Fig. 36. Since the two η-curves in Fig. 37 do not intersect, the occurrence of a second equilibrium temperature is not possible.

If, however, the two η-curves intersect, as in Fig. 38, a second equilibrium temperature T_2 can occur, the position of which is determined by the theorem of equation (17). The equality of the two surfaces *abc* and *dec* in Fig. 38 corresponds to this equality. Since in a cyclic process they are circumnavigated in an opposite sense, their sum is equal to zero. At the two equilibrium tem-

peratures $E_2 - E_3$ is negative and $E_2 - E_3$ must pass through a zero value at a temperature higher than T_2; this happens at a temperature at which *abc* equals *cfg* plus the rectangle to the left of *fg*. In this way, with the occurrence of a second equilibrium temperature, first $\eta_2 - \eta_3$, then $E_2 - E_3$, and finally $\zeta_2 - \zeta_3$ passes through the zero value.

g. The ζ-surfaces and the Neutral Curves

With the knowledge we have gained with respect to the ζ-isotherms and the ζ-isobars of a crystal and its melt, we are now in position to form a conception of the position of the ζ-surfaces above the pT-plane. The forming of such a conception will be greatly facilitated by the help of the sketch given in Fig. 39. The point of observation in this sketch is such that the observer looks down on the model the ζ-surface of which slopes from right to left. The curves lying nearest are completely drawn; the lines on plane surfaces are dotted. The ζ-isotherms t_1, t_2, t_3, and t_4 rise with increasing pressure; the ζ-isobars p_1 and p_2 fall off with increasing temperature and at $T = 0$ they intersect perpendicularly with the ζ, p-plane. The ζ-surface of the vapor, *abc*, intersects that of the anisotropic state in the curve *dge*, and that of the isotropic in the curve *adec*. This curve of intersection ends in the critical point *c*, and with it also ends the edge formed by the intersection of the ζ-surfaces of the vapor and liquid. Therefore at temperatures above that of the critical point *c* the ζ-isotherms run continuously from the smallest to the highest pressures, as, for example, the isotherm t_4, without the occurrence of a point of inflection such as occur with the transformation of vapor into liquid upon isotherms below the temperature of the critical point. The ζ-surface of the vapor thus is merely a portion of the ζ-surface of the liquid to which it is connected in a continuous way. The ζ-surface of the anisotropic state behaves in a different way; it is a wholly independent surface cutting the ζ-surface of the liquid—or rather of that of the isotropic state—in the curve *dfe*. In the space defined by the curve *dfe* the ζ-surface of the liquid lies over that of the anisotropic state. If there be substances at present unknown, the supercooled liquids of which are stable in the form of glass, their behavior will be represented by the piece of the ζ-surface between the ζ-isotherm at_1

and the curve of intersection ahf. It may be seen that not only the ζ-surface of the vapor but also the ζ-surface of the stable states of the amorphous substance are connected continuously with the ζ-surface of the liquid, forming the continuous surface of the isotropic state.

The projection of the curves of intersection of the ζ-surfaces upon the pT-plane, indicated in the figure by the corresponding

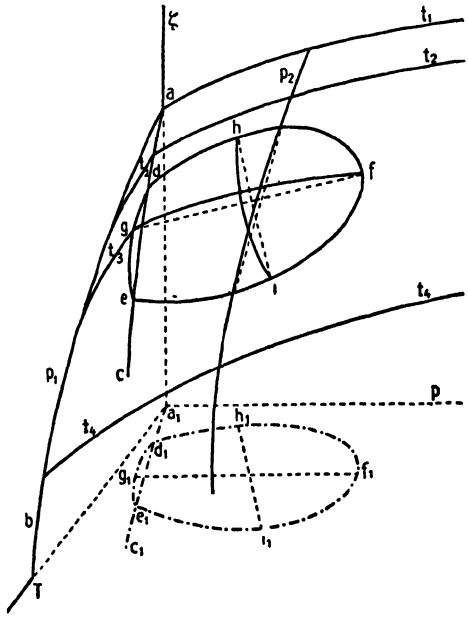


FIG. 39.

letters subscripted, are the equilibrium curves. The curve $d_1g_1e_1$ is the sublimation curve; the curve e_1c_1 is the vapor pressure curve; the curve a_1d_1 is the curve upon which the stable amorphous substance is in equilibrium with its vapor; and curve $e_1f_1d_1$ is the melting curve.

Tangential planes placed at the same pT-point upon the ζ-surface of a crystal and upon that of its melt will ordinarily intersect; at only one pT-point will the two tangential planes be parallel. Since at this point

$$\frac{d_T\zeta_2}{dp} = \frac{d_T\zeta_3}{dp} \quad \text{and} \quad \frac{d_p\zeta_2}{dT} = \frac{d_p\zeta_3}{dT},$$

then

$$v_2 = v_3 \quad \text{and} \quad \eta_2 = \eta_3 \quad \text{or} \quad R_p = 0.$$

In addition, other parallel tangents can be placed to the two ζ-surfaces. If the two tangents parallel to the p-axis on the two ζ-surfaces at points lying over each other on these surfaces be parallel to each other, it signifies that the volume of phase 2 will be equal to that of phase 3. Through these points upon the two ζ-surfaces pass two curves lying over one another, ih, the projections of which upon the pT-plane coincide in the neutral curve i_1h_1. At the points on this curve $v_2 = v_3$. If tangents drawn parallel to the T-axis upon each of the two ζ-surfaces on the same pT-perpendicular, be parallel, η_2 will equal η_3. The projections of the two curves gf coincide in the neutral curve g_1f_1 upon which $R_p = 0$.

Above the point of intersection of the two neutral curves, h_1i_1 and g_1f_1, lie two points, one on each of the two ζ-surfaces, the tangential planes to which are parallel to each other.

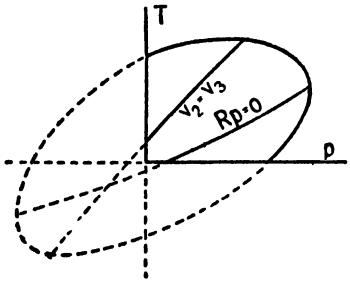


FIG. 40.

The points of intersection of the neutral curve h_1i_1 with the melting curve, the points h_1 and i_1, are distinguished by the fact that upon them $v_2 = v_3$. Therefore point i_1 is the maximal melting point, and the point h_1 is the minimal melting point. The point of intersection of the melting curve with the neutral curve f_1g_1, f_1, is the maximal melting pressure, at which $R_p = 0$.

The points upon the ζ-surfaces corresponding to the points h_1 and i_1 are unique in the fact that a tangent parallel to the ζp-plane at these points touches the curve of intersection of the two ζ-surfaces, and therefore simultaneously touches the two ζ-surfaces. Somewhat the same is true of point f.

The position of the neutral curves is very important with respect to the form and the development of the equilibrium curves. As regards its point of intersection we know that the point must fall into the section of the pT-plane embraced by the supposedly closed equilibrium curve. Two chief cases are to be distin-

guished. The point of intersection of the two neutral curves can fall within the field of realizable condition, as in Fig. 39 in which the parameter p and T possesses realizables values. It appears, however, that for the majority of substances the point of intersection of the neutral curves lies outside of the field of realizable states, as evident in Fig. 40, but still in the piece of the pT-plane embraced by the closed melting curve. Furthermore, the neutral curve upon which $v_2 = v_3$ runs more steeply than the neutral curve upon which $R_p = 0$. (See page 32.)

The tangential plane at the critical point c, Fig. 39, touches two ζ-surfaces, that of the vapor and that of the liquid. The conclusion to be drawn from this fact is that at the critical point c, $\eta_1 = \eta_2$ as well as $v_1 = v_2$. In addition, the critical point occurs upon an equilibrium curve and therefore at this point

$$\zeta_1 = \zeta_2,$$

and since

$$\zeta_1 - \zeta_2 = E_1 - E_2 - (\eta_1 - \eta_2)T + (v_1 - v_2)p,$$

for the critical point we also have the relation

$$E_1 = E_2.$$

Since the volume, entropy, and energy of the two phases at the critical point are equal, the two phases are identical at this point.

The point at which the two neutral curves intersect, the point at which

$$v_2 = v_3 \quad \text{and} \quad \eta_2 = \eta_3$$

does not lie upon an equilibrium curve; at this point

$$\zeta_2 > \zeta_3,$$

and since

$$E_2 - E_3 - (\eta_2 - \eta_3)T + (v_2 - v_3)p > 0,$$

then at this point

$$E_2 > E_3.$$

7. The Application of the Nernst[1] Heat Theorem to the Determination of Equilibrium Pressures in Condensed Systems

Let us first correlate the formula used by Nernst in the application of the heat theorem bearing his name, with the ψ-function of Gibbs. H. v. Helmholz in particular has demonstrated the application of this function, and has designated it as the free energy. The chief properties of the ψ-surface over the Tv-plane may be derived in the following way.

For a unit of mass of a chemically homogeneous substance occurring in a homogeneous phase we have

$$\psi = E - T\eta.$$

Differentiation of this equation produces

$$d\psi = dE - \eta dT - Td\eta,$$

which combined with the equation

$$dE = Td\eta - pdv,$$

in turn gives us

$$d\psi = -\eta dT - pdv,$$

from which follows:

$$\left(\frac{d\psi}{dT}\right)_v = -\eta; \quad \left(\frac{d\psi}{dv}\right)_T = -p$$

$$\left(\frac{d^2\psi}{dT^2}\right)_v = -\frac{c_v}{T}; \quad \left(\frac{d^2\psi}{dv^2}\right)_T = -\left(\frac{dp}{dv}\right)_T.$$

The curves of intersection of the ψ-surface parallel to the ψv-plane and parallel to the ψT-plane are therefore falling curves with increasing values of T and v; the ψ-isotherms are convex to the Tv-plane, and the ψ-curves of constant volume are concave to the Tv-plane.

The conditions for a two-phase equilibrium are:

$$\left(\frac{d\psi_1}{dm}\right)_T = \left(\frac{d\psi_2}{dm}\right)_T \quad \text{or} \quad \left(\frac{d\psi_1}{dv}\right)_T = \left(\frac{d\psi_2}{dv}\right)_T.$$

[1] W. Nernst, *Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes.* 1918.

If the substance be divided into two phases the possibility of a double tangent to the ψ-isotherm touching the ψ-isotherm in two points will necessarily exist; these two points will correspond to the specific volumes of the two phases, v_2 and v_3 (Fig. 41). The ψ-values of the substance occurring in one phase are greater than the ψ-values lying upon the double tangent and therefore represent less stable states than those represented by points upon the double tangent. For the equilibrium of a liquid with its vapor the ψ-curve is to be considered as a continuous curve, somewhat as given in Fig. 41. For the equilibria in which at least one anisotropic phase takes part, the continuity of the ψ-curve has no significance. The ψ-values of heterogeneous states correspond to the points of the double tangent. If for a unit of mass of a substance the fraction x be present as phase 1, and the fraction $1 - x$ as phase 2, the mean specific ψ-value is given by $x\psi_2 + (1 - x)\psi_3$ and the mean specific volume by $xv_2 + (1 - x)v_3$.

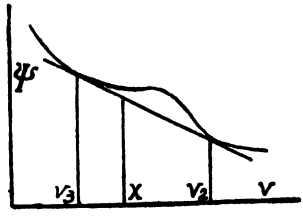


FIG. 41.

The two chief conditions of equilibrium, equality of temperature and of pressure in the two phases, are satisfied, for the ψ-curve is an isotherm and the pressure in both phases is the same since the tangent to the ψ-value of one phase again touches the ψ-curve, the second time at the ψ-value of the other phase.

The change in ψ at constant temperature is equal to $-pdv$, and consequently also to the external work furnished during the transformation of the mass dx from one phase into the other. Accordingly, v. HELMHOLZ has designated it as free energy.

The differentiation of

$$\psi_2 - \psi_3 = E_2 - E_3 - (\eta_2 - \eta_3)T$$

with respect to v at constant temperature gives us:

$$\left(\frac{d\psi_2}{dv}\right)_T - \left(\frac{d\psi_3}{dv}\right)_T = \frac{d_T(E_2 - E_3)}{dv} - \frac{d_T(\eta_2 - \eta_3)}{dv} \cdot T.$$

This equation is identical with the equation

$$A = U + \frac{dA}{dT}T,$$

used by NERNST.

A comparison of the members of the two equations will disclose that

$$A = \frac{d_T(\psi_2 - \psi_3)}{dv},$$

$$U = \frac{d_T(E_2 - E_3)}{dv},$$

$$\frac{dA}{dT} = -\frac{d_T(\eta_2 - \eta_3)}{dv}.$$

A, U, and dA/dT therefore, refer to the change of ψ, E, and η with the transformation of a quantity of a substance from one phase into another during which the volume changes by the volume unit. In order that two phases be in equilibrium, in accordance with the equilibrium conditions,

$$\frac{d_T(\psi_2 - \psi_3)}{dv} = 0,$$

and therefore when $p = 0$, $A = 0$; or for a finite value of p

$$A = p(v_2 - v_3).$$

At the absolute zero

$$\frac{d_T(\psi_2 - \psi_3)}{dv} = \frac{d_T(E_2 - E_3)}{dv}; \quad A = U$$

and to this the *Nernst Heat Theorem* adds, for the temperature $T = 0$,

$$\lim.\frac{dA}{dT} = \lim.\frac{dU}{dT} = 0,$$

or

$$-\frac{d_T(\eta_2 - \eta_3)}{dv} = \frac{d\left(\frac{d_T(E_2 - E_3)}{dv}\right)_v}{dT} = 0.$$

Upon the basis of this theorem, which is completely confirmed by experience, it is now possible to determine the unknown equilibrium temperature of two condensed phases.

If at constant pressure the volume difference of the two phases does not change noticeably with change in temperature it is permissible to introduce in the place of the differential quotients with respect to v, the differences

$$E_2 - E_3 = U \quad \text{and} \quad -(\eta_2 - \eta_3) = \frac{dA}{dT}.$$

The curve $U = f_v(T)$ can be calculated if U for a temperature T_1, and its quotient $\frac{dU}{dT} = c_2 - c_3$, be known. c_1 and c_2 indicate the specific heats at constant volume. If the U-curve be given, the curve $A = p_v(T)$ can be determined in the following way.[1]

From a point a upon the U-curve (Fig. 42) parallel lines are drawn to the T- and U- axes, and a straight line is drawn through the points of intersection b and c. This straight line is tangent to the A-curve. From Fig. 42 it may be seen that

$$\tan \beta = -\tan \alpha = -\frac{dA}{dT} = \frac{U - A}{T},$$

and that bc is a tangent to the A-curve. Proceeding from $T = 0$, at which $A = U$ and $\frac{dA}{dT} = \frac{dU}{dT}$, since the point c is always the point of intersection of tangents to the U-axis, as shown in the above case, a series of tangents is obtained with this construction defining the course of the A-curve. The point of intersection of the A-curve with the T-axis is the desired equilibrium temperature T_1 of the two phases at $p = 0$. At a finite value of p this point of intersection lies under the T-axis upon a curve removed from the temperature axis by distances equal to the work term $p(v_2 - v_1)$.

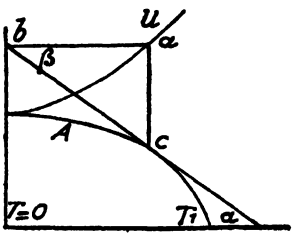


FIG. 42.

In special cases, where the U- and the A-curves are symmetrical with respect to the horizontal passing through the point of contact at $T = 0$, we have the relations.

$$U = U_{T=0} + \beta T^2$$
$$A = A_{T=0} - \beta T^2.$$

The difference of the specific heats of the two phases accordingly varies linearly with the temperature, $c_2 - c_3 = 2\beta T$, and since $\frac{dU}{dT} + c_2 - c_3 = 2\beta T$, for the equilibrium temperature T_2 we have

$$T_1(c_2 - c_3) = U_1.$$

[1] W. Nernst, *l. c.*, page 71.

At higher pressures, where $v_2 - v_3 > 0$, $\frac{d_T(E_2 - E_3)}{dv}$, or U is increased by the work of transformation; if $v_2 - v_3$ change its sign, these values will be diminished by the work done on transformation. At a pressure possessing two equilibrium temperatures the course of the U- and the A-curves would be that indicated in Fig. 43. At $T = 0$, A and U proceed from the same negative values. The A-curve has a maximum at the point where $\frac{dA}{dT} = 0$. At this point the two curves must of necessity intersect since here $A = U$ because $\frac{dA}{dT} = 0$. The two equilibrium temperatures, T_2 and T_1, are given by the point of intersection of the A-curve with a line running below the temperature axis at distances which are equal to the external work in calories.

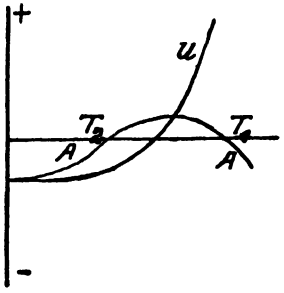


FIG. 43.

EQUILIBRIA IN CONDENSED SYSTEMS AT THE ABSOLUTE ZERO

For equilibrium in general we have

$$E_2 - E_3 = (\eta_2 - \eta_3)T - (v_2 - v_3)p.$$

In correspondence to the *Nernst Heat Theorem* at $T = 0$

$$(\eta_2 - \eta_3) = 0,$$

and accordingly

$$E_2 - E_3 = -(v_2 - v_3)p.$$

This equation has two solutions; since $v_2 - v_3$ changes its sign with increasing pressure the equilibrium pressures must likewise change in sign. $E_2 - E_3$ is regarded as independent of the pressure. If $v_2 - v_3$ be positive, p_1 will be negative, and if $v_2 - v_3$ be negative, p_2 will be positive.

According to the theorem already presented (Chapter IV, 5*b*), at $T = 0$ the surface *abc* and *cdf* must be equal (Fig. 44), so that if one equilibrium pressure be known the other may be determined. An estimation of p_2 upon the basis of the values of $E_2 - E_3$ and

$v_2 - v_3$ known for $p = 0$ is permissible only when the pressure at which the two volume isotherms intersect, $p\Delta v = 0$, is negative. In first approximation it may be assumed that the extrapolated value of $v_2 - v_3$ for $T = 0$ is independent of the pressure, and the estimation of p_2 is then possible. If, however, $p\Delta v = 0$ be positive, this approximation will lead to incorrect values of p_2. The approximation is permissible when $p\Delta v = 0$ is negaivte, the equilibrium curve running toward low temperatures with increasing pressure; it is not permissible if $p\Delta v = 0$ has a positive value, when the equilibrium curve would first go to higher temperatures with increasing pressure, and would then finally fall off.

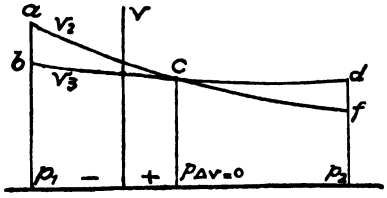


FIG. 44.

The direction of the equilibrium curves of condensed systems at $T = 0$ is given by the following rule, a result of the *Nernst Heat Theorem*. In general

$$\frac{dT}{dp} = \frac{v_2 - v_3}{\eta_2 - \eta_3}.$$

Since at $T = 0$, $\eta_2 - \eta_3 = 0$; $v_2 - v_3$, however, has a finite value so that at $T = 0, dT/dp = \infty$ and the equilibrium curves at $T = 0$ are then perpendicular to the p-axis.

The same thing is true for the isometric lines, since in the generally applicable expression

$$\left(\frac{dT}{dp}\right)_v = -\frac{\left(\frac{dv}{dp}\right)_T}{\left(\frac{dv}{dT}\right)_p}.$$

At $T = 0$, according to NERNST,[1] the isobaric expansibility has a zero value whereas the isothermal compressibility has a finite value.

8. ADIABATIC CHANGE IN STATE UPON THE EQUILIBRIUM CURVES OF CONDENSED SYSTEMS

A conception of the positions of the adiabatic curves of two phases in equilibrium with respect to their equilibrium curves is

[1] Nernst, *l. c.*, page 82.

given in the following discussion. A sudden increase in the pressure upon a two-phase system occurring in equilibrium, if the two adiabatics run more steeply towards higher temperatures than the equilibrium curves, will cause the temperature to enter the phase field of the phase stable at high temperatures; and if $\Delta v < 0$ the pressure increase will be followed by a rapid pressure decrease, as indicated by a sudden falling of the manometer indicator. This actually occurs upon the melting curve of ice and upon the transformation curve of hexagonal into regular AgI. If the adiabatics be flatter than the equilibrium curves and if $\Delta v = 0$, a similar retrogression will occur, though this case has never been found. In the other possible cases an initial pressure decrease would be obtained completing itself either more quickly or more slowly than the corresponding pressure decrease upon the equilibrium curve. Upon the observed curves of the pressure decrease with respect to time, however, no such difference is distinctly evident, and it is therefore probable that the direction of the two adiabatics absolutely or very nearly coincide with that of the equilibrium curve. We would then have

$$\frac{dT}{dp} = \left(\frac{dT_1}{dp}\right)_v = \left(\frac{dT_2}{dp}\right)_v,$$

or

$$\frac{\Delta v}{R_p} = \frac{1}{c_{1,\,p}}\left(\frac{dv_1}{dT}\right)_p = \frac{1}{c_{2,\,p}}\left(\frac{dv_2}{dT}\right)_p.$$

Of course, the observations with respect to the secondary pressure changes are not so accurate that this equation may be said to be absolutely correct. For if the two adiabatic quotients should deviate 10 per cent in dT/dp, the deviation would correspond to only 6 to 12 kg./cm.^{2} for a primary pressure increase of 300 kg./cm.^{2}, and since the secondary pressure changes are consummated more quickly in the beginning than afterwards, the deviations from each amount may be overlooked. For benzene, naphthalene, and *p*-xylene, rapid pressure changes are absorbed up to 500 kg. upon mixtures of crystal and melt at temperatures lying between the melting pressures 200–500 kg./cm.^{2}, and no retrograde motion is to be noticed on the part of the manometer indicator. No proof of the equation is possible on the basis of a direct determination of dv/dT, c_p, Δv, and R_p, because of the

difficulty attendant upon the experimental determination of the c_p-values.

When T_0 represents the equilibrium pressure, from the equation

$$\frac{\Delta v T_0}{R_p} = \frac{T_0}{c_{1,\,p}}\left(\frac{dv_1}{dT}\right)_p = \frac{T_0}{c_{2,\,p}}\left(\frac{dv_2}{dT}\right)_p,$$

we may obtain the relation

$$T_0\left(\frac{dv_1}{dT} - \frac{dv_2}{dT}\right)_p = \Delta v T_0 \frac{(c_{1,\,p} - c_{2,\,p})}{R_p}.$$

From this it follows if

$$T_0\left(\frac{dv_1}{dT} - \frac{dv_2}{dT}\right)_p = \Delta v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

that

$$T_0(c_{1,\,p} - c_{2,\,p}) = R_p. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental verification of equation (1) is more easily performed than that of equation (2), since changes in volume are easier to determine, and may be more accurately determined, than changes in heat content. The experimental testing of equation (1) has shown that for 36 substances the Δv-values calculated from equation (1) agree with the observed values with a maximum deviation of 10 per cent.

In the case of eight other substances, greater deviations were found, and the observed values were always smaller than the calculated.[1] Equation (1) is satisfied in an especially satisfactory way for the substances naphthalene and *p*-xylene, in which cases no reversals of the manometer reading were to be observed. The deviations are respectively 0.4, 1.6, and 4.0 per cent. For these substances, however, equation (2) will be confirmed to at least 10 per cent.

The testing of equation (2) with the values $c_{1,\,p}$ and $c_{2,\,p}$ as well as the latent heat of fusion, r_p, measured in heat units, can be performed in only a restricted way: the values introduced into the equation for $c_{1,\,p}$ are those determined from 20–50° above the melting point T_0, and those for $c_{2,\,p}$, 20–50° below T_0, since the presence of admixtures exerts such a great effect upon the specific heat values determined near the melting point, giving

[1] H. Block, *Z. phys. Chem.*, **78**, 387 (1911).

values much too great, that it is impossible to approach T_0 more closely. Tests have shown that with about half of the substances investigated an agreement within 20 per cent of equation (2) is obtained; greater deviations are found for the other half.[1]

Equations (1) and (2) are therefore only approximation formulas [2] that prove correct for a few substances, equation (1) proving more generally satisfactory than equation (2). In the case of higher melting substances, especially the silicates and borates, the specific heats at ordinary temperatures of the glassy and the crystalline states are only slightly different.[3] Ordinarily the difference $c_{1,\,p} - c_{2,\,p}$ decreases rapidly with temperature.

9. The Curvature of the Equilibrium Curves.[4]

By the help of the thermodynamic potential, the ζ-function, the equations for the two differential quotients of the equilibrium curves can be derived:

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta\eta}\left[\frac{d_T\Delta v}{dp} + 2\frac{d_p\Delta v}{dT}\left(\frac{dT}{dp}\right) - \frac{\Delta c_p}{T}\left(\frac{dT}{dp}\right)^2\right]. \quad . \quad . \quad (1)$$

$$\frac{d^2p}{dT^2} = -\frac{1}{\Delta v}\left[\frac{d_T\Delta v}{dp}\left(\frac{dp}{dT}\right)^2 + 2\frac{d_p\Delta v}{dT}\frac{dp}{dT} - \frac{\Delta c_p}{T}\right]. \quad . \quad . \quad (2)$$

$\Delta\eta$ is the entropy difference of the two phases and is equal to R_p/T, Δv and Δc_p are respectively the differences of the specific volumes and the specific heats of the two phases. (dT/dp) and (dp/dT) give the direction of the tangents to the equilibrium curve at the temperature T.

By differentiation of the equation

$$\frac{dT}{dp} = \frac{\Delta v}{\Delta\eta},$$

we obtain

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta\eta}\left[\frac{d_T\Delta v}{dp} + \frac{d_p\Delta v}{dT}\left(\frac{dT}{dp}\right) - \left(\frac{d_T\Delta\eta}{dp}\left(\frac{dT}{dp}\right) + \frac{\Delta c_p}{T}\left(\frac{dT}{dp}\right)^2\right)\right]. \quad (3)$$

which, however, is less suited for our needs than equations (1) and (2).

[1] *Kristallisieren und Schmelzen*, Table on page 45.
[2] Nernst, *l. c.*, pages 86 and 87.
[3] *Kristallisieren und Schmelzen*, Table on page 57.
[4] *Göttinger Nachrichten*, 1915. Pages 59–69.

By the introduction of dT/dp or d^2p/dT^2 into the known equations the radius of curvature of the equilibrium curve at every point can be calculated.

The sign of d^2t/dp^2 or of d^2p/dT^2 determines the nature of the curvature. If the sign be positive, the curve will be bent convexly to the p- or T-axis; if negatively, concavely.

If dT/dp pass through a zero value, the same will also be true for Δv, and at this point

$$\frac{d^2T}{dp^2} = \frac{1}{\Delta\eta}\frac{d_p\Delta v}{dp}.$$

If dT/dp pass through a zero value, $\Delta\eta$ will likewise pass through a zero value and then

$$\frac{d^2p}{dT^2} = \frac{1}{\Delta v}\frac{\Delta c_p}{T}.$$

The application of equations (1) and (2) to the different kinds of equilibrium curves results as follows:

1. At the critical point, the end of the vapor pressure curve, dT/dp has an indeterminate value, $dT/dp = \frac{0}{0}$, and since the expressions $d_T\Delta v/dp$, $dp\Delta v/dT$, $\Delta c_p/T$ here disappear, d^2T/dp^2 likewise has an indeterminate value, $\frac{0}{0}$, as follows from (1). The critical point is therefore the end of the vapor pressure curve.

2. For the melting curve we have the following:

From the change in sign of the member $2\frac{d_p\Delta v}{dT}\left(\frac{dT}{dp}\right)$ at the maximum upon the melting curve, it follows that the melting curve in the neighborhood of the maximum is not symmetrical to the perpendicular to the p-axis that runs through the maximum. In the second quadrant, the melting curve is curved more steeply with respect to this vertical line than in the first quadrant, for the reason that whereas in the first quadrant the positive member $2\frac{d_p\Delta v}{dT}\left(\frac{dT}{dp}\right)$ diminishes the negative value of d^2T/dp^2, in the second quadrant, when the member itself has become negative, the negative value of d^2T/dp^2 is increased. The

course of the melting curve of $Na_2SO_4 \cdot 10H_2O$ has confirmed this conclusion.

MAXIMAL MELTING POINT AT 32.83° AND 500 kg./cm.²

Equilibrium Pressure	Pressure in the First Quadrant	Pressure in the Second Quadrant
32 80°	+350	600
32 75°	+150	735
32.70°	1	780

The differences of the two equilibrium pressures from the pressure of the maximal melting point are:

32 80°	+150	−100
32 75°	+350	−235
32 70°	+499	−280

If the melting curve were to run symmetrically with respect to the vertical line at its maximum, the differences at the same temperature would be equal with opposite signs. It may be seen from the figures that in the second quadrant the equilibrium temperature decreases more rapidly with equal pressure increments than is the case in the first quadrant. The same thing has been found true for the transformation curve of red into yellow HgI_2. (See VII, 12, page 187.)

3. An analogous relation also holds for the course of the transformation curve in the neighborhood of the point at which $R_p/T = \Delta\eta$ passes through zero.

As long as dp/dT is positive, the term $2\frac{d_p\Delta v}{dT}\left(\frac{dp}{dT}\right)$ of equation (2) will remain negative; according as dp/dT is negative, the term will be positive. This member is affected by the negative character of $\Delta\eta$ in that the negative value of d^2p/dT^2 and the curvature of the curves are diminished. In fact, the curve of transformation of Ice I and Ice III rises with decreasing temperature more rapidly at higher pressures than it falls at lower pressures.

V. THE MELTING CURVE

1. Methods for the Determination of the Coordinates of the Equilibrium Curves

In Chapter IV, 3, we saw that properties divide themselves into two classes according to their behavior during a change in state; one portion of them changes discontinuously, and the other continuously. In the latter case points of inflection occur upon the isobars or isotherms at the point of change in state. The methods of practical value for the determination of the coordinates of the equilibrium curves intersected, make use almost exclusively of the properties that change discontinuously.

The vapor pressure curve and the sublimation curve may be determined by two methods, the static and the dynamic. The static method consists in the determination of the equilibrium pressure at constant temperature. In this determination it is necessary that both phases of the substance be present, a condition easily ascertained if the substance be contained in an apparatus made of glass. The dynamic method consists in determining the temperature of boiling at constant pressure. Both of these methods are founded upon the fact that during a change in the volume or in the heat content of one of two phases in a one-component system, for each T-value there is a definite value of p, and that during the transformation of the one phase into the other the volume and the heat content vary discontinuously.

In the determination of melting curves and of transformation curves, however, it is necessary to use very strong and therefore opaque vessels if the curves are to be determined over a wide pressure range. The most important methods make use of the discontinuous change of volume occurring when one phase is transformed into another. On the other hand, the discontinuous change in heat content may likewise be employed. Attempts have been made by Amagat [1] and Wahl [2] to observe the process

[1] *Compt. rend.*, **105**, 165 (1887).
[2] *Z. phys. Chem.*, **83**, 708 (1913).

of melting and crystallization through a glass window in the steel vessel, but these have been of little practical importance; such an apparatus can be constructed to withstand a pressure of 2000 kg./cm.^{2} [1]

The determination of the pressure-temperature coordinates by observation of the change in volume occurring during melting may be carried out in two ways: (1) by observing the change in pressure caused by an arbitrary change in temperature (at nearly constant volume), (2) by observing the change in pressure produced in consequence of melting or crystallization by an arbitrary change in pressure upon a mixture of solid and liquid in equilibrium (at constant temperature). The first method is applied as follows. The substance enclosed in a steel cylinder is placed in a suitable bath, the temperature of which can be raised with nearly constant velocity, and the pressure upon the substance is measured by means of a manometer. This method, known as the pT-curve method, is better suited than the second to give a survey over a large field. Since the temperature of the substance will not generally correspond to the temperature of the bath, the method is of value only in determining the orientation of the curve. It may be made more precise by decreasing this temperature difference, which may be done by diminishing the velocity at which the bath is warmed, and by diminishing the quantity of substance used. The method is to be recommended for the first orientation of the curve, especially at temperatures over 100° and under 0°, and also in cases where the volume change is small. It has the advantage of giving values for the volume changes besides furnishing the coordinates of the melting curve.

Upon the typical pT-curve given in Fig. 45 it may be seen that the pressure changes along line ab, as long as the whole mass is crystallized. When melting begins, the increase in pressure accelerates with temperature increase. When the temperature increase is sufficiently slow, the pT-curve at the moment of complete melting almost reaches the melting curve of the pure substance, ec; from here the pressure increases much more slowly along the line cd. The pressure change brought about by melting, Δp_T, can easily be found by prolonging ab and drawing a line parallel to the p-axis through c. The line lc is then the pressure change required, Δp_T.

[1] W. Wahl, *loc. cit.*

The volume change accompanying the pressure increase Δp_T can be determined by connecting the vessel containing the substance to a cylinder in which the pressure may be increased Δp_T by the action of a tightly fitting piston. If the displacement of the piston per 1 kg. increase in pressure amount to $\Delta s/\Delta p$ and if q be the cross-section of the piston, the volume change will be

$$\Delta v_T = \Delta p_T \frac{\Delta s}{\Delta p} \cdot q.$$

This Δv_T does not hold for constant pressure, but for a pressure which during melting increases from $p_1 - \Delta p_T$ to p_1, differing, therefore, from the $\Delta v p_T$, in the *Clausius-Clapeyron* equation. Between these two values we have the following relation:

$$\Delta v_{p,\,T} = \Delta v_T - \Delta p_T \frac{d_T v''}{dp},$$

where $d_T v''/dp$ represents the compressibility of the melt for which an approximate value may be introduced.

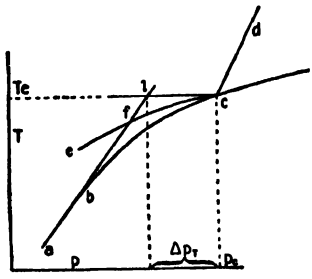


FIG. 45.

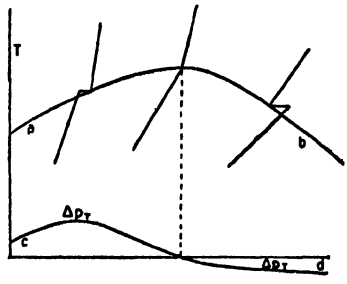


FIG. 46.

The application of this method to the determination of the course of an equilibrium curve in the neighborhood of its maximal temperature is illustrated by Fig. 46 in which *ab* is the equilibrium curve. The pT-lines are represented by the middle portions which are found by construction. The Δp_T section disappears in the pT-line that passes through the maximum upon the equilibrium curve; the direction of the pT-line before melting, however, is different from that after melting. The line *cd* gives the dependence of the pT-values upon the pressure.

In the second method the work is carried out at constant bath-temperature. The temperature upon the crystalline substance is

raised into the neighborhood of the melting curve and is melted in order to weaken as far as possible the influence of small quantities of admixture. At this point a definite pressure is automatically set up which corresponds to the equilibrium pressure at the temperature concerned. If insufficient time be allowed for the equalizing of the temperature of the substance and the temperature of the bath, the temperature of the substance, conditioned by the melting, will not agree with the temperature of the bath. In order to include the equilibrium pressure between two limiting pressures upon melting and crystallization, the pressure is raised and by repetition of the arbitrary pressure changes, but in decreasing amounts, it is possible to arrive at end-pressures by a pressure increase or a pressure decrease, which differ by only a few kilograms. Figure 47 illustrates this method for the determination of the equilibrium pressures for carbon dioxide and naphthalene. This method is especially suited for the accurate determination of the coordinates of the equilibrium curves; BRIDGMAN has applied it up to pressures of 12,000 kg./cm.^{2}

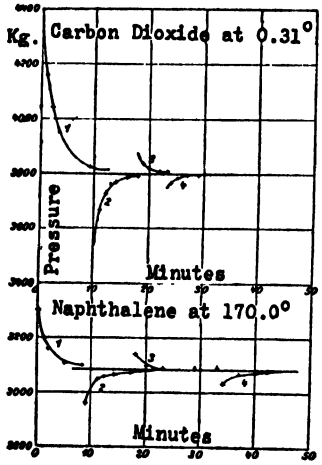


FIG. 47.

If the maximal linear crystallization velocity lie under 1 mm./sec., many substances with little supercooling crystallize so slowly that the method will no longer be practicable. In these cases the method of the pT-curves best gives the course of the melting curve, though the coordinates in such a determination are easily displaced a few tenths of a degree towards higher temperatures if the velocity of heating be not very low.

When the volume changes are very small (in the neighborhood of the maximal melting temperature) it is possible directly to measure the temperature of the mixture of crystal and melt by introducing a thermocouple. The experimental arrangement is shown in Fig. 48. The conical pieces *a* and *b*, made of the same material as the wires in the thermocouple, pierce the ebonite cone *c*.

The plug *dddd* is pressed against the support *ee* by means of a screw. When one junction of the thermocouple is immersed in partly molten Glauber's salt within the pressure cylinder, and the other junction likewise immersed in partly molten Glauber's salt at a pressure of 1 kg., an increase in pressure in the cylinder will set up a thermoelectric current, indicating that the temperature of the compressed Glauber's salt is higher than that of the uncompressed. However, when the pressure exceeds 500–600 kg., the temperature of the compressed Glauber's salt begins to fall, and sinks at 3000 kg./cm.^{2} to about 2° below that of the salt at 1 kg. This temperature behavior is likewise shown when the pressure is increased to 3000 kg. in the course of a minute. It is therefore evident that the equilibrium between crystal and melt sets in very quickly. Within the limits of error peculiar to it, this method gives the same results as the other methods.

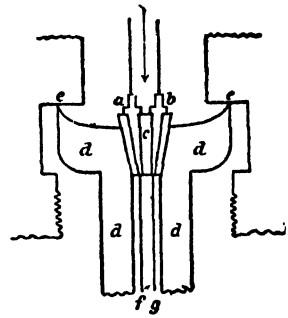


FIG. 48.

A fourth method, suitable for demonstration experiments, has been applied by MOUSSON [1] and also by the author.[2] The experiments by the author have been more systematically conceived, and have been carried out to 10,000 kg./cm.^{2} This method depends upon the fact that a solid body previously frozen within the substance to be investigated becomes mobile when the substance is melted, and upon tipping the cylinder the impact of the solid body against the wall of the steel cylinder can be heard. The results of these investigations show that the curvature of the melting curves is much less above 4000 kg. than below it. This result has also been obtained by the more accurate measurements of BRIDGMAN made above 4000 kg.

a. Determination of Melting Points at Ordinary Pressures

The melting point is the temperature at which under ordinary external pressure (1 kg./cm.^{2}) the crystal of a chemical substance is in equilibrium with its melt. This point of importance in

[1] *Pogg. Ann.*, **105** (1858), 105.

[2] *Kristallisieren und Schmelzen*, 1903, page 92 and the following.

practice differs from the triple-point, and ordinarily lies about 0.02° above the triple-point. With water and bismuth it lies a little lower than the triple-point, and in the case of water by about 0.0086°.

The most frequently used method for the determination of the melting point depends upon the change in viscosity produced by melting, and the method is used for the identification of various easily fusible preparations. Two experimental procedures are used; a few crystals are placed in a small tube fastened to a thermometer and are heated while the bath is stirred; or a drop of the melt is introduced into a capillary tube which is then closed at the end that did not come into contact with the melt, and the subsequent procedure is similar to that observed in the first method. When the substance is remelted as a consequence of the rising temperature of the bath, the expanding air enclosed between the closed end of the tube and the droplet of melt causes the droplet to be forced upward in the tube. According to H. LANDOLT [1] these methods give melting points that vary by a few tenths of a degree and that are higher than the results obtained when the melting point is determined directly in a mixture of crystal and melt (at least 20 gms.) upon the addition or subtraction of heat.

For the determination of the melting point at higher temperatures, for which it is difficult to construct a suitable transparent bath and with which the bodies measured begin to give off light making it difficult to recognize any changes taking place, the method commonly used is the cooling-curve method. This method is based upon the discontinuous change of the heat content upon melting (or upon crystallization). At the beginning of crystallization during cooling the heat of fusion of the melt is set free, and for a time arrests the fall in temperature. A suitable thermometric apparatus is introduced into the melt and the temperature is read at equal time intervals. Curve 1, Fig. 49, is a cooling curve and curve 2 is a heating curve, both made upon the same substance. If the thermal conductivity of the thermometric apparatus be good and the cooling and heating velocities not too great, the points of arrest upon both curves will lie at the same temperature, otherwise they will lie at two different temperatures. The form of the cooling curve is not wholly the same as that of the heating curve, for the conditions existing during crystallization

[1] *Z. phys. Chem.*, **4**, 389 (1889).

are not the same as those existing during melting. To the portion of the cooling curve parallel to the time axis (of unchanging temperature) a section of curve bent concavely towards the time axis is attached at the point of inflection by means of a small piece bent convexly towards the time axis. This is due to the fact that crusts of the crystallizing substance form on the thermometer and the crucible walls, so that during the process of crystallization the liquid-crystal interface moves away from the thermometer. Accordingly, the temperature read on the thermometer begins to sink before all has become crystalline. The last portion of the melt crystallizes at the turning point, from which point the cooling proceeds in the normal way. If this latter portion of the curve be prolonged until it intersects the prolongation of the horizontal section, the distance of the point of intersection from the point representing the beginning of crystallization gives the time required for crystallization, a measure of the heat of fusion.

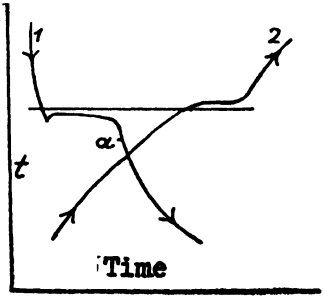


FIG. 49.

A comparison of these durations of arrest for substances of approximately equal melting points will furnish a quantitative measure of the heats of fusion, providing that the cooling curves be made upon equal quantities of the substance under similar cooling conditions.

If undercooling take place, the cooling curve will first sink below the temperature of the melting point, and when crystallization begins, will rise to temperature of the melting point, and remain there for a time (curve 1, Fig. 49). To have this case occur, the crystallization velocity must not be too small and the velocity of cooling must not be too great. If the maximal linear crystallization velocity sink below 3–4 mm. per minute, the velocity of the heat development will be insufficient, under a normal velocity of cooling, to raise the temperature to that of the melting point, and instead of a temperature horizontal a temperature maximum will be formed, the temperature of which will always lie below that of the melting point. Upon the heating curve (2, Fig. 49) there is naturally no evidence of undercooling.

Supercooling occurs so regularly that many substances can be recognized by the form of the cooling curves, by the temperature of arrest, and by the duration of the arrest.

If the linear crystallization velocity at the melting point be especially small, as in the case of substances the maximal C. V. of which lies below 2 mm. per minute, it is possible that a retardation of the velocity of cooling as a result of crystallization may not occur, or may be removed to a position far below the actual melting point. Upon the heating curve the retardation may lie at a temperature noticeably higher than the melting point. The determination of the true equilibrium temperature by the use of heating and cooling curves is therefore impossible. Other methods are selected in preference (see the chapter on the overheating of crystals).

2. The Determination of the Volume Change upon Melting

The determination of the volume isobar for a unit mass of a substance the pressure upon which is greater than that of the triple-point discloses a discontinuous change in volume upon the

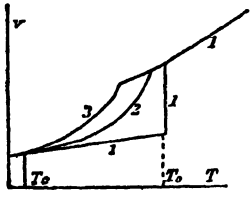


Fig. 50.

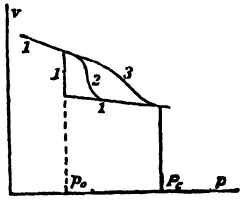


Fig. 51.

curve at the melting point. The same is true for the volume isotherm at the melting pressure. Actual substances show deviations from this simple ideal case because of the presence of admixtures which tend to lower the melting temperature and to raise the melting pressure, causing the volume change upon melting to become a continuous one.

In Figs. 50 and 51 the isobars 1, 2, and 3 and the isotherms 1, 2, and 3 represent the process of melting of a crystalline substance containing different percentages of admixture. The curves 1 refer to an ideally pure substance, the curves 2 and 3 to the same substance with increasing amount of admixture.

The isobars and isotherms of the pure liquid coincide in these diagrams with those of the liquids containing small amounts of admixture, because the difference in their ordinates disappears in comparison to the great volume change upon melting. The expansion coefficients, $d_p v'/dT$ and the compressibilities, $d_T v'/dp$, of the liquids are influenced only slightly by small amounts of admixture. On the other hand, if the admixture be insoluble in the crystal, the relations are wholly different. In this case the crystal present in excess crystallizes first, and the temperature falls slowly as the concentration of the admixture increases until the amount of liquid becomes small (invisible between the crystals), when the temperature sinks more rapidly to the eutectic point c. At temperatures below the eutectic point the coefficient of expansion $d_p v''/dT$ with small admixtures becomes only slightly different from the true $d_p v'/dT$ of the pure crystallized substance, and at pressures above the eutectic point, the same is true of the compressibility. In the melting range (T_c, T_0) and (p_c, p_0), however, the expansion coefficients and the compressibilities of the crystallized substance have values too great, because there is included in them the volume increase upon the melting of a portion of the crystals and the formation of a solution. Experiment has shown that the smaller the amount of arbitrarily added admixture, or the purer the substance has become by repeated recrystallization, the more steeply run the isobars and the isotherms during the melting. Finally the melting of the absolutely pure substance takes place without an unusual increase in the quotients $d_p v''/dT$ and $d_T v''/dp$ of the substance falsely taken for completely crystallized. The behavior of such a substance is represented by the isotherms and isobars 1; these show the sharp discontinuity of the volume change on melting.

Completely analogous relations are to be found in heat surfaces representing the quantities of heat related to the heating of a unit of mass of a substance under constant pressure with the performance of external work. It is necessary merely to substitute in the two former diagrams the heat-quantity Q_p for the volume v, obtaining for $d_p v/dT$ the quotient $d_p Q/dT$ which is equal to c_p the specific heat at constant pressure, and for $d_T v/dp$ the quotient $d_T Q_p/dp$. The change in heat content here is likewise discontinuous; the heat absorbed during melting, which is the heat of fusion r_p, is taken up at a constant temperature in the

case of a chemically homogeneous mass, and the specific heat of the solid, c''_p, for such a chemically homogeneous substance increases normally up to the temperature of the melting point. On the other hand, in case the substance be not chemically homogeneous, containing foreign material tending to lower the point of incipient crystallization, the specific heat measured to the temperature of the melting point of the pure solid will be considerable in error because of the inclusion at the temperatures near to the melting point of the heat of fusion. The heat of fusion is often a hundred times as large as c''_p and the amount of error introduced in this way may be considerable; too great a specific heat is found, and too small a heat of fusion. This is shown by measurements by L. BRUNNER,[1] in which the values found for c''_p, the specific heat of the crystal, for a few substances were greater than those found for the melt; further investigation by A. BOGOJAWLENSKI showed that this anomalous behavior disappeared upon further purification of the melt.

This lack of attention to the chemical homogeneity of substances investigated has given rise to many errors concerning the volume and energy changes on melting and as a result the conceptions of the processes of melting and crystallization have unfortunately been much confused.

In fact these errors have led to a belief in a continuity between solid and liquid, similar to that between liquid and vapor, and in many text-books volume isobars of substances doubtless chemically inhomogeneous have been given as typical for chemically homogeneous substances. This, of course, is unfortunate, and it is to be emphasized that any continuity must be due to chemical heterogeneity, and that all observations point to the fact that with chemically homogeneous substances a sharp discontinuity always occurs, not only upon the volume-surface, but also upon the surface of all other properties.

Curves like the isobars 3 (Figs. 50 and 51) would give the impression of continuity with melting if it were not precisely stated that in such cases the crystalline solid and the melt are not in equilibrium at a definite temperature but through a temperature interval, and that in the melting range $T_c - T_0$ the quantity of the melt varies considerably and consequently the concentration of the admixture in solution also.

[1] *Berichte der Deutschen chem. Ges. zu Berlin*, **27**, 2102 (1894).

a. The Elimination of the Effect of Admixture upon the Melting Point

The presence of admixtures not only makes more difficult the accurate determination of the form and the position of the volume- and heat-surfaces, together with the dependent quantities, Δv, r_p, $d_p v''/dT$, $d_T v''/dp$, and c''_p, but it also exerts an influence upon the coordinates of the melting curves that makes an accurate determination of them very difficult. The influence of admixtures changes the melting *point* of a chemically homogeneous substance into a melting *interval*, and similarly changes the melting pressure into an interval of melting pressure.

It is well known that melting points given in the literature for one and the same substance frequently differ from each other to an extent greater than would be expected from the thermometric accuracy of the methods used. The highest of these points corresponds to the melting point of the purest substance, provided that the impurity does not form solid solutions with the substance the melting point of which is measured. It is possible in the following way, however, to obtain the correct melting point of a substance containing admixture.

The interval between the prolonged isobar v'' (Fig. 52) of the crystalline solid and the isobar v' of the melt reproduces with sufficient accuracy in the neighborhood of the true melting temperature, t_0, the volume change on melting, Δv_0, of the pure substance. The intervals between the portion of the curve referring to a mixture of crystal and melt and the produced isobar of the crystalline solid are proportional to the quantity of melt. It follows for the lowerings of the freezing point, $t_0 - t_1$, that the concentrations of the solutions in equilibrium with the crystalline solid are $x\frac{\Delta v_0}{\Delta v_1}$ and $x\frac{\Delta v_0}{\Delta v_2}$, if x represents the concentration in gram-molecules of the admixture in the total quantity of material. If the freezing point lowering be proportional to the concentration, then

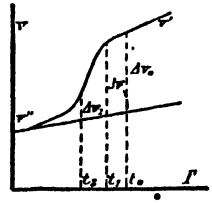


FIG. 52.

$$\frac{t_0 - t_1}{x\frac{\Delta v_0}{\Delta v_1}} = \frac{t_0 - t_2}{x\frac{\Delta v_0}{\Delta v_2}},$$

and

$$t_0 = \frac{t_1 \Delta v_1 - t_2 \Delta v_2}{\Delta v_1 - \Delta v_2}.$$

For such a determination a dilatometer is used (Fig. 53), the scale portion of which amounts to no more than 0.01 to 0.005 of the total volume. The dilatometer is filled with mercury and the substance to be investigated, as shown in the figure, and is then immersed with a sensitive thermometer in a bath and slowly heated. Six points are obtained on the volume curve: two when the substance is completely molten, two when completely solid, and two when the solid substance is in equilibrium with its melt. Stirring for the purpose of insuring equilibrium is accomplished by a tilting of the dilatometer, which causes the mercury to move and to stir the mixture thoroughly. The temperature is brought to constancy several times. The escape of the melt into the side tube is prevented by a bundle of iron wire which is forced into the neck a of the dilatometer tube. The value of Δv expressed in scale divisions may be introduced into the calculation. For the determination of Δv_1 and Δv_2 two temperatures are chosen in such a way that at the one the charge is half melted and at the other almost completely melted. From the difference $t_0 - t_1$ the quantity of admixture may be calculated in gram-molecules from the formula of RAOULT-VAN'T HOFF. As shown by the work of V. SSOBOLEWA [2] the true melting point for the ideally pure substance may be obtained in this way with an error of only $\pm 0.1°$ from observations upon a commercial product, or upon a preparation containing an intentionally added impurity.

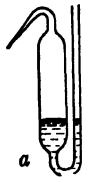


FIG. 53.

Melting point determinations at higher pressures refer always to the same ratio of crystal and melt. Inasmuch as commercial preparations frequently give melting intervals of 2°, corresponding to an interval in melting pressure of 100–400 kg./cm.^{2}, it is necessary to melt at least half of the material for the determination of the melting pressure at constant temperature in order that the determination be made as free as possible from the great influence exerted by admixtures upon small quantities of melt. If two determinations be made, one with the charge half melted and the

[1] V. Ssobolewa. *Z. phys. Chem.*, **42**, 75 (1903).

other three-quarters melted, the difference between the values obtained will be an indication of the influence of the impurity present upon the melting pressure.

If the pressure be lowered upon a crystallized substance containing impurity, an opposing increase in pressure, caused by an increase in volume on melting, will occur at a pressure higher than is the case with a pure substance. This is a very safe and very sensitive criterion for the homogeneity of a preparation. It is frequently difficult to procure a preparation of a substance the melting pressures of which differ by only 10–20 kg. between determinations made upon a mixture containing $\frac{1}{10}$ melt and a mixture containing $\frac{9}{10}$ melt.

It may be seen that in the case of a chemically inhomogeneous substance not one melting curve is concerned, but a host of them, corresponding to different partitions of the total quantity of material between the liquid and the solid phases. It is clear that if points on these different melting curves be regarded as belonging to a single curve, regardless of the amount of melt, a wholly erroneous conclusion will be obtained regarding the form of the true melting curve.

b. The Determination of the Volume Change on Melting at a Pressure of $p = 1$ kg./cm.^{2}

One of the chief difficulties attendant upon the accurate determination of the Δv-value is the formation of empty spaces between crystallites during crystallization. This difficulty has troubled all investigators that have made the determinations by means of a dilatometer. In order to avoid it a method was evolved that depended upon the fact that substances crystallizing very slowly near to the melting point in tubes 1.5 mm. inside diameter, crystallize in the form of crystal filaments which completely fill the interior of the tube.

In an actual determination of this kind it was found that the boundary between the crystal filament and its melt moved towards the upper open end of the tube a distance of 10 cm. during a period of twenty-four hours. The non-isomorphous impurities present in the melt were thus forced to the upper end of the tube and in consequence the crystallization of the last portions was greatly retarded by the lowering of the freezing point. When

such a retardation occurs the remainder of the melt may be removed from the tube. By repetition of this very slow crystallization it is possible to purify the substance very nearly completely and to obtain a reliable value for the volume of the crystal thread at a temperature very near to the melting point. A few further points upon the volume isobar of the crystal may then be determined by the suspension method, in which the substance is suspended in a liquid in which it is not soluble. The volume isobar of the melt is determined by the dilatometric method. The two isobars are thus obtained, and the distance between them at the melting point is equal to the value for Δv per one gram of substance. H. Block [1] has used this method for the determination of the Δv-values of about thirty substances the melting points of which lie between 30° and 100°.

c. The Determination of the Volume Change at High Pressures

The author has devised the following method for the determination of Δv at high pressures. A cylinder with a tightly fitting piston is connected with a steel cylinder which contains the substance brought from its original conditions of temperature and pressure to a point beneath and close to the melting curve, but not permitted to melt. When the pressure read from the manometer remains constant and when the bath-temperature changes no more the position of the piston is read upon a scale fixed to the cylinder. The piston is then drawn out a short distance, causing the melting to take place with rise in pressure. After the substance is completely molten (which can be easily ascertained) the pressure is brought back to the original value and the total displacement Δs of the piston determined. In order to eliminate the effect of the loss of the pressure-transmitting oil between the piston and the cylinder the determination of Δs made upon the melting of the substance is checked against the determination made upon crystallizing. If in both cases the filtration losses be the same, the mean of the two Δs-values gives the true value exclusive of loss. With a cross-section of the piston given in q square centimeters, the volume change in melting will be $\Delta s \cdot q$, which may be reduced to apply to one gram of substance. An ebonite piston screwed into a steel rod with a diameter of 0.5 cm.[2] may be forced

[1] *Z. phys. Chem.*, **78**, 385 (1912).

by means of a turning lathe into the steel cylinder and pressures of 3000 kg./cm.^{2} produced. BRIDGMAN has applied the same method to obtain pressures of 12,000 kg./cm.^{2} using a piston of the form given in Fig. 54. The piston P is 10 cm. long, has a diameter of 1.3 cm., and is made of hardened chromium-nickel-steel. It is pressed upon the ring R of the same material, which in turn is pressed upon the ring C of the soft steel under which lies the packing B of gum. By means of this contrivance, a high pressure is exerted upon a unit of surface of the front of the pistonhead A. This is a very considerable improvement over the older apparatus.[1]

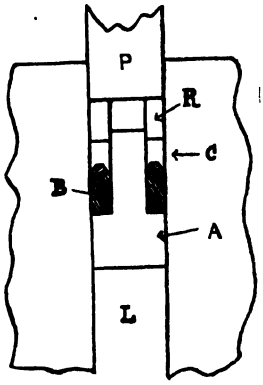


FIG. 54.

BRIDGMAN measured pressure by the resistance change produced in a wire the one end of which made electrical connection to the pressure-tight cylinder and the other to an insulated wire passing through the walls of the cylinder.

A pressure of 1000 kg./cm.^{2} was first produced in the pressure-tight steel cylinder by means of an auxiliary pump and at one stroke of the piston the highest working pressure of 12,000 kg./cm.^{2} was reached. The piston was driven into the cylinder by means of an hydraulic press, and during its progress it cut off the lateral hole through which the liquid had been introduced for the production of the initial 1000 kg./cm.^{2} pressure.

3. THE DETERMINATION OF THE HEAT OF FUSION

The determination of the heat of fusion at ordinary pressures is commonly carried out in the following way. The melt is cooled in a calorimeter and the heat given to the calorimeter is (1) the heat content of the melt from the initial temperature to that of the melting point, (2) the heat of crystallization, which is equal to the heat of fusion with opposite sign, and (3) the heat content of the crystalline substance from the melting point to the tem-

[1] Bridgman, *Proc. Amer. Acad.*, **49**, 627 (1914). Complete description of the stoppers, of the use of insulated wires, and of other improvements may be found in this paper.

perature of the calorimeter. It is evident, therefore, that in order to calculate the heat of fusion it is necessary to determine the mean specific heat of the liquid and of the crystalline solid. With the calculation made, r_p at the melting point at $p = 1$ kg. is obtained in cal./gm. In this case, likewise, it is necessary to be very careful of the presence of impurities, and when they are present, of the temperature to which the crystals are heated for the determination of specific heat, for if this temperature were chosen too near the melting point it is possible that a portion of the heat of fusion of the impure substance should be included in the specific heat, rendering the specific heat too great and the subsequently calculated heat of crystallization correspondingly too small.

O. PETTERSON has devised an excellent method for the determination of the heat of crystallization at temperatures near to the melting point.[1] The substance in thin-walled glass tubes is brought in an undercooled condition into a mercury calorimeter, and after heat equilibrium is established the melt is inoculated. If the heat of crystallization be large the heat set free upon inoculation will be quickly shared with the mercury calorimeter, and with considerable undercooling there is no danger of a residue of uncrystallized substance. Repetition of the determination at several calorimeter temperatures will give the dependence of the heat of fusion upon the temperature, and r_p can then be extrapolated to the melting point. The specific heat of the crystalline solid enters only as a trifling correction factor. By means of a suitable vapor bath the temperature of the mercury calorimeter can be changed at will.

The only direct determination of the heat of fusion at higher pressures has been made for benzene at 2000 kg./cm.^{2} by the author.[2] The crystalline substance enclosed in the lightest possible steel cylinder was introduced into a calorimeter and melted by a lowering of the pressure.

The chief method for the determination of the heat of fusion at high pressures is an indirect one. If the coordinates of the melting curve and the Δv-values be determined, R_p, the heat of fusion in mechanical units (kg. cm. per one gram of substance)

[1] *Berl. Ber.*, 1879, page 1718.

[2] *Kristallisieren und Schmelzen*, 1903, page 209; also *Ann. d. Phys.* 3, 165 (1900).

can be determined in the following way. If the values of Δv and T in the equation $\frac{dT}{dp} = \frac{\Delta v T}{R_p}$ be known and if the values of $\frac{dT}{dp}$ upon the melting curve for different values of T can be determined either by means of an interpolation formula in good agreement with the determined coordinate of the melting curve, or by means of geometrical construction, the value for R_p can be calculated. In order to determine $\frac{dT}{dp}$ graphically a chord is drawn to the melting curve tangent at the T-value desired, and the $\frac{dT}{dp}$-value read from the coordinate axes. With the appropriate Δv-value introduced into the equation, the value of R_p may be calculated. This method gives values for the heat of fusion that are more accurate than those determined directly.

4. The Coordinates of the Melting Curve

The first determinations of the direction of the melting curve at the triple-point were made by R. Bunsen,[1] W. Thomsen,[2] Hopkins,[3] Ferche,[4] and Visser.[5] These investigators tested qualitatively and quantitatively the requirement of the equation of Clausius-Clapeyron, that the melting point of a substance melting with volume increase should be raised by an increase in pressure, and conversely that the melting point of a substance melting with volume decrease (ice) should be lowered by an increase in pressure. After the development of the experimental technic for working at high pressures, Amagat[6] and Barus[7] succeeded in following the melting curve to pressures over 1000 kg./cm.^{2} Amagat observed the crystallization of CCl_4 through a glass window in a steel cylinder, and Barus determined the volume changes upon the melting of naphthalene. Barus proceeded in the following way, using a dilatometer of the form

[1] Pogg. Ann., **81**, 153 (1850).
[2] Pogg. Ann., **81**, 163 (1850).
[3] Athenaeum, 1854, 1207.
[4] Wied. Ann., **44**, 265 (1891).
[5] Rec. Pays-Bas., **12**, 101 (1893).
[6] *Compt. rend.*, **105**, 165 (1887).
[7] *Bull. Geol. Survey*, **96** (1892).

given in Fig. 55. The substance was placed in the annular space above the mercury, and in the inner tube above the mercury meniscus was placed a $ZnSO_4$ solution into which dipped a Zn-electrode. The wires *d* and *b* were led through the walls of the steel cylinder in which the dilatometer was placed. From the electrical resistance the position of the mercury meniscus could be obtained and the volume of the substance investigated could be calculated.

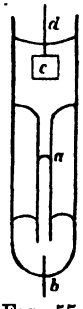


FIG. 55.

DAMIEN [3] and DEMERLIAC [4] have reported results which are impossible, and the errors in their work have been pointed out in a previous publication.[5] The author determined the course of the melting curves of about 40 substances up to 3000 kg./cm.^{2}, the coordinates of which were summarized in *Kristallisieren und Schmelzen*, published in 1903. These results in the greater part can be reproduced by means of an interpolation formula, $\Delta t = ap - bp^2$ in which Δt represents the melting point increase belonging to the pressure p.

Collectively, the melting curves curve in the expected manner, namely, concavely to the p-axis. The Δv-values were determined according to the described methods, and the very considerable decrease of Δv with increasing temperature likewise determined. By direct determination of the melting curve of benzene at 2000 kg./cm.^{2} it was found that R_p does not change noticeably upon the melting curve, and indirect determination according to the equation $dT/dp = \frac{\Delta vT}{R_p}$ led to the same result. For the determination of the Δv-values for the p- and T-values of the melting curves, the following interpolation formulas were employed:

$$\log \Delta v = \log \Delta v_{p=0} - ap,$$

$$\Delta v = \alpha - \beta(T - T_0),$$

$$\Delta v \cdot T = A - B(T - T_0),$$

$$\Delta vT = A_1 - B_1 p.$$

These represent the observed Δv-values with an approximation that does not often exceed the limits of error. If the last of

[3] *Compt. rend.*, **108**, 1160 (1889).
[4] *Compt. rend.*, **124**, 75 (1897).
[5] *Kristallisieren und Schmelzen*, pages 186–188.

these equations be introduced into the *Clausius-Clapeyron* equation, knowing from experience that R_p does not change upon the melting curve, we obtain

$$\frac{dT}{dp} = \frac{A_1}{R_p} - \frac{B_1}{R_p}p,$$

and after integration,

$$T - T_{p=0} = \frac{A_1}{R_p} \cdot p - \frac{B_1}{2R_p}p^2,$$

an equation with which the interpolation formula $T - T_{p=0} = a.p - b.p^2$, found for the melting curve, agrees.

When the equation is written in the form

$$T - T_{p=0} = \frac{\Delta vT}{R_p}p - \frac{1}{2R_p}\left(\frac{d(\Delta vT)}{dp}\right)p^2,$$

it may be seen that for the calculation of the coordinates of the melting curve up to 3000 kg./cm.^{2} it is necessary to have only the values R_p, Δv and $d(\Delta vT)/dp$.[1]

However, when these formulas were proposed it was appreciated that in the case of benzene the decrease in ΔvT for equal pressure increases between 2500 and 3500 kg./cm.^{2} is smaller than at lower pressures, and that the determinations of Δv upon other substances showed the same relation. It therefore seemed that the interpolation formula reproduced with good approximation the parabolic course of the melting curves up to only about 2000 or 2500 kg./cm.^{2} In order to test this, the melting curves of a few substances were followed up to 10,000 kg./cm.^{2} for the purpose of controlling the coordinates of the maximal melting point which could be derived from each interpolation formula. These points were found by determining the temperatures at which under definite pressures, platinum pegs frozen in the investigated substance became audibly mobile. (See *Kristallisieren und Schmelzen.*)

With dimethyl-ethyl carbinol an interpolation formula was obtained for the course of the melting curve up to 3000 kg., $t = 8.54 = 0.02205p - 0.000050260p^2$, and from this it appeared that the pressure of the maximal melting point is at 4250 kg.,

[1] With regard to other forms of the melting curve, corresponding to other laws for the change of v upon the melting curve, see *Kristallisieren und Schmelzen*, pages 82–86.

and that this melting point is equal to 44.5°. However, it was shown by the former method that the melting curve still rises, though slowly, at 60° and 10,000 kg. In an analogous manner it was shown that for trimethyl carbinol, orthocresol, sodium, and potassium, the maxima of the melting curves lie at higher pressures and higher temperatures than would be expected according to the interpolation formula that reproduced the course of the melting curve to 3000 kg. These results have since been completely confirmed by the measurements of BRIDGMAN.

The maxima of the melting curves therefore ordinarily lie at very high pressures, with most substances probably over 20,000 kg./cm.^{2} It is more interesting to note that there are some substances possessing especially small Δv-values (salt hydrates) the maximal melting points of which lie at pressures easily reached by measurement. This may be shown by the test that if at the maximum upon the melting curve Δv passes through a zero value, R_p has a value which does not differ noticeably from that at $p = 0$.

P. W. BRIDGMAN has repeated the determinations of the coordinates of the melting curves and has also repeated the derivation of the phase diagrams. Using the methods of the author, he has not only obtained coordinates of the melting curve and the Δv-values, but has also extended some of these measurements to 12,000 kg./cm.^{2}. This extension was made possible by substituting for the manometer, electrical resistance measurements upon a manganin wire enclosed in the cylinder, and also by the construction of the piston described above. BRIDGMAN'S experimental technic is model. It was actually determined that the curvature of melting curves about 3000 kg./cm.^{2} is much less than the curvature below this pressure. Therefore, the maximum lies at very much higher pressures than would be indicated by the quotient a/2b, obtained from the interpolation formula $\Delta t = ap - bp^2$.

As already stated, however, there are some substances, the melting curve maxima of which lie at obtainable pressures; these are the salt hydrates and the tertiary alcohols. In the case of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, the maximum lies at about 460 kg./cm.^{2}, and the melting curve has accordingly been accurately investigated. For another salt hydrate, $Cd(NO_3)_2 \cdot 6H_2O$, as a consequence of the small volume change upon melting at a

pressure of 1 kg., the maximum upon the melting curve appears to lie at considerably lower pressures than is the rule with the most important carbon compounds investigated. It is to be regretted that BRIDGMAN did not investigate a few substances of this class.[1]

In the group of salt hydrates there are also substances that melt with a volume diminution, such as the analogue of Glauber's salt, $Na_2CrO_4 \cdot 10H_2O$, which decomposes upon melting into a very little $Na_2CrO_4 + 6H_2O$ and a saturated solution that contains but little less anhydrous salt than the crystallized decahydrate. $Na_2SO_4 \cdot 10H_2O$ forms the anhydrous salt and a saturated solution upon melting. Since the two decahydrates form a continuous series of isomorphous crystals, then, as R. HOLLMAN [2] has shown, for one member of the isomorphous series, Δv must be equal to zero, and for the crystals rich in $Na_2SO_4 \cdot 10H_2O$, Δv must be positive and for those poor in $Na_2SO_4 \cdot 10H_2O$, Δv must be negative. The volume surfaces of the isomorphous series in the neighborhood of the melting interval will have the form given by R. HOLLMAN in Fig. 56. The $Na_2SO_4 \cdot 10H_2O$ melts with a volume increase, the $Na_2CrO_4 \cdot 10H_2O$ with a volume decrease. For the isomorphous mixture of about 65 per cent $Na_2SO_4 \cdot 10H_2O$, $\Delta v = 0$. The volume of this crystal decreases at first upon melting and then increases, as can be clearly seen in the model (Fig. 56). The melting intervals for crystals with more than 65 per cent $Na_2SO_4 \cdot 10H_2O$ are at first with increasing

[1] The Δv-values of the stable crystal forms ordinarily are so great that the maximum upon the melting curve lies at very high pressures. However, unstable crystal forms are occasionally found the Δv- values of which are small and in some cases the Δv-values must be very small, since the spherulites of these crystalline forms are so transparent that they easily evade detection. The opacity of spherulites is probably to be traced to the fissures which are not filled by melt, and the greater the contraction upon crystallization, the more turbid or opaque appear the spherulites. If, then, the spherulite is almost as transparent as the melt, its Δv must have a very small value. Such transparent spherulites are formed from melts of menthol, and in this case upon further cooling they become strongly opaque as a consequence of a transformation into a stable form. Besides the many turbid crystals that form in the melts of betol, there is sometimes found spherulites completely transparent the presence of which can be detected only by means of crossed Nicols. Unfortunately these structures are so little stable that the course of the melting curve cannot be determined.

[2] *Ann. d. Phys.*, **13**, 337 (1903).

pressure displaced towards higher temperatures, for crystals with less than 65 per cent the displacement is towards lower temperatures, whereas no displacement occurs with the composition containing 65 per cent $Na_2SO_4 \cdot 10H_2O$. With increasing pressure the displacement for the first series towards higher temperatures becomes smaller and passes over to a displacement towards lower temperatures. The pressure at which this change occurs grows from a zero value for the crystal containing 65 per cent $Na_2SO_4 \cdot 10H_2O$ to about 500 kg. for the pure $Na_2SO_4 \cdot 10H_2O$. Although at $p = 1$ kg. the value of Δv for the 65 per cent $Na_2SO_4 \cdot 10H_2O$ crystal is zero, the heat of fusion has a very high value that lies between the values for the two pure salts. This

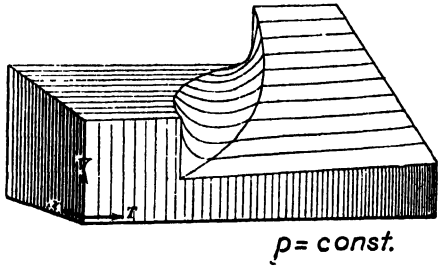


FIG. 56.

is a case, then, that serves happily to illustrate without complicated apparatus the fact that for the equilibrium of an isotropic phase with an anisotropic, the condition of $\Delta v = 0$ is not sufficient as a criterion for the presence of a critical point.

a. The Melting Curve of Glauber's Salt

The melting of 100 gms. of $Na_2SO_4 \cdot 10H_2$ at $p = 1$ kg. produces 18.1 gms. of the anhydrous salt and a saturated solution. When the pressure is 3000 kg./cm.^{2}, the amount of anhydrous salt formed amounts to 10.4 gms. The solubility of the anhydrous salt therefore increases upon the melting curve, but none of the three phases disappears. Since this equilibrium is a complete one and has but one degree of freedom, the equation of CLAUSIUS-CLAPEYRON is applicable, just as it is in the two-phase equilibrium.

Since the volume changes upon melting are very small, the determination of the volume change during melting at constant

temperature is not suitable for the defining of the melting curve, and the pT-curve method is used instead. The pT-curves given in Fig. 57 were obtained by heating 90 gms. of $Na_2SO_4 \cdot 10H_2O$ at a velocity of 0.1° per minute.[1] A curve drawn through the middle portions of these pT-curves will be the melting curve. It is evident that the pressure increases upon melting are positive at small pressures; at 460 kg. no change in pressure takes place, and at higher pressures Δp assumes increasing negative values, corresponding to the variation of Δv upon the melting curve.

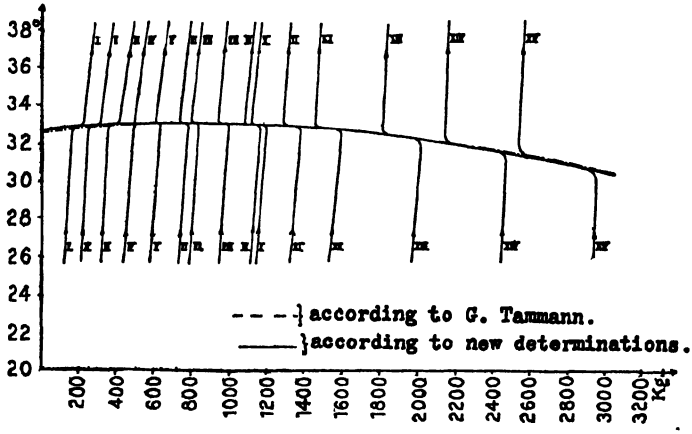


FIG. 57.

The dotted curve in Fig. 57 passes through a series of points determined by the author in the following way. The determinations of Δv by the movable piston method may be reproduced by the equation

$$\Delta v = 0.0037 - 0.000008p.$$

If this equation be introduced into the equation $\frac{dT}{dp} = \frac{T}{R_p}\Delta v$, and if we also introduce the values $T = 305$, $R_p = 43 \times 51.5$ kg. cm. $\left(\text{that is, } \frac{T}{R_p} = 0.137\right)$, after integration we obtain

$$t = 32.6 + 0.000507p - 0.00000055.p^2.$$

The curve calculated from this equation is the dotted one in Fig. 57, and it is to be noted that it corresponds to the one

[1] E. A. Block, *Z. phys. Chem.*, **82**, 429 (1913).

experimentally determined by E. A. BLOCK within the limits of error peculiar to the experimental determinations.

This curve may also be determined by the thermometric method, in which the temperatures of compressed and non-compressed charges of Na_2SO_4 are determined by a thermo-couple. The coordinates of the melting curve determined in this way agree with those determined as above within the limits of error.[1]

The most notable thing about the melting curve of Glauber's salt is that Δv decreases with increasing pressure in the first quadrant of the melting curve, but that in the second quadrant it assumes increasing negative values; whereas in the first quadrant dT/dp decreases with pressure, in the second it increases. This is true of all melting curves determined up to the present time, which of course are known only in the first or in the second quadrants. Curves of the second quadrant are those of ordinary ice, of bismuth, and of $Na_2CrO_4 \cdot 10H_2O$.[2]

It is therefore permissible to conceive the known pieces of the melting curves as sections of a closed curve formed by coordinate displacement, as explained on pages 31–33.

b. The Interpolation Formulæ

In the following table are given the interpolation formulas, determined by the author and his coworkers, for melting up to 3000 kg. Following these, there are listed the coordinates of the melting curves as determined in 1000 kg. steps by BRIDGMAN and also their Δv-values and the derived values of R_p in mechanical units, kilogram-meters per one gram.

From the Δv determinations by BRIDGMAN upon the melting curves, where the temperature increases with increasing pressure, it may be seen that Δv from 1–12,000 kg. ordinarily decreases to about the half value. In the cases of potassium, benzene, and CCl_4 the relative decrease is considerably greater.

The value of the heat of fusion, R_p in kg. m./gm., ordinarily decreases slightly except with the three substances named above, with which Δv decreases especially strongly with increasing pressure. In these cases a distinct decrease in R_p with growing pressure is observed.

[1] *Z. phys. Chem.*, **46**, 818 (1903).

[2] *Kristallisieren und Schmelzen*, page 203.

INTERPOLATION FORMULAS, $t = t_{p=0} + ap - bp^2$, FOR THE COURSE OF THE MELTING CURVES FROM 0–3000 kg./cm.² *†

	$t_{p=0}$	$a \cdot 10^4$	$-b \cdot 10^8$	$\frac{a}{2b}$
Benzene	5 43	283	198	7,146
Naphthalene	79 95	365 7	180	11,500
p-Xylol	13 2	343.8	171	10,500
Carbon tetrachloride	−23 0	350	147	11,900
Ethylenedibromide	9 85	252	125	10,500
Hydrocyanic acid	−13 4	218.7	147	7,400
Nitrobenzene	5.67	234 4	116	10,100
Aniline	− 6 1	203	112	9,080
Acetophenone	19 2	235	152	7,730
Benzophenone	48 11	275 7	136	10,150
Formic acid	7 75	127 6	80	8,000
Erucic acid	31 3	206 4	100	10,320
Lauric acid	42 5	230	150	7,660
Myristic acid	51 8	237	160	7,420
Monochloracetic acid	62 0	165	88	9,400
p-Cresol	33 3	228	63	18,100
Diphenylamine	53 4	245	100	12,250
Formanilid	46 6	202	143	7,050
p-Toluidine	43 3	259	135	9,600
Trimethylcarbinol	24 9	343 6	372	4,620
Dimethylethylcarbinol	− 8 45	220 5	260	4,230
Phosphorus	43 95	275	50	27,500
Orthophosphoric acid	38 0	80		
$CaCl_2 \cdot 6H_2O$	29 7	116 3	60	9,690
$Na_2SO_4 \cdot 10H_2O$	32 6	5 07	55	460
Veratrol	22 31	216 7	101	10,727
Chlorotoluene	6 85	265 9	122	10,897
Iodotoluene	33 85	304 1	138	11,018
Bromotoluene	26 50	291 1	131	11,110
Anethol	22 27	204 3	875	11,674
Diphenylmethane	26 90	255 6	116	11,017
Dichlorbenzene	52 28	266 3	126	10,567
Benzylaniline	35 55	232.4	108	10,759
Thymol	49 20	202 5	185	5,471
Menthol ‡	41 10	240 5	180	6,679
$Cd(NO_3)_2 \cdot 4H_2O$ §	58 7	81 3	50	8,130
Betol	93 0	330	314	5,255
Triphenylmethane	92 8	355	250	7,100
Erythritol	117 0	80	55	7,250
Guaiacol	28.4	178	100	8,900
Salol	42 0	288	130	11,100
Benzoic anhydride	41 2	258	55	23,450

* *Kristallisieren und Schmelzen*, pages 215–265.

† E. A. Block, *Z phys. Chem* **82**, 429 (1913).

‡ Puschin, *Nachrichten des Polytechn. Inst. Petersburg*, 1907, Vol II, page 1.

§ W. Denecke, *Z. f anorg. u. allgem. Chem.*, 108, 1 (1919).

c. *The Measurements of Bridgman* *

p kg./cm.²	Nitrobenzene			Diphenylamine			Benzene			Carbon tetrachloride		
	t	$\Delta v \cdot 10^4$ cm.³/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^4$ cm.³/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^4$ cm.³/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^4$ cm.³/gm.	R_p kg.m./gm.
1	5.6	813.6	9 60	54 0	958	11.24	5 4	1317	12 88	−22 6	258 0	1 67
1,000	27.2	732 6	10 00	79 1	807	10 67	32.5	1026	12 94	14 2	200 6	1.72
2,000	48.1	663.9	10 36	103 0	708	10 33	56 5	872	13 06	45 9	165 3	1 77
3,000	68 3	605 2	10 66	124 7	638	10 29	77.7	759	13 24	75 8	140.1	1 78
4,000	87.6	555 2	10 92	144 9	586	10 40	96 6	675	13 47	102 7	119 7	1.76
5,000	105 5	517 2	11.21	163.6	541	10 49	114 6	614	13.70	126 8	101 9	1.72
6,000	122.3	488.5	11 58	180 9	504	10 54	131 2	564	13 90	149 5	86.2	1.65
7,000	138 1	464.1	11.91	197.3	472	10 55	147.2	522	14 05	171 0	73 0	1.56
8,000	153.8	441.5	12.16	212 9	448	10 57	162 2	485	14 15	192.1	62 2	1.46
9,000	169.3	421.0	12.39	.....	.....	.....	167.7	451	14.20	211.9	53.8	1.37
10,000	184.5	402 8	12 59	.....	.....	.....	190 5	422	14.21			
11,000	198.6	386.4	12.73	.....	.....	.....	204.2	394	14 20			

* *Phys. Rev.* 3, 127 (1914) and 6, 1 (1915).

THE MEASUREMENTS OF BRIDGMAN—*Continued*

p kg./cm.^{3}	Bromoform			Silicon tetrachloride			Chlorbenzene			Brombenzene		
	t	$\Delta v \cdot 10^4$ cm.^{3}/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^4$ cm.^{3}/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^4$ cm.^{3}/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^4$ cm.^{3}/gm.	R_p kg.m./gm.
1	7.78	391	4 477	.....	.....	.....	−45 5	.....	.....	−31 1		
1,000	31.5	355	4.699	.....	.....	.....	−28 0	.....	.....	−12 1	486	7.010
2,000	53.8	322	4 852	−10 0	522	5 23	−12 0	565	9 58	5 3	428	7.134
3,000	74.9	292	4 982	16 7	470	5 20	2 9	511	9 90	21 3	382	7 375
4,000	94.7	266	5 097	42 6	428	5 28	16 7	469	10 22	35 9	345	7.615
5,000	113.3	243	5.217	67.9	395	5 42	29 7	432	10 47	49 4	315	7.756
6,000	130.8	221	5.252	92 5	368	5 56	41 9	400	10 76	62 0	288	7 845
7,000	147.3	203	5 267	116 3	347	5 78	53 3	372	10 93	74 1	266	7 827
8,000	163 2	188	5 242	139 4	330	5 97	64 0	349	11.10	85 7	248	7 868
9,000	178.7	176	5 151	161 8	317	6 23	74 4	328	11 18	96 9	234	7.943
10,000	194.0	166	5 118	183 8	306	6 44	84 5	311	11 24	107 6	222	8.050
11,000	209.1	157	5 047	205 4	297	6 67	94 2	297	11.31	117 9	212	8.127
12,000	.....	.....	.....	.....	.....	.....	103 6	285	11.42	127.9	205	8.389

THE MEASUREMENTS OF BRIDGMAN—*Continued*

p kg./cm.²	Potassium			Sodium			Carbon dioxide		
	t	$\Delta v \cdot 10^5$ cm.³/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^5$ cm.³/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^5$ cm.³/gm.	R_p kg.m./gm.
1	62 5	2680	5.51	97 6	2787	12 90	−56 6		
1,000	78.7	2368	5 81	105 9	2555	12 46	−37.3		
2,000	92 4	2104	6 02	114 2	2362	12 16	−20 5		
3,000	104.7	1877	6 15	121 9	2203	12 00	− 5 5	10,710	19.92
4,000	115.8	1676	6 22	129 8	2072	11 93	8 5	979	20.77
5,000	126.0	1504	6 21	135 8	1968	11 94	21 4	896	21.39
6,000	135.4	1347	6 12	142 5	1873	11 99	33 1	922	21.77
7,000	144.1	1205	6 00	148 9	1790	12 10	44.2	755	21.90
8,000	152 5	1073	5 85	154 8	1711	12.22	55 2	697	21.84
9,000	160.1	950	5 67	161 0	1634	12 35	65 8	644	21 90
10,000	167.0	838	5 43	166.7	1556	12.48	75.4	602	22 06
11,000	173 6	738	5 16	172 2	1476	12 60	84 6	564	22 28
12,000	179.6	642	4 83	177.2	1398	12.72	93.5	531	22 54

THE MEASUREMENTS OF BRIDGMAN—*Continued*

Mercury				Chloroform				Aniline			
p kg./cm.^{2}	t	$\Delta v \cdot 10^5$ cm.^{3}/gm.	R_p kg.m./gm.	p kg./cm.^{2}	t	$\Delta v \cdot 10^4$ cm.^{3}/gm.	R_p kg.m./gm.	t	$\Delta v \cdot 10^4$ kg.m./gm.	R_p kg.m./gm.
2,000	−28.66	252.5	2.848	1	−61 0	.....	.....	−6 4	854	11.20
4,002	−18 48	251.2	2.951	1,000	−45.7	.....	.....	13 1	784	11 94
6,005	− 8.31	248 6	3.041	2,000	−28 3	.....	.... ..	31 6	724	12.66
8,018	1 87	244 3	3.114	3,000	−12 1	530	8 70	48 7	673	13 33
10,034	12.06	237.7	3.154	4,000	3 4	498	9 10	64 5	631	13 95
12,064	22.24	229.6	3.165	5,000	18.2	467	9 43	79 0	594	14.48
				6,000	32 4	438	9 65	93 2	561	14 93
				7,000	45 6	412	9 81	106 5	530	15.36
				8,000	58 6	389	9 93	119 1	502	15.73
				9,000	71.3	368	10 00	131 5	476	16 06
				10,000	83.7	350	10 08	143 2	451	16 38
				11,000	96 1	334	10 20	154 7	427	16.60
				12,000	107.9	321	10 35	165.3	405	16.69

THE MEASUREMENTS OF BRIDGMAN—*Continued*

p kg., cm.^{2}	Benzophenone			Paratoluidine			Methyloxalate			Bismuth		
	t	$\Delta v \cdot 10^4$ cm^3 gm.	R_p kg.m. gm.	t	$\Delta v \cdot 10^4$ cm.^{3} gm	R_p kg m gm.	t	$\Delta v \cdot 10^4$ cm.^{3} gm.	R_p kg.m gm.	t	$\Delta v \cdot 10^5$ cm.^{3} gm	R_p kg.m. gm.
1	47 77	904	10 20	43 6	1413	1651	54 24	1453	21 03	271 0	345	5 49
1,000	74 6	773	10 56	69 0	1195	1717	75 8	1115	18 71	267 5	354	5 36
2,000	98 9	689	11 00	91 5	1037	1766	95 8	957	18 13	263 8	362	5 24
3,000	121 3	624	11 48	112 0	931	1804	114 7	862	18 19	260 0	370	5 11
4,000	142 0	571	11 85	131 3	852	1819	132 6	798	18 52	256 0	378	4 98
5,000	161 3	532	12 26	150 0	789	1801	149 6	745	18 87	251 9	386	4 85
6,000	179 6	498	12 63	168 4	736	1774	165 9	696	19 08	247 6	394	4 72
7,000	197 0	468	12 90	186 6	688	1748	181 6	650	19 14	243 2	401	4 59
8,000	213 7	442	13 17	204 6	647	1722	196 8	606	19.03	238 6	407	4 44
9,000	.....	.....	.....	.....	.....	.....	.....	.....	.....	233 8	413	4 30
10,000	.....	.....	.....	.....	.....	.....	.....	.....	.....	228 8	419	4 16
11,000	.....	.....	.....	.....	.....	.....	.....	.....	.....	223 6	424	4.01
12,000	.....	.....	.....	.....	.....	.....	.....	.....	.....	218 3	429	3 88

The measurements of BRIDGMAN have shown, in agreement with the measurements of the author, that over 3000 kg. the melting curves run more nearly linear than under 3000 kg. For this reason their maxima lie at much higher pressures than was first supposed from the examination of the curves up to 3000 kg. The maximum lies lowest with potassium and even here the pressure is around 20,000 to 30,000 kg. As we have stated above, it is to be expected that the maxima in the case of salt hydrates lies at much lower pressures, and this is also true of the tertiary alcohols, the melting curves of which would therefore be of interest.

d. The Course of the Melting Curve in the Hypercritical Region

At pressures and temperatures greater than the critical, the properties of the liquid phase change continuously. The course of the melting curve in the critical region accordingly gives no hint of the fact that the critical temperature has a special significance for the substance concerned. It may be asked whether in reality the melting curves enter into this hypercritical region. For most substances this question cannot be answered with assurance. There are two substances, however, for which the course of the melting curve has been determined in the hypercritical region. These are phosphonium chloride, PH_4Cl, and carbon dioxide, CO_2. Figure 58 gives the equilibrium curves for PH_4Cl. In order to represent the sublimation, the melting, and the vapor pressure curve in the same diagram, $\sqrt{p}$ instead of p is plotted upon the pressure axis. For this reason the curvature of the equilibrium curves is abnormal. $\frac{d^2T}{dp^2}$ is negative here, as it always is in the first and second quadrants. The critical point lies between 49° and 50°, and 74 and 75 atm.;

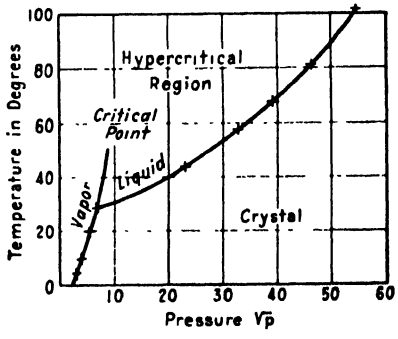


FIG. 58.

it is clearly evident that the melting curve extends beyond the critical temperature, far into the hypercritical region.[1]

In the case of CO_2 the critical point lies at 31.4° and 72.9 atm.; the melting curve has been followed by the author to 20° and 5000 kg./cm.^{2} and by BRIDGMAN to 93.5° and 12,000 kg./cm.^{2}

5. The Constitution of the Heat of Fusion

The heat of vaporization, l_p, of a normal liquid consisting of only one kind of molecule is made up of only two work terms, the external work A_a, and the internal work A_i, which is expended during vaporization in opposing the attractive forces of the molecules. It is therefore to be assumed that upon vaporization at the critical point, because of the identity of the liquid and the vapor there obtaining, the energy content of the molecules themselves does not change. The heat of vaporization in mechanical units may then be represented by the equation

$$l_p = A_a + A_i.$$

In the case of the heat of fusion two new terms are to be added provided that a normal liquid be formed, the first representing the change in potential energy, $\Delta\pi$, which enters as a result of the transformation from the lattice structure to the complete disorder of the liquid, and the second, ΔE, the possible change in energy content of the molecules in consequence of the destruction of the lattice. Accordingly, the heat of fusion measured in mechanical units may be expressed,

$$R_p = A_a + A_i + \Delta E + \Delta\pi.$$

At the maximum of the melting curve $A_a + A_i = 0$ and therefore $R_p = \Delta E + \Delta\pi$.

The values of A_a and A_i may be accurately calculated for a few substances, the volume surfaces of which are known.[2] Between $p = 0$ and 3000 kg. A_i amounts to only 2–20 per cent of the heat of fusion, and A_a to only 0–35 per cent. The greater portion of R_p, therefore, is to be found in the terms ΔE and $\Delta\pi$.

[1] The coordinates of the three equilibrium curves as found by experiment are given in *Kristallisieren und Schmelzen*, pages 284–294.

[2] *Z. phys. Chem.*, **85**, 273 (1913).

Although the quantitative separation of the two terms is impossible at the present time, it may be assumed that $\Delta\pi$ is smaller than ΔE. The difference in the heats of fusion of the forms presumably built up of one and the same kind of molecules (forms of the same thermal crystal groups, see page 122) amounts to only approximately 10 per cent, a difference which evidently occurs only in members ΔE and $\Delta\pi$.[1] If the change of potential energy, $\Delta\pi$, with the change in the grouping of the molecules from the orderly arrangement upon a lattice to the disorder of a melt, have the same order of magnitude as that occurring when one kind of lattice is transformed into another, then ΔE must represent the chief part of the heat of fusion.

Upon crystallization the vectorial properties of the crystal appear in the place of the scalar properties the liquid, and it must be assumed that this change in properties is conditioned by the appearance in the molecules of polar forces which tend to hold the lattice together —and it must likewise be assumed that the molecule itself becomes anisotropic. The quantity ΔE in this way represents the energy loss resulting from the transformation of one gram of molecules from the liquid to the crystalline state, from the state of isotropy existing in the melt to the state of anisotropy existing in the crystal.

The process of fusion differs from that of vaporization in the fact that upon fusion a change in nature of the distribution of the molecules, from the order of the lattice to the disorder of the melt, takes place, whereas upon vaporization this remains the same, both the liquid and the vapor states possessing a random distribution of molecules. And an additional, more important difference lies in the fact that upon fusion the molecules lose a portion of their energy due to their loss of anisotropy.

The probability of spontaneous crystallization depends, as we shall see on page 213, upon the temperature to which the melt is heated before its undercooling. This fact suggests that the transformation of the anisotropic molecules into isotropic molecules is not completed upon fusion, but that there remains in the melt molecules more especially qualified to crystallize than the majority of the molecules. This observation is in accordance with our conception of the constitution of the heat of fusion.

[1] *Z. phys. Chem.*, **85**, 280–281 (1913).

6. The Behavior of Substances Consisting of Two Kinds of Molecules of Similar Constitution and of Low Transformation Velocity.[1]

If the different kinds of molecules constituting a liquid intertransform very rapidly, the liquid will behave with reference to its vaporization and crystallization as if it were actually composed of but one kind of molecule, for upon isothermal vaporization the pressure will remain constant, and upon isobaric crystallization the temperature will remain constant to the conclusion of the process. On the other hand, if the transformation velocity be low the liquid will behave as if it were a mixture of two different substances, for upon vaporization the pressure will sink, and upon crystallization the temperature fall will be retarded at the point of the first separation of crystal, and will then sink to an eutectic point.

A series of liquids is actually known in which this behavior is shown. They consist either of two isomeric or two polymeric forms. Figure 59 represents the relations at the beginning of crystallization of a liquid in which two forms, α and β, are very slowly intertransformable at low temperatures, but at somewhat higher temperatures are rapidly intertransformable. The molecular composition of the liquid is represented upon the abscissa, and the temperature upon the ordinate. The line AC is the liquidus representing the temperature of the first appearance of the α-form from the liquid mixture of α and β, and the line BC is the liquidus of the β-form. The line cd gives the molecular composition of the liquid at different temperatures when equilibrium between the two kinds of molecules α and β is reached. Its direction depends upon the sign of the heat of transformation of α into β. If with the transformation of α into β an absorption of heat take place, then cd will run from left to right, and in the

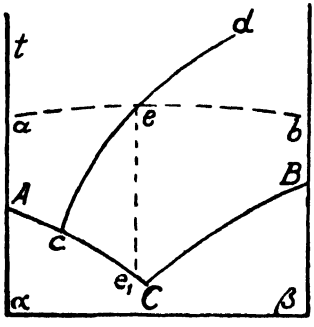


Fig. 59.

[1] Bancroft, *Journ. Phys. Chem.*, **2**, 143 (1897). Roozeboom, *Z. phys. Chem.*, **28**, 289 (1899).

other case from right to left. The line *ab* gives the temperature at which the velocity of transformation becomes high. If the liquid be cooled quickly from the point *e* crystallization will begin at the point e_1, since the equilibrium between α and β would not be noticeably shifted during the cooling. On the other hand, if the liquid be cooled very slowly so that the equilibrium between the α- and the β-form follows the line *ec*, crystallization will begin at *c*. The temperature of the beginning of crystallization thus depends upon the rapidity of cooling between the temperatures of the points *c* and *e*. Above *e* no such dependence will obtain since at temperatures above this point the velocity of the establishment of equilibrium is very high.

If the two forms composed of α- and β-molecules can be partly separated by fractional crystallization the crystals obtained will show sharp melting points, though the temperature of the beginning of crystallization of the heated melt will as before depend upon the previous history of the melt. In the case of acetoacetic ethyl ester, which consists of two tautomeric molecules, the *keto* and the *enol*, the relations are essentially as described. KNORR[1] succeeded in separating these two forms by fractional crystallization and also succeeded in determining the course of the two liquidus curves. As an additional example we have benzaldoxime, the *anti* and *syn* modifications of which can be prepared in a pure form with melting points at 34° and 130°. The liquidus lines *AC* and *BC* for the mixtures of these two forms can be easily determined on account of the low velocity of transformation. Mixtures of all compositions upon heating to a temperature at which equilibrium between the two forms is established show the same temperature of beginning crystallization, 27.7°. In this equilibrium mixture there is present 95 per cent of the *syn* and only 5 per cent of the *anti* modification.[2]

With polymeric substances the relations are similar in principle. The influence of the transformations occurring in such substances upon the temperature of the beginning of crystallization has been studied in an exhaustive way by R. HOLLMANN.[3]

The observation of L. KNORRS is of great significance, namely, that no *enol* molecules form in the crystals of the *keto* during long

[1] *Liebig's Ann.*, **293**, 88 (1896).
[2] Carneron, *Journ. Phys. Chem.*, **2**, 409 (1898).
[3] *Z. Phys. Chem.*, **49**, 129 (1903).

heating at temperatures close to the melting point. On the other hand, the *enol* molecules form quickly in the melt just above the melting point, as shown by addition of $FeCl_3$, which gives an intense red color with the *enol* form. It is evident from this that the structure of crystals can be much simpler than that of the melt.

7. Methods for Distinguishing Isotropic from Anistropic Bodies

Until recently the methods available for the distinction of isotropic and anisotropic bodies depended upon a few special criteria not always infallible. The development of the methods of investigation of substances in very short Rontgen rays has made it possible now to make the distinction in a much more general way.

The beginning of crystallization in a melt ordinarily makes itself evident by a loss of complete transparency, the mass no longer appearing clear and homogeneous. If an undercooling greater than 100° take place, ordinarily fissures will suddenly appear, and the mass will become vitreous, will assume a state of frozen isotropy. The melt of an easily fusible substance cooled in a narrow glass tube forms upon the upper surface a deep funnel-shaped crater. This is caused by the volume diminution of the substance, great in comparison to that of the glass tube; the warmer and less viscous melt in the central portion of the tube is pressed down into the deeper parts of the tube by the air pressure. With further undercooling cracks are suddenly formed in the brittle mass. The fact that the heat of crystallization is latent in such glassy masses may be ascertained, provided that the crystallization velocity (C. V.) be great enough, by the taking of a heating curve. If this fail, however, sufficiently slow heating, or exposing the glass to the temperature of its maximal nuclei member, will bring about a significant change in the appearance of the glass: it becomes opaque, porcelain-like, through the formation of spherulites or scattered single crystals.

If the substance in the anisotropic state possess a transformation point (transformation points have never been observed in glassy, isotropic substances), and if the substance be present in a finely divided condition, investigation between crossed Nicols

yielding no information, the question of whether the substance is isotropic or anisotropic can be decided by any suitable method for the detection of the transformation or the transformation product. For example, freshly precipitated AgI has been shown to be anisotropic by the discovery that it has a transformation point at 149°. By the measurement of the amount of the heat of transformation evolved or of the volume change upon transformation, the anisotropic fraction of the total mass can be determined.

The microscopic investigation of thin sections of rock has led to some important results. It has shown that in the younger eruptive rocks varying amounts of the glassy magma is always present; in the older eruptive rocks the residue of the mother substance is no longer present, having been consumed in the process of crystallization. This indicates that the glassy residue is unstable and that it exists in the younger rocks only by virtue of the extremely low C. V.

Another method for obtaining the answer to our question may be illustrated by the so-called amorphous silicon. From solutions of Si in Al that contain more than 10 per cent Si, the silicon crystallizes in large primary crystals. Finally, the eutectic contains the Si in a very finely divided condition. Solutions containing less Si than the eutectic amount contain the finely divided form of the Si alone. An alloy containing more than 10 per cent Si and one containing less than 10 per cent Si upon solution in HCl therefore deposit in the first case large grey crystals and in the second, a grey powder which has been called amorphous. In a chemical way these two preparations differ in reaction velocity, which is much greater with the "amorphous" form.

This, however, can be explained by the great difference in the amount of surface exposed. Upon the formation of an eutectic, the two phases in equilibrium with the liquid must be crystalline. If one of them were amorphous, that is, if one were a supercooled liquid, the equilibrium diagram of the mixture of the two substances would have to be completely different from that given for Al — Si, by which we are told that both are miscible in the liquid state in all proportions and are not noticeably soluble in the solid state.

The method of DEBYE and SCHERRER,[1] developed from the LAUE method and permitting the use of a finely powdered sub-

[1] *Physik. Zeitsche.*, **17**, 277 (1916).

stance for the purpose of investigation, is of general applicability. The powder to be investigated is placed in a little tube of very thin paper and illuminated with a beam of monochromatic X-rays. If the distance between adjacent layers in the space lattice be a whole multiple of the wave length, the reflected rays will not interfere. One portion of the particles oriented at random for a given group of lattice planes accordingly will reflect in the first, second, and so forth, order; another portion will reflect in another set of planes. The beams belonging to a given reflection angle form a mantle-like cone the axis of which is the beam of X-rays, since the particles are randomly oriented with respect to the beam and reflect only from a given group of lattice planes for which the reflection conditions are fulfilled. If the light reflected from the particles be caused to fall upon a light-sensitive plate, a series of black, concentric circles will be obtained. DEBYE and SCHERRER, however, caused the light to fall upon a film bent into the form of a cylinder with the glass tube containing the substance forming the axis of the cylinder. The distance of the black lines from the primary beam could then be measured and from it the reflection angle of the beam corresponding to any line could be calculated. From the positions of the lines the positions of the reflecting lattice planes could be derived. Besides the positions of the lines, their intensity and breadth is likewise of importance. The intensity of the blackening is proportional to the frequency of the reflecting lattice planes which in turn is proportional to the frequency of the parallel crystal planes of the lattice. Thus the intensities of the beams reflected by the lattice planes of the cube are related to those of the octahedron and to those of the rhombdodecahedron as 6 : 8 : 12.

The width of the lines increases with the angle of reflection, and is also dependent upon the size of the particles, increasing with decrease in grain-size. Investigations by SCHERRER [1] have shown that finely divided gold powder consists of small crystals the size of which varies in different preparations from 1.9 to 10$\mu\mu$. Likewise, " colloidal " silver consists of little crystals, the lattice of which does not differ from that of compact silver; this is also true of " colloidal " gold.

Freshly precipitated silica-gel, according to S. KYROPOULOS,[2] is

[1] *Physik. Zeitschr.*, **19**, 27 (1918).
[2] *Z. anorg. Chem.*, **99**, 197 (1917).

isotropic, whereas a dried, aged preparation contains many interspersed ultramicroscopic crystallites. Some varieties of glass give only a broadened black halo about the impact of the primary beam upon the photographic plate. Such an X-ray photograph is similar to those obtained for liquids. Other kinds of glass show in addition to this halo fine dark lines, indicating the presence of a noticeable number of centers of crystallization.

So-called amorphous silicon and amorphous boron prove, as expected, to be wholly crystalline. Also the so-called amorphous carbon, wood charcoal, sugar charcoal, or lampblack, prove to be crystalline, and in fact their lattice structures are closely related to that of graphite. The especially dense carbon resulting from the action of mercury upon the halogen compounds of carbon [1] alone shows no reflection lines upon the Rontgen photograph, and gives only black halos similar to those obtained by SCHERRER for glass without crystallization centers. Caoutchouc, gelatine, acetyl cellulose, are isotropic whereas starch, cellulose, cotton, flax are crystalline.[2]

If a substance consist of aggregates of parallel rods, double refraction will obtain, according to O. WIENER.[3] Such aggregates behave as uniaxial crystals. According to H. AMBRONN,[4] double refraction due to a rod-like structure can be distinguished from genuine double refraction by immersing the concerned body in a liquid of equal coefficient of refraction. If the double refraction be due to the rod-like structure alone it will disappear, if both effects are present the double refraction will be retained.

[1] *Z. anorg. Chem.*, **115**, 115 (1920).
[2] Herzog and Jancke, *Berl. Ber.*, **53**, 2162 (1920).
[3] *Abh. d. Sachs. Ges d. Wiss.*, **32**, 6 (1912).
[4] *Zeitschr. f. wiss. Mikroskopie*, **32**, 43 (1905).

VI. POLYMORPHISM

Since the discovery of the dimorphism of sulphur and of mercuric iodide by E. MITSCHERLICH [1] (the discoverer of isomorphism), two and in some cases more than two forms have been found for many substances; and other substances have been shown definitely to be monomorphic. The ability of a substance to occur in different crystal forms depends upon the nature of the substance, and is very different in different groups of substances.

In the following discussion, by crystal forms (phases) is meant the forms of a substance characterized by a definite set of specific physical properties. In this sense a cube and an octahedron of NaCl are not different crystal forms, but different growth-forms, the difference brought about by the presence of admixtures in the mother liquid. The physical properties of the cubic and of the octahedral sodium chloride are otherwise identical.

The physical limits of a crystal are of value in identifying it and in judging the conditions obtaining during its formation, but for an intimate knowledge of the substance itself these limits are of little significance. In fact the polyhedral form itself is not characteristic of the crystalline state. There are substances, metallic substances especially, that solidify at high temperatures from solutions in spheroidal or ellipsoidal forms, owing to the fact that the surface tension overpowers the forces of the solid state. If the forces tending to arrange the molecules upon lattices decrease strongly with increase in temperature, round forms may be obtained.[2]

The inner structure of anisotropic substances is manifestly more fundamental than the external form. It is ordinarily true that if substances belong to different crystal classes their lattices are of a different kind, though it is possible that the lattices of two forms of the same substance differ only concerning the lattice parameter, in correspondence to the differing specific volumes of the two forms.

[1] *Berl. Akad. Abh.*, **43**, 1822; and *Pogg. Ann.*, **28**, 116 (1833).

[2] *Göttinger Nachrichten*, 1912. Page 557.

At the present time it is customary to make a division of crystal forms in a way that, as we shall see, is insufficient. Two kinds of polymorphism are distinguished. In the first of these the forms are reversibly intertransformable, and in the second the forms are irreversibly intertransformable. O. LEHMANN has named the reversible transformation enantiotropic, and the irreversible monotropic. This division is not wholly unequivocal because the conditions of state alone determine whether a phase is to transform reversibly or irreversibly.

For example, the transformation of Ice I into Ice III between $-22°$ and $-40°$ at a pressure of 2200 kg. is reversible (see the transition curve of these two kinds of ice in the phase diagram of water, page 159). If Ice I at $-30°$ be changed completely into Ice III by an increase in pressure up to 2500 kg., and then cooled to $-180°$, the pressure may be decreased to atmospheric without the occurrence of the retransformation into Ice I; this transformation is brought about when the temperature is raised to $-130°$. Such behavior is quite common. A phase is reversibly transformable into any phase with which it can come into equilibrium, upon the equilibrium curve limiting the respective phase fields. An irreversible transformation is possible only outside the phase field of the phase concerned. It is quite plain that a division into crystal groups cannot be made upon the basis of the reversibility or irreversibility of transformation. A satisfactory division cannot be made upon the nature of the transformation, but can be made upon the basis of the stabilities of the forms concerned.

Some measure of the stability is therefore necessary in order that such a division may be made. Vapor pressures are commonly taken as a comparison of stability, but it is clear that the method is of no service when the pressure existent upon the system is greater than that of the saturated vapor. It is therefore necessary to have at disposal a more general method for the measurement of stability. The thermodynamic potential referred to the unit of mass fills this need. This is the ζ-surface of GIBBS (compare IV, 6), which is a function of the two independent variables p and T, and is therefore better suited for our purpose than other thermodynamic functions; better than, for instance, the ψ-function which gives the free energy in dependence upon v and T. For our purpose it is necessary to know merely that the ζ-function gives the order of stability of the different phases,

the unstable phase possessing a greater ζ-value than the stable. The ζ-surface of any phase is obtained by protracting the various ζ-values for a unit of mass upon perpendiculars over the pT-plane. Upon the non-plane curve of intersection of two ζ-surfaces, the ζ-values of the two phases will have the same value, the same stability as we have seen, and therefore at the values of p and T for each point upon the equilibrium curve the two phases will be in equilibrium. The projection of the non-plane curve of intersection upon the pT-plane is therefore the equilibrium curve. It is possible that these ζ-surfaces may intersect, producing an equilibrium curve, or on the other hand it is possible that they may not intersect.

A rational division of different forms can be made upon the basis of their different stabilities. In order that we may finally obtain such a rational division it is necessary that we first derive a few laws determining the positions of the equilibrium curves of the forms of different stabilities. The equilibrium curves refer to the equilibria of the two forms of different stability with a reference phase. The chief law from which the others follow, is:

1. *The equilibrium curve of the unstable form always has its course within the phase field of the stable form.*

The proof of that general law can be carried out in the following way. In Fig. 60 two planes of intersection, T_x and p_x, are passed through the ζ-surfaces respectively of the stable form 3, the totally unstable form 3′, and the phase 2. In order to avoid complications which need not be discussed here it is assumed that the indicated ζ-surfaces are not intersected by the ζ-surfaces of the other phases of the hypothetical substance. The arrow upon the T-axis points towards falling temperature; in this direction the ζ-values increase upon the ζ-isobars. Similarly the ζ-values increase with rising pressure upon the ζ-isotherms. The ζ-surface of the phase 2 intersects the ζ-surface of the form 3′ in the non-plane curve 2 3′, and the ζ-surface of form 3 in the non-plane curve 2-3. The projections of these two non-plane curves upon the pT-plane give the equilibrium curves 2-3′ and 2-3.

Since the ζ-surface of form 3′ lies over the ζ-surface of form 3 (our assumption made 3′ totally unstable with reference to 3), the projection of the non-plane curve 2-3 will of necessity enclose the projection of the non-plane curve 2-3′, and the two equilibrium curves cannot possibly intersect. The phase field of the totally

unstable form thus falls completely within the phase field of the stable.

The correctness of these conclusions may be directly obtained from a consideration of the planes of intersection, p_x and T_x. It can be seen from the figure that the equilibrium temperatures of the form 3′ with the phase 2, T_1' and T_2', fall between the equilibrium temperatures T_1 and T_2 of the form 3 with the

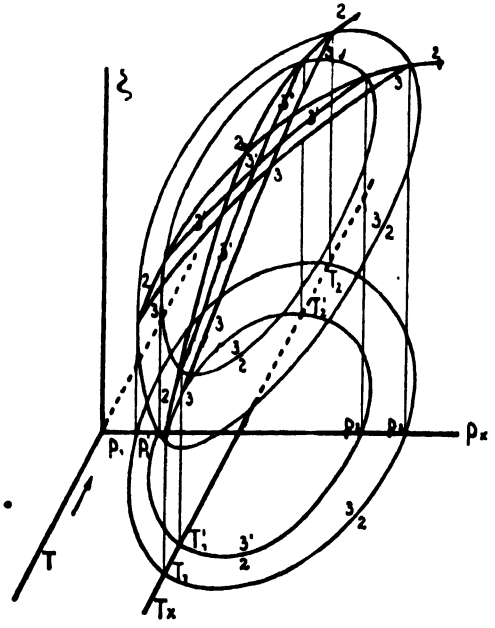


FIG. 60.

phase 2. In the same way the equilibrium pressures of the totally unstable form 3′, the pressures p_1' and p_2', fall between the equilibrium pressures of the stable phase, p_1 and p_2.

If the equilibrium curve of the totally unstable form with the phase 2 be conceived as divided into its four quadrants by the two neutral curves it is possible to formulate the special rule that regardless of how the two neutral curves of the two forms lie with respect to each other, the equilibrium pressure of the stable form with phase 2 is smaller in the first and fourth quadrants than that of the unstable form with the same phase, and that in the second

and third quadrants this relation is reversed. The equilibrium temperature of the unstable form in the first and second quadrants of the equilibrium curve of the unstable form always lies below the equilibrium temperature of the stable form, and in the third and fourth quadrants, always above the equilibrium temperature of the stable form.

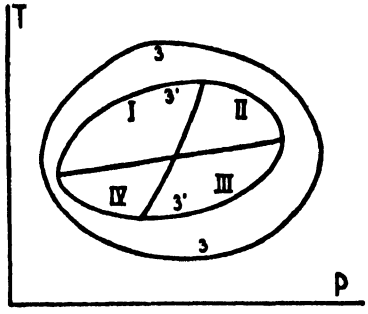


Fig. 61.

It is therefore possible that if the fourth quadrant of the equilibrium curve of the unstable form be in the region of unrealizable negative absolute temperatures and pressures, the equilibrium curve of the unstable form will remain in the region of realizable condition.

1. Division into Thermal Crystal Groups

With the criteria at hand for the determination of the order of stability of different forms we are enabled to look more closely into the question of the division of forms upon the basis of stability relations. As we have seen, two cases are possible with respect to the positions of the surfaces of the thermodynamic potential: either they intersect or they do not intersect. In the first case, a change in the stabilities of the two forms occurs upon crossing the transition curve, each of the two forms is partly stable and partly unstable; the designation stable or unstable changes for the same form with the crossing of the transition curve. In the second case the one form is stable in the whole phase field; it is designated as totally stable whereas the other form is totally unstable.

Experimental investigation has shown that some substances show no transformation curves to high pressures (12,000 kg.) whereas others exhibit one or more such curves. It is possible that this difference is not absolute but merely quantitative, that in the first class the transformation curves occur at very high pressures and in the second class at much lower pressures. The designation of total stability presupposes a knowledge of the whole field of the anisotropic state though actually this is not at our disposal.

The problem is somewhat different with respect to total instability. In this case there are forms unstable in the field of state of a stable form, and the equilibrium curves of the unstable form with the neighboring phases with which the stable form may also come into equilibrium run parallel to the equilibrium curves of the stable form with the same neighboring phases. This parallelism indicates a close relationship between the ζ-surfaces of the two forms and therefore also between their equations of state. To the present time only one case of this kind has been accurately investigated, namely, Ice III and Ice III'. In addition to these two forms the melting curves of still more unstable forms have been followed to 3000 kg., and have been found to run close beneath the melting curve of the stable form and not to intersect it (Chapter VII). In addition to the investigations on ice, the fields of state of substances that form one or more unstable forms from their melts have been investigated with respect to the existence of transformation curves, and it has been found that no such curves occur. It follows that the forms unstable at $p = 1$ kg. remain so at higher pressures, otherwise a transformation curve would obtain upon which a change in stability would take place, stable into unstable. Since this is the case, the unstable forms of the substances listed in the table below are probably totally unstable.

In order to designate a form as totally unstable it is named according to the form in the field of state of which falls its melting curve, sublimation curve, and other equilibrum curves, and its unstability is indicated by one or more accent marks.

As examples, the melting points of a few forms with their appropriate designations are given in the following table:

	I	I'	I''	I'''	I''''
Benzophenone	48 5	46	26		
Salol	42 0	38 8	28 5		
Betol	95 0	95	93	91	?
$CH_2ClCOOH$ (monochloracetic acid)	61.2	56	50	43 7	

In the case of sulphur, besides the two stable forms, there are still more unstable forms[1] existing in fields not distinct from those of the stable forms.

[1] Brauns, *N. Jahrb. f. Mineralogie.* Supplementary Volume, **13**, 39 (1900).

A definite relation as regards the equilibrium curves exists between a part of the unstable forms and the stable form accompanying each: the equilibrium curves of the unstable form accompany those of the stable in long pieces though always remaining completely within the phase field of the stable form. The forms that bear this relation to each other can be designated as members of a thermal crystal group. The forms of different groups can come into equilibrium with each other but not with members of the same group. This division of crystal forms is much more fertile than the first, according to which crystal forms are either enantiotropic or monotropic. The greater part of the monotropic forms belong to the group of one known stable form, though in all probability some monotropic forms belong to another group, the field of state of which lies at higher pressures; for example, the diamond, unstable at low pressures, does not belong to the group of graphite, and aragonite does not belong to the group of calcite, as may be seen from the following discussion.

Besides the association of the equilibrium curves of members of one thermal crystal group as described above, there are other criteria for the range of activity of two forms in the same or in different crystal groups. Namely, if the v-values of the unstable form be smaller than the Δv-value of the stable form, and if the same relation hold for the heat of fusion, it is very probable that the unstable form remains unstable over a wide interval of pressure with respect to the second, stable form.[1] On the other hand if the Δv-value of the unstable form be greater than that of the stable it is probable that the unstable form attains at higher pressures a phase field in which it is stable. If the heat of fusion of the unstable form be greater than that of the stable it is probable that the unstable form attains at higher temperatures a field in which it is stable. This will be considered again in § 4.

Our knowledge of polymorphism is still very incomplete, especially with respect to unstable forms. The inadequacy of the division of the forms into enantiotropic and monotropic is not commonly felt in the consideration of unstable forms. Limited, as so often is the case, to investigation at ordinary pressures, the investigator is commonly satisfied with the information that a new

[1] *Zur Thermodynamik der Gleichgewichte, II. Der Polymorphismus.* (The Thermodynamics of Equilibrium. II. Polymorphism.) *Ann. d. Physik.*, **40**, 297 (1913).

form is less stable than the form already known, in a temperature range extending to the melting point, or that the new form has a transition point at higher temperatures at which it changes into a form stable above the transition temperature. For this requirement in the majority of cases the classification of enantiotropic and monotropic is sufficient. But if a form, the phase field of which lies at higher pressures, can be realized at ordinary pressures, on sufficient temperature elevation this form will pass into the form stable at ordinary pressure and will therefore behave like a monotropic substance, though at higher pressures it is actually enantiotropic with reference to the form stable at ordinary pressures. As an example, Ice III and Ice II at ordinary pressure below $-130°$ are monotropic with reference to Ice I, though at higher pressures they stand in the relation of enantiotropy with respect to Ice I. In the cases of diamond and aragonite, of course, the equilibrium curves with graphite and calcite running to higher pressures are not known, but since both diamond and aragonite are denser than the forms stable at ordinary pressures the existence of these equilibrium lines is very probable. Both diamond and aragonite have been designated as monotropic, but they might just as well be called enantiotropic. If the criteria of total instability be considered and only those forms be designated as monotropic that show in the light of these criteria a condition of total instability, then the term monotropic would be synonomous with total instability and nothing could be said against the use of the term. Since the designation "total instability" almost always asserts more than we know, the forms with the indications of total instability are called shortly "unstable."

2. The Determination of Transition Points and the Experimental Differentiation between Unstable and Stable Crystal Forms

In Chapter IV, 3, page 36, it was shown that some properties of a substance change discontinuously upon a change in the state of aggregation and that others do not show such discontinuous change, a discontinuous change marking the change in state in the latter case only in the differential quotient with respect to temperature or pressure. This behavior is of importance

for the investigation of transition points. Since a discontinuous change upon a curve is easier to detect than a point of inflection, corresponding to a discontinuous change in the first differential, the properties of the first class are given preference over those of the second for the purpose of determining transition points.

Such discontinuously changing properties are the heat content, the specific volume, the optical properties, the magnetisability and the electrical conductivity; and an investigation of the dependence of these properties upon the temperature will yield the information desired. Of course, the change in one or more of these properties can be so small that it can be discovered only by use of great quantities of substance and by refinement of the method of investigation. For example, nickel has a transition point at 330° at which it passes from a ferromagnetic state to a paramagnetic. This transition point can easily be observed by rough methods. On the other hand, the change in the heat content and in the specific volume are very small. For this reason a retardation in the cooling velocity can be observed only with the use of large quantities (1 kg.), and an elongation of a nickel rod as a result of the transformation can be observed only when the rod has considerable length.

The great difference between the change in different properties occurring upon transformation may be illustrated by another example. $K_2Cr_2O_7$ crystallizes from its melt in magnificent red crystals which upon cooling break up into a fine powder, indicating a large volume change upon transformation. However, upon the cooling curve of $K_2Cr_2O_7$ no retardation in the cooling velocity can be recognized.[1]

It is a fact worthy of notice that in some cases an expected transition will not occur, or will occur very irregularly, under ordinary conditions, but that in the presence of some medium the transition will take place promptly and completely. Such a case is the transition of ordinary tin into grey tin (transition point 20°) which ordinarily occurs very irregularly and with a great amount of supercooling. In contact with a solution of $SnCl_4$ the transition is regular, though requiring a good length of time for completion.[2] Evidently the number of transition centers on the surface of the tin is greatly increased by the medium.

[1] *Kristallisieren und Schmelzen.* Page 40.

[2] E. Cohen. *Z. phys. Chem.*, **14**, 53 and 535 (1894).

The influence of dissolved admixture upon the transition point is also of interest. The crystal Hg_5Tl_2, m. p. 14.5°, in the pure state shows no transition point. An addition of 0.0038 per cent Pb causes the appearance of a very significant transition point upon the cooling curve at 12-13°, accompanied by a discontinuous change in volume.[1]

Ordinarily transformations occur with great regularity upon cooling as well as upon heating. On the other hand, the lack of such regularity does not safely preclude the possibility of transformation.

a. Methods that Make Use of Discontinuously Changing Properties

A transition in the solid state occurring without undercooling or overheating will make itself manifest by the appearance of a point of arrest upon the cooling curve and heating curve in addition to that of the melting point. The duration of arrest caused by a transition in the solid state is ordinarily considerably shorter than that due to fusion or crystallization, for the reason that the heat of transition is ordinarily smaller than the heat of fusion. The reverse may be true, however, as in the cases of Na_2SO_4 and Li_2SO_4.[2] Undercooling and overheating has the effect of changing the form of the cooling curve and the heating curve at the point of halt from a horizontal to a maximum or minimum. If the temperature of the point of halt upon the heating curve differ from that upon the cooling curve there will be a question as to the actual position of the equilibrium temperature. A great amount of undercooling with little overheating would give an average value too low, and the reverse condition too high. Suitable inoculation, or strong local heating or cooling of a small portion of the mass, will diminish this difference and will permit the determination of the true equilibrium temperature. A low linear

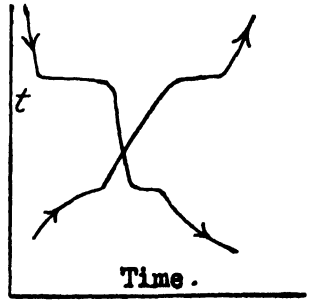


FIG. 62.

[1] G. D. ROOS. *Z. anorg. Chem.*, **94**, 358 (1914).
[2] *Z. anorg. Chem.*, **43**, 273 (1905).

transformation velocity will change the point of halt to an interval of delayed cooling velocity.

Occasionally a point of halt other than that of the melting point will occur upon the heating curve but not upon the cooling curve (Fig. 63). This may be caused by a transformation of an unstable form into a stable, or by the formation of a stable form, in the time between the taking of the cooling and the heating curve, that undercools so greatly that no indication of it appears upon the cooling curve. In the case of an irreversible transition of an unstable form, inoculation of the melt will cause the freezing point to be raised and the temperature and duration of arrest of the upper point of halt to be increased. After this treatment the lower point of halt will not be found upon the heating curve.

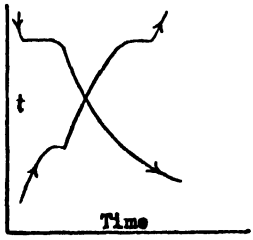


Fig. 63.

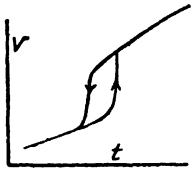


Fig. 64.

For the determination of the transition point upon the basis of volume change, VAN'T HOFF [1] has made frequent use of a simple dilatometer. Figure 64 represents graphically in scale divisions the height of the dilatometer liquid in dependence upon temperature, with rising temperature in one case and falling temperature in the other. The greater the transformation velocity the steeper will be the curve of volume change upon transition and the more closely will correspond the transition temperatures obtained upon heating and cooling. If the substance investigated behave normally as represented in Fig. 64, in order to obtain an accurate determination of the equilibrium temperature it will be necessary first to transform a portion of the substance and then to determine the volume change resulting from a very slow change in bath-temperature. Under these conditions an almost perpendicular line can be obtained at the temperature of the transition point.

[1] *Z. phys. Chem.*, **17**, 50 (1895).

The change in orientation and in double refraction in a thin layer of substance as observed between crossed Nicols is very striking, but unfortunately the microscope is an obstacle to accurate temperature control and determination.

The electrical resistance also changes discontinuously with transformation but the method can be used only for relatively good conductors.

b. Methods Founded upon the Measurement of the Temperature Dependence of Properties that Do Not Change Discontinuously upon Transformation

Such properties are the vapor pressure and the solubility in a liquid. If the values of these properties be plotted in dependence upon temperature, two lines intersecting at the transition point will commonly be obtained. Of course the vapor pressure below the melting point is ordinarily so small that this method is of little importance. The solubility likewise is of little importance in this respect because of the trouble inherent to its determination.

A determination of the electromotive force in a circuit composed of ordinary tin, a stannous salt, and grey tin, in dependence upon temperature will furnish two curves with a break, a point of inflection which is the transition point, at which the electromotive force is zero.[1]

3. Quantitative Relations between the Positions of the Equilibrium Curves of a Series of Forms of Different Stabilities and the Stabilities of these Forms

a. The Measure of Stability

For two forms of different stabilities coming into equilibrium with one and the same third phase, the following equation may be derived to express the relation between the ζ-values of the two forms, their equilibrium pressures with the third form, and the volumes of the stable forms and that of the third form, as is evident from the positions of the ζ-isotherms in Fig. 68*b*:

$$\zeta_3{}'_{p_1'} - \zeta_{3p_1} = \int_{p_1}^{p_1'} \frac{d_T\zeta^2}{dp}\,dp = (\zeta_3' - \zeta_3)_{p_1'} + \int_{p_1}^{p_1'} \frac{d_T\zeta_3}{dp}\,dp. \quad (1)$$

[1] E. Cohen. *Z. Phys. Chem.*, **14**, 53 (1894).

From this equation may be obtained:

$$(\zeta_3' - \zeta_3)_{p_1'} = \int_{p_1}^{p_1'} \left(\frac{d_T\zeta_2}{dp} - \frac{d_T\zeta_3}{dp}\right)dp = \int_{p_1}^{p_1'} (v_2 - v_3)dp. \quad (2)$$

These equations are equally valid for partially and for totally stable forms, because both equations permit a converging or a diverging of the ζ-isotherms of the forms 3′ and 3 with increasing pressure.

If ζ_2 and ζ_3 in the interval p_1 to p_1' can be expressed as a linear function of the pressure, as is the case when the pressure nterval $p_1' - p_1$ gives vanishing values for

$$\frac{d_T v_2}{dp} \text{ and } \frac{d_T v_3}{dp},$$

equation (2) can be written

$$(\zeta_3' - \zeta_3)_{p_1'} = (v_2 - v_3)\cdot(p_1' - p_1). \quad . \quad . \quad . \quad (3)$$

This equation, as well as those following, in the derivation of which it is assumed that the ζ-isotherms or ζ-isobars are linear, may be applied only to pieces of the equilibrium curves that may be regarded as straight lines. In accordance with this assumption the corresponding ζ-surfaces will be plane surfaces and their lines of intersection and the projections of these lines upon the pT-plane will be straight lines.

For a series of unstable forms 3′, 3″, etc., the ζ-values of which at the same pT-point stand in the relation $\zeta_3' > \zeta_3''$, etc., we have

$$(\zeta_3' - \zeta_3)_{p_1'} = (v_2 - v_3)\,(p_1' - p_1)$$
$$(\zeta_3'' - \zeta_3)_{p_1''} = (v_2 - v_3)(p_1'' - p_1)$$

And it follows that:

$$(\zeta_3' - \zeta_3)_{p_1'} : (\zeta_3'' - \zeta_3)_{p_1''} = (p_1' - p_1) : (p_1'' - p_1). \quad (4)$$

A series of unstable forms coming into equilibrium with one and the same phase at different equilibrium pressures will exhibit differences in ζ-values as compared to the ζ-values of the stablest form, which are proportional to the corresponding differences in the equilibrium pressures at the same temperature, and since at the same pT-point the greater stability corresponds to the smaller ζ-value, the distances of the equilibrium curves from the pT-plane measure the stabilities of these forms.

Analogous relations are obtained in the investigation of the ζ-isobars of the forms 3 and 3′ which come into equilibrium with one and the same plane 2 at the temperatures T_1 and T_1'. It may be seen from Fig. 65 that

$$\zeta_3'_{T_1'} - \zeta_{2T_1} = \int_{T_1}^{T_1'} \frac{d_p\zeta_2}{dT} dT = (\zeta_3' - \zeta_3)_{T_1'} + \int_{T_1}^{T_1} \frac{d_p\zeta_3}{dT} dT, \quad (5)$$

and from (5) may be obtained

$$(\zeta_3' - \zeta_3)_{T_1'} = \int_{T_1}^{T_1'} \left(\frac{d_p\zeta_2}{dT} - \frac{d_p\zeta_3}{dT}\right) dT = -\int_{T_1}^{T_1} (\eta_2 - \eta_3) dT. \quad (6)$$

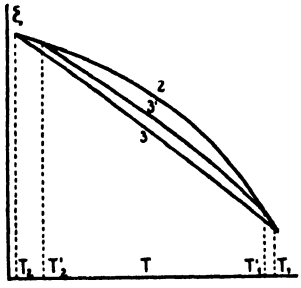


Fig. 65.

If η_2 and η_3 in the temperature interval $T_1 - T_1'$ be independent of the temperature, then

$$\eta_2 - \eta_3 = \frac{R_{3,p}}{T_1},$$

and the following approximation formula may be obtained:

$$(\zeta_3' - \zeta_3)_{T_1'} = (\eta_2 - \eta_3)(T_1 - T_1') = \frac{R_{3,p}}{T_1}(T_1 - T_1'). \quad (7)$$

For a series of unstable forms 3′, 3″, etc., an equation similar to (4) may be obtained:

$$(\zeta 3' - \zeta_3)_{T_1'} : (\zeta_3'' - \zeta_3)_{T_1''} = (T_1 - T_1') : (T_1 - T_1''). \quad (8)$$

At the equilibrium temperatures at which a series of unstable phases come into equilibrium with one and the same phase, the instability of the forms increases with respect to that of the stablest form proportionately to the differences of the equilibrium temperatures of the forms as referred to the equilibrium pressures of the stablest form.

Equations (4) and (8) are valid regardless of the nature of the phase with which the forms of different stability come into equilibrium; it may be gaseous, liquid, or crystalline. The differences of the equilibrium curves from one another in the direction of the p- and T-axes will, of course, be a measure of the relative instabilities of these forms only when the forms come into equilibrium with one and the same phase.

The formulation of these laws for special cases has already been given elsewhere.

From the positions of the vapor pressure curves of the forms of different stabilities, VAN'T HOFF [1] inferred that the triple-point at which the unstable form is in equilibrium with its vapor and its melt must lie at a lower temperature than that of the analogous triple-point of the stable form, and the author simultaneously arrived at the same result [2] in the statement that the order of melting points gives the order of stability for a series of unstable crystalline solids.

In equations (3) and (7),

$$(\zeta_3' - \zeta_3)_{p_1'} = (v_2 - v_3)\,(p_1' - p_1)$$

$$(\zeta_3' - \zeta_3)_{T_1'} = (\eta_2 - \eta_3)\,(T_1 - T_1')$$

the indices p_1' and T_1' may refer to the same point of state upon the equilibrium curve of the stable form 3′, and in this case the equation $(\zeta_3' - \zeta_3)_{p_1'} = (\zeta_3' - \zeta_3)_{T_1'}$ will be fulfilled and we have

$$\frac{T_1 - T_1'}{p_1' - p_1} = \frac{v_2 - v_3}{\eta_2 - \eta_3} = \left(\frac{dT}{dp}\right)_{2,3} \quad . \quad . \quad . \quad (9)$$

Thus the relation of the distances of a point upon the equilibrium curve of the unstable form 3′ in the direction of the T- and p-axes from the equilibrium curve of the stable form will give the direction of the equilibrium curve of the stable form. This relation may be had directly from Fig. 66. It can be seen that this relation is valid only when the equilibrium curve 2–3 is linear in the pressure interval $p_1' - p_1$; this condition is included in our original assumption, namely, that the ζ-isotherms and ζ-isobars are straight lines and that the ζ-surfaces are planes, since the

[1] J. H. van't Hoff, *Vorlesungen über theoretische und physikalische Chemie*, Section 2, first edition, 1899, page 127.

[2] *Z. phys. Chem.*, **29**, 67 (1899).

lines of intersection of the surfaces and also their projections upon the pT-plane, the equilibrium curves, are straight lines.

Let us further investigate the relations of the equilibrium pressure of two unstable crystal forms to the equilibrium pressure of two stable forms, the one unstable form belonging to the crystal group of one of the stable forms, and the other unstable form to the crystal group of the other stable form. In accordance with this assumption the ζ-isotherms of the forms 3 and 4 (Fig. 67) intersect those of the forms 3′ and 4′, whereas the ζ-isotherms of the forms of the same crystal group, the isotherms of 3 and 3′ and those of 4 and 4′, do not intersect. With the further assump-

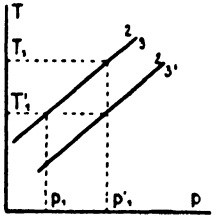


Fig. 66.

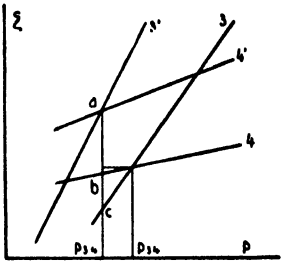


Fig. 67.

tion that the ζ-isotherms are linear as in the first case, the difference of the two equilibrium pressures, $p_{3,4} - p_{3',4'}$, in the pressure interval concerned will be given by equation (10).

From Fig. 67, $bc = ac - ab$, and since

$$ac = (\zeta_{3'} - \zeta_3)_{p_{3',4'}},\quad ab = (\zeta_{4'} - \zeta_4)_{p_{3',4'}},\quad \zeta_{3'p_{3',4'}} = \zeta_{4'p_{3',4'}},$$

and

$$bc = (p_{3,4} - p_{3',4'})\left(\frac{d_T\zeta_3}{dp} - \frac{d_T\zeta_4}{dp}\right),$$

it follows that

$$(\zeta_4 - \zeta_3)_{p_{3',4'}} = (p_{3,4} - p_{3',4'})\,(v_3 - v_4). \quad . \quad . \quad (10)$$

Since, as we shall see in section 4, the sign of the difference $v_3 - v_4$ at the equilibrium pressure $p_{3,4}$ must always be positive, the order of magnitude of $p_{3'}, {}_{4'}$ as compared to $p_{3,4}$ is determined only by the sign of the difference $(\zeta_3 - \zeta_4)_{p_{3',4'}}$. The equilibrium pressure of the two unstable forms 3′ and 4′, $p_{3'}, {}_{4'}$, then falls into the field of state of the stable form that at the pressure $p_{3'}, {}_{4'}$ has the smaller ζ-value.

Since

$$(p_{3,4} - p_{3',4'}) = \frac{[(\zeta_3' - \zeta_3) - (\zeta_4' - \zeta_4)]_{p_{3',4'}}}{v_3 - v_4},$$

in which the sign of the left-hand member is determined by that of the numerator of the right-hand member, the difference of the relative instabilities $(\zeta_3' - \zeta_3) - (\zeta_4' - \zeta_4)$ of the forms 3′ and 4′ at their equilibrium pressure determines the difference of the two equilibrium pressures in such a way that the equilibrium pressure of the two unstable forms falls into the field of state of the stable form the accompanying unstable form of which has the greater instability.

A completely analogous result can be obtained by considering the ζ-isobars of two forms in two different crystal groups. By means of the method described above we obtain:

$$(\zeta_3 - \zeta_4)_{T_{3',4'}} = (T_{3'4'} - T_{3,4})\,(\eta_4 - \eta_3). \quad . \quad . \quad (11)$$

or

$$T_{3',4'} - T_{3,4} = \frac{[(\zeta_3' - \zeta_3) - (\zeta_4' - \zeta_4)]_{T_{3',4'}}}{\eta_3 - \eta_4},$$

from which can be drawn conclusions analogous to those obtained from equation (10). In this case likewise the equilibrium temperature of the unstable form falls into the field of state of that stable form, the accompanying unstable form of which has the greater instability.

The differences in the ζ-values of the two forms of the same crystal group given by equations (3) and (7) can be obtained in another manner. Namely, we have the equation

$$(\zeta_3' - \zeta_3)_{p_1'} = -\int_0^{T_1'} (\eta_3' - \eta_3)_{p_1'}\, dT$$

and

$$(\zeta_3' - \zeta_3)_{T_1'} = \int_0^{T_1'} (v_3' - v_3)_{T_1'}\, dp.$$

If these equations be combined with equations (3) and (7) the following equations are obtained:

$$(v_2 - v_3)\,(p_1' - p_1) = -\int_0^{T_1'} (\eta_3' - \eta_3)_{p_1'}\, dT. \quad . \quad . \quad (12)$$

and

$$(\eta_2 - \eta_3)\,(T_1 - T_1') = \int_0^{p_1'} (v_3' - v_3)_{T_1'}\, dp. \quad . \quad . \quad . \quad (13)$$

The values of the two integrals, difficult to determine experimentally, can be replaced by the more easily determinable left-hand members of equations (12) and (13).

4. The Conditions of Total Instability and of Partial Stability

A form 3′ will be totally unstable with respect to another more stable form 3 when the ζ-surface of form 3′ lies completely above the ζ-surface of form 3. If, however, the ζ-surfaces of the two forms intersect in the field of state defined by the melting curve, the two forms are partially stable.

In order to distinguish between total and partial stability it is therefore necessary to know not only the positions of the two ζ-surfaces but also the limits of the field of the anisotropic state. For it is possible that the ζ-surface of a totally unstable form should cut the ζ-surface of the stable form outside of the field of state of the unstable form. If this case appear, however, the two forms will be unstable with respect to a third form in the points of state that correspond to the curve of intersection of their ζ-surfaces and ordinarily the two forms will be no longer realizable at these points of state.

Bearing in mind the positions of the ζ-isotherms and ζ-isobars let us conceive the different possibilities of the positions of the curves of these two forms in order that we may discuss in an exhaustive way the cases in which a third phase is to be considered in addition to the curves of the two original forms.

With respect to the positions of the ζ-isotherms there are four cases to be distinguished, since two orders of magnitude can obtain for the volume of the unstable form 3′ and that of the stable form 3, and also for the compressibilities of the two forms. The order of magnitude of the volumes given in the following discussion represents that obtaining for 1 kg./cm.^{2}, and it is assumed that the compressibilities do not change with increasing pressure. After the introduction of these assumptions limiting the possible cases, and in matter of fact these assumptions are confirmed by experience, there are still four thermodynamically possible cases to distinguish:

$$(a)\quad v_3' > v_3 \quad \text{and} \quad \frac{d_T v_3'}{dp} < \frac{d_T v_3}{dp},$$

$$(b)\ v_3' > v_3 \quad \text{and} \quad \frac{d_T v_3'}{dp} > \frac{d_T v_3}{dp},$$

$$(c)\ v_3' < v_3 \quad \text{and} \quad \frac{d_T v_3'}{dp} > \frac{d_T v_3}{dp},$$

$$(d)\ v_3' < v_3 \quad \text{and} \quad \frac{d_T v_3'}{dp} < \frac{d_T v_3}{dp}.$$

To these four possibilities there corresponds four cases for the positions of the two ζ-isotherms with respect to each other. These are given in Figs. 68*a*, *b*, *c*, and *d*.

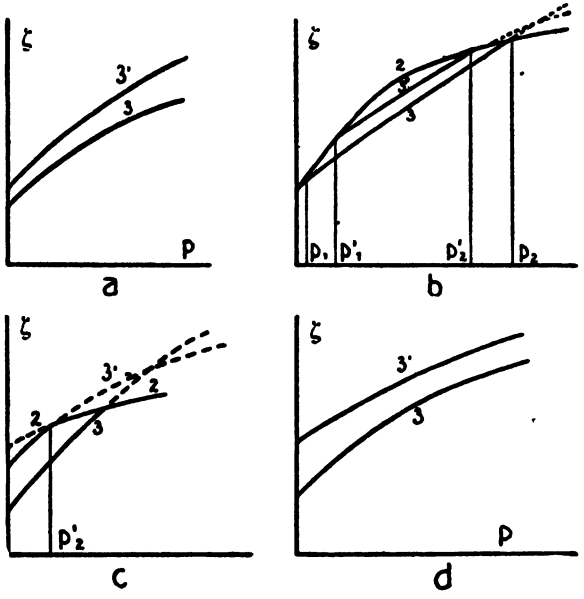


FIG. 68.

Case (*a*) is distinguished by the fact that the two ζ-isotherms cannot intersect, and case (*d*) by the fact that they do not intersect. In these two cases, therefore, the position of the ζ-isotherm of the third phase with respect to those of the two forms 3 and 3′ is of no importance. If their positions be those indicated in Fig. 68*a* and *d*, the form 3′ in relation to the form 3 will be totally unstable for all pressures at the temperature of this intersection through the ζ-surfaces. In the cases (*b*) and (*c*), however, the

position of the ζ-isotherm of phase 2 is of decisive importance for answering the question of whether form 3′ is totally or only partially stable. If the point of intersection of the isotherms ζ_3' and ζ_3 lie above the ζ-isotherm of phase 2, form 3′ is totally unstable, in other cases, partially stable.

Just as a change in sign can take place in $v_2 - v_3$ with rising pressure, if at low pressures v_2 be greater than v_3, a change in sign can likewise take place in $v_3' - v_3$, if v_3' be greater than v_3 at low pressures.

If the volume of the unstable form melting with volume increase at a pressure of 1 kg. be greater than the volume of the stable form, in the case of the stable substance melting with a volume decrease, the volume of the unstable form can be smaller than that of the stable form. But classic thermodynamics is unable to decide this question; nor can it state at which pressure the reversal of the concerned order of magnitude appears.

For the ζ-isobars of the forms 3′ and 3 there are wholly analogous relations. As in the first case there are here also four cases to be distinguished with the limitation that the relation in size of c_{p3}' and c_{p3} does not reverse with rise in temperature. These four cases are

$$(a)\quad \eta_3' > -\eta_3 \quad \text{and} \quad -\frac{c'_{p_3}}{T} < -\frac{c_{p_3}}{T},$$

$$(b)\quad \eta_3' > -\eta_3 \quad \text{and} \quad -\frac{c'_{p_3}}{T} > -\frac{c_{p_3}}{T},$$

$$(c)\quad \eta_3' < -\eta_3 \quad \text{and} \quad -\frac{c'_{p_3}}{T} > -\frac{c_{p_3}}{T},$$

$$(d)\quad \eta_3' < -\eta_3 \quad \text{and} \quad -\frac{c'_{p_3}}{T} < -\frac{c_{p_3}}{T}.$$

We will now derive the analytical and geometrical conditions of total and partial stability, chiefly with reference to case (*b*). Case (*b*) is of especial interest because conditions derived for it will hold for the other simple cases.

Form 3′ in comparison to form 3 will be unstable at constant temperature if its ζ-values, Fig. 68*b*, in the whole pressure interval between the two equilibrium pressures of the two phases 3′ and 2

be greater than the ζ-value of form 3. For the total instability of form 3 there must be the relation:

$$\zeta_{3p_1'} + \int_{p_1'}^{p_2'} \frac{d_T\zeta_3'}{dp}dp > \zeta_{3p_1'} + \int_{p_1'}^{p_2'} \frac{d_T\zeta_3}{dp}dp.$$

If we write

$$\zeta_{3p_1'} - \zeta_{3p_1'} > \int_{p_1'}^{p_2'} (v_3 - v_3')dp,$$

and remember that according to equation (2), page 128,

$$(\zeta_3' - \zeta_3)_{p_1'} = \int_{p_1}^{p_1'} (v_2 - v_3)dp,$$

we obtain

$$\int_{p_1}^{p_1'} (v_2 - v_3)dp > \int_{p_1'}^{p_2'} (v_3 - v_3')dp. \quad . \quad . \quad . \quad (14)$$

This relation in magnitude of the two integrals is then the condition for the total instability of form 3′ in relation to the form 3.

If the order of magnitude be reversed, the two forms will stand in the relation of partial stability. In order to distinguish in the following discussion a form that is partially stable in relation to a form 3, from a form 3′ which is totally unstable in relation to the form 3, we will designate it as form 4. The condition of partial stability is then given by the equation:

$$\int_{p_1}^{p_1'} (v_2 - v_3)dp < \int_{p_1'}^{p_2'} (v_3 - v_4)dp, \quad . \quad . \quad . \quad (15)$$

The conditions of total and partial stability may likewise be derived from the ζ-isobars.

From Fig. 65, page 129,

$$\zeta_3'{}_{T_1'} + \int_{T_1'}^{T_2'} \frac{d_p\zeta_3'}{dT}dT > \zeta_{3T_1'} + \int_{T_1'}^{T_2'} \frac{d_p\zeta_3}{dT}dT.$$

If we write

$$(\zeta_3' - \zeta_3)_{T_1'} > -\int_{T_1'}^{T_2'} (\eta_3 - \eta_3')dT,$$

and combine this relation with equation (6), page 129, we obtain

$$-\int_{T_1}^{T_1'} (\eta_2 - \eta_3)dT > -\int_{T_2'}^{T_2'} (\eta_3 - \eta_3')dT, \quad . \quad . \quad (16)$$

as the condition for partial instability of the form 3′ as compared to the form 3; and as the condition for partial stability, the relation:

$$-\int_{T_1}^{T_{1'}}(\eta_2-\eta_3)dT < -\int_{T_{1'}}^{T_{2'}}(\eta_3-\eta_4)dT. \quad . \quad . \quad (17)$$

If the equilibrium temperature T_2 fall below the absolute zero, it is to be replaced by $T = 0$.

In case the relations (14) and (16) be fulfilled at all pressures and temperatures for the forms 3′ and 3, the form 3′ will be totally unstable as compared to form 3, and with fulfillment of

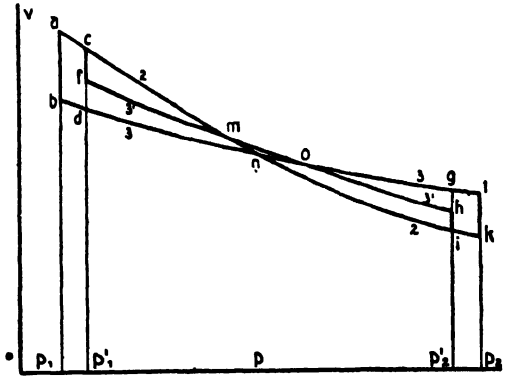


Fig. 69.

the relations (15) and (17) in a given region of state, the forms 3 and 4 stand in the relation of partial stability.

The relations obtained are made clear by the geometric interpretation of the conditions of total instability. Figure 69 represents the volume isotherm of phase 2 intersecting those of the two forms 3′ and 3; in fact the volume isotherms of the forms 3′ and 3 likewise intersect.

The relations given in (14) require that for the pieces of surface *acdb*, *ogh*, and *odf* the inequality

$$acbd > ogh - odf$$

be valid. Furthermore, an inequality analogous to (14), ob-

tained in a manner wholly analogous to that used for (14), is here valid, namely the equality:

$$-\int_{p_2}^{p_2'}(v_2 - v_3)dp < -\int_{p_1'}^{p_2}(v_3 - v_3')dp.$$

The geometric interpretation of this inequality is

$$glki > ogh - odf.$$

Besides this, according to page 45,

$$abn = nlk$$

and

$$cfm = mih.$$

The geometric interpretation of (16) is represented in Fig. 70, in which the η-isobars are given. If relations corresponding to those given above are fulfilled for the pieces of surface *abcd*, *odf*, *ogh*, the form 3′ will be unstable with respect to form 3 at all pressures, and similar to the above, the inequality obtains:

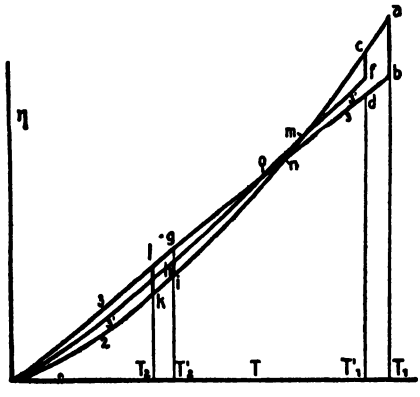


FIG. 70.

$$abcd > odf - ogh$$

and

$$glki > ogh - odf.$$

Furthermore, according to equation (5) of the first part, we have the following equations:

$$abn = nlk$$

$$cfm = mih.$$

5. The Position of the Phase Fields of Partially Stable Forms is Regulated by the Volume and the Heat Content of the Forms, and the Relative Magnitudes of these Properties Point to Total or to Partial Instability

Upon the crossing of an equilibrium curve as a result of isothermal pressure increase a system leaves the phase field of the form with the greater volume and enters the field of the form of smaller volume. Upon isobaric temperature increase a system leaves the phase field of the form of lower heat content and enters that of the form of higher heat content.

The proof of these two generalizations may be obtained by the help of the ζ-function in the following manner.

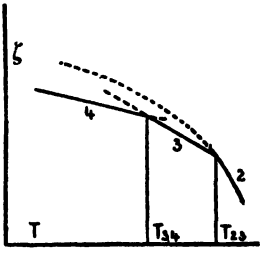


Fig. 70a.

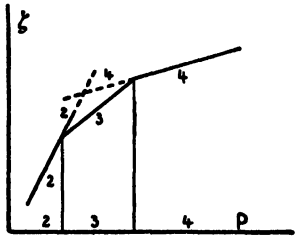


Fig. 70b.

Figure 70*a* gives the isotherm of the liquid, curve 2, and the isotherms of the partially stable forms, curves 3 and 4. The directions of these curves at the points of intersection are given by the relations

$$\frac{d_T\zeta_2}{dp} > \frac{d_T\zeta_3}{dp} \quad \text{and} \quad \frac{d_T\zeta_3}{dp} > \frac{d_T\zeta_4}{dp},$$

and therefore

$$v_2 > v_3 \quad \text{and} \quad v_3 > v_4.$$

It may be seen, if these relations be valid and if the ζ-isotherms intersect, that each of the phases 2, 3, and 4, possesses a pressure interval in which it is stable in comparison to the two other phases, because a pressure interval exists for each phase with the fulfillment of the stated conditions in which the ζ-isotherm of the phase lies lower than those of the other two phases. These pressure intervals must then follow each other in a series according to decreasing volume.

In an analogous way there may be obtained for the ζ-isobars of the phases 2, 3, and 4, Fig. 70*b*, the rule that the phase stable at higher temperature forms from the phase stable at lower by an absorption of heat; the series of temperature intervals in which the ζ-isobar of each of the three phases lies lower than those of the other two phases, that is, the temperature interval in which the phase concerned is stabler than the other two, will require that

$$\frac{d_p\zeta_4}{dT} > \frac{d_p\zeta_3}{dT} > \frac{d_p\zeta_2}{dT},$$

or that

$$-\eta_4 > -\eta_3 > -\eta_2;$$

from it which it follows that

$$\eta_3 - \eta_4 > 0 \text{ and } \eta_2 - \eta_3 > 0,$$

and for the heat of transformation at constant pressure,

$$(\eta_3 - \eta_4)T_{34} > 0 \text{ and } (\eta_2 - \eta_3)T_{23} > 0.$$

These two rules become of practical importance when it is desired to prognosticate the fields of state of absolute stability of two forms the transformation curves of which at present lie beyond the approach of experiment. At this point we need merely to mention the cases of diamond and graphite.

In close relation to these universally valid rules there stands two other rules to which, however, only a certain likelihood is to be accorded. These are as follows: The probability that the ζ-isotherms of two forms will intersect upon increasing pressure is much less if they diverge at low pressures than if they converge. Accordingly, if the volume of the unstable form be greater at low pressures than that of the stable form it is probable that the unstable form remains less stable than the stable form at all pressures, and if the reverse order of magnitude in volume obtain, it is probable that the two forms are partially stable. Similarly, it is less likely that the ζ-isobars of the two forms will intersect at lower temperatures if at the melting point of the unstable form the two ζ-isobars diverge, than if they converge. If the entropy of the unstable form at its melting point be greater than that of the stable form, or if the heat of fusion of the unstable form be

greater than the heat of fusion of the stable form at the melting point of the unstable, it is then probable that the unstable form at all temperatures below its melting point will remain less stable than the stable form, and if the opposite relation in size obtain for the heats of fusion it is probable that a change in stability will occur, that both forms are partially stable.

It is evident, therefore, that the relative magnitudes of the volumes and of the heats of fusion of two forms differing in stability are to be regarded as indications of total or partial stability. If the unstable form have the greater volume and the smaller heat of fusion, a change in stability probably will not occur. On the other hand, a change in stability is not to be expected if the reverse order of magnitude obtain for the volumes and the heats of fusion.

6. The Melting Curves of Unstable Forms

If the specific volume and the specific heat content of an unstable form be greater than the corresponding quantities of the stable form, then, as we have seen, the melting curve of the unstable form has its course wholly within the phase field of the stable form. This has been confirmed by all experimental investigations made to the present time. Of course, the experimental testing of this law is hampered by difficulties caused by the instability of the unstable form.

1. Benzophenone occurs in three forms with melting points of 48.5°, 46°, and 26°. The melting curve of the 48.5° form has been followed to 3500 kg. without finding a triple-point upon the melting curve, and a thorough investigation of the phase field of this form showed that no transformation curves exist there. It follows from this that in the phase field concerned the form with the melting point of 48.5° remains always the most stable. Since the form with the melting point of 26° has the greater specific volume and the smaller heat of fusion, the law given above applies to these two forms.

2. The substances discussed in the following paragraphs display unstable forms having specific volumes and heat contents greater than those of the stable forms, and it can be directly shown that the melting curve of the less stable form runs within the phase field of the more stable.

The two melting curves of the forms of menthol with melting points 42.5° and 36.5°, according to HULLET,[1] run linearly up to a pressure of 310 kg. and are parallel throughout.

The melting curves of the two forms of dibrompropionic acid with melting points 64° and 51° diverge significantly with increasing pressure, according to the measurements of W. WAHL.[2] The determinations were carried out in a pressure apparatus with glass windows, and the substance was investigated with crossed Nicols.

The melting curves of the two forms of acetamide and ethyl aminocrotonate have been determined by F. KÖRBER[3] to a

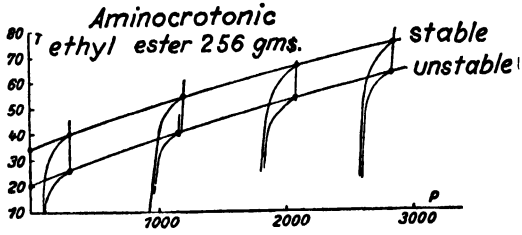


FIG. 71.

pressure of 3000 kg. At an undercooling of 20–40° the less stable forms crystallize from the melt, at − 20° these change rather quickly to the more stable. In this way the unstable form can be prepared first in a pressure-tight cylinder, and its pT-line can be determined upon heating, as shown by Fig. 71. After the determination has been carried out for the unstable form the substance is cooled to − 180° in order to change the unstable into stable, and then the pT-line of the stable is determined.

The melting points of the two forms are recorded in the table at equal pressures, the equilibrium pressures of the two forms. For the two substances investigated the difference of the equilibrium temperatures decreases with increasing pressures, though the difference of the equilibrium pressures increases.

Of the two forms of these substances the less stable has the greater volume and the smaller heat of fusion and it is therefore

[1] *Z. phys. Chem.*, **28**, 668 (1899).
[2] *Phil. Trans.*, Series A, **212**, 140 (1912).
[3] *Z. phys. Chem.*, **82**, 45 (1913).

Substance	p	Melting Point		Melting Point Difference
		Stable	Unstable	
Acetamide	1	80 1	69 4	10 7
	600	91 6	81 3	10 3
	1600	103 0	92 8	10 2
	2800	111 8	103 2	8 6
Ethyl aminocrotonate	1	34 0	19 9	14 1
	300	39 2	25 7	13 5
	1200	53 1	40.3	12 8
	2100	64 9	52 5	12 4
	2800	72.6	60.2	12 4

Substance	T'	Melting Pressure		Melting Pressure Difference
		Stable	Unstable	
Acetamide	80	520	1	520
	85	910	260	750
	90	1370	520	850
	95	1810	870	940
	100	2380	1330	1050
	103	2830	1600	1230
Ethyl aminocrotonate	33	800	1	800
	35	870	50	820
	40	1170	340	830
	45	1530	660	870
	50	1900	1000	900
	55	2320	1340	980
	60	2800	1730	1070

very probable that the melting curve of the less stable form in its whole course falls within the phase field of the more stable form, and the differences of the equilibrium pressures can either decrease or increase with rising pressure. In the latter case the difference is to be expected to continue to increase at still higher pressures. The differences of the equilibrium pressures perhaps always increase with temperature.

The equilibrium curves of the unstable forms of the ices will be discussed on page 167.[1]

7. Atomic Explanation of Thermal Crystal Groups

The equilibrium curves of the forms of one crystal group with neighboring phases are arranged in such a manner that the equilibrium curves of the unstable forms fall within the phase field of the stable, and accompany the equilibrium curve of the stable form in a series of nearly parallel lines. This fact indicates a close relationship between the equations of state of the forms of one group, and this close relationship may be ascribed to the fact that the various forms in one crystal group consist of similar molecules arranged upon different lattices, whereas in different groups of the same chemical substance, different molecules are arranged upon different lattices.

a. These different molecules may be isomers or polymers. If they were always polymeric it would be expected that substances showing normal behavior as liquids, that is, substances possessing a normal heat of vaporization and a value for the temperature coefficient of the molecular surface energy $\frac{d\alpha(Mv)^{2/3}}{dT}$ greater than 2.0 which is independent of the temperature, would give but one crystal group, whereas associated liquids should display two or more crystal groups. If the condition exist that a liquid contains but two kinds of molecules and the molecule of smaller volume manifests itself at low pressures by forming crystals, it is possible that only one crystal group may obtain. On the other hand if no isomeric molecules exist in the melt of a substance forming a normal liquid, it is to be expected that the forms of only one group will be produced upon crystallization. This expectation is satisfied in general, but as a result of the occurrence of isomeric molecules the presence of which is not shown by the criteria for association, some apparently normal liquids display two or more crystal groups, as, for example,

[1] Lists of unstable (monotropic) forms are given by Lehmann, *Molekularphysik* (1888); G. Tammann, *Z. phys. Chem.*, **25**, 442 (1898); A. H. R. Müller, *Z. phys. Chem.*, **86**, 178 (1913); and K. Schaeling, *Dissertation*, Marburg, 1910, who investigated 550 carbon compounds and of these recognized 80 as monotropic.

benzene, carbon tetrachloride, carbon tetrabromide, and methylene iodide. Inasmuch as no method exists at the present time for the detection of isomeric molecules in liquids, these cases must remain at the present time as exceptions to the general rule.

b. The existence of several kinds of molecules in a liquid, such as water or phenol, may be inferred from an abnormally great decrease in the volume isobar over a strip of the pT-plane; such a decrease indicates that molecules of large volume are transformed by the pressure increase into those of smaller volume.

The direction of this strip upon the pT-plane, its dT/dp value, must be equal to the quotient of the volume change, Δv, and the entropy change R_p/T referred to the transformation of a unit of mass of the molecules of the greater volume into that of smaller volume. For the change in the equilibrium constant K of a reaction at constant pressure we have:

$$\frac{d \ln K}{dT} = - \frac{R_p}{RT^2}$$

and for the transformation with which we are concerned, at constant temperature:

$$\frac{d \ln K}{dp} = - \frac{\Delta v}{RT}$$

and for the same change in the equilibrium constant K, we have

$$\frac{dT}{dp} = \frac{\Delta v T}{R_p},$$

which gives the simultaneous change of p and T which must be undertaken in order that the concentration of the two kinds of molecules remain unchanged. This equation is identical with that for the equilibrium of two kinds of crystal consisting of the same kind of molecule. It differs in the fact that in the transformation of crystal varieties, Δv and R_p refer to a unit of mass of substance, whereas with the transformation in homogeneous liquids these quantities do not refer to a unit of mass of the liquid, but to a greater quantity, since besides the two kinds of molecules in question there can be present considerable quantities of other molecules. Still, it is to be expected that if the transformation be evident upon the volume surface, the direction of its strip upon the

pT-plane will coincide with the corresponding transformation curve and the strip will intersect the melting curve in the neighborhood of the transformation curve of the two forms. This actually occurs in the cases of water and phenol (see their equilibrium diagrams), and it may be considered as confirmation of the assumption that only such molecules form into crystals as are present in the liquid prior to crystallization, and that no new molecules form for the purpose of crystallization. The liquids from which several crystal groups separate accordingly appear to be mixtures of several kinds of molecules each of which is capable of forming a crystal group. In the pressure-temperature region of the melting curve of a given crystal group the melt is rich in the molecule that possesses the lattice of this group. Upon the transformation to the melting curve of another group the liquid becomes impoverished of the former molecules and the concentration of the molecules now making themselves evident by crystal formation increases.

c. Finally, another fact points towards our conclusion that the molecules evincing themselves by crystal formation must be present in the liquid prior to crystallization. An increase in pressure results in a decrease in the concentration of the molecules of larger volume, and in the light of the preceding statement it is to be expected that the only kind of molecule manifesting itself at higher pressures by crystallizing would be those of smaller volume. And from this it follows that the transformation curves that intersect the melting curve will always lie under the parallel to the p-axis passing through the concerned triple-point. If the transformation curves were to lie above this parallel, as in Fig. 72, Form II would then have a greater volume than Form I and it would be developed from the liquid at higher pressures than Form I, which is in contradiction with the assumption that the liquid with increasing pressure becomes impoverished in the molecules of greater volume. It is therefore to be expected that the position of the transformation curve which intersects the melting curve as represented in Fig. 72, does not actually occur,

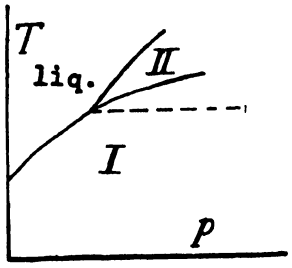


Fig. 72.

and in fact such a position of the transformation curve has never been observed with certainty, though thermodynamically it has the same probability as other positions.

In summary, then, normal liquids (that is, liquids that contain only one kind of molecule and therefore contain neither polymeric nor isomeric molecules) upon crystallization deposit the forms of only one crystal group, C, C', C''. . . . Abnormal liquids are able to deposit the forms of different crystal groups, C_1, C_1', C_1'' . . . and C_2, C_2', C_2''. . . . The conclusion that the molecules present in a liquid can become manifest by the formation of crystals independently of each other is commonly confirmed by experience.[1]

8. Determination of the Molecular Weight of Crystal-Building Molecules

The term molecule is used to designate the masses of a substance that move about independently in the vapor of the substance. At temperatures far below the melting point the molecules are fixed in lattices in which their atoms vibrate about a fixed point representing the position of the atom in the lattice. The energy of this vibration at lower temperatures appears to be very small, since the law of Neumann-Kopp is applicable to the specific heat of compounds. The conception of molecules at low temperatures is without significance, and it may therefore be said that the molecular weight of a substance in crystalline form is equal to the weight of the crystal.

At temperatures near the melting point, however, even with crystals of complex composition, demonstrable diffusion occurs, and in this temperature range the molecular weight of the crystal may properly be discussed. It appears that generally only one kind of molecule crystallizes from the melt even though the melt contain more than one kind.

The molecular entropy-change on melting, $r_p \cdot M/T_1$ (r_p is the heat of fusion per one gram in cal., M the molecular weight, and T_1 the absolute temperature of the melting point), fluctuates for normal liquids, according to P. Walden,[2] around the value

[1] *Z. f. Elektroch.*, **14**, 713 (1908).
[2] *Z. phys. Chem.*, **82**, 172 (1913).

13.5 cal. This is true for substances, the molecules of which are built up of 6–8 atoms. In the case of the crystallization of liquids containing more than one kind of molecule there is to be added the heat of transformation of the molecules that change during crystallization into those forming the crystals. This amount of heat is the product of the heat of transformation, w per one gram, multiplied by the weight of the transformed molecules, $\Delta\alpha$, in one gram of the melt. For such a mixture of molecules we have

$$\frac{r_p M}{T_1} \pm \frac{\Delta\alpha \cdot w}{T_1} = 11 \text{ to } 16 \text{ cal.}$$

With normal liquids $\Delta\alpha = 0$, the rule of WALDEN holds, and it is possible to determine the molecular weight of the crystallizing molecules. With abnormal liquids the determination is likewise feasible if w have a negligibly small value. This is the case for the modifications of ice, I, III, V, and VI, and since these modifications have nearly the same value for r_p/T, their molecular weights cannot be different. The molecular weight calculated in this way for the modifications of ice has a value of 53–60, corresponding to the formula $(H_2O)_3$, the molecular weight of which is 54. It is to be remembered, however, that the simple formula for water has only three atoms and accordingly the rule of WALDEN with respect to water is of doubtful applicability; the molecular weight 54 is therefore questionable. It appears certain, however, that the molecular weights of the various modifications of ice are not different and that therefore the difference between the various modifications is to be ascribed to isomerism rather than to polymerism.

The isomerism occurring in these cases need not be a different grouping of the atoms in the molecule. It may be merely a difference in the distances between the atoms within the molecule, corresponding to the volume change obtaining when one form is transformed into another.

This kind of isomerism occurs several times with water and has also been observed for phenol, *o*-cresol, acetic acid, urethane, silver iodide, potassium chlorate, acid ammonium sulphate, and benzene. In these cases the equilibrium curves between two forms run very steeply, their dT/dp values are very great, and therefore the energy difference of the two forms is nearly equal to

the external work of transformation. These forms may be compared to elastic springs, which with compression maintain a constant temperature or become only slightly heated.

If this isomerism were a common property of molecules it would be expected that the transformation curves of all would be similarly steep. With one portion of these substances, these transformation curves would appear at relatively low pressures, and with the rest at very much higher pressures.

It is noticeable that this kind of isomerism occurs especially often in associated liquids for which the temperature coefficient of the molecular surface energy is smaller than 2.0. Accordingly the molecules favorably disposed towards association would be those most likely to show this isomerism, whereas the molecules of normal liquids either do not decrease their volume as described, or do so at very much higher pressures. A noteworthy intermediate position is occupied by benzene, for which BRIDGMAN found a steeply running transformation curve at $p = 12{,}000$ kg.

9. THE TRIPLE-POINT

a. The Directions of the Sublimation and the Vapor Pressure Curves at the Triple-point

The vapor pressure curve and the sublimation curve must intersect at the triple-point, that is, at this point the tangents to the two curves must have different directions. For both curves we have:

$$\frac{dp'}{dT} = \frac{R_p'}{\Delta v' T} \quad \text{and} \quad \frac{dp''}{dT} = \frac{R_p''}{\Delta v'' T} .$$

The heat of sublimation minus the heat of vaporization of the liquid is equal to the heat of fusion, $R_p'' - R_p' = R_p$. If this be remembered, and the volume difference Δv upon melting be disregarded, so that $\Delta v' = \Delta v = v$, the specific volume of the vapor, we obtain

$$\frac{dp''}{dT} - \frac{dp'}{dT} = \frac{R_p}{vT} .$$

The angle at which the sublimation and the vapor pressure curves intersect will be very small when v is large. In fact it is difficult to show the application of this equation to water and ice.

JUHLIN [1] has measured the difference $p' - p''$ for supercooled water and ice and has found an expected maximum.

t_0	$p' - p''$
− 2.5	0.083 mm.
− 6.0	0.135
− 10.0	0.198
− 15.5	0.214
− 20.0	0.199

If the triple-point lie at a much greater pressure, as in the case of PH_4I, v becomes very much smaller. In this way the difference in the direction of the vapor pressure and the sublimation curves becomes very much greater, and it must be calculated without the use of the approximation $\Delta v' = \Delta v'' = v$.

b. The Volume-Entropy Diagram

The phase diagram upon the pT-plane suffers by being incomplete, for it says nothing with respect to the quantities of the substance divided among the different phases. If these data be desired, it is necessary to use an additional parameter. Of all possible diagrams, that of the volume-entropy has the most merit.

For a unit of substance the volumes v are protracted upon the abscissa, and the entropy of the substance upon the ordinate, and instead of a triple-point there are obtained three separate points, the coordinates of which give the volumes and the entropies of a unit of mass of the substance, namely, the points, 1, 2, and 3 (Fig. 73), the joining of which forms a triangle. If the entropies and the volumes of the unit of mass of the three phases, η_1, η_2, η_3 and v_1, v_2, v_3 be given, and if x, y and $1 - x - y$ designate the fractions of the unit of mass divided into the three phases 1, 2, and 3, the volume and the entropy of the system consisting of the phases may be expressed by the equations

$$v = xv_1 + yv_2 + (1 - x - y)v_3,$$

$$\eta = x\eta_1 + y\eta_2 + (1 - x - y)\eta_3.$$

[1] *Bihg. Svenska. Ak. Handl.*, **17** (I), 1 (1894).

The coordinates v and η give the center of gravity of the triangle when the masses x, y and $1 - x - y$ are present in the vortices of the triangle. All possible conditions of a substance that divides itself into three phases, assumed with a change in volume, are represented by points falling within the triangular surface 1, 2, 3. If one of the phases be made to disappear entirely by a change in volume the state of the substance, now existing in two phases, will be represented by a point on one of the sides of the triangle.

A slight change in pressure and temperature that does not destroy the state of equilibrium between two phases will result in a shifting of the point representing the state of the substance from the side of the triangle into one of the three two-phase spheres. These are limited by two curves. A straight line connects two accompanying points upon the curve-pairs. Each of these two points is determined by the η- and v-values of the two phases occurring in equilibrium. The systems with variable quantities of the two phases are represented by the points upon the straight lines. The quantities of the two phases are related inversely as the lengths of the two pieces of the straight line.

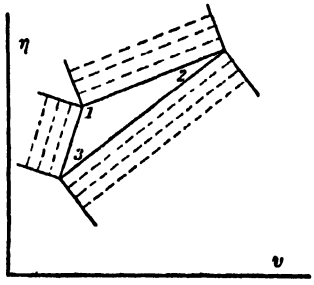


FIG. 73.

The direction of the three curve-pairs is perpendicular to the accompanying sides of the triangle and the straight lines joining the point-pairs on any curve-pair are parallel to the sides of the triangle.

The direction of a side of the triangle is given by the quotient

$$\frac{\Delta\eta}{\Delta v} = \frac{\eta_2 - \eta_1}{v_2 - v_1}.$$

This is equal to the tangent of the angle that the side of the triangle forms with the v-axis. $\Delta\eta$, however, is equal to the corresponding heat of transformation, R_p, measured in mechanical units, divided by the temperature of the triple-point: $\Delta\eta = R_p/T_0$. It follows therefore, that

$$\frac{\Delta\eta}{\Delta v} = \frac{R_p}{T_0 \Delta v},$$

and for the direction of the perpendicular to the sides of the triangle we have

$$-\frac{\Delta v}{\Delta \eta} = \left(\frac{dT}{dp}\right) \quad \text{or} \quad \frac{\Delta v}{\Delta \eta} = -\left(\frac{dT}{dp}\right).$$

Lines drawn from any point within the triangle perpendicular to the three sides of the triangle and impressed upon the pT-plane will give a system of curves which after a rotation of 180° around the η-axis gives the direction of the equilibrium curves upon the pT-diagram. See Fig. 74*a* and *b*.

The sections of these perpendiculars from the sides of the triangle to the point at which they intersect correspond to the

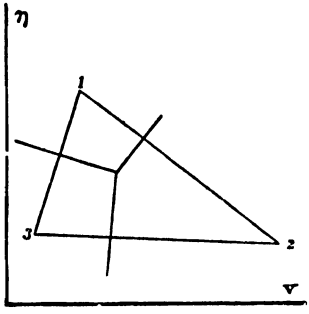


Fig. 74*a*.

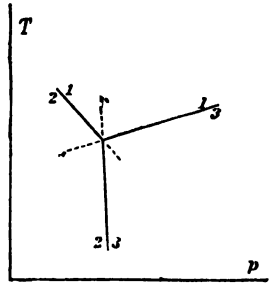


Fig. 74*b*.

equilibrium curves of absolute stability, and the prolongations of these curves beyond the point of intersection (dotted curves in Fig. 74*b*) are realizable in part but do not represent absolute stability. Since these prolongations must always fall between the other two perpendiculars, it follows that in the pT-diagram the prolongation of one of the curves of absolute stability, must fall between two curves of absolutely stable equilibrium. Thus we have arrived at the proof of this law in a manner different from that used on page 56.

For the case of two melting curves and a transformation curve the law assumes the following special form: The melting curve, which at temperatures above the triple-point represents absolutely stable equilibrium, must run more steeply than the other melting curve, that is, it must have a greater dT/dp value. Consequently, a bending of the melting curves towards the pressure

axis can never be due to the occurrence of a new polymorphic modification.

c. *The Position of the Transformation Curves of the Forms of Two Crystal Groups*

Two systems consisting of two intersecting equilibrium curves that have one phase in common will display above the point of intersection of the two equilibrium curves upon the pT-plane a point of intersection of the three ζ-surfaces, and in consequence the point of intersection of the two equilibrium curves is a triple-point. The fulfillment of this condition, that one phase be common to the systems of two intersecting equilibrium curves, is sufficient reason for the point of intersection possessing the properties of a triple-point. If this condition be not fulfilled, two equilibrium points may intersect and the point of intersection will not be a triple-point. Accordingly, a third equilibrium curve meeting at this point will not be found.

Inasmuch as two intersecting sublimation curves, or the vapor pressure curve and a sublimation curve, as well as two melting curves, will represent systems having one phase in common, vapor or liquid, the intersection of two of these curves will produce a triple-point. It does not matter whether only absolutely stable phases occur in the systems of equilibrium curves, or the phases of different orders of stability. In the case of transformation curves, however, when unstable forms occur in addition to the absolutely stable forms, it is possible that two transformation curves intersect, the systems having no phase in common, and the point of intersection will not have the properties of a triple-point.

The forms the ζ-surfaces of which do not intersect we will gather into one group and give the group the name *crystal group*. To one crystal group belong a totally and absolutely stable form besides a series of totally unstable forms of different orders of stability, the ζ-surfaces of which do not intersect among themselves nor with the ζ-surface of the absolutely stable form.

Let us now investigate the positions of the four transformation curves formed by the intersection of the ζ-surface of the forms 3, 3′, 4 and 4′, the forms 3 and 3′ belonging to the same crystal group, and the forms 4 and 4′ likewise belonging to the same crystal group; the primed figures representing the unstable forms,

and the unprimed the stable. There is given, then, two stable forms 3 and 4, and two unstable forms 3′ and 4′. The ζ-surfaces of the forms 3 and 3′ as well as those of forms 4 and 4′ will not intersect each other whereas the ζ-surfaces of forms 3 and 4, 3′ and 4, 3 and 4′ as well as those of 3′ and 4′ will intersect.

The field of state of form 4 is given as totally surrounded by that of form 3. If in reality this condition does not exist, the actual cases may easily be derived from this hypothetical case by

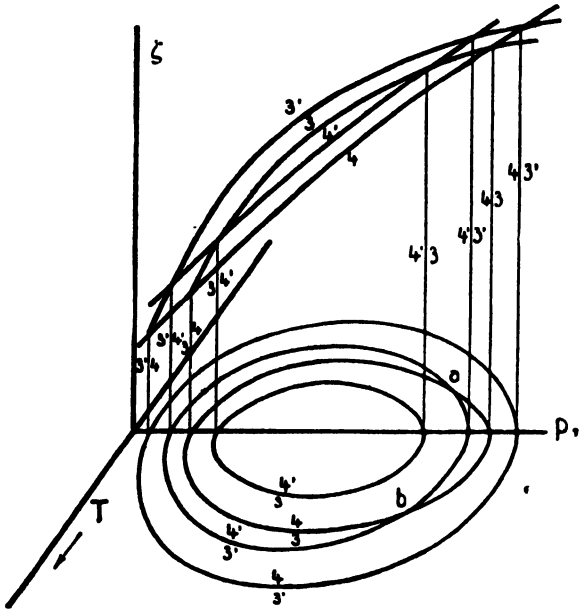


FIG. 75.

displacement of the pT-curves towards the equilibrium curves, for the purpose conceived as stationary.

Figure 75 represents a section through the ζ-surfaces of the four forms 3, 3′, 4, and 4′ for a constant temperature. The equilibrium curves of these forms upon the pT-plane are likewise represented. Each of these equilibrium curves cut through the straight line p_1, parallel to the p-axis, in 2 points. These points are the projections of the points of intersection of the two ζ-isotherms, and of necessity the equilibrium curves of the two-phase systems must pass through them.

It may be seen that the equilibrium curve of the two most stable forms, 3 and 4, of two different crystal groups, which is the curve 3–4, is enclosed by the equilibrium curve of the stable form 4 and the unstable form 3′, that is, by the curve 4–3′, since the ζ-surface of form 3′ lies over that of 3 and since both surfaces are intersected by the lower surface of form 4. Therefore, the projections of the two non-plane curves of intersection of the ζ-surfaces, 3 and 4 as well as 3′ and 4′ cannot intersect.

If, however, the two ζ-surfaces of the forms of one crystal group that lie over each other be cut by the ζ-surface of the most stable form of another crystal group, and if the field of state of this form enclose those of the two other forms, the positions of the two equilibrium curves will be reversed. The equilibrium curve of the two stable forms 3 and 4 surrounds the equilibrium curve of the two forms 3 and 4′ since now the two ζ-surfaces of the forms 4 and 4′ are cut by a surface that lies above them, whereas in the first case the two ζ-surfaces of form 3 and 3′, were intersected by the surface of the form 4 which lay under them.

Figure 76 shows a section of the ζ-surfaces of the same four forms perpendicular to the p-axis (at constant pressure) and of course the relations given in this figure are the same as those given in Fig. 75, in which a section perpendicular to the T-axis (at constant temperature) is represented.

If, therefore, in a two-phase system one of the two forms the phase field of which is surrounded by the phase field of the other form be replaced by an unstable form of the same crystal group, the field of state of the unstable form will then fall completely within that of the stable form; and if of the two forms the other be replaced by an unstable form the field of state of the unstable form will never reach to the limits of that of the stable form. It therefore follows that an unstable form can come into equilibrium with a stable form of another crystal group only at such points of state that lie outside of the phase field of the stable form. In other words, an absolutely stable form of one crystal group can come into equilibrium with a partially stable form of another crystal group only in points of state at which the absolutely stable form has lost its absolute stability.

We have now seen that with the substitution of one of the stable forms by each of the unstable forms, the equilibrium curves of the three possible systems cannot intersect. However, if the

two stable forms of different crystal groups be simultaneously replaced by two unstable forms of each of the two crystal groups, it is possible for the equilibrium curves of the stable and of the unstable pairs to intersect. These points of intersection, however, can never have the properties of triple-points, since there is no accompanying intersection of the ζ-surfaces. The non-plane curve of intersection of the two ζ-surfaces 3′ and 4′ lies above the curve of the intersection of the ζ-surfaces 3 and 4, and it is only

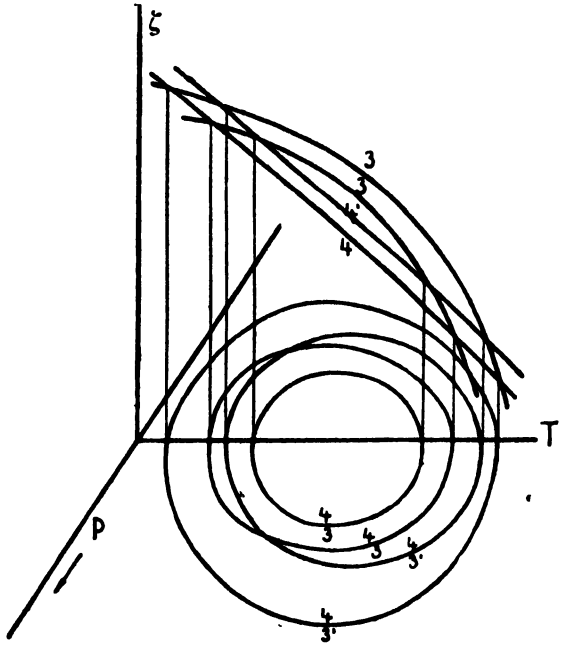


FIG. 76.

the projections of these curves that intersect, not the curves themselves. In the case represented in Fig. 75 it may be seen that of the pressures at which the ζ-isotherms of the forms 3′ and 4′ intersect, the one lies outside and the other inside of the pressure interval which the equilibrium curves 3–4 cuts out of the straight line p_1. The consequence of this is that the two equilibrium curves 3–4 and 3′–4′ must intersect twice, in the points a and b. Analogous relations are found with the inspection of the ζ-isobars given in Fig. 76.

Finally the law that determines the conditions for the forma-

tion of a point of intersection of the two equilibrium curves to which the properties of a triple-point are lacking can be reversed: if two equilibrium curves intersect and their point of intersection lacks the properties of a triple-point, the two forms of one equilibrium curve will be less stable than the two forms of the other.

d. The Volume Change and the Heat of Transformation at the Triple-point

The equations combining the volume changes and the heats of transformation at the triple-point are the following:

$$\Delta v_{12} + \Delta v_{23} - \Delta v_{13} = 0. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If a cyclic process be completed at the triple-point by transforming a unit of mass of a substance that originally occurred in Phase 1, into Phase 2, then into Phase 3, and finally into Phase 1, the sum of the external work in this isothermal and isobaric process, if equation (1) hold true, will be equal to zero. It follows from this with respect to the heats of transformation that

$$R_{12} + R_{23} - R_{13} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Furthermore,

$$\left(\frac{dT}{dp}\right)_{12} = \frac{\Delta v_{12} T_0}{R_{12}}, \quad \left(\frac{dT}{dp}\right)_{23} = \frac{\Delta v_{23} T_0}{R_{23}}, \quad \left(\frac{dT}{dp}\right)_{13} = \frac{\Delta v_{13} T_0}{R_{13}}. \quad (3)$$

If each two of the Δv- and R-values be known, the triangle of the ηv-diagram will be determined, and the dT/dp values can be constructed. Practically, however, it is much easier to determine the direction of the equilibrium curve than to carry out the determination of the volume change or of the heat of transformation, especially at higher pressures. If the dT-dp values be known, a series of triangles will be possible which are similar to the fundamental triangle. If in addition a Δv-value or, which is less frequent, an R-value be known, the fundamental triangle will be determined. All the remaining Δv- and η-values can then be read directly from the Δv-diagram, and the R-values computed. In connection with these principles papers by E. RIECKE,[1] L. NATANSON,[2] and H. W. BAKHUIS ROOZEBOOM[3] are of interest.

[1] *Z. Physik. Chem.*, **6**, 411 (1890).
[2] *Wied. Ann.*, **43**, 178 (1891).
[3] *Die Heterogenen Gleichgewichte*, **1**, 94 (1901).

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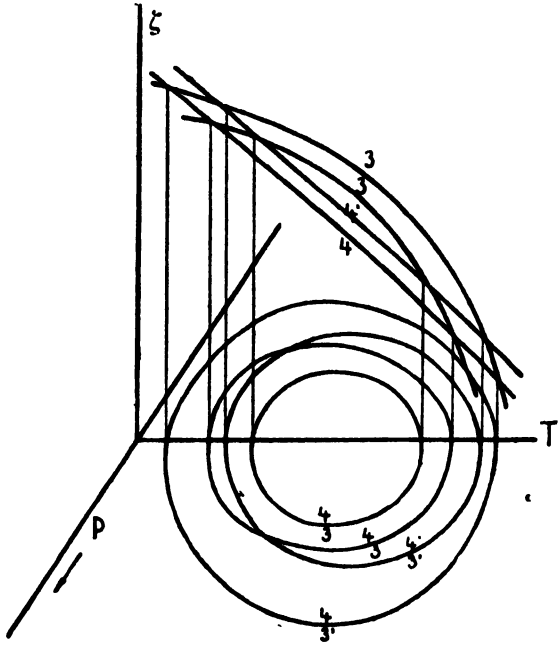


FIG. 76.

the projections of these curves that intersect, not the curves themselves. In the case represented in Fig. 75 it may be seen that of the pressures at which the ζ-isotherms of the forms 3′ and 4′ intersect, the one lies outside and the other inside of the pressure interval which the equilibrium curves 3–4 cuts out of the straight line p_1. The consequence of this is that the two equilibrium curves 3–4 and 3′–4′ must intersect twice, in the points a and b. Analogous relations are found with the inspection of the ζ-isobars given in Fig. 76.

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Furthermore,

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[3] *Die Heterogenen Gleichgewichte*, **1**, 94 (1901).

VII. THE PHASE DIAGRAM

1. The Phase Diagram of Water

If the pressure upon ordinary ice be raised at a constant rate at − 30°, a critical point will be reached at 2220 kg., where in consequence of a considerable diminution in the volume of the compressed ice, the pressure decreases momentarily and then remains constant until the volume change is completed. This volume diminution corresponds to the formation of a denser modification of ice, Ice III′. When the transformation is complete the pressure again rises regularly. If the pressure be then allowed to decrease it will fall at a regular rate corresponding to the volume increase until at a pressure of 1800–1500 kg., the indicator of the manometer suddenly returns to 2200 kg. and remains constant at this pressure while the volume increases until the whole quantity of the denser ice is transformed into ordinary ice. After this transformation is completed, the pressure falls evenly to that of atmospheric.

The pressure 2200-2220 kg. is evidently the equilibrium pressure of the two kinds of ice. According as the research is carried out between − 30° and − 50°, or − 70° and − 80°, one of two different equilibrium curves will be encountered: the equilibrium curve of ordinary ice, Ice I, with the denser Ice III′, or that of Ice I with Ice II, which is slightly denser than Ice III′.

From these investigations it may be seen that the expansive force of ice is a limited one. The pressure exerted by it cannot exceed 2500 kg. since at this pressure occurs the spontaneous formation of Ice III′.

In this way the existence of two new modifications of ice was shown.[1] These new forms, Ice II and Ice III′, may be obtained at ordinary pressures by slowly decreasing the pressure in the steel cylinder cooled by liquid air, in which the forms were prepared at the higher pressure, until atmospheric pressure is reached.

[1] *Ann. d. Phys.*, **2**, 1 (1900).

The cylinder may then be opened and the denser forms withdrawn. On warming, Ice III′ goes over into Ice I at about − 130°, as shown by the transformation of the compact pieces into a fine meal of considerable volume.[1]

Ten years after the discovery of Ice III′ and Ice II, BRIDGMAN [2] took up the investigation and extended the pressure range to 20,000 kg. He found that Ice III′ can be transformed into a denser form, Ice V, at 3700 kg., and that in turn Ice V can be transformed into a still denser Ice VI at 6300 kg. After the appearance of this work, the author again took up the investigation of the forms of ice, for the possibility presented itself of the proof of the total instability of particular forms and of the coordination of these forms with definite thermal crystal-groups.

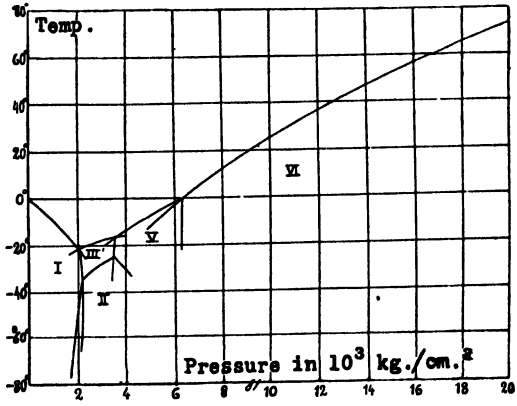


FIG. 77.

Figure 77 is the phase diagram of water for the stable forms I, II, V, and VI according to BRIDGMAN. Ice III′, formerly regarded as completely stable, has proved to be less stable than another form of the same group discovered later. It seems preferable, therefore, to designate this form as III′ rather than III. The coordinates of the melting curve of Ice I and Ice III′, as well as those of the equilibrium curves, I–II, I–III′, which were determined by the author in 1900, differ from those obtained by BRIDGMAN in 1912 in the neighborhood of the triple-point by

[1] *Z. anorg. Chem.*, **63**, 285 (1909).
[2] *Proc. Amer. Acad.*, **47**, 441 (1912).

about 62 kg./cm.[2] The manometer used in 1900 registered a pressure higher than BRIDGMAN'S by about this amount; this difference cannot be represented in the scale used in Fig. 77.

It may be seen from the figure that four stable forms of ice can come into equilibrium with water. The melting curve of Ice I, as is well known, is a falling one, whereas those of III′, V and VI are all rising. The melting curve of Ice VI has been followed by BRIDGMAN to 20,670 kg. and 76.35°. The cooling of compressed water does not always result in the formation of that modification, the melting curve of which is crossed by the decreasing temperature. For example, at a pressure of 2700 kg. Ice I is formed on cooling in preference to Ice III′, and the latter does not appear until the pressure exceeds 2700 kg., though the melting curves of these two forms intersect at 2100 kg.[1] Similarly, upon crossing the melting curve of Ice V at 4000 kg., crystallization centers of Ice III′ are frequently formed, and above 5000 kg., those of Ice VI are formed.[2] The melting curve of one kind of ice may thus be followed far into the phase field of another.

The equilibrium curves of Ice III′ and Ice I may be followed for a considerable distance into the phase field of Ice II, because no nuclei of Ice II are formed from Ice III′ upon cooling. At higher pressures also the formation of these nuclei does not occur in Ice III′ upon cooling, and water may thus be cooled at a pressure of more than 2700 kg. far into the phase field of II without the formation of the modification there stable. Ice II can be formed upon the equilibrium curve III′–II by compressing Ice I below − 70°, transforming it into Ice II, and warming the product to the temperature of the equilibrium curve. Crystallization centers of Ice III′ are formed in this case by the crossing of the transformation curve II–III′ and it is in this way that the curve is determined.

a. The Curves of Realization

The equilibrium curves I–II, I–III′, III′–V, and V–VI run very steeply to low temperatures. With decreasing temperature

[1] *Z. phys. Chem.*, **75**, 618 (1910).

[2] It happens, though seldom, that Ice V forms from Ice I under 3000 kg., and then passes into a form of the group III [*Z. phys. Chem.*, **84**, 282 (1913)]. In presence of NH_4Cl, this occurrence is much more frequent [*Z. anorg. Chem.*, **108**, 37 (1919)].

the linear transformation velocity decreases very strongly, until finally the transformation is indefinitely delayed. This diminution in the transformation velocity is noticeable in the presence of both phases with the transformation curves I–II and I–III at 70°–80°. The final pressure in different experiments, after volume increase on the one hand and diminution on the other, differ by about 100 kg., and it is accordingly impossible to follow the curves to lower temperatures.

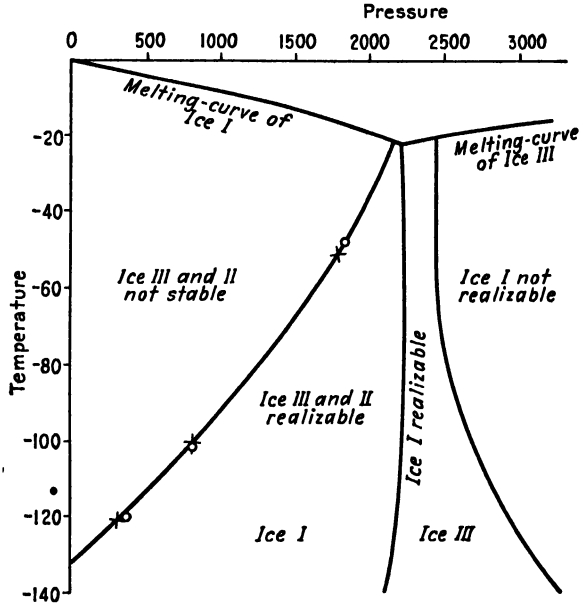


FIG. 78.

If only one of the two forms that are concerned in the equilibrium be present, the pressure can increase considerably above that of the equilibrium curve until finally the formation of the denser form begins; in turn, the pressure upon the denser form can be diminished considerably before the appearance of the less dense form. These pressures depend upon the temperature, the differences between them increasing very considerably with decreasing temperature. The two curves which limit the phase field in which each of the two forms, Ice I and III′, can exist in the absence of the other, are given in Fig. 78. It may be seen that

below − 130°, Ice I can be realized up to 3000 kg., and that Ice III′ can be obtained at ordinary pressure, as stated before, and at still lower temperatures Ice V and VI can be realized at ordinary pressure. The velocity of the attainment of equilibrium of these two forms in the presence of each other decreases rapidly as the field of realizability broadens. These relations are repeated with the equilibrium curves of the other forms of ice, although they have not been exhaustively investigated. More complete investigations have been made with phenol and AgI.

b. The Specific Volumes and the Heats of Fusion

The two following tables give the specific volumes of water and the modifications of ice that are in equilibrium with it, and in addition the heats of melting and of transformation at the respective triple-points.

TABLE 1

SPECIFIC VOLUME OF WATER AND THE MODIFICATIONS OF ICE IN EQUILIBRIUM AT p AND $t°$ *

p kg./cm.²	$t°$	v of Water cm.³/gm.	v of Ice cm.³/gm.	Δv cm.³/gm.	Compressibility	
					Ice	Water
			Ice I			
0	0	1.0000	1 0900	0 0900	0 0,35	0 0,52
500	− 4.1	0 9777	1 0775	0.0998		
1,000	− 8 7	9588	1.0684	0 1096	0.0,16	0 0,37
1,500	−14 0	9414	1 0615	0 1201		
2,000	−20.3	9253	1.0571	0 1318	0 0,8	0.0,29
			Ice III′			
2,000	−22.5	0.9250	0.8774	0.0476		0 0,30
2,500	−20.1	9099	8726	373	0.0,91	26
3,000	−18.3	9874	8688	286		24
3,500	−17.0	8867	8636	231		21
			Ice V			
3,500	−17.0	0.8879	0.8085	0.0785		
4,000	−13 6	8781	8048	733	1.0,72	0.0,190
5,000	− 7 0	8610	7976	634	53	164
6,000	− 1.6	8478	7929	549	47	140
6,500	+ 0.6	8418	7902	516		

* Bridgman, *Proc. Amer. Acad.* 47, 537 (1912).

TABLE 1—*Continued*

SPECIFIC VOLUME OF WATER AND THE MODIFICATIONS OF ICE IN EQUILIBRIUM AT p AND $t°$

p kg./cm.²	$t°$	v of Water cm.³/gm.	v of Ice cm.³/gm.	Δv cm.³/gm.	Cxmpressibility	
					Ice	Water
			Ice VI			
4,500	−18 0	0 8689	0 7705	0 0985		
5,000	−12 5	8604	7636	968	0 $0_4$102	0.$0_4$164
6,000	− 3 2	8472	7544	928	0.$0_5$72	140
7,000	5 0	8370	7488	882	55	126
8,000	12.6	8271	7455	816	48	120
9,000	19 5	8156	7401	755	43	110
10,000	26 0	8055	7358	697	37	104

TABLE 2

THE MELTING CURVE OF ICE *

$t°$	p kg./cm.²	Δv cm.³/gm.	dp/dt	r_p cal./gm.
−15 0	4,790	0 0980	99 6	59.0
−10 0	5,280	960	106.5	63 0
− 5 0	5,810	938	113 8	67.1
0 0	6,360	916	120 0	70.4
+ 5 0	7,000	884	125 8	72.5
10 0	7,640	844	132 7	74 4
15 0	8,310	798	140.0	75.5
20.0	9,000	751	148 5	76 6
30.0	10,590	663	167.3	78 8
40 0	12,390	590	188.7	81.7
50.0	14,430	523	215.4	85.3
60 0	16,690	477	242 9	90.5
64.30	17,840			
67.5	18,500			
72 15	19,670			
76.35	20,670			

* Bridgman, *Ibid*, page 521.

TABLE 3

THE COORDINATES OF THE TRIPLE-POINT AND THE VOLUME CHANGE Δv *

Water = W Phases	$t°$	p kg./cm.^{2}	Δv cm.^{3}/gm.		
III, W, I	−22.0	2115	III–W 0 0466	W–I 0.1352	III–I 0.1818
II, III, I	−34 7	2170	II–III 0.0215	III–I 0.1963	II–I 0.2178
V, III, W	−17.0	3530	V–III 0.0547	III–W 0 0241	V–W 0 0788
V, II, III	−24.3	3510	V–II 0.0401	II–III 0.0145	V–III 0.0546
VI, V, W	+ 0.16	6380	VI–V 0.0389	V–W 0.0527	VI–W 0.0916

* Bridgman, Proc Amer. Acad., **47**, 524 and 526 (1912)

HEATS OF FUSION AND OF TRANSITION IN CALORIES PER GRAM AT THE SAME TRIPLE-POINTS

Phases			
III, W, I	III, W 50.9	W, I −56.1	III, I − 5.2
II, III, I	II, III 12.3	III, I − 2.2	II, I 10.1
V, III, W	V, III 0 9	III, W 61 4	V, W 62.3
V, II, III	V, II −16 0	II, III 16 9	V, III 0.9
VI, V, W	VI, V 0.2	V, W 70.1	VI, W 70 3

c. The Point at which R_p is Zero

The points on the equilibrium curve at which $R_p = 0$ though Δv have a finite value are of especial interest. The existence of these points was assumed in harmony with the point of view that critical points do not occur upon an equilibrium curve that represents an equilibrium between two phases at least one of which is anisotropic. Although many equilibrium curves have been investigated upon which R_p attains very small values, to the present time the curves Ice I–III′ and Benzene I–II are the only ones that have been found upon which R_p actually passes through a zero value. The coordinates in the following table were obtained from the determinations of the author for these equilibrium curves,

from which the values of r_p in cal. per gram are calculated for the heat of transformation when $\Delta v = 0.19$ cm.^{3}/gm.

$t°$	p kg.	$\frac{dp}{dT}$	r_p
−22	2200	−3 1	+3.6
−30	2225	−3 0	+2 9
−40	2255	0	0
−46	2255	+1 2	−1.2
−50	2250	+1.4	−1.4
−60	2236	+1.6	−1.7
−70	2220		

BRIDGMAN found the following values:

$t°$	p kg.	$\frac{dp}{dT}$	Δv	r_p
−20	2103	−5.3	0.1777	+5.6
−30	2156	−3.2	1919	+3.5
−40	2178	−0 6	1992	+0.7
−50	2160	2.0	2023	−2.1
−60	2117	5.4	2049	−5.5

According to the determinations of the author, r_p passes through zero at − 46°, whereas BRIDGMAN's data give −43°.

That r_p becomes zero in the neighborhood of −45° upon the transformation curve I–III′ is shown by the fact that during the transformation, which is accompanied by a rapid volume change, the pressure remains constant at $-45° \pm 5°$, whereas during a volume increase at a higher or lower temperature the pressure increases, and during a volume diminution, decreases, according as the temperature of the equilibrium mixture moves up or down upon the equilibrium curve under the influence of the heat of transformation.

d. The Volume-Surface of Water and of the Modifications of Ice

The volume surface of water and of Ice I and Ice III′ in the region of the triple-point is reproduced in Fig. 79. At the triple-

point D, the specific volume of Ice I is greater than that of water and the latter is greater than that of Ice III′.

BRIDGMAN [1] has determined the volume surface for water from the melting curves of the four forms of ice to 40° and from 0–13,000 kg. In comparison to the volume surfaces of normal liquids, a series of abnormalities were found, a portion of which had been previously determined by AMAGAT.[2] These abnormalities have become of importance for the determination of association in water. We will here concern ourselves only with those abnor-

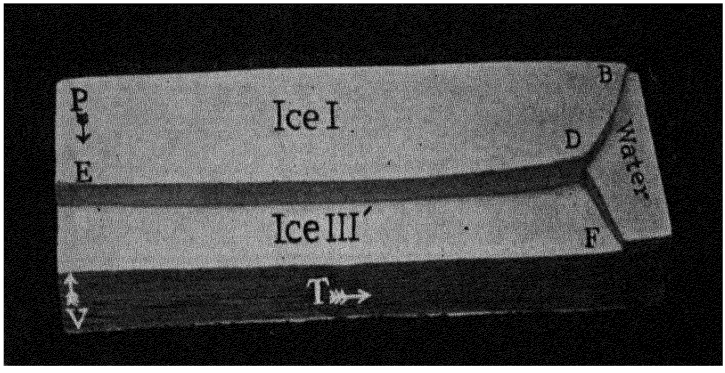


FIG. 79.

malities which are related to the different kinds of ice. At pressures that are almost independent of the temperature, the compressibility of water decreases more rapidly than at pressures higher or lower than this critical pressure interval. The explanation given for this is that within this pressure interval, the transformation of a molecule of greater volume into one of smaller is especially great. (See page 145*b*.) Figure 80 gives three pT-lines that serve to illustrate a few of the abnormalities observed.

The greatest volume change among the transformations of the stable modifications of ice occurs with the transformation of Ice I into Ice III′ and II. This maximal volume change probably corresponds to the abnormal behavior of compressibility represented by line 1.

[1] *Proc. Amer. Acad.*, **48**, 310 (1912).
[2] *Ann. chim. phys.*, **6**, 29, 345. Table Number 63 (1893).

Upon line 2 the transformation of the molecules II and III into V is noticeable, and upon line 3, the molecules V into VI. It therefore appears that water is relatively rich in molecules of the type V only in a small pressure interval; besides the molecule V it contains also molecules II, III and VI. It would follow that the separation of the molecules of V from water upon the production of the crystalline form would be very much hindered, and experiment shows that this is the case. After line 3 is crossed the water becomes rich in the molecules of the form VI, and the solid modification then formed upon crystallization is that of form VI.

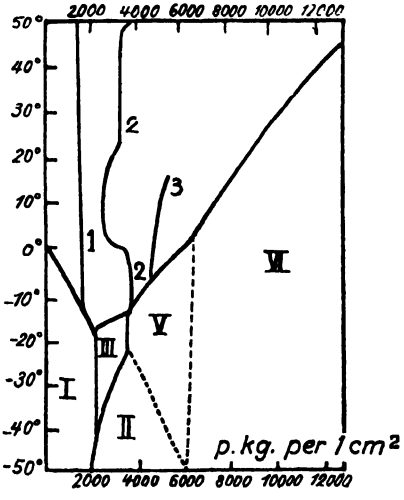


FIG. 80.

In the more rapid decrease of the compressibility of water with increasing pressure may be seen an increase in the concentration of the molecules of smaller volume. The volumes of the molecules concerned are in the order of the volumes of the solid modifications. Since the pressure is almost constant upon the lines 1, 2, and 3, the heats of transformation of these molecules are small, and this has been found experimentally for the solid modifications.

The position and the course of the pT-lines of the abnormal compressibility of water are therefore in agreement with the transformation curves of the solid phases. It may be concluded from this that a solid phase can form only when its molecules are present in the water prior to crystallization.

e. The Unstable Forms of the Group of Ice I and of Ice III

If the assumption be correct that there are crystal groups and that the members of each group are closely related in the condition that the surfaces of thermodynamic potential do not intersect, it is to be expected that the equilibrium curves with

water, Ice I, Ice II, and Ice V of an unstable form III′ of the group III would run nearly parallel to the corresponding curves of the known stable form of Group III, and fall collectively within the phase field of this form. This expectation can be confirmed by experiment,[1] and accordingly the existence of a totally unstable form can be rigorously proved. The heavily drawn lines in Fig. 81 indicate the equilibrium of the most stable form. The more finely drawn lines refer to equilibria in each of which at least one

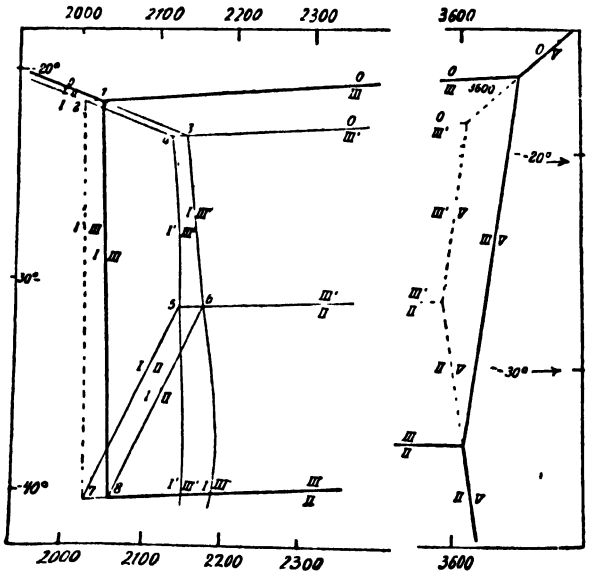


Fig. 81.

unstable form takes part. The equilibria represented by the dotted lines have not been realized.

The compression of ordinary ice at − 80° to 2500 kg. leads to the production of Ice II. If a mixture of Ice I and Ice II be warmed, the temperature and pressure will vary along the line I–II (Fig. 81).[2] At the triple-point 6 both pressure and tem-

[1] *Z. phys. Chem.*, **84**, 257 (1913).

[2] The pressure determined by the author in 1911 for the triple-point, water, Ice I, and Ice III′, lay at about 20 kg. smaller pressure than that determined by Bridgman. Bridgman designated Ice III′ as Ice III because he had not recognized the existence of a more stable form of the group of Ice III.

perature will remain constant for a long time and finally will follow line I–III′ until at the triple-point 3 the pressure remains constant during the melting of I or III′. Under a greater pressure, and smaller volume, I melts and the pressure rises along the melting curve O–III′; under smaller pressure, and greater volume, III′ melts and the pressure decreases along curve O–I.

However, if ordinary ice is compressed between −22° and − 30°, the pressure does not rise upon the equilibrium curve I′–III′. The coordinates of these two equilibrium curves, though nearly the same, are distinctly different, and the difference between the two equilibria is also shown in the different velocities of establishment. These differences lead to the conclusion that one of the two phases is different from that which took part in the equilibrium I–III′. Ice I is not formed from Ice III′, but a new closely related form, Ice I′, as will be seen from facts introduced later.

Upon slowly cooling water compressed to 2800–3200 kg. crystallization occurs during a pressure decrease. The melting points of this dense ice obtained from different experiments carried out under strictly similar conditions, differ by about 2.5°. The higher melting points fall upon the curve O-III, the lower upon the curve O–III′. The melting curve of the unstable form III, curve O–III′, intersects the two equilibrium curves I–III′ and I′–III′ at the points 3 and 4. Since 3 is a triple-point, the melting curve of ordinary ice must end there, and this has been found by experiment to be the case. At 4 must obtain the melting curve of an unstable form, Ice I′, closely related to ordinary ice. The melting curve of this modification, which is seldom formed from water but regularly from Ice III′ upon increase in volume (decrease in pressure), has been found to run about 0.5° below the melting curve of ordinary ice, Ice I. Since this melting curve ends at point 4 it is evident that Ice I′ is formed from Ice III′ upon volume increase. From the fact that upon dilatation following the compression of Ice I, the pressure always rests on the curve I′–III′, it is to be inferred that Ice I′ always forms from Ice III′, whereby III′ is enveloped by I′ preventing the formation of I.

If Ice III be produced from water and the pressure be then lowered, the pressure will finally rise to 2060–2040 kg. at − 25°, upon the equilibrium curve I′–III or I–III. A line drawn through

this point and point 2 will intersect the line I′–II at point 7, through which as the third equilibrium line curve III–II must pass. This system is usually produced by the cooling of a saturated solution of KCl under pressures of 2400–3000 kg. Under these conditions, according to W. DENECKE,[1] Ice III′ is first formed and then with rise in temperature Ice III′ changes into Ice III. The points of the equilibrium curve II–III determined by DENECKE are in accord with line II–III predicted by the author (Fig. 81). The positions of the equilibrium lines of unstable and stable equilibrium are those demanded by thermodynamics. The equilibrium line of the stable system I–III lies between the equilibrium lines I′–III and I–III′, and the equilibrium line of the two unstable forms I′–III′ likewise falls between these two lines.

The closing of the phase fields of forms III and III′ at higher pressures is indicated at the right of Fig. 81.

As may be seen from the positions of the surfaces of thermodynamic potential, not all points of intersection of two equilibrium lines are triple-points. The triple-points of interest to us are numbered with Arabic numerals.

The phase field of form III′ is totally enclosed, and it is the first totally enclosed field of an unstable crystalline form that has been found; this total enclosure proves the total instability of the form. It must be noted in connection with this that the equilibrium curve III′–V has not been experimentally determined, but as the existence of curves I–III′, O–III′, and II–III′, which have all been determined, and the existence of Ice V, is given, the existence of line III′–V must be admitted, and the line must correspond very closely to the one indicated.

For the purposes of inspection, the relations in Fig. 81 are reproduced in the approximate diagram, Fig. 82. Alongside of the completely drawn equilibrium curves, the coordinates of which have been measured, are written Roman numerals designating the various modifications of ice. The triple-points are indicated by Arabic figures.

Besides Ice I′ of the group I, another form, Ice I″ has been observed in rare cases. This form melts between 1400 and 1100 kg. about 4.2° lower than ordinary ice. In addition to the second form, a third still less stable form, I‴, has been observed, which

[1] *Z. anorg. Chem.*, **108**, 1 (1919).

in each pressure interval melts at a temperature about 5.2° lower than the melting point of ordinary ice. All of these forms, of which there are probably seven, belong to one crystal group; they all melt with volume decrease, and their melting curves all run parallel to that of Ice I. The same is also true for their equilibrium curves with Ice II and Ice III, which accordingly run fairly parallel to the equilibrium curves I–II and I–III.

It has thus been proved that besides the six stable forms of ice there are at least four, perhaps seven, forms in the group of Ice I, and two forms in the group of Ice III. In all probability unstable forms exist in the remaining four groups and further

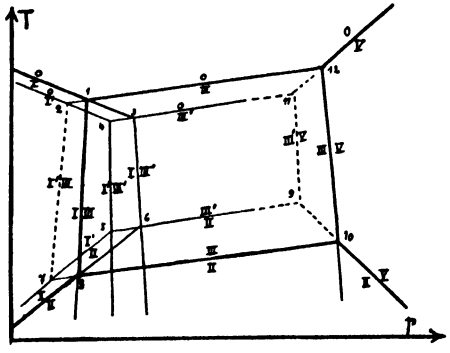


FIG. 82.

investigation would no doubt disclose them. In any case the conception of crystal groups has proved a useful one.

2. THE PHASE DIAGRAM OF PHENOL

Phenol occurs in two forms differing in volume by 0.0315 cm.^{3} per gram at 40.0° and 1980 kg. Figure 83 gives the phase diagram for two preparations, C and A. Preparation A contained more admixture than preparation C and the influence of the admixture may be seen in the diagram. The solubility of the admixture in the two crystal-forms can be determined by the displacement of the transition curve.

If C_0, C_1, and C_2 indicate the concentrations of the foreign substance in the liquid and in the two crystal-forms, I and II, W_p the osmotic work with isothermal transport of a unit mass

of the solvent into the solution of concentration 1, and if the value of r represents the heat of transition concerned, then the effects of the foreign substance upon the temperatures of the three equilibrium curves will be

$$\Delta_{01}t_p = (c_0 - c_1)W_p\frac{T_p}{r_{01}};$$

$$\Delta_{02}t_p = (c_0 - c_2)W_p\frac{T_p}{r_{02}},$$

and

$$\Delta_{12}t_p = (c_1 - c_2)W_p\frac{T_p}{r_{12}}.$$

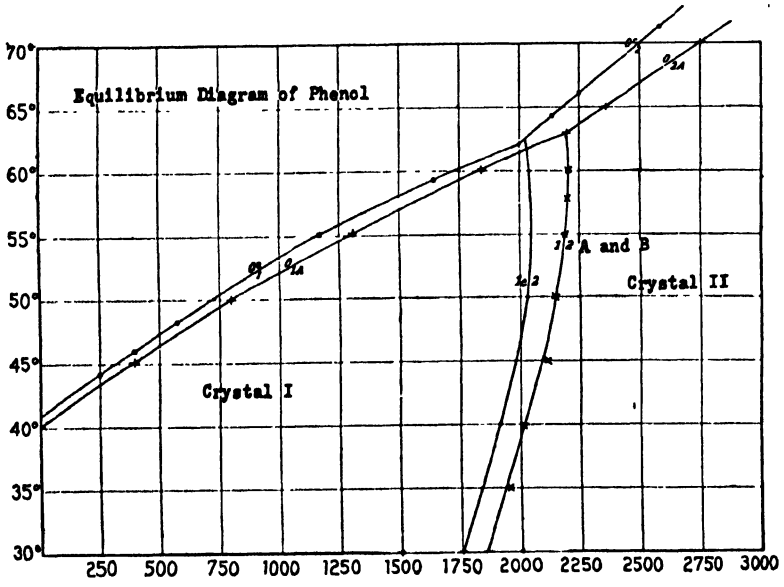


FIG. 83.

If the foreign substance be soluble in the liquid alone, then $C_1 = C_2 = 0$, and it follows that

$$\Delta_{01}t_p = c_0W_p\frac{T_p}{r_{01}};$$

$$\Delta_{02}t_p = c_0W_p\frac{T_p}{r_{02}},$$

and

$$\Delta_{12}t_p = 0.$$

In this case the position of the equilibrium curve I–II will not be changed. If $C_1 > C_2$, the equilibrium curve will be displaced to higher pressures, if $C_1 < C_2$ to lower pressures. The admixtures present in preparation A are accordingly distinctly more soluble in I, which has the greater volume, than in II.

Each of the two forms may be realized in the phase field of the other.

Between 0° and 40° the pressure can be raised upon the ordinary crystals of phenol to 2500 kg. without the formation of the denser crystal-form II; at this point a rapid decrease in pressure to the transformation curve 1-2 will occur and at 35° a velocity of pressure decrease amounting to 400 kg. per minute was observed, corresponding to the formation of 20 gms. of the denser modification per minute. It is therefore possible to realize Phenol I in the unstable state in a portion of the phase field of Phenol II, and it is also possible to realize Phenol II in the absence of the less dense crystal-form in the phase field of the latter form, although the latter endeavor is considerably more hazardous than the former. Forty grams of Phenol II at a temperature of 60° were compressed at 3000 kg. for an hour, the bath temperature then brought to 40°, and the pressure slowly lowered to 1200 kg. The spontaneous formation of the less dense crystal occurred suddenly at this temperature and the manometer momentarily registered a considerably higher pressure, and after a few fluctuations finally indicated 1900 kg. In this case the transition of a polymorphic crystal-form into another less dense form, a pressure

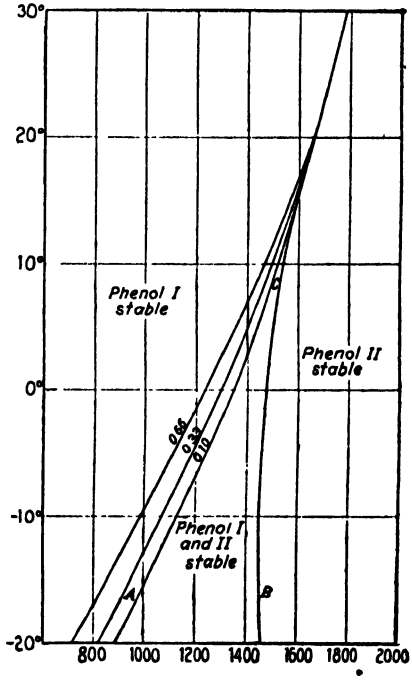


FIG. 84.

increase of 700 kg. is brought about in a fraction of a second, therefore with a velocity characteristic of reactions of explosive substances. The rapidity of this transition is made possible by a small heat of transition. Similar, although smaller and slower, pressure changes are observed in the transformation of ordinary ice into Ice II and in the reverse transformation.

Between 60° and 30° the equilibrium between the two crystal-forms is reversible, but below 30°, the equilibrium pressure is no longer produced. If the pressure upon a mixture of the two forms be increased beyond curve *B*, Fig. 84, it will subsequently return to curve *B*, and upon a decrease in pressure, will reach one of the *A*-curves. Upon which one of these the mixture will arrive depends upon the relative quantities of the two crystal-forms. If crystal-form I amounts to 0.66 of the total quantity, the pressure will take a position upon the curve farther to the left, and with decreasing quantity of I this end-pressure increases, as shown by the two other *A*-curves. In the phase field between curves *A* and *B* two kinds of crystal are stable in the presence of each other for a considerable length of time because the transition velocity in this field is very low, although at a temperature 50° higher the transition velocity assumes extraordinarily high values.[1]

3. The Phase Diagram of Silver Iodide [2]

The complete equilibrium curves for the three forms I, II, and III are given in Fig. 85; the volume surfaces are given in Fig. 86. The crosses above the curves I-II and III-II represent temperatures at which the transformation I into II or III into II takes place upon warming, and the circles represent the reverse transformation. The line *ef* gives the points of state at which transformation I into III takes place upon compression, and the line *hg* refers to the reverse transformation effected by diminution of the pressure upon the form III.

A rise in temperature upon a mixture of the two forms I and III will cause the pressure to follow the line *3*, and a fall in tem-

[1] Concerning the experimental curves of the crystal forms I and II, as well as the preparation of form II at ordinary pressure, see *Z. phys. Chem.*, **75**, 75 (1910).

The melting curve of Phenol II has been followed by *Bridgman* to 209.2° and 12,000 kg./cm.² (*Proc. Amer. Acad.*, **51**, 112 (1915).

[2] *Z. phys. Chem.*, **75**, 733 (1911).

perature will cause it to move along line 2. Between these two curves lies the true equilibrium curve, which can be approached

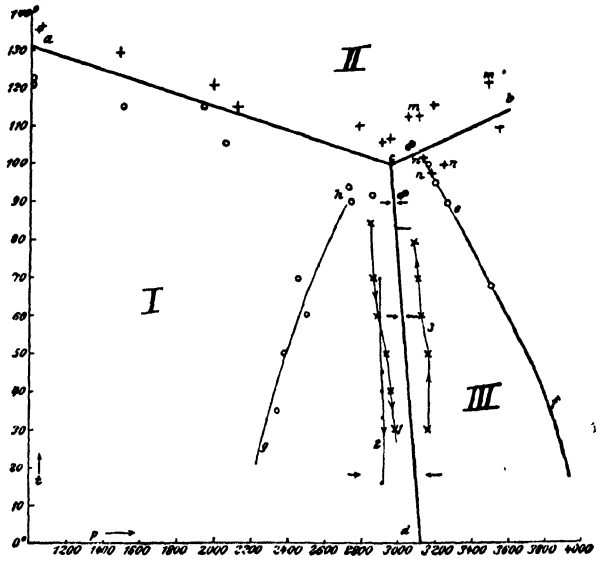


FIG. 85.

about as closely as indicated by the arrows upon volume increase or decrease. At 20° the velocity of transition at pressures dif-

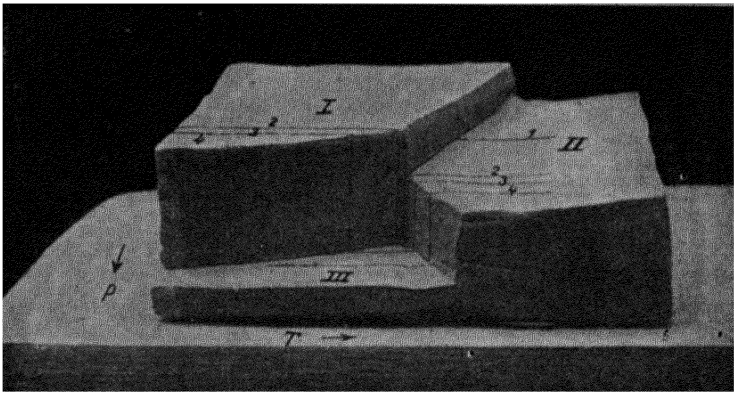


FIG. 86.

fering from the equilibrium pressure by about 150 kg. is so small that transition seems indefinitely delayed.

Silver iodide does not behave as a normal single-component system upon its transition from I into III or from III into I, as, for example, the system composed of Ice I and Ice III. It cannot be maintained that the abnormality in AgI lies in the fact of a decrease in the velocity of transformation with decrease in temperature, such as obtains for the analogous transformations in ice and phenol, in which cases the transformation velocities are equal to the velocity of volume change imposed upon the system and only at lower temperatures do the transformations become abnormal in the sense that after each change in pressure an opposing pressure change is set up, due to a partial transformation. In the case of silver iodide there is a whole temperature range from 90° to 20° in which the transformation of I into III takes place at a definite pressure with a velocity which depends only upon the velocity of volume change. This pressure is 3200 kg., and with the transformation of III into I, the maximal velocity, which does not decrease very much with falling temperature, is reached at 2700 kg. and is actually independent of the temperature. In fact at − 80° the transition of III into I takes place at a considerable velocity though at a smaller pressure, 1800 kg. The peculiarity in silver iodide lies in the fact that besides the pressure of maximal velocity there is also a pressure interval in which the transformation is completed at a much smaller velocity; in this interval it is necessary to change the pressure in order to accelerate the transformation. At the end of the transformation of I into III, it is necessary that the pressure become greater than 3200 kg. in order that the transformation may be completed, and with the transformation of III into I the pressure must be greatly decreased in order to transform all of the crystal-form I.

Fused AgI has been recognized as distinctly crystalline though the freshly precipitated curdy form has frequently been described as amorphous. With reference to the transformations into the forms II and III, however, the two forms do not differ; the points of state upon the equilibrium curves concerned are the same. It follows that the so-called amorphous forms and the crystalline form are identical.

The determinations of BRIDGMAN [1] and those of the author are essentially in agreement. The transformation curve I–III has been followed by BRIDGMAN to 6000 kg.

[1] *Proc. Amer. Acad.*, **51**, 97 (1915).

4. The Phase Diagram of Sulphur [1]

Figure 87 gives the course of the three curves of stable equilibrium, that of the monoclinic with the rhombic, the liquid with the rhombic, and the liquid with the monoclinic. These three curves intersect at 152° and 1400 kg. The upright crosses refer to determinations made at constant temperature with the most rapid pressure change possible; the inclined crosses refer to determinations in which the pressure upon the substance was held for a

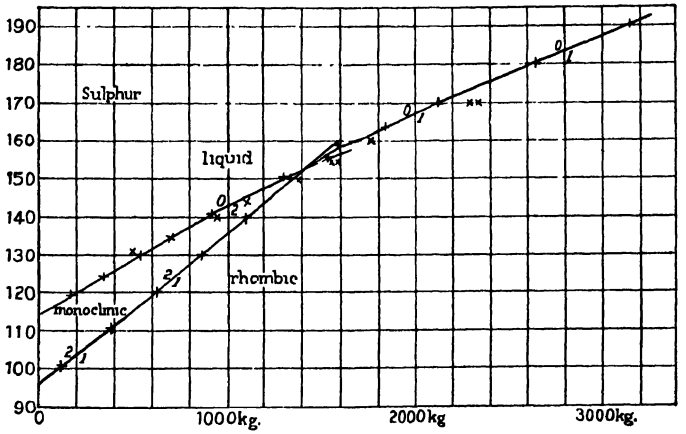


Fig. 87.

longer time at the point of state in question, permitting the establishment of the inner equilibrium in the liquid sulphur. The equilibrium temperature especially at the higher temperatures falls rapidly with time, and the equilibrium pressure increases because the quantity of the form of sulphur soluble in carbon disulphide increases.

The melting point of monoclinic sulphur at $p = 1$ kg. extrapolates to 115.0°, though with rapid warming it was found to be at 119.2°. With slow heating temperatures as low as 114.0° have been observed.[2]

Monoclinic sulphur easily undercools and the transformation to rhombic sulphur occurs very slowly at room temperature. The

[1] *Kristallisieren und Schmelzen.* Pages 269–275.
[2] R. H. Kruyt, *Z. phys. Chem.*, **64**, 550 (1908).

rhombic sulphur may be overheated, though rather seldom, and with rapid heating melts at 112.8°. This melting point lies upon the prolongation of the melting curve of rhombic sulphur.

As obtained from extrapolation of determinations obtained at higher pressures, the transformation point of rhombic into monoclinic sulphur at $p = 1$ kg. lies at 95.4°, whereas the temperature found experimentally by KRUYT and SMIT is 95.3°.

The volume changes and the heats of transformation upon melting and transition have been given elsewhere.[1]

Sulphur crystallizes not only as monoclinic and rhombic sulphur but also in a mother-of-pearl form, the melting point of which lies at 106.8° when free from the insoluble sulphur, and at 103.4° when containing 3.1 per cent of the insoluble form. In addition to these forms several unstable forms have been observed by BRAUNS.[2] However, nothing has been learned with respect to the relation of these unstable forms to the crystal groups of the stable forms.

Sulphur has an anomalous behavior in the fact that in the liquid state two kinds of molecules occur, one of which is insoluble in carbon disulphide. Sulphur, therefore, behaves not as a one-component, but as a two-component system.

5. THE PHASE DIAGRAM OF PHOSPHORUS

Phosphorus occurs in three groups of forms: yellow phosphorus I, graphitic (black) phosphorus II, and a form varying in color from red to violet. The transformation velocity of I (regular) into II (probably hexagonal), and that of liquid into I, are determined as usual by the flow of heat. On the other hand, the transformation velocity of the liquid into the red forms is much less and the same is true of the reverse transformation.

Graphitic phosphorus, Phosphorus II, forms from yellow phosphorus, Phosphorus I, at 1200 kg., and at a temperature of 200° will not retransform into the yellow at pressures as low as 4000 kg. and lower. Red and violet phosphorus, on the other hand, do not change into the graphitic even upon heating with iodine as a catalyst. At higher temperatures the graphitic changes into the yellow and then into the red.

[1] *Kristallisieren und Schmelzen.* Pages 269–275.
[2] *N. Jahrb. Mineral.*, **13**, 39 (1900).

Preparations of different colors can be obtained from liquid phosphorus by heating. A bright-red variety is obtained by heating in an atmosphere of nitrogen, and violet by the addition of sodium. The following values for the melting curve of yellow phosphorus and the transformation curve of Phosphorus I into II have been given by BRIDGMAN.[1]

MELTING CURVE

kg./cm.^{2}	$t°$	$\Delta v \cdot 10^5$ cm.^{3}/gm.	R_p kg.·m./gm.
1	44.2	1927	2.09
1,000	72 2	1792	2 27
2,000	99 3	1667	2.41
3,000	124.4	1549	2.52
4,000	148.2	1436	2 63
5,000	170 5	1326	2.72
6,000	191.9	1218	2.78
	TRANSITION CURVE I–II		
1	−76 9		
6,000	− 2.4	858	18.61
7,000	9.6	825	19.45
8,000	21.4	799	20.24
9,000	32.7	772	21.04
10,000	43.7	746	21 82
11,000	54.4	720	22 58
12,000	64.4	694	23 29

The melting curve of yellow phosphorus could be followed to only 6000 kg., because the beginning of the formation of red phosphorus is noticeable at a temperature as low as 175° and as a result the equilibrium pressure is not sharply defined.

The vapor pressures of the different modifications of phosphorus are given in the accompanying table, a summary by BRIDGMAN.[2]

At the same temperature the various forms of phosphorus exhibit vapor pressures in the following ascending order: the graphitic form (Phosphorus II), the dense red form of BRIDGMAN, the two red forms investigated by HITTORF, the red of TROOST

[1] *Phys. Rev.*, **3**, 186 (1914).
[2] *J. Amer. Chem. Soc.*, **36**, 1349 (1914).

VAPOR PRESSURE CURVE IN CENTIMETERS MERCURY

Temperature, °C.	Bridgman		Hittorf		Troost and Hautefeuille	
	Graphite-like P.	Dense, Red P.	Ordinary Red P.	Crystalline Red P.	Yellow P.	Ordinary Red P.
357.1	2.3	5.2				
358	.....	.....	3 15			
360	.....	.....	.....	.....	243 0	9.1
409	.....	.....	37 1			
440	.....	.....	.....	.....	570 0	133 0
443.7	.....	73.2				
445.2	58.5					
447	.....	.....	164 0	93 0		
487	.....	.....	.....	.....	.....	517.0
494	.....	.....	.....	.....	1370.0	
503	.....	.....	.....	.....	1660 0	
510	.....	.....	.....	.....	.....	820.0
511	.....	.....	.....	.....	1990.0	
530	.....	.....	614.0	413 0		
550	.....	.....	.....	.....	.....	2360 0
577	.....	.....	.....	.....	.....	4260.0

and HAUTEFEUILLE, which probably contains a little yellow, and finally the yellow (Phosphorus I). The variety of phosphorus that has been known for the longest time, yellow Phosphorus I, is therefore the least stable, and it appears to be stable only because between 0–100° the crystallization centers of the red and the graphitic are very few in number, and chiefly because the linear transformation velocity is very low.

Although the maximal linear crystallization velocity of yellow Phosphorus I is the highest crystallization velocity that has been observed, the crystallization velocity of the red form in the liquid yellow is very low. For this reason the determination of the melting point of red phosphorus is difficult. A. STOCK and STAMM [1] found that the red form melts to the liquid yellow between 579° and 601° and that it crystallizes between 540° and 520°.

[1] *Berl. Ber.*, **46**, 3497 (1913).

The graphitic (black) form discovered by BRIDGMAN has a density of 2.69, whereas the red has a value of 2.34 and the yellow of 1.9. The graphitic form conducts electricity whereas the red and the yellow are insulators. The specific resistance of graphitic phosphorus is 0.711 ohm at 0° C. and decreases with increasing temperature.

6. THE FORMS OF SILICIC ACID ANHYDRIDE

At ordinary temperatures three forms are stable in the presence of each other; α-quartz, α-tridymite, α-cristobalite, and silica-glass. At higher temperatures the intertransformation of these three forms is very sluggish, and often it is possible to effect transformation only in the presence of a solvent such as Na_2WO_4. In spite of this slowness in the intertransformation of the three forms, each of the α-forms can change into a β-form with a velocity limited only by the flow of heat; for upon the cooling curves of the β-forms points of arrest are found. These transformation points are as follows: for α- into β-quartz, 575°; for α- into β-cristobalite, 275-220°; and for α- into β-tridymite, 117°.

Each of the three α-forms, therefore, possesses a capacity for transforming into a β-form at low temperatures, although the intertransformations of the β-forms, which require much higher temperatures for completion, are very slow. This slowness of transition obtains also for the transformation of the three β-forms into the isotropic form, silica-glass, though the melting process is regulated only by the flow of heat. The viscosity of the melt is then uncommonly high; at the melting point of cristabolite, 1625°, the melt is extraordinarily viscous.

The various modifications of silica possess the ability to transform, and that even at relatively low temperatures, but the transformation takes place with ordinary velocity only in a definite direction whereas in other directions it is considerably restrained. The assumption seems plausible that the molecules of the α- and β-forms are the same and that they are different in the forms of quartz, tridymite, and cristobalite, and that the molecules in these forms also differ from those in silica-glass, isotropic silicic acid anhydride. The nature of this difference cannot be stated, since many possibilities exist.

The stability relations of the forms of SiO_2 are given by the

diagram of the vapor pressure curves, Fig. 88, according to C. N. FENNER. In fact the vapor pressure of the forms is immeasurably small, but the relative positions of these curves can be obtained from a study of the transformation processes, especially as relates to the points of intersection, the transition points. At the same temperature the stability is greater the smaller the vapor pressure, and it is therefore easy to learn the stability relations of the several forms at any temperature. Besides the vapor pressure curves the directions of the transformation curves

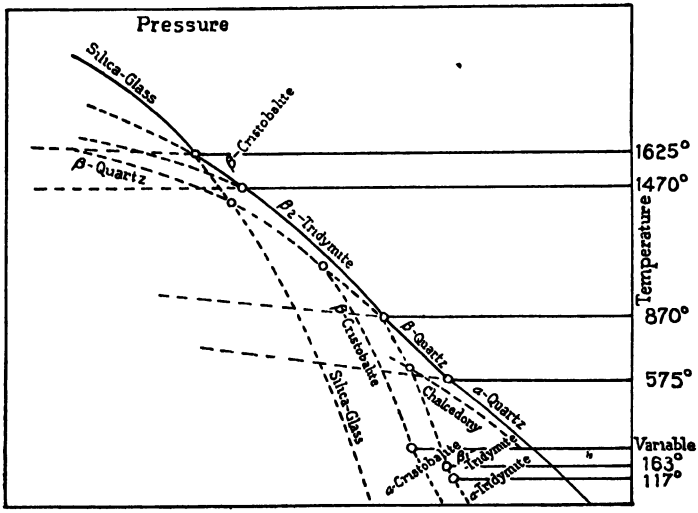


FIG. 88.

are indicated in the diagram by dotted lines almost perpendicular to the T-axis.

By heating quartz with Na_2WO_4, β-tridymite or β-cristobalite can be obtained according as the temperature interval of stability for β-tridymite or β-cristobalite is chosen, and in addition, tridymite can be transformed into quartz and cristobalite, and the latter can be transformed into quartz or tridymite. The mechanism of the reaction using Na_2WO_4 does not consist in the formation of nuclei of crystallization of the second form in the first form, but in a solution and subsequent nuclei formation of the new form in the solution. Inasmuch as the transformation without the use of solvent is so slow that it cannot be awaited, either the

number of transition nuclei in the original form is very small, or the transition velocity is very low. To which of these two factors the slowness of the transformation is due has not been determined.

Because of the multiplicity of the transformations here possible an opportunity is afforded for testing the law of stages (see page 236). With several of the transformations, the law is apparently satisfied. According to FENNER, however, there are cases for which it does not hold true.

From a mixture of amorphous silica and Na_2WO_4 there can be obtained after the lapse of a few hours tridymite alone; after a longer time β-quartz appears, but cristobalite, the formation of which would be expected to take place first according to the law of stages, does not form.

Silica-glass, or precipitated silicic acid, changes upon heating without a flux always to cristobalite, even above 1470°, where according to the law of stages, tridymite should be formed first. β-quartz forms cristobalite at 1300° in conformity with the law of stages, the transformation taking place very slowly; in the presence of Na_2WO_4 transformation takes place much more rapidly, but β-tridymite is formed.

In the absence of a solvent, cristobalite alone is obtained from silica-glass and β-quartz; the transformation likewise proceeds slowly. The devitrification of silica tubes is caused by the formation of crystallization centers of cristobalite; the life of such tubes would be prolonged by the addition to the silica of a substance inhibiting the formation of such centers of crystallization.

In comparison to the transformations without the use of a solvent, silica-glass forms tridymite or quartz in the presence of a solvent (Na_2WO_4 or water), below 870° quartz alone is formed. This latter transformation is perhaps the cause for the wide distribution of quartz in granite and other plutonic rocks.

α-quartz has a density of 2.65 and is the densest form of SiO_2; with the transformation of α- into β-quartz the density decreases by about 2 per cent. At ordinary temperatures the densities are: α-cristobalite, 2.33; α-tridymite, 2.27;* and silica-glass, 2.20. Regarding geologic questions related to the transformations of the various forms of SiO_2 reference is made to the work by FENNER and a paper by MÜGGE.[1] The transformation of β- into α-quartz

[1] *Göttinger Nachrichten*, 1919, Professional contributions, page 79.

is probably one of the transformations produced by the considerable tensions in the upper strata of the earth, the release of which leads to seismographic phenomena, to which reference has already been made.[1]

7. Remarks upon the Phase Diagram of Carbon

It is well known that diamond is not stable at high temperatures under ordinary pressure but changes noticeably into graphite at 1000°. If the melting curves of graphite and diamond with increasing pressure rise to higher temperatures, then diamond must be stable under high pressures at temperatures much above the melting point of graphite at $p = 1$ kg. Since the only point upon the transformation curve of graphite into diamond, the position of which can be given approximately for $T = 0$ lies at the relatively low pressure of about 6000 kg./cm.^{2}, it is very improbable in the light of other experience, that by slight increase of pressure the temperature range of the stability of diamond should be raised as much as from 1000° to 4000°. Ice III, which is stable above 2000 kg., changes at ordinary pressure into Ice I at − 130°.

If the melting curve of graphite should fall off, the difficulty would be raised that in this case the density of liquid carbon would be greater than that of graphite; the phase field of diamond would then be displaced towards lower temperatures. Such a case would be given by the formation of an especially dense form of carbon, the density of which exceeds that of graphite. If the melting curve of graphite and that of diamond do not intersect above 1500° the case would correspond to our experience with reference to the transition of Ice III into ordinary Ice I at $p = 1$ kg.

As a matter of fact, the course of the melting curve of graphite is unknown. If actually the curve does not fall off steeply it is possible that at temperatures higher than 1500° the phase field of an unknown form, of density between that of graphite and that of diamond, exists above the phase field of diamond, just as the phase field of Ice III lies above that of Ice II. At the present time this possibility seems the most likely.

E. Bauer [2] has calculated the equilibrium pressure of graphite

[1] *Kristallisieren und Schmelzen*, 1903, page 183.

[2] *Z. anorg. Chem.*, **92**, 313 (1915).

and diamond from the energy difference, as determined by ROTH,[1] and the volume difference, Δv. According to *Nernst's Heat Theorem*, at $T = 0$ and $p = 6200$ kg.,

$$E_{\text{graphite}} - E_{\text{diamond}} = \frac{p\Delta v}{43},$$

$$288 \text{ cal. per mol.} = \frac{p \cdot 2.0 \text{ cm.}^3}{43}.$$

Figure 89 summarizes what has been said about the phase diagram of carbon. The diagram is legitimate first of all with respect to the transformability of diamond into graphite at relatively low temperatures, and is also reconcilable with the geologic occurrence of diamond.

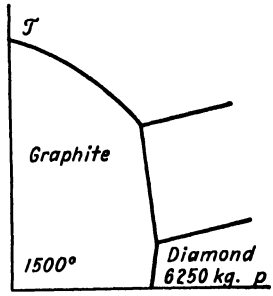


FIG. 89.

The blue earth in which diamonds are found imbedded may have worked up as olivine from a depth of 20–30 km., corresponding to a pressure of 6000–9000 kg./cm.^{2} and a temperature of 1300–1500°. Rapid cooling to 1000° could have produced the diamond as such.[2] But there still remains a degree of uncertainty about the matter, for the beginning of the formation of graphite in diamond at 1000° C. is distinct after a period of twenty-four hours, whereas the half-liquid magma must have maintained a temperature above 1000° for a period considerably greater than twenty-four hours after the pressure had fallen to small values, and yet no paramorphs of graphite or of diamond have been found in the blue earth. Laboratory experience has shown that the important factor in the production of a new crystalline form is the temperature to which the original crystalline form is allowed to fall. At a definite temperature, in the course of the cooling, the number of crystallization centers increases very greatly, and in view of this fact it may be seen that a diamond crystal that had been once cooled would be much less stable at a temperature of 1300–1500° than one that had never been permitted to cool.

[1] *Berl. Ber.*, **46**, 896 (1913).

[2] Doelter, *Mineralchemie*, **1**, 48 (1912).

With respect to the artificial preparation of diamond it may be said that the transformation velocity of diamond decreases rapidly with the temperature upon a steep transformation curve, as, for example, upon the transformation curve of Ice I into Ice II. Experimental difficulties are multiplied by the fact that cylinders made of material with the greatest strength at high temperatures are likely to expand so greatly at a temperature of 1000° with pressure as low as 3000 kg. that the desired pressure rise of 6000–10,000 kg. becomes impracticable. Whether or not the transformation velocity of graphite into diamond at 1000° is noticeable cannot be said. At best such an artificial production of diamond would produce no large crystals but only a fine-grained crystalline conglomerate which could find use as an abrasive.

A series of notices exists in the literature relating to the successful production of diamond crystals from solutions of carbon in liquid iron or liquid silicates.[1] It appears, therefore, that carbon can crystallize as diamond at ordinary pressures. The assumption that quenching liquid iron containing carbon produces a very high pressure cannot be accepted, for in this case crystallization would take place with contraction and not expansion. The production of diamond at pressures outside of its phase-field is similar to the production of Ice V at relatively low pressures. The phase-field of Ice V lies above 3500 kg., yet its formation in pure Ice I occasionally occurs at 2300 kg., and in the presence of NH_4Cl the formation of Ice V from Ice I at 2300 kg. is more frequent than the formation of Ice III.[2] It seems possible, therefore, that substances may be discovered, the presence of which could make the formation of crystallization centers of diamond outside of its field of state of very frequent occurrence.

8. The Phase Diagram of Carbon Tetrachloride, Carbon Tetrabromide, Methylene Iodide

It is surprising that the phase diagrams of these liquids show the occurrence of several crystal-forms, for the liquids themselves, judged by our criteria for normal molecular composition (which do not recognize the presence of isomeric molecules), would be considered as normal. It appears that this peculiarity occurs

[1] Doelter, *Mineral chemie*, **1**, 42 (1912).
[2] Denecke, *Z. anorg. Chem.*, **108**, 35 (1919).

regularly with the halogen derivatives of the hydrocarbons that contain large amounts of the halogen. Yet chloroform, $CHCl_3$, does not display polymorphism, although C_2Cl_6 probably does.

Figure 90 is the phase diagram of CCl_4 according to BRIDGMAN.[1] Three stable crystalline modifications occur, the transformation curves of which are almost linear; the melting curve is noticeably curved and Δv decreases rapidly upon it, whereas Δv upon the transformation curves decreases very much less rapidly with increasing pressure.

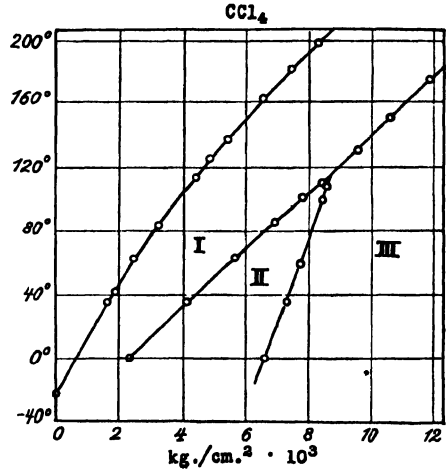


FIG. 90.

Figure 91 represents the phase diagram of CBr_4 according to BRIDGMAN.[2] Here again there are three different stable crystalline forms, and the three transformation curves run almost linearly, since Δv changes very little.

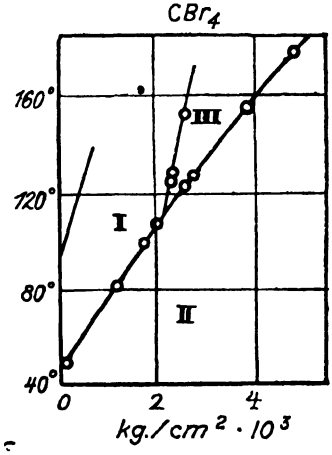


FIG. 91.

Figure 92 gives the phase diagram for CH_2I_2 as obtained by the author and R. HOLLMAN.[3] It is surprising that the transformation curve 1–2 is a rising one. The type of triple-point 0, 1, 2 has never been found elsewhere. In explanation of this (page 146c) it may be adduced that with this position of the equilibrium curves the molecules

[1] *Phys. Rev.*, **3**, 175 (1914).
[2] *Proc. Amer. Acad.*, **51**, 95 (1915).
[3] *Ann. d. Phys.*, **6**, 74 (1901); and *Kristallisieren und Schmelzen*, page 278.

of the form of greater volume would make themselves manifest by the formation of crystals at higher pressures, although with rising pressure the liquid becomes poorer in these molecules. An error of experiment of 1° may account for the relative positions of the triple-points 0, 1, 2 and 1, 2, 4, and an adjust-

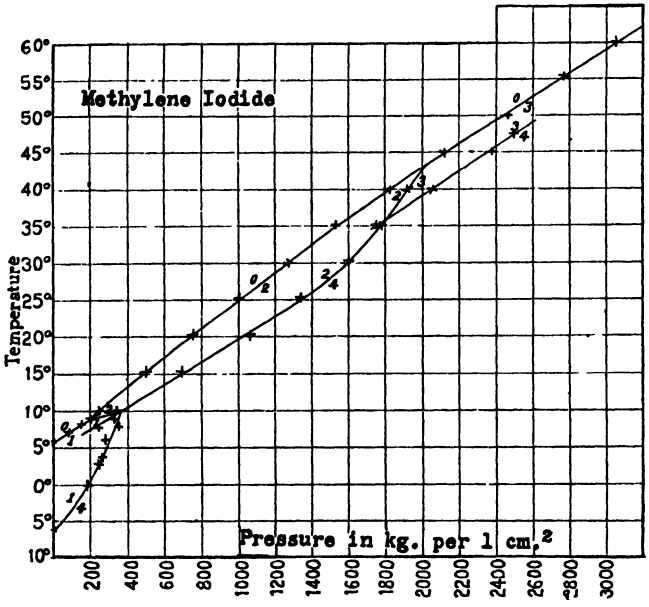


FIG. 92.

ment of this error might make the equilibrium line 1–2 descending rather than ascending as shown in the diagram.

9. THE PHASE DIAGRAM OF URETHANE

Figure 93 gives BRIDGMAN'S phase diagram for urethane.[1] The course of the melting curve of form I was formerly determined by the author (KRISTALLISIEREN und SCHMELZEN, page 239) when indistinct signs of a second form were found. The investigation was not completed because these signs lay at the limit of the working pressure. The phase field of form III is very small.

[1] *Proc. Amer. Acad.*, **51**, 118 (1915).

10. The Phase Diagrams of a Few Nitrates

Figure 94 gives the phase diagrams for six nitrates as determined by Bridgman.[1]

In the case of NH_4NO_3 six stable modifications have been

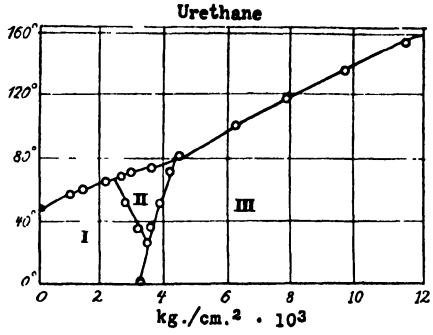


Fig. 93.

found, and a notable abnormality has also been shown to exist. Whereas in other cases Δv decreases upon ascending equilibrium curves, and increases upon falling curves, in this case Δv increases

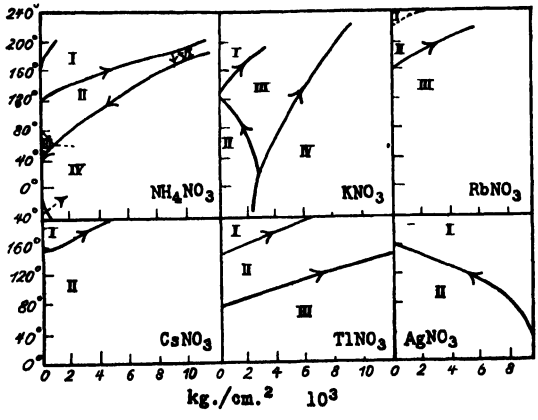


Fig. 94.

exceptionally upon the three equilibrium curves III–IV, II–IV, and II–VI; though the increase for curve II–IV is very slight. The arrows upon the equilibrium curves in Fig. 94 point in the

[1] *Proc. Amer. Acad.*, **51**, 620 (1916).

direction of decreasing Δv values. With other substances this abnormality does not exist. With silver nitrate, R_p passes through a zero value slightly under 0° and Δv increases with increasing pressure.

Although for the compressibility $\left(\frac{dv}{dp}\right)_T$, the expansibility $\left(\frac{dv}{dT}\right)_p$, and the specific heat C_p upon the melting curve, the rule ordinarily holds good that at the same point of state the phase stable at higher temperatures has values for these quantities greater than those for the phase stable at lower temperatures, the rule has many exceptions when applied to transformation curves. For the transformation curve NH_4NO_3 III–IV the exception has been known for some time, and since it has been found that other substances likewise show the same exceptional behavior, it appears that no rule similar to the one for melting can be formulated to apply to such transformations.

11. The Transformation Curve of Benzene

The course of the melting curve for benzene has been followed by Bridgman to 10,000 kg./cm.² (page 101). At this point it unexpectedly meets a steep transformation curve [1] which runs to 12,000 kg./cm.². At 180° this curve becomes retrograde, in that R_p passes through a zero value at appreciable values of Δv. These relations are similar to those described by the author for the transformation curves Ice I and Ice III.

The transformation curve of benzene is defined by the following values:

p kg./cm.²	t°	Δv cm.³/gm.	R_p kg.·m./gm.
12,260	100	0 01048	−3.7
12,080	120	0.01110	−3.4
11,950	140	0.01168	−3.0
11,860	160	0.01219	−2.0
11,810	180	0.01269	−0.5
11,840	200	0.01281	+1.4

[1] *Phys. Rev.*, **3**, 172 (1914).

12. The Transformation of Red into Yellow Mercuric Iodide

The volume change in this transformation is small and it is therefore to be expected that the maximum lies at attainable pressures. The transformation is very slow and considerable undercooling occurs. The following table gives the coordinates of the transformation curve as obtained by Bridgman: [1]

HgI_2

p kg./cm.^{2}	$t°$	Δv cm.^{3}/gm.	$\frac{dt}{dp}$	R_p kg.·m./gm
1	127 0	0 00342	0.0267	0 513
1,000	149 8	217	187	0 491
2,000	165 2	127	122	0 456
3,000	174 9	065	069	0.420
4,000	179 9	024	028	0 390
5,000	181.2	−008	−010	0 365
6,000	178 2	−045	−059	0 345
7,000	169.7	−100	−134	0 330
8,000	152 4	−175	−234	0 318
9,000	122 3	−270	−361	0 296
10,000	79 4	−390	−495	0 278

[1] *Proc. Amer. Acad.*, **451**, 107 (1915).

VIII. THE DEFORMATION OF CRYSTALS AND ITS CONSEQUENCES

1. The Flowing of Crystalline Bodies

The deformation of a body is called homogeneous when points equally distant from each other and arranged in parallel lines remain equally distant, the actual distance having changed, and as a result again appear in parallel lines.

The permanent deformation of crystals caused by straining above the elastic limit is characteristically homogeneous, whereas permanent deformation in amorphous substances is characteristically non-homogeneous. During a permanent deformation of a plastic crystal the parts of the crystal move over each other upon gliding planes without losing their coherence.

There are two cases to be distinguished:

1. *Translation*, a sliding of the parts of a crystal over each other in such a way that the optical orientation of the parts is not altered.

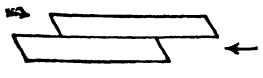


Fig. 95.

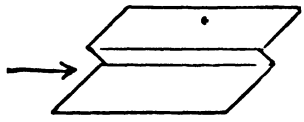


Fig. 96.

2. "*Simple Slip*," a combination of sliding, translation, with a rotation of the parts of the displaced layer to the formation of twin laminæ.

A gliding plane, upon which displacement occurs, is defined by its position among the atom-planes in the crystal and by the direction of the minimal force that produces it. Under equal conditions, the greater the number of parallel gliding planes formed in the unit of volume, and the greater the number of the sets of such parallel gliding planes, the more plastic will be the crystal, that is, the greater will be the amount of deformation to which the crystal can be subjected without loss of coherence. This capacity

for displacement of portions of plastic crystals protects them from breaking and prevents confusion of their lattice structure. It is very likely that in this way a crystal is enabled to flow without melting.

Attempts have been made to explain the flowing of crystalline bodies by a transient melting, and in support of the idea various proposals have been presented, the object of which is to show that a substance will melt upon compression beneath a loosely fitting piston at pressures much lower than those required with compression under a tightly fitting piston.

These attempts have led to demonstrably mistaken results, and the experiments themselves have not been conclusive. On the other hand, there is a satisfactory explanation for the flowing of crystalline bodies and for the property changes caused by it. Despite this, however, the assumption of partial melting during flow continues to be made occasionally, and frequently the incorrect conclusions resulting from it are presented in other fields as scientific truth.

a. Theoretical Investigations

First let us examine closely the theoretical foundation for the hypothesis of partial melting during the flow of crystalline bodies. Attempts have been made in three ways to show that when the opportunity is found for the separation of the melt from the crystal during compression, a substance melts at a pressure lower than that obtaining when this opportunity is absent.

1. POYNTING [1] carried out an isothermal cyclic process with this end in view. The substance was first compressed, in this imaginary process, under a porous piston and at the pressure P a unit mass of the substance melted whereupon the piston sank to the volume of the crystalline substance, v''. The withdrawn melt was then crystallized under a tightly fitting solid piston at the pressure p, which caused a rise or a fall on the part of the piston according as the volume difference of the substance in the two states, $vp'' - vp'$, was positive or negative.

Therefore,

$$-Pv_P'' + (v_p'' - v_p')p = 0 \quad \text{or} \quad P = \frac{v_p'' - v_p'}{v_P''} \cdot p. \quad . \quad (1)$$

[1] *Phil. Mag.*, (5), 12, 32 (1881).

From this it may be concluded that substances melting with volume diminution would melt upon compression beneath loosely fitting pistons at considerably smaller positive pressures than if the piston were solid and tightly fitting, and it may also be concluded that substances melting with volume increase, under similar conditions, would melt at negative pressures.

This cyclic process of POYNTING is probably not isothermally reversible since pressed crystals cannot be liberated from the melt and hence the piston cannot be raised. In addition, it cannot be understood why the substance should have such a pronounced sensitiveness to the porosity of the enclosing case; it therefore seems likely that some error is present in the above deduction.

The first and second laws of thermodynamics may be expressed in the form: the sum of the work terms in an isothermal cyclic process is zero; and they may be applied only to reversible cyclic processes. According to the above proposal, at a temperature $T°$, the crystalline substance must be in equilibrium with the melt at the pressure p and also at the considerably smaller pressure P, and this equilibrium is determined only by a property of the casing, the degree of porosity. This improbability is directly asserted and it is necessary that we examine more closely the error which evidently lies in a complete misconception of the two laws.

CARNOT has expressed the efficiency of his cyclic process as $\frac{Q_1 - Q_2}{Q_1}$, where Q_1 indicates the heat given up by the warmer state and Q_2 the heat taken up by the cooler; this quotient may be completely determined. CLAUSIUS has shown that the efficiency of the Carnot cyclic process is also given by the quotient $\frac{T_1 - T_2}{T_1}$, where T_1 represents the absolute temperature of the warmer state and T_2 the absolute temperature of the cooler. From the equivalency of these two quotients there follows:

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0.$$

According to the first law, A, the work obtained by a cyclic process, is equal to $Q_1 - Q_2$. Since both laws are applicable to complicated cyclic processes, the sum of the work terms must equal zero, $\Sigma A = 0$.

Thus the second law may be applied to a cyclic process in the form $2A = 0$, if the efficiency of each process be determinable. This condition, however, does not suffice for the foregoing isothermal irreversible cyclic process. The efficiency of this process, given by the work Pv_p'', is as indefinite as the porosity of the casing involved.

Equation (1) might represent the application of the second law to steam-engines with porous pistons. This fallacious application of the second law leads to the unbelievable result that a property specific to every substance, such as melting pressure, should depend upon a chance peculiarity of the casing surrounding the substance.

2. OSTWALD [1] attempted to arrive at the same conclusion in another way.

A theory due to *Schiller* [2] was used which states that an external pressure tends to diminish the vapor pressure of a liquid. If a gas insoluble in the liquid exert upon the liquid the pressure p, then the vapor pressure of the liquid may be expressed as:

$$\pi_p = \pi_{p=0} \cdot \frac{v}{v - v'},$$

where v represents the specific volume of the vapor and v' that of the liquid.

OSTWALD drew upon the πT-plane the vapor pressure curve of the liquid and of the crystalline solid for different external pressures, and found that the vapor pressure curve of the undercooled liquid of pressure p_1 intersected that of the crystalline solid of pressure p_2 at temperature T. From this he concluded that under these conditions both phases are in equilibrium with each other and that between the pressures p_1 and p_2 a definite relation exists.

In order to investigate this contention let us consider the dependence of the vapor pressure π upon the external pressure p and the temperature T for the three phases, vapor, liquid, and crystal, represented as surfaces in the coordinate system π, p, and T.

For the π-surface of the vapor, $\pi = p$. If $p > \pi$, then π is no longer measurable; however, this virtual vapor pressure may be

[1] *Lehrbuch der allgemeinen Chemie*, II, 2, 374 (1902).
[2] N. Schiller, *Wied. Ann.*, **53**, 396 (1894).

regarded as a function of p and T. Each of the three faces has a π-surface (Fig. 97). The surface of the vapor, $T_1e'c'T_2$, is a plane which the pT-plane intersects in the T-axis at an angle of 45°.

The π-plane of the vapor intersects that of the liquid, $c_1be'g'$, in the non-plane curve $e'b'c'$, and the π-surface of the crystal, $d'b'a'f'$, in the non-plane curve $b'a'$. The surfaces of the liquid and the crystal intersect in the non-plane curve $b'd'$. The projections of these curves upon the pT-plane are the familiar equilibrium curves, *ebc* the vapor pressure curve of the liquid, *ab* the vapor pressure curve of the crystal, and *bd* the equilibrium curve of the crystal with its melt.

If it be inquired whether or not at a definite temperature the virtual vapor pressure of the crystal π'' and that of its melt π' can be equal to each other, it will be seen that for an infinite series of pressures p_1, a similar series of p_2-values obtains. A straight line parallel to the p-axis generally meets the π-surface of the crystal as well as that of the undercooled liquid. However, the projections of these points upon the πT-plane do not fall upon a curve, but cover an area. A definite relation between π and T for the condition $\pi' = \pi''$ therefore exists only for the points of the curve of intersection of the π-surfaces for crystal and melt. OSTWALD arrived at his conclusion by considering only the projections of a few sections perpendicular to the p-axis upon the πT-plane, and hence misunderstood the conditions for the establishment of equilibrium.

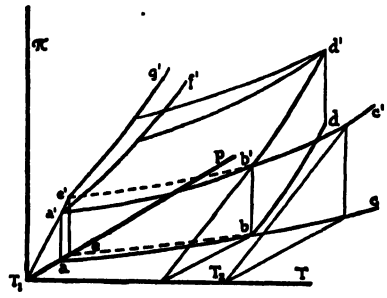


FIG. 97.

3. Recently P. NIGGLI [1] sought to solve the question of the equilibrium between pressed crystalline substances and their less pressed melts by the help of the thermodynamic potential. He equated the potential of the unit of mass of the crystalline substance at a pressure P and that of its melt at a pressure p,

$$\mu_P'' = \mu_p'$$

[1] *Z. anorg. Chem.*, **91**, 197 (1915).

and differentiated the one side of the equation with respect to P and T and the other with respect to p and t,

$$\frac{\partial \mu_P''}{\partial T} dT + \frac{\partial \mu_P''}{\partial P} dP = \frac{\partial \mu_p'}{\partial T} dT + \frac{\partial \mu_p'}{\partial p} dp.$$

At constant temperature, $dt = 0$, and since

$$\frac{\partial \mu_P''}{\partial P} = v_P'' \quad \text{and} \quad \frac{\partial \mu_p'}{\partial p} = v_p',$$

there results

$$\frac{dP}{dp} = \frac{v_p'}{v_P''}.$$

From this it follows:

$$\frac{P}{p} = \frac{r_p'}{v_P''} \quad \text{or} \quad p - P = \frac{v_P'' - v_p'}{v_P''} p.$$

According to NIGGLI, therefore, POYNTING'S value for P should apply to the difference $p - P$.

In Fig. 98 μ [1] is represented as a function of p and T for the three states of aggregation. The three μ-surfaces intersect in three curves, $a'b'$, $b'c'$, and $b'd'$, the projections of which upon the $p\pi$-plane are the three equilibrium curves—the vapor pressure curve of the crystal, ab; the vapor pressure curve of the melt, bc; and the melting curve, bd. At any point upon any of the three equilibrium curves, two phases are in equilibrium and their potentials are therefore equal. It is not permissible to reverse this proposition, however, assuming that if in two different points of state the potentials be equal the two phases will be in equilibrium. For a crystal and its undercooled melt at one and the same temperature there is an infinite series of pairs of points of state, the potentials of which are equal to each other. A plane perpendicular to the ζT-plane (Fig. 97) intersects the ζ-surfaces of the crystal and its undercooled melt in two curves. For each point upon one curve there is a corresponding coordinate point upon the second

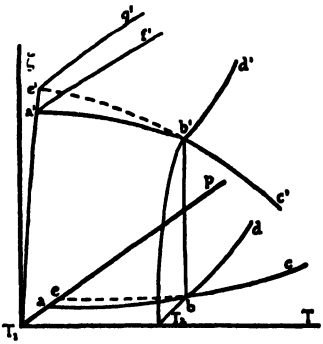


FIG. 98.

[1] μ is equal to the function ζ referred to the unit of mass.

curve, in accordance with the requirement $\mu_p'' = \mu_p'$. The equation $\mu_p'' = \mu_p'$ therefore asserts nothing definite, and its mathematical transformations can lead to no definite results. If, however, the statement of NIGGLI held true, that the equation $\mu_p'' = \mu_p'$ characterizes the state of equilibrium, then the phase rule must be altered, since a change in pressure would in that case correspond to two degrees of freedom of the system rather than to one, as is demanded by the rule.

With regard to the influence of pressure upon a solid phase in equilibrium with its solution analogous considerations would apply, and NIGGLI treated this case in a manner similar to that in which he discussed the equilibrium of a pressed crystal with its melt.

It has thus been seen that the several formulæ, derived in various ways, for the representation of the influence of the pressure on a crystal upon the equilibrium of the crystal with its melt, are incorrect because in their derivation the conditions of equilibrium were misunderstood.

4. J. W. GIBBS [1] and E. RIECKE [2] have treated this subject in an appropriate manner and with correct formulation of the question: how will p and T be influenced for the equilibrium of a crystal with its melt by a force exerted upon the crystal? The course of their derivation is given in the following.

Let there be cut from a crystal a prism in known orientation, of 1 cm.^{2} cross-section and of the volume of the unit of mass. This prism is brought into the melt at the temperature T and the equilibrium pressure p, and at the ends of the prism is exerted a pressure or tension of X kg./cm.^{2}, working parallel to the axis of the prism. The problem is this: are the conditions of equilibrium, p and T, changed by this force, and if so, in what way. In order that equilibrium shall still exist after the application of the force X between the crystal and its melt, the changes of the thermodynamic potential μ or of the ζ-function of the crystal and of its melt must be the same.

These changes are:

$$d\zeta'' = -\eta'' dT + v'' dp + X dx$$

and

$$d\zeta' = -\eta' dT + v' dp.$$

[1] *Scientific Papers.* I. Page 184 and the following.

[2] *Wied. Ann.*, **54**, 731 (1895).

η'' and η' signify the specific entropies and v'' and v' the specific volumes of the crystal and its melt, and dx is the change in length of the crystal prism effected by the force X.

For the equilibrium of the prism under tension with its melt we then have,

$$-(\eta' - \eta'')dT + (v' - v'')dp - Xdx = 0.$$

The work Xdx, the increase of the potential energy of the crystal prism, is always positive, for when X is positive dx is positive, and when X is negative dx is negative.

Therefore, with the application of the force X, the equilibrium temperature is lowered, as long as $\eta' > \eta''$, and the equilibrium pressure will be increased as long as $v' > v''$.

At constant pressure the influence upon the equilibrium temperature, and at constant temperature the influence upon the pressure, are respectively

$$dT = -\frac{Xdx}{\eta' - \eta''} \quad \text{and} \quad dp = \frac{Xdx}{v' - v''}.$$

At the point upon the equilibrium curve in which $v' - v''$ passes through a zero value, dp changes from $+\infty$ to $-\infty$, but it has a definite finite value. The quantity dT shows the same behavior for the point where $\eta' - \eta'' = 0$, and at this point dp has a definite finite value.

It follows that if two crystals of the same size occur in association with their melt, and the unstressed crystal is in equilibrium with the melt, the stressed crystal with the greater potential energy will then melt and the portion melted will deposit on the unstressed crystal; this process will lead to an equilibrium in which the potential energies of the two crystals will be the same, since the potential energy of the unstressed crystal increases as a result of the increase in size, while that of the stressed crystal decreases.

Since the equations hold only for processes in which the equilibria are changed, the force X may be raised only to the elastic limit of the crystal, X_e. This must be borne in mind in the integration of the last two equations.

Carrying this out, and setting

$$d\zeta' = -\eta' dT + v' dp.$$

where R_p represents the heat of fusion measured in kg./cm., we obtain

$$\Delta T = \frac{T}{R_p}\int_{X=0}^{X_\epsilon} X dx \quad \text{and} \quad \Delta p = \frac{1}{v' - v''}\int_{X=0}^{X_\epsilon} X dx.$$

In the evaluation of the integral it is to be remembered that $x = \alpha X$, and then

$$\int X dx = \frac{\alpha}{2} X^2,$$

where α is equal to the change in length of the crystal prism produced by a tension or pressure of 1 kg. per 1 cm.^{2}, if the prism have a cross-section of 1 cm.^{2} and if its volume be equal to that of the specific volume of the crystal.

Determinations of α and X_ϵ at the temperature of the melting point are lacking for any substance whatever. However, it may be assumed in approximation that X_ϵ ordinarily lies between the limits 10 and 100 kg. per cm.^{2}, and X between the limits 0.0001 and 0.00001.

If $T = 300$, $r_p = 30$ cal., and R_p in consequence amounts to 1200 kg./cm., there result for ΔT values of $-0.00012°$ to $-0.12°$; whereas if $v' - v'' = 0.05$ cc. per one gram, values of 0.02 to 20 kg. per cm.^{2} are obtained for Δp.

The influence upon the equilibrium temperature and the equilibrium pressure of pressure and tension exerted on crystals in equilibrium with the liquid phase is therefore so slight that even upon raising the force to the elastic limit of the crystal, the effect produced rarely exceeds the errors in the experimental determinations of p and T for the equilibrium state. It is not permissible to apply the equation of GIBBS and RIECKE outside of the pressure limits O and X_ϵ, for it is applicable to reversible processes only.

b. Empirical Results

If a slowly increasing force be allowed to work upon a cube cut from a plastic crystalline conglomerate, such as copper, there will be seen upon microscopic investigation of the polished plane of the crystal parallel to the direction of pressure, fine, dark, parallel lines, in the individual crystallites. These gliding-lines are the traces of gliding-planes upon which the portion of each crystallite are displaced with respect to each other, and are so

oriented to the direction of pressure that they exert a minimum of resistance to permanent deformation. The pressure at which the gliding-lines appear corresponds to the elastic limit, which may be exactly determined in this way. The elastic limit obtained for the operation of a pressure agrees with that found upon the application of tension.[1] If the pressure be raised further, these gliding-lines appear in other crystallites, and with increasing pressure the angle of the gliding-line with the direction of pressure becomes sharper, and finally new sets of gliding-lines appear in the crystallites, intersecting the original set of parallel lines.

The explanation of the fact that the gliding-planes do not form in all crystallites at the same pressure (with copper the first gliding-lines appear at 203 kg./cm.^{2}, and the last at 2000 kg./cm.^{2}) lies in the fact that the force at which gliding takes place in a crystal depends in great degree upon the orientation of the crystallites with respect to the direction of the force.

Accordingly, all crystallites are finally divided by several systems of gliding-planes, and in this condition each crystallite can endure further deformations of a much greater magnitude. The piece, now divided into numberless small elements—as high as 1000 to 1,000,000 elements have been counted in a single crystallite—has obtained the ability to flow. With copper, the pressure at which flow begins, lies at about 2780 kg./cm.^{2}, and therefore exceeds the elastic limit thirtyfold.

A crystalline conglomerate is prepared for flowing by degrees in the manner described. The plasticity is due to the division of the crystallites by gliding-planes into very much smaller elements, the coherence of the crystallites being preserved during this process. In a brittle body deformation causes cracks and loss of coherence, but in a plastic crystalline conglomerate a displacement along gliding-planes occurs instead.

The greater the capacity of a crystallite to form gliding-planes, that is, the greater the number of gliding-planes formed in a unit of volume under a given force, the more plastic will be the substance concerned and, therefore, the more ductile, the more malleable, and the more easily rolled will it be.

Observation of plastic materials during deformation therefore teaches that it is not necessary to assume a transient melting in order to understand the process of plastic flow.

[1] *Z. phys. Chem.*, **75**, 108 (1910).

c. *The Behavior of Ice*

The fact that large quantities of substances ordinarily considered brittle can flow is illustrated by the behavior of glaciers. It has been shown even in the case of ice that displacement can occur easily in one direction along gliding-planes. O. MÜGGE [1] cut bars of quadratic cross-section (1 cm.^{2}) with the optical axis parallel to the length of the bar, and placed these upon two wooden supports. Around the unsupported section of the bar he wound a cord and attached to it a weight of 5 kg. Gradually a piece was

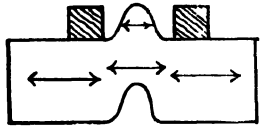


FIG. 99*a*.

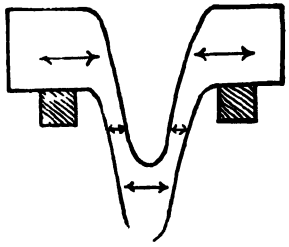


FIG. 99*b*.

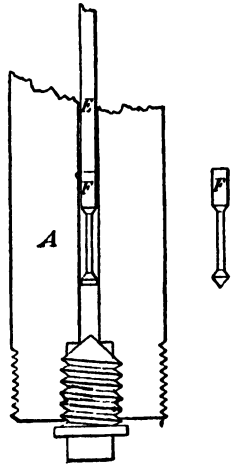


FIG. 100.

pressed out of the bar, corresponding to the thickness of the cord. Figure 99*a* represents the beginning, Fig. 99*b* a later stage of the process. No cracks occurred in the bar. The pieces pressed out were streaked with fine lines parallel to the base of the bar, and, as shown by the arrows, the optical axis had not changed.

In order to measure the velocity of flow of ice in dependence upon pressure and temperature, the apparatus in Fig. 100 was constructed for the production of a constant velocity of flow.[2] Water was introduced into the space under the pressure-pin *F*, and after it was frozen the pressure-pin was introduced. By

[1] *N. Jahrb. f. Min.*, 1895, II, page 211.
[2] *Ann. d. Phys.*, **7**, 198 (1902).

means of a lever apparatus a predetermined pressure was exerted upon the ice through the steel rod E and the pressure-pin F, causing the ice to flow in the form of a small tube through the annular space between the cylinder wall and the pressure-pin. The quantity of ice discharged in this manner was accurately determined by measurement of the drop of the loaded end of the lever by means of a screw which made electrical contact with the end of the lever. A unit graduation upon the circumference of the screw corresponded to 0.0858 cm.^{3} of ice. The cross-section of the steel cylinder amounted to 0.1988 cm.^{2}, and that of the front of the pressure pin to 0.1847 cm.^{2}; the cross-section of the annular opening was therefore 0.0141 cm.^{2}. The velocities of flow observed are given in the following table, represented by divisions upon the circumference of the screw per minute in dependence upon pressure and temperature:

p kg./cm.^{2}	−5.7°	−10 7°	−15 7°	−21.7°
100	0 9	0.03		
200	4 1	0 3		
300	11 8	2 0	0 1	
400	22 5	4.1	0 3	0 15
500	49 5	8.3	1.5	0.3
600	95.0	19	5.1	0 5
700	.....	34	12.6	2 5
800	.....	60	22 0	7.0
900	.....	101	.....	13 5
1000	.....	170	.....	20 5
1100	.....	.....	.....	30
1200	.....	.....	.....	53
1300	.....	.....	.....	65

The velocity of flow increases very quickly with both temperature and pressure. The melting of the ice at high pressures showed itself in the sudden drop of the piston when the critical pressure was reached. The critical temperature and pressures at which the drop took place are represented in the table on the following page.

It may be pointed out that the pressures obtained in this way correspond within the errors of measurement to the melting pressures obtained in the working out of the melting curve.

$t°$	Pressure at which the Plunging of the Lever Took Place in kg./cm.²	Highest Pressure at which a Constant Velocity was Measured	Melting-pressure,* in kg./cm.²	Δ
− 5 7	665	642	678	+13
−10.7	1130	1116	1225	+95
−15.7	1729	1611	1681	−14
−21.7	2100	2000	2170	+70
−27.6	2240	2220		

* *Ann. d. Phys.* **2**, 1 (1900).

If a second melting curve existed, which represented the melting of water under conditions such that it could flow away freely, then according to the formula of POYNTING, this melting should occur, under a pressure of 230 kg./cm.², at the temperature − 21.7°, and under a pressure of 118 kg./cm.² at − 10.7°. However, at these points upon the flow-velocity isotherm,[1] indicated in Fig. 101 by arrows, no sudden rise occurs; melting begins only when the melting curve is crossed.

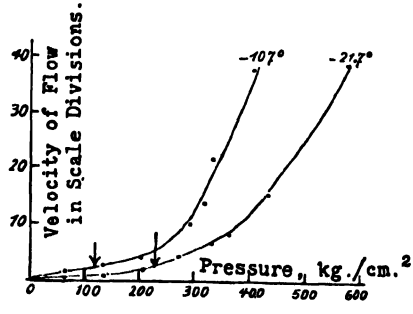


FIG. 101.

The question of the flow of glacial ice has been very carefully discussed by H. VON HELMHOLTZ.[2] It was presupposed that the temperature of the glacial ice of the Alps does not sink much below 0°. Under this condition a relatively small pressure increase favorably exerted upon a portion of the ice crystals would be sufficient to cause them to melt at the point of critical pressure, and the water formed, the temperature of which would be a little

[1] These flow-velocities were determined with the pressure pin pictured in Fig. 100 alongside of the chief figure; the cross-section of the annular opening was 0.0389 cm.², therefore almost three times as large as that used in the measurements of the table on page 203.

[2] *Populär Wissenschaftl. Vorträge*, 1865, pages 117, 129.

lower than 0°, would then deposit as ice in places of smaller pressure. From the measurement quoted it appears that ice can flow even in the phase field in which it is stable and at relatively low temperatures. A difference in the velocity of flow alone is to be expected in the cases of warm and of cold glaciers, when the gradient is the same in both instances.

For the explanation of the effect of unsymmetrical pressure upon rock, reference is continually made to the formula of POYNTING and to the inadmissible conceptions connected with it. In fact many valid objections to these conceptions have been met in noteworthy cases. As is known, carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$, decomposes upon melting into KCl and a liquid. If a partial melting of carnallite occur during deformation under unsymmetrical pressure, it should be possible to detect at least traces of KCl. F. RINNE [1] has pointed out that no such traces are to be found. H. E. Boeke [2] has shown that in other similar cases the products of melting do not appear during the action of unsymmetrical pressure.

2. RECRYSTALLIZATION

Cold work upon a piece of metal causes the formation of laminated fragments to take place within the metal. With sufficient temperature increase very small, new crystallites appear at the boundaries of the laminated fragments, and these new crystallites increase in size until finally the whole piece consists of well-developed grains. Corresponding to the structural changes there also occur changes in the physical and chemical properties of the metal. In metallography this process is termed *recrystallization.*[3] A somewhat similar process takes place in the union of the particles of amorphous bodies, and in the combination of liquid droplets to larger drops, but between the agglomeration or coalescence of isotropic particles and the union of anisotropic particles, a difference exists with respect both to the beginning of the process and to the structure of the end-product. At the beginning of the combination of anisotropic fragments there are formed, as has been shown with iron [4] and copper,[5] minute new grains at the

[1] V. Koenen, *Festschr.*, Stuttgart, 1907, 369.

[2] *Grandl. d. Phys.-Chem. Petrographie.* 1915, pages 26–30.

[3] *Tammann, Lehrbuch der Metallographie*, 3rd Edition, 1923, pages 98–118.

[4] Chappel, *Ferrum*, **13**, 6 (1915).

[5] Rassow and Velde, *Z. f. Metallkunde*, **12**, 309 (1920).

boundaries of the fragments, whereas in the combination of amorphous fragments the process consists merely in a combination of two or more grains into a larger grain. The end-product of recrystallization is a crystalline conglomerate, the crystallites of which are separated from each other either by voids or by layers of varying thickness made up of non-isomorphous admixtures, whereas the combination of isotropic surfaces of the same composition leads to a physically homogeneous mass.

The process of recrystallization plays a dominant rôle in many geological processes, such as the formation of glaciers, the production of marble from limestone, and the formation of crystalline schists. The process is of importance in the technology, not only of metallography, but also of ceramics. Unfortunately the workers in fields differing so much as these have little opportunity for the exchange of observations, and the valuable facts known to the one group have often remained unknown to the other.

With the subdivision of a crystal, a portion of the applied work is changed into heat and another portion enters into the products of division and increases their energy content. The products of division will therefore have a thermodynamic potential greater than that of the original undivided crystal, and accordingly, the products of division will tend to unite into a single crystal. It follows that any crystalline conglomerate tends to transform itself into a single crystal. As regards this, however, special cases will require special conditions for the occurrence of the process; the thermodynamic potential cannot furnish information as to the course of the process, but only with regard to the relative stabilities of the initial and final states. More detailed information as to the course of the process can be obtained only upon the basis of atomistics.

a. The Fundamental Conceptions

Two contiguous crystals of the same substance are in general not in equilibrium with each other if, at the plane of contact, the essentials of the lattice structure are not satisfied. If two crystals of the same chemically homogeneous substance be brought into contact in such a way that the crystallographically equivalent lattice planes in the two crystals are made continuous, the *two* crystals will form *one* crystal, since at the plane of contact the

same forces will act which act upon any one of the crystallographically similar planes within the crystal and which tend to hold the lattice together. If the contact take place in a different manner, that is, if the lattice planes of the two crystals intersect at the plane of contact, the field of force at the contact surface will be very different from that obtaining upon a lattice plane within the crystal. As long as the molecules vibrate about lattice points and do not leave them, a regrouping of the molecules on the plane of contact need not take place. Increasing temperature, however, will tend to release the molecules from their anchor positions and diffusion will begin. In this way a regrouping of the molecules will take place at the plane of contact, due to the different field of force obtaining there, and this will lead to the formation of a new lattice. A layer of molecules possessing mean orientation can then form at the crystal boundary, and the surfaces of this newly formed crystal with the original crystal will encroach upon older crystals; in other words, the densely filled lattice-plane absorbs the molecules from the less densely filled planes, and moves forward with considerable velocity into the crystal with the less densely filled planes. The determination of the orientation of the newly developed crystal in dependence upon the orientation of the two original crystals, and the determination of the velocity of growth of the new crystal, that is, the motion of the two new boundary planes in dependence upon the original orientation of each of the two crystals, is a problem in crystallography, and one of which the solution will be by no means easy. Connected with this would be the determination of the dependence of the linear crystallization velocity upon the temperature and the pressure.

At the present time little is known relating to these problems. It has been observed in metals that a slight deformation followed by recrystallization causes the displacement of crystal boundaries, whereas greater deformation leads to the formation of very small crystallites. As a result slight deformation induces the formation of grains larger than the original grains, whereas severe deformation brings about the formation of smaller grains.

Our fundamental postulate in the following consideration is this: in general two crystals touching one another in any manner will not be in equilibrium. As a result of this postulate, we must believe that at the boundary surface a third crystal must form, or that the one crystal must encroach upon the other. A limitation

to this conclusion is necessary in the case of twin-crystals where two crystals are in contact upon a definite plane, the twinning plane. Since during the growth of twin-crystals the twinning plane remains constant as the contact plane it must be concluded that crystals in contact upon a twinning-plane are actually in equilibrium. Again it is a problem for crystallography to determine the positions of these twinning-planes for crystals of different substances. Conditions during formation of crystals from liquids are not favorable for the formation of twins, since contact between the crystals rarely occurs. On the other hand, twinning occurs very often during the recrystallization of crystalline fragments where the amount of contact is often very slight. In this case a regrouping of differently oriented lattices takes place until the lattices either meet upon a definite twinning-plane or are separated from each other by material between the crystals.

The influence of the orientation of two contiguous crystals upon the nature of their combination has been closely investigated by A. HEIM.[2] From a clear, crystallographically uniform plate of sea ice a number of cubes were cut, which were then superimposed over one another in different orientations and loaded in each case with a weight of 1 kg. (Unfortunately the size of the cube-planes is not stated.) After having stood pressed lightly together in this manner for twenty-two hours at $0 - 4°$ they were placed between the faces of a press in such a manner that the distinguishable planes of union stood parallel to the direction of the pressure.

After a slow increase in pressure all cube pairs that had been placed crystallographically parallel regardless of the direction of the contact plane to the crystal axis, proved to have merged into one piece. Fissures which occurred frequently during the pressing never ran along the plane of union, but through it, even if the plane of union were met at a sharp angle. In the case of pairs the chief axes of which did not lie parallel, it first appeared that the behavior was similar, but upon increasing pressure the cubes soon broke apart and always along the original planes of union.

The fracture produced in pairs placed parallel was always conchoidal whereas the surface of fracture in the second case

[1] *Handbuch d. Gletscherkunde.* Stuttgart, 1885, page 230.

showed numerous complementary unevennesses indicating that new grains had formed at the plane of contact.

The results of this investigation are in accord with the fundamental principle of recrystallization. The complete union of the cube pairs with similar orientation is to be expected. The formation of grains upon the plane of union with dissimilar orientation is to be ascribed partly to unevennesses upon the surfaces in contact and partly to the division of the newly formed ice into small regions upon the contact surface by means of the salt solution present.

b. The Relation of the Work of Division to the Raising of the Vapor Pressure and the Lowering of the Melting Point

In order to explain recrystallization it is necessary to recall the fact that the vapor pressure of a liquid increases with diminishing radius of curvature, and that accordingly small drops have a greater vapor pressure than have larger ones. This has been simply carried over to apply to small and large crystals. It must be remembered, however, that crystals are different from liquid drops in that they are bounded by planes, provided the temperature range of formation be below that in which the form is determined by surface tension, and that therefore a complete analogy between the two as regards vapor pressure is not to be expected and no difference between the vapor pressures of small and of large crystals is necessarily entailed.

Any difference is evidently due to the work of division performed upon each of the large crystals during the process of subdivision. This work is equivalent to the increase of the energy content and hence of the thermodynamic potential during an isothermal process. It is necessary, if a relation between the work and the change in vapor pressure be sought, that the work of division be wholly definite; so that, for example, no relation can be stated for the work of division performed during the powdering of a crystal, since in such a process the amounts of work expended upon different crystals, and even upon different portions of the same crystal, are different.

A relation between the work of division and the vapor pressures p_0 of the undivided crystal, and p of the divided crystal, may be obtained by the following cyclic process. At the

temperature T_0 the crystal is divided and during the process of division the work A is furnished each mole of the substance. The product of the division is then vaporized and the pressure of the vapor diminished from p to p_0, resulting in a gain in work $RT_0 \ln \frac{p}{p_0}$. Finally the vapor is condensed to an undivided crystal. Since the sum of the work terms in this isothermal cyclic process is zero, therefore

$$A = RT_0 \ln \frac{p}{p_0} \quad \text{or} \quad \frac{A}{RT_0} = \frac{p - p_0}{p_0} \quad . \quad . \quad . \quad . \quad (1)$$

For the relation of the work of division to the lowering of the melting point, $T_0 - T$, caused by the diminution in the size of the crystals, we have [1]

$$A = (T_0 - T)\frac{R_p}{T_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where R_p represents the molar heat of fusion.

This equation is applicable only to cases where the melt is not itself finely divided. In this latter case an additional term, A', representing the work of division of the melt, must be taken into consideration. Equation (2) then becomes

$$A - A' = (T_0 - T)\frac{R_p}{T_0}. \quad . \quad . \quad . \quad . \quad . \quad (2')$$

The lowering of the normal melting point, T_0, as a consequence of a definite degree of division of a crystal has been determined by F. MEISSNER, [2] using a method devised by the author.

The method is the following. The melt of the substance to be measured is placed between a cylindrical lens and a metal plate and is there caused to crystallize. After the melt has completely crystallized a temperature gradient is produced in such a way that the isotherms perpendicularly intersect the line of minimal thickness of the layer of crystalline filaments. In the stationary state the limit between the liquid and the crystalline layers is not a straight line, as are the isotherms, but shows a convexity towards lower temperatures, because the thin crystal layers

[1] *Z. anorg. Chem.*, **110**, 167 (1920).
[2] *Z. anorg. Chem.*, **110**, 169 (1920).

have a lower melting point than have the thicker ones. Since the thickness of the layer and the temperature at the boundary between liquid and crystal may be determined it is possible to obtain a relation between the thickness and the lowering of the melting point, and from this to calculate the work of division. The lowering of the vapor pressure may also be determined from equations (1) and (2′). The relation is

$$\frac{p - p_0}{p_0} = \frac{T_0 - T}{T_0} \frac{R_p}{RT_0} \frac{A}{A - A'}.$$

With the kind of division obtained in this process, azobenzene, the substance among those investigated which showed the greatest effect of division upon the melting point, gave a melting point lowering of 0.355° in a layer 0.8μ thick. That is, $\frac{T_0 - T}{T_0} = \frac{0.355}{342} = 0.001$, from which it follows that $\frac{p - p_0}{p_0} = 0.0078 \frac{A}{A - A'}$.

If, for example, $A = 2A'$, then $\frac{p - p_0}{p_0} = 0.016$.

It is to be emphasized that these values hold only when the division is of the type just described. It seems probable that if division of the crystal could be brought about by cleaving or by rolling, the depression of the melting point would be much greater, and accordingly the work of division would be greater.

c. The Influence of Division upon Solubility

The cyclic process used for the derivation of the relation between the work of division and the resulting elevation of the vapor pressure can likewise be used for the derivation of the relation between the work of division and the resulting increase in solubility, and in this way there is obtained the equation

$$A = RT_0 \frac{l - l_0}{l} \quad \ldots\ldots\ldots \quad (3)$$

where l_0 represents the solubility of the undivided crystal and l the solubility of the divided.

If formulas (1) and (3) be compared, we find that with equal

work of division the relative vapor pressure lowering is equal to the relative solubility increase:

$$\frac{p - p_0}{p_0} = \frac{l - l_0}{l_0}. \quad \ldots\ldots (4)$$

Experimental determinations of the increase in solubility due to decrease in grain-size have been made by W. OSTWALD [1] and by HULETT.[2] A solution made by agitating finely divided gypsum in water was found by HULETT for a mean grain-size of 0.2μ to give a value for conductivity of 0.00252. In time the grain-size increased to 2.0μ and the conductivity decreased to 0.00221. The relative solubility increase amounted to 0.19. Still greater values were found for $BaSO_4$, namely 0.49, and mercuric oxide, 2.0. All of these values are much greater than the value calculated for azobenzene from the depression of the melting point in consequence of diminution of grain-size to 0.8μ, namely, $\frac{p - p_0}{p_0} = 0.048$. Even though the grain-size and the work of division in HULETT'S experiments be very different, it is still remarkable that the values found by HULETT should be 4 to 40 times as great as those found for azobenzene.

The explanation of this discrepency may lie in the fact that the work of division is largely dependent upon the nature of the division. In the case of azobenzene the division consisted in the production of very flat crystalline layers during crystallization, no further treatment being given the crystalline layers after their formation. In comparison to this, powdering in a mortar is probably the most severe kind of cold work to which a body can be subjected. Cold work on metals brings about changes not only in physical properties, but also in chemical properties. This change in chemical properties is especially noticeable in the case of metallic solid solutions, the compositions of which lie close to the reaction limit of the reagent employed.[3]

In order to determine the influence of the work of division without the disturbing effect of cold work it would be necessary to determine the solubility of the unimpaired crystallites pro-

[1] *Z. phys. Chem.*, **34**, 495 (1910).
[2] *Z. phys. Chem.*, **37**, 385 (1901), and **47**, 350 (1903).
[3] *Mischkristallreihen und ihre Atomverteilung.* Leipzig, 1919, pages 171–181.

duced from a supersaturated solution and to compare it with the solubility of the larger unimpaired crystals.

The disturbing influence of cold work upon the solubility of small crystals might be successfully determined by heating the cold-worked powder to a temperature sufficient to reinstate the normal properties of the crystalline substance. If no grain-size increase be introduced as a result of the cohering of the particles, the difference between the solubility of the unheated and that of the heated crystalline powder would give the change in solubility resulting from the cold work.

It should be quite possible, therefore, to separate the influence of cold work upon solubility from that of grain-size.

A simple method for the demonstration of the different behavior of fresh and aged cleavage planes has been given by PETER RIESS.[1] Water vapor was blown upon fresh cleavage planes of mica, gypsum, and calcite, where it condensed in a continuous layer. On aged cleavage planes, however, the water formed small droplets. This difference in behavior was possibly due to the presence of countless molecular fragments upon the aged cleavage planes which attracted water and in time increased to larger particles. The second possibility is apparently supported by the following observations: A small drop of water ages a fresh cleavage surface of mica immediately and the first washing with water removes more substance from the cleavage plane than do following washings, which under similar conditions dissolve equal quantities of substance. Two to three layers of mica molecules are rendered supersoluble by cleavage.[2]

d. The Increase in Size of Ultramicroscopic Particles of Ag and Au under Water

Such an increase has been often observed.[3] There is a temptation to ascribe the increase simply to the greater solubility of the particles of smaller size. To maintain such a contention, however, it would be necessary to show that the diffusion streams caused by the difference in solubilities of the very slightly soluble particles of Ag or Au in water are sufficient to effect the increase in

[1] *Pogg. Ann.*, **67**, 354 (1846).
[2] *Z. anorg. Chem.*, **130**, 200 (1923).
[3] R. Zsigmondy, *Kolloidchemie*, 1912, page 131.

size observed. This requirement, however, cannot be fulfilled, and it is probable that the chief cause for the observed increase is not the difference in solubility, though it may be of considerable importance.

The increase in size in silver and gold suspensions of ultramicroscopic particles of Ag and Au, respectively, the lattices of which according to SCHERRER are identical with those of compact Ag and Au, is well known. In these Ag- and Au-mother liquors, containing no genuinely dissolved Ag or Au, the growth of ultramicroscopic particles to microscopic dendrites, especially in the case of Ag, is often observed, whereas in compact Ag at the same temperature, 20°, during the same time no indications of crystal-growth can be obtained. The beginning of grain-size increase in this case is most easily recognized by a decrease in electrical resistance. This difference in behavior between suspended ultramicroscopic particles of silver and compact silver is probably due chiefly to the lively molecular motion of the suspended Ag particles. Whereas the particles in hardened Ag-wire are so arranged that points of contact are unfavorable for union, the high mobility of the Ag particles in water favor union in an extraordinarily high degree, such a union taking place when two particles meet so that equivalent lattice planes coincide. An additional favorable circumstance consists in the possibility of rotation, which upon collision would permit adjustment to correct orientation of the colliding particles. The forces of cohesion of the lattice, which are free at the surface of the particles, also assist the union of the latter.

The fact that the mobility of crystallites is a favorable condition for recrystallization is demonstrated by the following experiment. Dried Ag powder is warmed and stirred at a constant rate by means of a rotating stirrer. With this treatment agglomeration of the powder takes place at 104–106°, causing the stirrer to be raised out of the mass.[1]

e. The Maturing Process in Silver Bromide Emulsions

The silver bromide used in photographic plates is made by precipitating silver nitrate with potassium bromide. The suspension of AgBr obtained, mixed with gelatine, is warmed, and

[1] *Z. anorg. Chem.*, **126**, 119 (1923).

after the grain-size of the AgBr has increased, more gelatine is added. The precipitated particles of AgBr are in all probability anisotropic. In the case of freshly precipitated AgI it has been shown that the transformation point lies at 141° when $p = 1$ kg./cm.^{2}, the point characteristic for crystal formed from the melt. The pT-curves for the two preparations are identical.[1] EDER [2] reported a grain size increase from 0.0008 to 0.003 mm. during a five-day maturing. These observations have been confirmed by K. SCHAUM.[3] The lively motion of the AgBr crystallites assists the union of favorably colliding particles, resulting in a branched, incompact structure.

f. Recrystallization of Carbon Compounds

Recrystallization in metallic bodies takes place at temperatures below the temperatures of noticeable vapor pressure. In the case of Cu, the beginning of definite recrystallization lies at 200°; with Ag and Au the temperature is somewhat lower, namely, 150°. The beginning of noticeable distillation in high vacuum in the case of Cu lies at 1315°, according to F. KRAFFT, in the case of Ag, at 1200°, and in that of Au, at 1375°. Thus the migration of the atoms of Cu, Au, and Ag in their lattices is quite lively 1000° below the temperatures of noticeable vapor pressure. On the other hand, in the cases of non-metallic substances, especially those the molecules of which possess a complex structure, the difference is very much less and investigation of a series of carbon compounds shows that rapid recrystallization takes place only at temperatures where very considerable sublimation occurs.

Inspection of a collection of organic substances after a storage of ten years at widely varying temperatures disclosed the fact that one portion had acquired a form of disconnected, or loosely connected, crystals, whereas the crystals of the other (smaller) portion had become so firmly united that a heavy blow was required to separate them, though no cementing mother-liquid could be recognized between them.

This of course, does not prove that mere contact between crystals had effected recrystallization, for the existence of small

[1] *Z. phys. Chem.*, **75**, 740 (1911).
[2] Eder's *Handbuch*, **3**, 56 and 101 (1902).
[3] *Physik. Z.*, **4**, 4 and 40 (1902).

quantities of mother liquor doubtless occurs in all preparations except the most carefully purified, and temperature fluctuations upon such thin layers of mother liquor might produce crystalline bridges between the separate crystals, favoring a union of the crystals.

Preparations, the crystals of which stick together, ordinarily show rapid recrystallization in the neighborhood of the melting point, if not at room temperature. This may be demonstrated in the following way. The crystals reduced to small pieces are warmed in a glass tube and stirred at a constant rate. During the stirring the temperature is observed at which the particles of the powder begin to stick together. The formation of new grains in a crystalline aggregate may actually be seen by pressing a crystal into the thinnest possible layer and observing it during the heating by means of a microscope. This method is somewhat limited by the impossibility of satisfactorily pressing crystalline layers that are thinner than 0.5 mm., and by the fact that the image obtained from thicker layers is never sharp, whence it is impossible to recognize finer details, such as the formation of very small crystallites around the borders of the larger fragments (as in the cases of copper and ice).

Among the substances that readily form new grains at room temperatures are the following: pinene hydrochloride, camphor, phenol, and dichlorbenzene. In the case of benzoic acid rapid formation of new grains first takes place at 90°. When the substance recrystallizing at room temperature is observed by transmitted light in the form of a pressed-out layer, no uniform structure can be seen at first, but after a few moments a polyhedric structure begins to appear upon the surface of the piece. These polyhedral grains have a mean diameter of 0.005 to 0.03 mm. At higher temperatures the small grains grow rapidly, especially in phenol (m. p. 43°) and *p*-dichlorbenzene (m. p. 52.7°), forming comparatively very large grains of about 0.1 mm. diameter. The phenomena are extraordinarily manifold, and the observation of them must be a pleasing task for the microscopist. No detailed description of the process will be given here, though especial reference must be made to one important point, namely, that it is not possible to state which of two crystals, one large and one small, will increase in size at the expense of the other. For example, a small crystallite has been observed to remain unchanged

between three larger ones while the boundary between two of these larger crystals disappeared.

g. Crystalline Grains in Glaciers

The weight of the many layers of snow deposited upon glaciers causes the snow crystals to form a grain-like glacier ice. In time this coarsely crystalline aggregate becomes clear, and in the course of years the size and character of the grains alter considerably. Accordingly, the undermost ice at the end of the glacier is made up of grains quite different from the grains formed first. Besides the grains of the size of a pine-head or a hazel-nut present in old glacier ice, there are frequently found gigantic grains 10 cm. in diameter. The grain-like structure of artificial ice or of the clear glacial ice formed first upon the compression of the snow crystals is quite easily seen, especially when the grains in the ice are displaced relatively to one another by compression. In the new glacier ice the grains are generally irregularly oriented with respect to one another. In time, however, in addition to the growth of the grains, a re-orientation takes place so that in large masses of ice all of the grains have parallel optical axes. Investigation of this at different points upon Alpine glaciers has given different results with respect to the spreading of the sphere of similar grain-orientation. (A. Heim, *Study of Glaciers.*) E. v. Drygalski[1] observed in old inland ice and in the deeper layers of icebergs of the antarctic the presence of grains varying in size from that of a pinhead to that of a hazel nut, which were optically similarly oriented.

It follows from this that after their formation, the glacier grains, surrounded by a very thin layer of salt solution, came into contact in consequence of a deformation exceeding the elastic limit, and that upon this contact the grains re-oriented themselves to give an optically uniform crystal, though the original surface of separation remained visible; the newly formed grain accordingly appears to be a double grain, the actual connection between the grains occurring at only one or at only a few points. In this way older glacier ice may be optically single-grained over wide areas, though the surfaces of separation of the individual grains appearing in the original younger ice may be evident here also.

[1] *Deutsche Südpolarexpedition*, 1901–1903, 1 (1920).

The conditions obtaining in glaciers for the growth of the fine crystal of ice to the gigantic grain of the old glacier are manifestly very favorable. The substance between the grains must be a liquid solution of different salts. The motion of the glacier causes the deformation of the grains leading to actual contact between them, and effecting another division of the easily mobile substance between the grains. From this point of view, a glacier is comparable to a mass of metal that recrystallizes at its working-temperature, in which grain-growth is brought about in the same way. A difference between the two cases exists only with respect to the substance between the grains; in ice this substance is liquid, whereas in metals it doubtless must be solid since recrystallization takes place far below the temperature of melting.

h. The Crystalline Schists

Structurally, the crystalline schists stand between the plutonic rocks, formed from melts, and the neptunic sedimentary rocks. With respect to the history of the crystalline schists there has been a great deal of dispute.

These schists could not have originated directly from a fluid magma because of their characteristic exfoliation; it is possible that they have been produced from plutonic as well as sedimentary rocks. Fracture and displacement in plutonic rocks, processes analogous to cold-working in metallic bodies, could have produced exfoliation, and together with subsequent recrystallization, could have produced a grain similar to that obtaining in plutonic rock, thus preserving the characteristic property of exfoliation more or less distinctly. An increase in temperature of the mass due to a covering by sediment would have accelerated recrystallization tremendously. Of course the processes are complicated in comparison to cold-work and recrystallization occurring in the sedimentary rocks. Only seldom have we to deal with recrystallization in chemically homogeneous masses, as, for example, the formation of marble from finely grained limestone.[1]

The important factors in the explanation of the formation of crystalline schists seem to be the lowering of the melting point and the raising of the solubility in consequence of unequal pressure stresses, and also the raising of the solubility in consequence of

[1] F. Rinne and H. E. Boecke. *Tschermaks Mitt.*, **27**, 345 (1908).

diminution in grain size.[1] However, the effect of these two factors is probably very small in comparison to that of recrystallization.

Pressure is of significance with respect to recrystallization in so far as it effects the contact of the crystalline fragments or of the fine grains. The conditions for recrystallization and for chemical change between crystals of different composition are the same, namely, the temperature must be raised sufficiently to permit the exchange of individual molecules within the lattice upon which they vibrate or, more concisely, the temperature must be raised sufficiently to permit internal diffusion.

The formation of crystalline schists from plutonic rocks is essentially analogous to the processes occurring in a crystalline conglomerate produced at the melting point and containing several metals capable of forming chemical compounds, which is first cold-rolled and then caused to recrystallize by an increase in temperature.

The formation of crystalline rock from sedimentary rock is comparable to the processes occurring in a block formed by compressing the mixed powders of several metals, when this, either in its original state, or after further cold-working, is warmed to a temperature not sufficient to form the final product which would be obtained from the melt of the metals concerned. In both cases, that of the mixture of metal powders and that of the crystalline schists, the many components make possible numerous complicated chemical changes and in addition render more involved the processes of recrystallization. Obviously the practical geologist may benefit greatly from the experience of the metallographer.

[1] N. Grubenmann, *Die Kristallinen Schiefer.*, Berlin, 1904, I, pages 42 et seq.

IX. THE TRANSITION OF AN UNSTABLE INTO A STABLE STATE OF AGGREGATION

If a substance be taken from a phase field in which it is completely stable into a field where the original phase loses its stability, the possibility of transformation will exist. This transformation does not occur throughout the whole mass at the same moment, but always proceeds only from a few nuclei. The fact that transition occurs in this way is in support of atomistics. The number of these nuclei, in comparison to the total number of molecules present, is extremely small; and it may therefore be concluded that a series of conditions must be fulfilled in order that spontaneous transformation may take place. The smaller the number of these conditions, the greater will be the number of transition nuclei formed.

Spontaneous transformation is subject to the laws of probability, whereas non-spontaneous transformation in uniform substances is governed by the flow of heat and by a linear velocity dependent upon the temperature.

Condensation will take place immediately upon a liquid droplet introduced into a supersaturated vapor, just as crystallization will occur on the introduction of crystals into an undercooled melt. An undercooled crystal-form or a crystal-form that is not stable, is likewise forced into transition by contact with the more stable form. Transition can be thus brought about in phases that have become unstable by the introduction of very small particles of the stable phase, whereas without such treatment, transition would occur only after a considerable and indefinite length of time. This process is known as inoculation.

The more stable phase in some way influences the less stable at the surface of contact, known as the interface. In the absence of this more stable phase no such effect is brought about and spontaneous transformation into the stable form is an event of uncertain occurrence.

The decisive factor in the spontaneous transformation of a less stable into a more stable state is the number of transition nuclei

which form in the unit of mass during the unit of time, whereas in the case of non-spontaneous transformation, the linear crystallization velocity plays the most important rôle.

With the formation of transition centers of an isotropic in another isotropic phase, the transition velocity is scalar; such a transition is the condensing of a vapor into small drops. If one of the phases be anisotropic, then the linear transformation velocity will be vector; this fact is clearly shown in the crystallization of an undercooled liquid or in the transformation of an unstable crystal-form into one more stable.

With the formation of an isotropic phase in another isotropic, such as with the separating of liquid drops from vapors, the number of transition centers is disproportionately large compared to the transformation of an isotropic state into an anisotropic, or with that of an anisotropic into another anisotropic. Evidently in the first case there are fewer conditions for the formation of a transition center to be fulfilled than in the second case, and therefore the formation of a transition center in the second case must take place considerably less often than in the first.

1. The Condensation of Vapors

The number of condensation centers in vapor depends upon the removal of the point of state of the vapor from the vapor pressure curve. Since this number increases very quickly from infinitesimal values, with the distance from the vapor pressure curve, no counting has ever been made—approximations alone have been attempted. Observers have given attention especially to the influence of dust [1] upon condensation, and also to the influence of gaseous ions produced by α-particles or X-rays. It has been established, in the case of water vapor where slight undercooling was produced by adiabatic expansion, that the number of condensation centers is extremely small in absence of dust or of ions. With greater expansion, corresponding to a fourfold supersaturation, the number of condensation centers becomes very great (cloud-like condensation).[2]

If a vapor dispersed in air be cooled by adiabatic expansion to a temperature below the triple point, either liquid drops or crystals —rain or snow—can form.

[1] Aitken, *Nature*, **23**, 195 (1880).

[2] R. v. Helmholz, *Wied. Ann.*, **27**, 508 (1886) and **32**, 1 (1887).

The question of whether droplets or crystallites are formed can be decided by an experiment in which condensation of the vapor is caused to take place above an undercooled melt of the substance. If the formation of snow occur the liquid will be inoculated and will crystallize; if rain be formed, the undercooled liquid will not be inoculated.

Benzophenone vapor (m. p. 45°) causes no inoculation in undercooled benzophenone between 40° and 0°, and the same is true of nitrophenol (m. p. 45°). Since it is difficult permanently to undercool large quantities of water, lower than − 4°, the experiment with water can be carried out only to this temperature. Water vapor condensed between 0° and − 4° does not cause inoculation in undercooled water and, therefore, not snow but rain is formed.

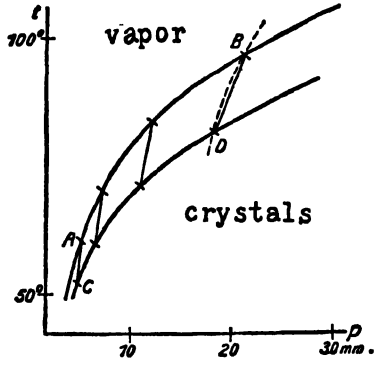


FIG. 102.

Not all liquids permit undercooling for a length of time sufficient for the performance of the described test and it is often necessary to apply other methods less sensitive in the diagnosis of the condensation product. F. BECKER [1] was unable to observe in the condensing vapors of camphor (m. p. 178°), borneol (204°), and isoborneol (214°), with good illumination, refraction rings such as are caused by liquid droplets, but saw only the glittering of crystallites. The results of the observations on camphor are made clear in Fig. 102. *AB* is the vapor pressure curve, the dotted curve *BD* represents the adiabatic followed by the mixture of air and camphor-vapor during expansion. At the point *D* the glittering of the camphor crystals occurred. If a curve be laid through the points corresponding to *D* the curve of incipient condensation for adiabatic changes of state of the air-vapor mixture is obtained. The denser the vapor, the lower must the air-vapor mixture be cooled in order to introduce the formation of crystals. If rain be formed instead of snow, the undercooling decreases with increasing density of the vapor, and therefore the vapor pressure

[1] *Z. phys. Chem.*, **78**, 39 (1912).

curve and the curve of beginning condensation converge with rising temperature. Liquid drops are formed from the vapor of nitrophenol, camphene, menthol and water.

The condensation of vapors in crystalline form upon a glass wall takes place at the same temperature (with the same degree of undercooling) as it occurs from the air-vapor mixture, upon adiabatic pressure diminution.

	In Air-vapor Mixture	Pure Vapor
Isoborneol.....	85 0°	85 1°
Camphor.....	82 2°	82 3°
Borneol.....	77.4°	77 3°

The phenomena occurring with iodine vapor in a mixture with air are represented by Fig. 103.

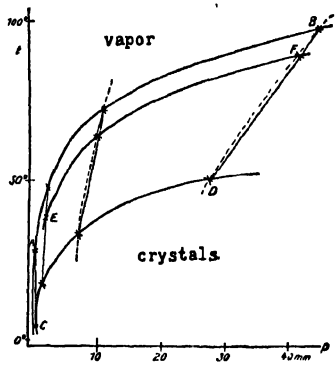


FIG. 103.

AB is the vapor pressure curve of iodine; when the undercooling reaches a point on the curve *EF* the vapor becomes almost colorless. Whether the condensation product formed in this way consists of drops or of crystals remains undecided. The curve *CD* gives the points of state in which visible crystallites appear. If the vapor pressure be very small, a condensation as a result of adiabatic dilatation cannot be observed.

a. The Formation of Glass from Vapor.[1]

A condenser was placed in a vessel which could be evacuated to 15 mm. and through the condenser was run a stream of water, the temperature of which could be varied at will between 0° and 100°. In this vessel the substance to be investigated was placed. At the end of the condenser a glass or mica plate was fixed with screw clamps in such a way that it could easily be replaced. In order to avoid any spraying of the liquid on the condensation plate a protection plate was inserted between the condensation

[1] Starinkewitsch and Tammann, *Z. phys. Chem.*, **85**, 573 (1913).

plate and the substance investigated. In this way the substance could be easily brought to a given temperature, chosen first above the melting point, and second below it. Furthermore, the temperature of the condensation plate could be easily changed by regulating the temperature of the water.

By the use of a glass plate it was found with betol (m. p. 95°), that at condensation temperatures between 70° and 10°, 1 to 60 drops had crystallized in the 2000 to 3000 drops present, after a period of 8 minutes. Since the most careful cleaning of the glass plate could not assure the absence of particles of betol upon its surface, the glass plate was replaced by a freshly cleaved mica plate.

Upon this plate the formation of a crystal nucleus was never observed after condensation upon the plate had proceeded for 8 minutes. With decreasing temperature of the condensation plate, the number of drops decreased very considerably, but the size of the drops increased.

Temperature of the Condensation Plate	Number of Drops upon 0 1 mm.^{2}
20°	2–3
32°	2
42°	50
54°	250
63°	160

The first crystallization in the drops upon the plate occurred only after a lapse of 15 minutes; ordinarily more time than this was required and in one case no drops had crystallized after the passing of seven days.

Betol vapor, therefore, condenses upon a freshly cleaved mica plate only in the form of drops, and in fact this is true of betol throughout the temperature range 0°–90°, regardless of whether the vapor forms from the crystallized or the liquid substance. After some time crystallization begins in a very few drops. From the crystallized drops hair-like filaments grow over the plate inoculating the liquid droplets that they touch. In Fig. 104, in the upper part of the preparation, may be seen liquid droplets exclusively. In the middle part it may be seen that the greater part of the drops has crystallized and that these drops have sent out fine filaments. From this evidence it is to be concluded that upon the mica plate there is, besides the drops themselves, a very

thin layer of liquid betol which is drawn to the filaments by capillarity. In the under part of the preparation crystallization completed itself in another way. The small drops which were here originally have changed into a network of fine filaments so that the original form of the droplets is no longer to be recognized.

Papaverine (m. p. 147°, temperature of softening 47°) after heating to 150° will condense at a temperature of 17° upon the mica plate in a glassy layer in the course of 15 minutes.

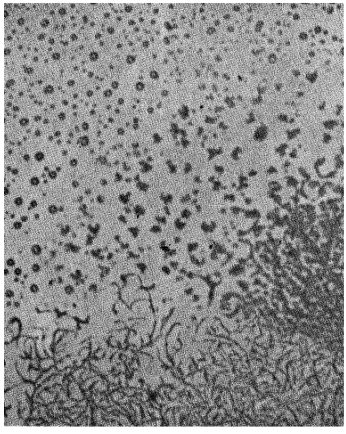


FIG. 104.—Betol. (× 68)

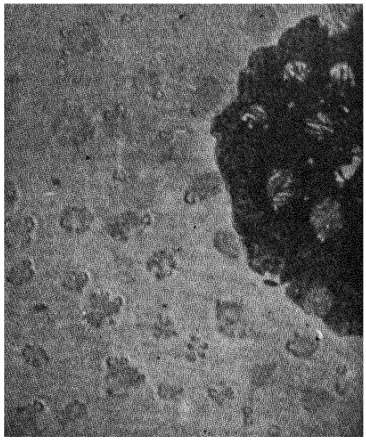


FIG. 105.—Papaverine. (× 68.)

The bright part of Fig. 105 is the glassy layer and in it may be seen a number of irregular gaps. Two hours after the preparation of the film a crystallization center formed from which crystallization proceeded with approximately the same velocity in all directions upon the glass film. The gaps in this part of the preparation occur in the crystallized part as bright patches upon a dark background, while in the glassy part, in comparison, they stand out as dark patches upon a bright background. The amorphous particles in the gaps of the film of glass have transformed themselves, in the crystallized part, into thin filaments. That there is concerned in this case no transformation from an unstable into a stable form is shown by the following experiment. When the mica plate is introduced into undercooled papaverine at 100°, only the dark portion of Fig. 105 grows into the undercooled

to visible structures that may easily be counted. These structures, grains, are often spherulites, consisting of numerous needles radiating from a point. The points of these needles lie on the spherical surface of the spherulite. Substances differ in the forming of grains in that the number of needles constituting a single spherulite differs. In addition to the spherulites there are formed single small crystals which grow as such. A substance sometimes forms different kinds of spherulites distinguishable by their different transparency, and since there is also a difference in the melting points, it is evident that they are different crystalline forms of the substance concerned.

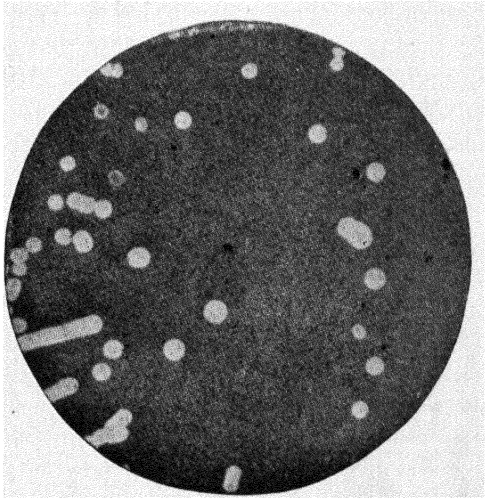


FIG. 106.

Figure 106 is a photograph of a layer of fused betol in the state of spontaneous crystallization. A drop of betol was placed upon a warmed glass slide and covered with a warmed cover-glass. It was then cooled to room temperature and warmed above a lamp for a few minutes, when, owing to the increased crystallization velocity, flat-pressed grains—disks of radially oriented crystal prisms—developed. (Fig. 106.) Two kinds of grains may be distinguished in the photograph: the dark patches corresponding to the white grains, m. p. 91°, and the brighter patches corresponding to the satin-like grains, m. p. 93°. Within the grains may be seen concentric circles, due, no doubt, to temperature

variations during the formation of the grains. The elongated grains in the lower right of the photograph were formed by the merging of crystal grains that grew from nuclei formed close to one another in a straight line. A great many interesting and beautiful structures may be seen in observing the crystallization of undercooled melts.

The results for the counting of the grains in piperine (m. p. 129°) are plotted in Fig. 107. The piperine was fused at 135° in closed thin-walled glass tubes, exposed for ten minutes to the temperatures given in the figure, and the number of grains counted after the crystallization centers had been developed by heating to 100° for 4 minutes. It may be seen that the nuclei number possesses a sharply defined maximum; the tendency towards spontaneous crystallization is therefore greatest at + 40°, and sinks to insignificant values at 80° and 0°. The temperature of the maximum is independent of the quantity of substance investigated and does not change if instead of cooling to the temperature of exposure from 135°, the substance be warmed to this temperature from 0°, with subsequent development of grains at 100°, although the number of grains itself per unit of weight increases about tenfold.

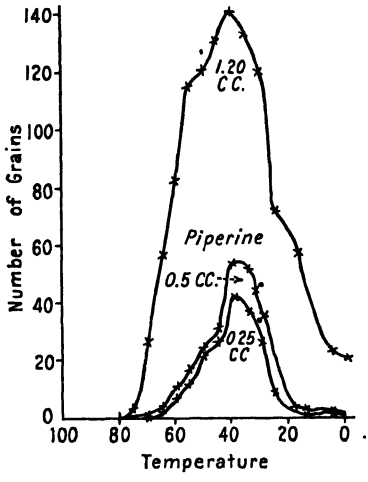


FIG. 107.

With betol, two varieties of grains, corresponding to the two crystal modifications, ordinarily formed during the treatment which consisted of fusion at 110°, two-minute exposure, and development at 70°. These two varieties were then counted; but we shall trace here only the milk-white grains which melt at 91°. Thus we again note in Fig. 108 the pronounced maximum. Measurements were made on a sample purified from the commercial preparation by one recrystallization and the results are given by curve *4*. After two further recrystallizations the nuclei number increased significantly and the maximum was displaced

to a somewhat higher temperature (curve *1*). With the addition of 0.2–0.5 per cent salicin, or of 5 per cent cane sugar, the formation of grains was prevented during the usual two minutes, and, in fact, for a period of five minutes. An addition of 10 per cent naphthalene lowered the maximal temperature slightly, but affected the nuclei number itself very little (curve *2*); 0.1 per cent perchlorethane depressed the nuclei number slightly (curve *8*); whereas 0.1 per cent anisic acid (curve *6*) increased the nuclei

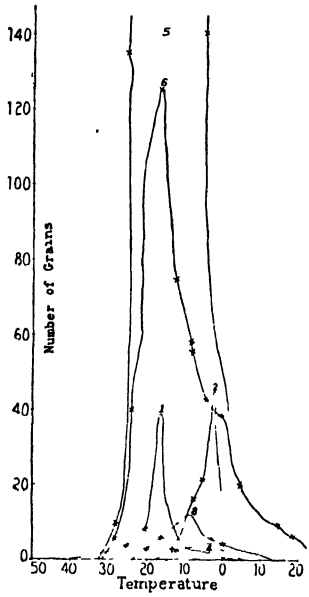


FIG. 108.

1. Betol recrystallized three times
4 Betol recrystallized once
6. Betol + 0 1 per cent anisic acid.
2 Betol + 0 5 per cent naphthalene.
5 Betol + 5 per cent benzamide.
8 Betol + 0 1 per cent perchlorethane.

number very greatly, and an addition of 5 per cent benzamide had a still greater action. Foreign substances, therefore, have an effect upon the tendency towards spontaneous crystallization in betol which varies considerably with the nature of the substance, although the temperature of the maximum itself is very little affected.

The nuclei number is also influenced by insoluble powders, although microscopic examination has shown that these solid

particles occupy positions wholly at random with respect to the grain formed. This behavior is illustrated in Fig. 109; although an addition of glass powder depresses the nuclei number to zero, emery powder, and transparent quartz powder increase it very greatly (curves *2* and *3*). Fused feldspar increases the nuclei number whereas crystallized feldspar decreases it somewhat (curves *4* and *5*). Although such insoluble powders exert a con-

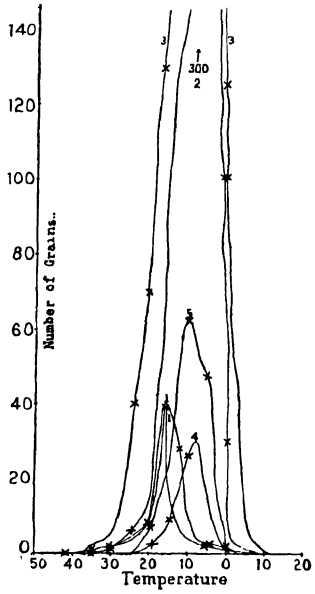


FIG. 109.

1 and 1 Betol recrystallized twice
2 Betol +0 5 per cent emery.
3 Betol +0 5 per cent transparent quartz
4. Betol +0.5 per cent feldspar.
5. Betol +0 5 per cent feldspar (fused).

siderable influence upon the nuclei number, the maximum of the nuclei number itself remains at almost the same temperature.

Carefully cleaned, annealed metal wires ordinarily increase the nuclei number, although even here the grains only rarely form upon the metal.[1]

Investigation upon the tendency towards spontaneous crystallization has shown that this property at first increases with increasing removal from the melting point, but begins to decrease

[1] *Z. anorg. Chem.*, **91**, 241 (1915).

after the passing of a certain temperature which is characteristic of each substance, and which is changed slightly by the presence of foreign bodies. Therefore, if a substance be cooled rapidly, so that its temperature passes as quickly as possible this critical temperature, at which the greatest number of crystal ization centers form in the unit of time, it should then be possible to obtain the substance in the form of a glass, since the inner friction grows rapidly with decreasing temperature. It must therefore be *possible to obtain all substances in the form of glass*, whereas it was formerly assumed that only mixtures could be obtained in this condition.

In order to throw more light upon this question a statistical investigation of 153 carbon compounds was undertaken.[1] Each of these compounds was enclosed in a thin-walled glass tube, fused, and exposed to different temperatures beneath its melting point. The results are as follows:

Of 153 Substances

22 or 14 per cent permit undercooling up to 10° for a few seconds.
54 or 35 per cent permit undercooling of about 10–20° for a few seconds.
19 or 13 per cent permit undercooling of about 20 for more than a minute.
59 or 38 per cent can be obtained in the glassy state.

It appears, therefore, that substances belong to wholly different groups with respect to undercooling. In every case the process of cooling could be considerably improved, that is, the substance could be cooled more rapidly than actually was the case in these experiments. Since with comparatively slow cooling more than a third of the substances investigated were transformed into the amorphous state, it seems possible that with more rapid cooling the majority of these substances could be obtained as glasses. Single groups of substances, such as the acid silicates, can easily be obtained in the glassy state. The hydrocarbons, and their halogen- and nitro-derivatives permit only slight undercooling, as is also the case with the mono- and dicarboxylic acids. The tendency to undercool increases directly with the number of hydroxyl-groups. The meta substitution

[1] *Z. phys. Chem.*, **25**, 472–478 (1898).

products of benzene permit greater undercooling than do the ortho, and the latter greater than the para.

These facts are of importance to the organic chemist. It often happens that after the removal of the solute by distillation the reaction product remains behind as a viscous mass, the crystallization of which does not take place at room temperature in the course of days. However, if the mass be heated and if its temperature during the heating correspond to a temperature at which the nuclei number has a noticeable value, the formation of crystallization centers will occur. If, then, the mass be brought to the temperature at which the linear crystallization velocity has reached its maximal value, the transformation of the viscous liquid into a crystalline solid will be easy.

The sugars are notable for their small tendency towards spontaneous crystallization and for their very small crystal ization velocity. These properties make it very difficult to separate and identify the sugars. E. FISHER introduced a method which has made the task very much easier. The method consists in converting the sugars into the corresponding osazones, with subsequent separation and identification. These new compounds, the osazones, may be more readily separated and identified than the sugars themselves, and if desired, may be reconverted into the parent sugars.

In order to facilitate crystallization recourse has sometimes been had to the addition of foreign bodies that tend to increase the nuclei number. Thus, for example, gall may be crystallized after the addition of ether.

a. The Transformation of Inorganic Substances into the Glassy State

Metals do not commonly greatly undercool. Undercooling in the cases of iron and nickel has been observed to the extent of 100°. The ability to undercool among metals is also dependent in a high degree upon admixtures. In liquid antimony, crystallization begins regularly after an undercooling of 5–10°. Undercooling frequently occurs in the crystallization of gold. In all cases among metals it is comparatively slight and in no case has it been possible to obtain a metal in a glassy state, for the spontaneous crystallization tendency of metals increases very rapidly with increasing undercooling. In fact, the tendency must be

abnormally great with very slight undercooling since metals deposited from electrolytes at ordinary temperatures are crystalline throughout.

Of the elements, only a few metalloids have been transformed into the glassy state, such as sulphur, selenium, and oxygen. Liquid oxygen becomes viscous before crystallization begins, in this case with a small crystallization velocity.[1]

So-called amorphous boron, carbon, and silicon are cryptocrystalline bodies. Their crystalline structures have been shown by the method of DEBYE and SCHERRER. Vanadium pentoxide may be obtained in small quantities in the glassy state. Of the oxides, boron oxide, silicon dioxide, phosphorus pentoxide and arsenous oxide may be obtained as glasses. The ability to undercool persists in the salts of these acid anhydrides, and is the greater, the smaller the amount of the basic oxide combined in the salt. The acid silicates and borates, for example, may be obtained in the glassy state with slow cooling, and the same is true of the salts of metaphosphoric acid and those of pyrosulphuric acid ($K_2S_2O_7$). The more basic the silicate or borate, the more rapidly must it be cooled in order to obtain it as a glass. In the younger eruptive rocks there is still to be found a considerable residue of glass which had not succeeded in crystallizing during cooling because its temperature sank too rapidly.[2]

Of the sulphides, antimonous and arsenous sulphide have been prepared as glasses.

The melts of salt hydrates frequently permit considerable undercooling and may be prepared as hard glasses, e.g., $Na_2S_2O_3 \cdot 5H_2O$. If the melts of these substances be viscous at room temperature they ordinarily become vitreously solid upon cooling to $-80°$ (the temperature of the freezing-mixture used).

Whereas many substances are unknown in the glassy condition, because their tendency towards spontaneous crystallization is too great, or because the maximum of this tendency lies at very low temperatures, there is one well-known substance, boric anhydride, which has not yet been obtained in an anisotropic state, but which is known only in the isotropic state. Boric anhydride glass softens at about 580° and has a noticeable vapor pressure at 1000°. Whether this substance cannot crystallize at small pres-

[1] W. Wahl. *Z. phys. Chem.*, **84**, 116 (1913).

[2] Doelter, *Phys.-Chem. Mineralogie*. Leipzig. Page 7.

sures in particular because it is not stable in the form of crystals, its melting curve not intersecting the vapor pressure curve, or because its tendency towards spontaneous crystallization is very small, cannot be decided. Since this substance is prepared in large quantities by the dehydration of the hydrate $B(OH)_3$, the formation of crystallization centers would be expected, though crystalline boric anhydride has never been prepared despite many attempts with this end in view.

b. A Process for the Forcing of Spontaneous Crystallization [1]

For this purpose a temperature gradient is produced in a column of the vitreous liquid which is to be investigated, within which lies the temperature of the maximal nuclei number. Under these conditions crystallization becomes noticeable after some time by the appearance of a turbidity in the clear mass in the neighborhood of the temperature of the maximal number of crystallization centers. In time this turbidity proceeds towards both ends of the liquid column and crystallites visible to the naked eye sometimes form. If the liquid column is contained in a glass tube it is merely necessary to break the tube at the point at which the turbidity exists in order to obtain a few crystallites, and to use these to inoculate the mass in which crystallization is to be forced, at a temperature somewhat higher than that which prevails in the temperature gradient at the place of turbidity. By vigorous stirring the whole mass can be brought to crystallization at this temperature.

Figure 110 should clarify the connection between the temperature gradient, and the linear crystallization velocity together with the tendency towards spontaneous crystallization.

The line *ab* represents the length of the column of the undercooled liquid. If the temperatures prevailing in the cross-sections of this column be plotted perpendicular to *ab*, the curve *cd* is obtained, which gives the change in temperature of the column, the one end of which is warmed and the other held at room temperature.

The curve *s.c.t.* represents the dependence of the tendency towards spontaneous crystallization upon the temperature, which of course is also that of the dependence of the nuclei number in the

[1] *Z. anorg. Chem.*, **87**, 248 (1914).

unit of mass during the unit of time upon the temperature, and the curve *l.c.v.* gives the temperature dependence of the linear crystallization velocity.

Between the temperatures of the maxima of these two curves incipient crystallization is recognizable by the appearance of a turbidity, or by the formation of visible crystals, usually spherulites, since between these two temperatures the conditions are more favorable for the formation and growth of crystallization centers than they are outside of this temperature interval.

Lines drawn through the maxima of the two curves *s.c.t.* and *l.c.v.*, parallel to *ab*, intersect the temperature curve *cd* at the points t_1 and t_2, the projections of which upon *ab* give the points 1 and 2. Between the sections of the column corresponding to these two temperatures crystallization first makes itself visible. From here it proceeds outward towards both ends of the column.

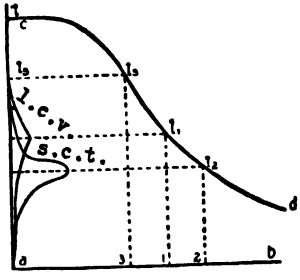


FIG. 110.

At higher temperatures it will make a halt at the point 3 upon the column at which the equilibrium temperature t_s, of the crystals with the melt, prevails. Towards lower temperatures the limit between the clear glass and the turbid devitrified melt will be sharp only when the linear crystallization velocity has an appreciable value at the temperature concerned, although the number of crystallization centers is not very great.

If, however, the reverse relations obtain, the limit will not be very sharp, the turbidity will end in a porcelain-like layer which, on account of the smallness of the spherulites, finally concludes in a deep blue color. This blue color is especially beautiful in tubes of difficultly fusible Jena glass that have been heated unequally.

The nature of the temperature gradient that is applied for the forcing of crystallization is of importance. A steep gradient, *ceteris paribus*, is considerably less favorable than a more gradual, because with the former the amount of substance to be devitrified occurring within the definite temperature interval is smaller than with the latter. In order to diminish the gradient, tubes made of material with especially high heat conductivity are to be recommended.

The applicability of the method may be illustrated by two examples.

A mixture of 66 per cent boric anhydride and 34 per cent borax ($Na_2B_4O_7$) was poured into a platinum boat and fused to a difficultly fusible glass rod before it was allowed to cool. The one end of the boat was then heated in a gas oven to 750° and the other projected out of the oven into the free air.

After four hours a spherulite was formed which attained the length of one centimeter in the course of two days. The temperature at its boundary with the liquid mixture amounted to about 700°. After cooling, the mass was treated with boiling water. The glass dissolved much more quickly than the crystallized mass, which crumbled to long fine needles. The melting point of these needles lay at 688°; analysis showed them to contain 10.89 per cent sodium. Whether there was formed here a highly acid borate, or a mixture of borax with boric anhydride, could have been determined only by a systematic investigation of a series of glasses with varying content of the anhydride.

Upon the fusion of equivalent quantities of potassium carbonate and silicon dioxide, the latter expels about 95 per cent of the carbon dioxide at a partial pressure of carbon dioxide of 0.07 atmosphere. This mixture of potassium carbonate and silicate has not up to the present time been crystallized and the pure silicate likewise appears to be known only in the form of a glass. Crystallization first becomes noticeable in the mixture of these two substances by the appearance of a turbidity during a heat treatment to 750° similar to the one described in the former example. The very small spherulites change in the course of two days into larger transparent crystals between which may be seen opaque portions of potassium carbonate.

c. The Law of Stages

If a state of aggregation that has become unstable pass into other states of different stabilities the question arises as to which of these states will be assumed. It has been believed that the less stable state is first formed and then the more stable. This, however, is indefinite since it does not take account of the kind and the manner of the transformation. Doubt remains as to what is meant by this rule, whether it means that after a certain length

of time crystallization centers of the least stable form appear, regardless of the temperature, and that after another period of time centers of a more stable form appear, and so on, or whether it means that with slight undercooling crystallization centers of the least stable should form and with greater undercooling, the more stable, and so on.

Inasmuch as the process of spontaneous transitions is an atomic one it will be subject to the laws of probability. Therefore, only the *probability* of the formation of crystal-centers, the forms of which have different stability, may properly be discussed.

The thought lying at the base of this law of stages is a question of fact and may therefore be directly tested by experiment. Since quite frequently several forms of crystal appear during the crystallization of an undercooled melt, the validity of the rule, respecting the probabilities of the formation of crystallization centers of different stabilities, can be tested.

Even if the probability for the formation of grains of the stablest form were much greater than for that of the less stable, this could hardly be known to us. From the fact that there is known a series of less stable forms it follows that the relation just named does not always obtain.

Thus, for example, benzophenone occurs in two forms with melting points of 48.0° and 25.0°. The nuclei number of the more stable is very small, that of the less stable between $-20°$ and $-30°$ is fairly large. Accordingly it is easy to prepare the less stable form.

Ordinarily, however, grains of the forms with different stability appear simultaneously. The relation between the numbers of grains is very sensitive to the presence of foreign substances. Oftentimes one recrystallization is sufficient to change this relation considerably, and in some cases the effect is so great that the nuclei of one form are no longer observed. The grains of the more stable as well as the grains of the less stable may disappear in this way.

It has been pointed out that the temperature of the maximal nuclei number does not greatly change in consequence of admixture. It might be expected, therefore, according to the law of stages, that with one and the same substance the temperatures of these maxima would decrease with increasing stability of the forms concerned. In the following table are given the melting

points and the temperatures of the maxima of the nuclei numbers for a series of substances:

TEMPERATURES OF THE MAXIMA OF THE NUCLEI-NUMBERS

(Above which are given the Melting-points of the Substances Concerned)

Piperine.....	129 40	Allylthiourea.....	74 <−20	73–74 15	70 0
Betol.....	91 20	Quinic acid.....	157–158 <−15	153 50	
Cinchonidine..	210 100	Chlorurethane.....	102 15	101 40	
Dulcite.....	188 80	Dextro-camphoric acid...	171 120	159 70	153
Mannite.....	166 40	Santonin.....	170 40	120 50	
Narcotine.....	175 140	4-Brom-1-Dinitrobenzene.	59.5 0–20	34.8 20–25	
Resorcinol....	110 −10	$Na_2S_2O_3 \cdot 5H_2O$.....	48 −40	33 −60	
Vanilline.....	81 0	Triphenylmethane.....	stable −30	unstable −10	

Eight of these substances exhibit two forms, and with five of them the temperature of the maximal nuclei number of the less stable form lies above that of the more stable; with three of these eight substances the reverse relation obtains, that is, the relation is not that demanded by the law of stages.

The fact that the formation of a nucleus of crystallization occurs very seldom in comparison to the number of molecules present would indicate either that many conditions must be satisfied for its formation, or that the number of molecules capable of crystallizing must be a very small one. If the latter possibility were the case it would be necessary to assume that only a few of the molecules are able to arrange themselves upon a lattice,

and that for the formation of the first nucleus the meeting of about eight of these susceptible molecules would be necessary. Under these conditions, the formation of a grain would be relatively rare, and if, in addition, limiting conditions were placed upon the manner in which the molecules meet, the formation of a nucleus would occur still less frequently. Such limiting conditions might relate to the velocity of the colliding molecules, the directions from which they approach collision, and so on. If these conditions actually suffice to explain the relatively small probability of the formation of a nucleus, it is obvious that the process is so complicated that any simple relation between the probabilities and the stabilities of the forms produced is not to be expected.

If the formation of crystal grains be a process governed by the laws of probability it is evident that: (1) the nuclei numbers obtained from several experiments conducted under strictly similar conditions should vary about a mean value, as do other quantities subject to chance, as, for example, the sum of the number of spots turned upwards on thrown dice varies around a mean value; (2) the relative variations of the nuclei numbers from the mean value should decrease with increasing nuclei number, as is the case with other quantities subject to chance.

For the investigation of criterion (1) the number of grains in undercooled piperonal (m. p. 37°) was determined[1] after the treatment described in the following paragraph.

The preparation was melted in a bath at 50°, and the nuclei were formed by exposure to a temperature of 25° for a period of 0.5 minute. In order to prevent the grains from growing into each other the substance was placed in a 35° bath, and the grains were counted. Between each two experiments the substance crystallized completely at room temperature.

For carrying out the comparison between the nature of the occurrence of nuclei and the manner in which an event subject to chance occurs there is given a typical collective series, the single events of which are subject to the laws of chance, and which possesses a mean value approximately equal to that found for piperonal. If the manner in which these two events occur be the same, i.e., if the formation of crystalline nuclei in piperonal be subject to the laws of chance, it is to be expected that the events of this typical collective series shall vary about a mean value in the

[1] P. Othmer. *Z. anorg. Chem.*, **91**, 219 (1915).

same way as the formation of the nuclei in piperonal. This is criterion (1). The collective series consisted in the sum of the spots displayed by six dice in each of fifty throws, and the mean value of these sums was 19.40, which came close to the mean value of the nuclei number in piperonal obtained from 50 tests, 19.44.

The largest number of nuclei was 27, the greatest number of spots was likewise 27; the smallest number of nuclei was 11, the smallest spot-sum was 10. The distribution of nuclei numbers and spot-sums is given in the accompanying table. The number

Nuclei Number	Number of Determinations	Sum of Each 6 Determinations	Sum of Spots	Number of Dice Throws	Sum of Each 6 Determinations
10	0		10	1	
11	1		11	0	
12	1	9	12	1	7
13	3		13	2	
14	3		14	2	
15	1		15	1	
16	2		16	2	
17	5		17	9	
18	6	25	18	3	25
19	3		19	7	
20	4		20	3	
21	5		21	1	
22	5		22	5	
23	0		23	4	
24	3	16	24	3	18
25	5		25	5	
26	2		26	0	
27	1		27	1	

of equal deviations is greatest in the neighborhood of the mean value and smallest for the extreme values. In both experimental series 50 per cent of the deviations lie in the middle third, with therefore only 50 per cent in the extreme thirds. Furthermore, in the third of extreme values in which lie the greatest nuclei numbers and spot-sums there occur respectively 16 and 18 deviations, whereas in the third containing the sma lest numbers there are found deviations of only 9 and 7. Evidently, then, the

variations among the lower nuclei numbers and spot-sums are greater than among the higher ones.

For these two series of experiments the mean error in the single measurement is determined by the formula:

$$\epsilon = \pm\sqrt{\frac{S}{n-1}},$$

in which S is the sum of the squares of the differences from the arithmetical mean, n is the number of trials, from which may be obtained:

Mean error of the nuclei numbers = + 4.12
Mean error of the spot-sums = + 3.90

These values also agree well. The most probable error, $\frac{2}{3}\epsilon$, is ± 2.75 for the nuclei number. The values that approach most closely, + 2.6 and − 2.4, together form 20 per cent of all errors. With the spot sum the most probable error is ± 2.6. The values corresponding to it, + 2.6 and − 2.4 together furnish 28 per cent of all of the errors.

It may therefore be stated that there exists an extensive similarity between these two experimental series.

Number of Experiment	I		II	
	Nuclei Number	Deviation	Nuclei Number	Deviation
1	19	+ 6 7%	32	−3%
2	15	−16	33	±0
3	13	−27	32	−3
4	18	+ 1	34	+3
5	23	+29	32	−3
6	22	+23 6	34	+3
7	15	−15 7	35	+6
8	18	+ 1	34	+3
9	14	−24 4	32	−3
10	21	+18	32	−3
Mean.....	17.8	15.9%	33.0	3%

For the application of the second criterion a small (I) and a large (II) quantity of piperonal were investigated in capillary tubes under similar conditions. The substance was melted at 50° and the grains formed by exposure to a temperature of 30° for 50 seconds. The nuclei number found are given in the following table. It is evident that the theory of probability is satisfied also in this case. The deviations of the single experiments from the mean value with a nuclei number of 18 have an average value of 16 per cent; with a mean nuclei number of 33 the deviations are only 3 per cent and vary less than is the first case.

d. The Dependence of the Tendency towards Spontaneous Crystallization upon the Temperature in the Neighborhood of the Melting Point

The atomistic conception of the formation of crystallization centers leads to the assumption that the nuclei number increases with increasing undercooling from very small values immediately below the melting point. It has been maintained, however, that the nuclei number is actually zero within a certain temperature interval below the melting point, and that it begins to increase only after the passing of this interval. This temperature interval has been designated as the sphere of metastability, and in it only contact with the solid phase has been thought sufficient to bring about crystallization.[1]

This conception is based upon misunderstood observations upon salol and phenol, the nuclei numbers of which in the neighborhood of the melting point sink to such small values that the tendency towards spontaneous crystallization appears to be wholly absent. Ostwald was of the opinion that the metastable state in undercooled phenol extended from 24 to 42° below the melting point. P. Othmer [2] determined the time necessary at different temperatures for the formation of the first grains in fused phenol (see table on next page).

It may be seen from these data that the metastable sphere can be very materially diminished by merely extending the time

[1] Ostwald, *Z. phys. Chem.*, **22**, 302 (1897), and *Verwandtschaftslehre*. Second Edition, page 349.

[2] *Z. anorg. Chem.*, **91**, 219 (1915).

PHENOL, 6 gms.

Formation-Temperature of the Nuclei	Time in Seconds					
	Single Values					Mean
20°	14	11	17	15	15	13 4
	13	12	14	11	12	
22°	60	105	45	36	22	38 8
	30	29	20	21	20	
26°	300		100	194		322
	440		82	814		
30°	120		1620	840		2810
	4200		5580	4500		
PHENOL, 30 gms.						
30°	40	30	30	32		33
35°	840	420	780	1320		820

of observation, i.e., crystallization centers will finally appear if the observer have the patience to wait for them.

With other substances, the formation of grains can be followed to temperatures much nearer the melting point. Lauric acid (m. p. 43.2°) was investigated by OTHMER, and the time T, elapsing before the appearance of the first grain in one gram of the acid, was determined.

Temperature.....	40.00°	41 00°	41.50°	42 00°	42 60°	42 70°	42 80°
T' (seconds).....	2 5	3 5	5.5 °	10 0	95	120	1200

It may be seen, therefore, that the crystallization of lauric acid takes place at least within 0.4° of the melting point.

Although the extensive metastability postulated by OSTWALD has been shown not to exist, a limited metastability of a few tenths of a degree must exist because of the increase in solubility resulting from decrease in particle-size. It would be of interest to determine the range of undercooling within which the nuclei number is disappearingly small, owing to decrease in grain-size, in the case of substances which permit very little undercooling.

In this way a conception of the sizes of crystallization centers might be obtained.

e. The Influence upon the Number of Crystallization Centers of the Temperature to which the Melt is Heated before Undercooling

If the process of crystallization actually consist of two processes the first of which is the loss in energy by the molecules in becoming anisotropic, and the second, the arrangement of the molecules upon a lattice, it is possible that a small number of anisotropic molecules exists in an undercooled melt. If this be the case, the number of crystallization nuclei formed with a given degree of undercooling must be a function of the temperature to which the melt is heated before undercooling, and must decrease with increase in this temperature.

This dependence of the nuclei number has been actually found in an investigation by P. Othmer. Piperonal (m. p. 37°) is especially suitable to such experiments because of its reproducible nuclei number. Three tubes containing 0.13, 0.7, and 0.4 gm., respectively, of piperonal were heated to different temperatures for a period of one minute, cooled to 24.3 for a half-minute for the formation of nuclei which were then developed at 35° and counted. The nuclei numbers are reduced to 1 gm. of piperonal in the following table:

Heating Temperature	Nuclei Number			Mean
	I	II	III	
40°	206	236	282	228
50°	164	175	196	178
60°	65	67	92	75
65°	44	43	44	44
70°	34	29	35	33

The higher the temperature to which the melt was heated preceding its undercooling, the smaller was the number of nuclei formed under otherwise similar conditions.

With the duration of the heating the nuclei number decreased

distinctly, as would be expected. Furthermore, it was shown that cooling above the melting point did not increase the number of nuclei in the melt.

Other substances, namely, 4-brom, 1, 3-dinitrobenzene, betol, and palmitic acid, likewise exhibited this decrease in the nuclei number due to the disrupting effect of the high temperature.

f. Abnormal Dependence of the Tendency towards Spontaneous Crystallization upon the Time

The number of crystallization centers which form with a definite undercooling is usually directly proportional to the time. In the case of the fatty acids and their esters, however, the nuclei number increases much more quickly than is required by this simple proportionality. Moreover, it is dependent upon the temperature to which the preparation is heated after fusion and also upon the duration of this heating. The nuclei numbers of palmitic acid [1] given in the table are in illustration of this:

Temperature before Undercooling, 75° 1 min.	Duration of Undercooling, Minutes.	Amount of Undercooling	Palmitic Acid, Melting Point 62°							
			0 5	1 0	1 5	2 0	2 5	3 0	4 0	5 0
			Grains							
100° 1 min.		1 5°	0	0	0	1	4	14	>37	>80
		1 6°	0	0	0	3	8	21		
		2 0°	20	>40						
		1 5°	0	0	0	0	0	3	11	28
		1 7°	0	0	0	4	8	18	>40	
		2 0°	2	18						

This abnormality with respect to time appears with those substances for which the expression $\frac{M \cdot r_p}{T_p}$ is significantly greater than 13.5 cal., r_p designating the heat of fusion per one gram, T_p the melting temperature, and M, the molecular weight. When

[1] P. Othmer, *Z. anorg. u. allgem. Chem.*, **91**, 235 (1915).

this expression has its normal value, the melt probably contains only one kind of molecule. If it is greater or smaller, transformations probably take place in the melt during crystallization, accompanied by either development or absorption of heat. The rapid increase in the nuclei number with time indicates that these transformations take place rather slowly.

g. The Influence of Pressure upon the Nuclei Number

The probability for the formation of a center of crystallization in an undercooled melt is extremely small in comparison to the number of molecules present. It is concluded, therefore, that the formation of a center of crystallization is not only conditional upon the favorable meeting of a definite number of molecules but that in addition other limiting conditions must be satisfied, which still further depress the probability for its formation. The following supposition might represent such a limiting condition. Not all of the molecules are capable upon favorable collision of forming a center of crystallization, but only a relatively small number which depends upon the nature of the substance and the temperature. These molecules may be designated as anisotropic and may exhibit the following properties. The difference of their volume per gram from that of the isotropic molecules may be represented by $\Delta v'$ and this difference may be set equal to Δv the volume change upon crystallization. Their heat of transition R_p', may likewise be equated to the heat of fusion, R_p. The pT-lines for equal concentration of anisotropic molecules would thus run parallel to the melting curve, since the equation of CLAUSIUS-CLAPEYRON is applicable to the case. That the curves of equal concentrations of anisotropic molecules are parallel to the melting curve would also be indicated by the relation $\frac{\Delta v'}{R_p'} = \frac{\Delta v}{R_p}$. Since according to our conception of the process of crystallization, equal concentrations of anisotropic molecules correspond to equal nuclei numbers, the pT-curves of equal nuclei numbers should be parallel to the melting curve. In other words, with equal undercooling, the nuclei number should be independent of the pressure.

M. HASSELBLATT[1] verified this conclusion experimentally.

[1] *Z. anora. u. all. Chem.*, **119** (1921).

Betol has the same nuclei number at $p = 1$ kg. and 34° as it has at $p = 1000$ kg. and 59°. In this pressure interval the melting point of betol rises from 93.0° to 122.9°, an increase of 30° as compared to increase in temperature along the curve of equal nuclei numbers of 25°.

The maximum of the nuclei number for papaverine lies at 40° and rises with increase in pressure to 60° at $p = 1000$ kg., the nuclei number not having changed noticeably; presumably, the influence of the pressure upon the melting point is of the same order of magnitude.

For piperine, the maximum of the nuclei number lies at 35° when $p = 1$ kg., and at 70° when $p = 1000$ kg., although the number itself is doubled during the rise in pressure.

There are some substances, then, such as betol and papaverine, with which the pT-curves of equal nuclei number run parallel to the melting curves, although this rule does not apply to all substances.

3. The Change in Viscosity with Undercooling

The viscosity of a liquid at first increases slowly with increasing undercooling and then reaches a critical temperature, at which the rate of increase mounts rapidly until finally a hard, brittle glass is formed. Quantitative measurement of the change in viscosity during undercooling has shown that although the viscosity increases very rapidly, though continuously, with falling temperature, that is, with an increasing rate of change, other properties show no variations in rate during the formation of the brittle glass. For example, the expansion coefficient for betol or piperine shows no change during this abnormal increase in viscosity.

It is therefore justifiable to consider glasses as *undercooled liquids.*

The velocity of fall of a small sphere in a viscous liquid is inversely proportional to the viscosity of the liquid. The viscosity for betol and for piperine have been determined in this way.[1] Figure 111 gives the time in seconds, plotted against the temperature, for the movement of a small glass rod under the force of 0.087 gm. a distance of 1.02 mm.

[1] *Zeit. phys. Chem.*, **28**, 22.

If all of the curves in Fig. 111 except that of piperine be moved parallel to themselves to a point where the piperine curve is met, a narrow bundle is obtained—only the curves of betol and dextrose fall out. That is, for the same order of magnitude in viscosity, the viscosity curves show a nearly equal rate of change with temperature.

	Beginning of Motion	Velocity of 1.02 mm. in 100 Sec.	Melting Point	Temperature of Maximal Nuclei Number
Piperine	37 0	44 9	127	40
Betol	2 1	6 4	95	20
Alphol	3 4	9 6	80 4	
Peucedamin	−1 8	1 5	81	0?
Cocaine	10 0	15 6	98	
Santonin	46 2		170	42
Narcotine	64.5		175	140
Allylthiourea	−7.5		74	0 and −20
Chlorurethane	5 5		102	40
Quinic acid	36 8		161	60
Papaverine	47.3	53 0	147	
Brucine	125 2	132 2	178	
Cane sugar	108 6	113 3	160	

The preceding table gives the temperatures at which the small rod began to move, and the temperatures at which it attained a velocity of 1.02 mm. in 100 sec., and, in addition, the melting temperatures and the temperatures of maximal nuclei number. The temperature of equivalent viscosities which may be interpolated by the help of Fig. 111 refer to a velocity of motion of the small rod amounting to 1.02 mm. in 100 sec.

It may be seen that the temperature of softening lies on the average 90° below the melting point, although this difference in temperature varies considerably from substance to substance. With santonin and narcotine it rises to 120°, with brucine and sucrose it sinks to 50°.

It is to be noted that in many cases the liquids lose their mobility with respect to small external forces exactly at temperatures where the tendency to form crystals is the greatest. On the other hand, with some substances the tendency towards spontaneous

crystallization is greatest when the melt has become rigid, as with santonin and a modification of allylthiourea. With other substances the maximum of nuclei number occurs at temperatures far above the softening range of the glassy liquid, and this is the case especially with narcotine, chlorurethane, quinic acid, etc.

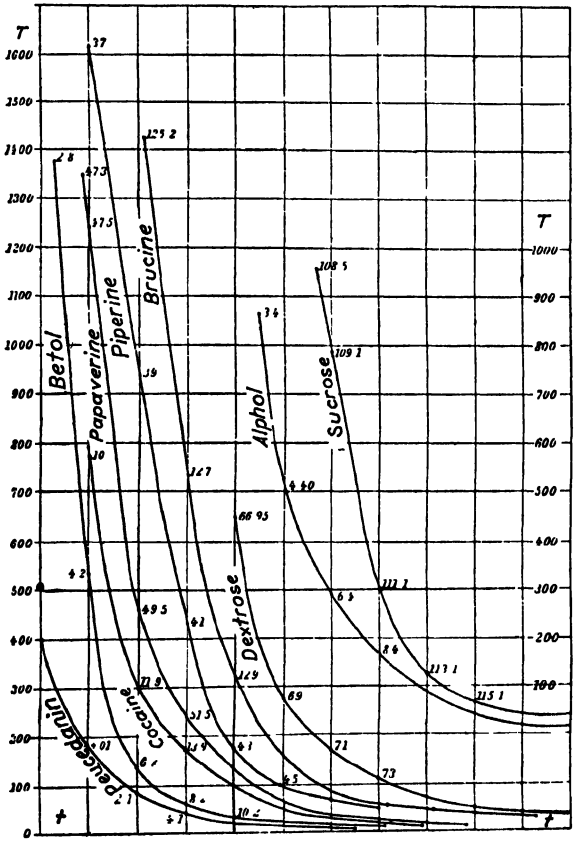


FIG. 111.

It is evident that the temperatures of the greatest tendency towards spontaneous crystallization do not lie at temperatures of equal inner friction.

The maximum of the nuclei number is to be explained by the increase in viscosity due to increased undercooling. The greater the viscosity the more difficult it is for the molecules to group

themselves upon a crystal lattice, and therefore the smaller is the nuclei number. If the ability to form grains finally disappears, by virtue of its high inner friction the glass will obtain a stability, which, thermodynamically considered, does not rightfully belong to it.

a. The Dependence of Viscosity upon Pressure

The influence of pressure upon viscosity has been investigated by a number of workers, notably, WARBURG and VON BABO,[1] ROENTGEN,[2] WARBURG and SACHS,[3] COHEN,[4] HANSEN, [5] FAUST.[6]

The work of the first of these investigators is concerned chiefly with the influence of pressure upon the viscosity of water up to a pressure of 700 kg. FAUST determined the influence of pressure upon the viscosity of ether, carbon disulphide, and alcohol up to 2000 kg.

At temperatures below 40° the viscosity of water diminishes with small pressure changes, above this temperature it increases in keeping with the behavior of all other liquids. The viscosity isotherm of water shows a minimum at 0° which is displaced towards smaller pressures with rising temperatures, and at 40° it lies at $p = 1$ kg.

The measurements of FAUST show that upon the isometric lines, those of unchanging volume, the viscosity of ether and carbon disulphide do not change.

The influence of the increase in pressure from 1–2000 kg. upon the viscosity of these liquids is very considerable.

At 0° the viscosity increases to about three times its normal value. Inasmuch as the temperature rises more rapidly with equal increase in pressure upon isometric curves than upon melting curves, the melt will become more viscous with increasing pressure in the points of state upon the rising portions of the melting curve, if the viscosity have the same value at equal volumes. At pressures above the maximum of the melting curve, the viscosity of the melt would begin to increase rapidly with increasing pressure

[1] *Wied. Ann.*, **17**, 390 (1832).
[2] *Ibid.*, **22**, 510 (1884).
[3] *Ibid.*, **22**, 518 (1884).
[4] *Ibid.*, **47**, 666 (1892).
[5] *Dissertation.* Tübingen, 1900.
[6] *Z. phys. Chem.*, **86**, 479 (1914), and *Göttinger Nachr.*, 1913, page 489.

upon the melting curve, because in addition to the effect caused by rising pressure there would be the increase due to falling temperature. Accordingly, it would often be more correct to designate the melt in this region as a solid isotropic body.

4. The Linear Crystallization Velocity

(Abbreviated to C. V.)

The fact that crystals are polyhedra indicates that the C. V. must be dependent upon direction; for if it were independent of direction, crystals would be bounded by spherical surfaces. The direction to which any value of C. V. refers is that defined by a line perpendicular to the series of surfaces formed by successive additions of atom-planes to an original crystal-face during the growth of the crystal. The distances of the crystal-faces from the center of crystallization have the same relation to one another as the values of the linear C. V. of the respective faces.

There is another crystallization velocity of the character of a vector, determined[1] by introducing the substance into a dilatometer and reading the change in volume in the unit of time. This "three-dimensional velocity," however, depends upon the number of crystallization centers, upon their positions with respect to each other, and upon the conditions for the withdrawal of the heat of crystallization. In consequence of this, the determinations do not give consistent results.

If a crystal that has formed slowly be compared to one that has formed more rapidly it will be found that the first crystal has distinctly the greater number of faces. Crystals form slowly from slightly undercooled melts or from slightly supersaturated solutions, and quickly from greatly undercooled melts or highly supersaturated solutions.

It is therefore evident that the C. V. for each crystal-face is dependent in a characteristic manner upon the conditions existent during formation. If the velocity-vectors were the same for all faces under similar conditions, then all surfaces would advance during crystal growth at the same speed, and the external limits of a crystal would not depend upon the conditions of formation. If, however, the different velocity-vectors be different functions

[1] E. Cohen, *Z. phys. Chem.*, **30**, 617 (1899); **33**, 61 (1900).

of the undercooling in crystallization from a pure melt, or of the supersaturation in crystallization from a supersaturated solution, then the external limits must change with change in the undercooling or the supersaturation. This would be shown by the suppression of those faces the C. V. of which increase slowly with increasing undercooling or supersaturation, by those of which the increase is more rapid. In order to be able completely to describe the development of a crystal in its pure melt at different temperatures it would be necessary to know the temperature dependence of all of the velocity-vectors. The solution of this problem is still very uncertain. So far it has been possible to determine only the greatest vector at only one temperature, that of the melting point, and this only with substances that undercool greatly. A correct conception of the temperature dependence of the maximal vector has been obtained for such substances.

D. GERNEZ [1] made the first measurements of the linear C. V. in dependence upon the degree of undercooling. For this purpose a glass U-tube was used, with a scale attached, upon which the motion of the visible limit between the undercooled melt and the crystal could be followed. Crystallization of the melt was caused by inoculation. GERNEZ measured the C. V. of rhombic sulphur and yellow phosphorus, and showed that in both cases the C. V. increased with increased undercooling, that is, with decreasing temperature. The reason for this anomalous temperature dependence of a transformation velocity remained unexplained. After B. MOORE had found that the C. V. of phenol and acetic acid is independent of the diameter of the tube (between 1 and 7 mm.) in which the crystallization proceeds, it became customary to measure the true temperature dependence in tubes of this size.

The researches of GERNEZ and MOORE extended over only a small temperature interval (about 20°) below the melting point. In an investigation by the author with J. FRIEDLÄNDER the temperature interval was considerably increased and results were obtained which are of value in explanation of the abnormal temperature dependence.

Figure 112 gives the dependence of the C.V. upon the *bath-temperature* for substances of considerable C. V. The C. V. increases with undercooling, as GERNEZ had found, but becomes

[1] D. Gernez, *Compt. rend.*, **95**, 1278 (1882).

independent of the temperature of the bath after the undercooling exceeds 20—30°.

It was possible to investigate benzophenone to a temperature 100° below its melting point, because of its especially low tendency towards spontaneous crystallization, and it was found that the C. V of this substance decreases rapidly at an undercooling of 100°, and that its value is negligibly small at the temperature of the carbon dioxide-ether freezing-mixture. A tube of 1 mm. diameter, filled with benzophenone at a temperature of 0° where crystallization proceeds with maximal velocity (55 mm. per minute), was immersed in an alcohol-carbon dioxide bath and crystallization was thereby stopped immediately. Upon warming, the boundary between liquid and crystal began to move at —35°, and with increasing temperature it rose quickly to its constant maximal value. Such a temperature dependence, as the investigation of numerous substances has shown, is typical for all substances, the maximal C. V. of which amount to more than 3 mm. per minute.

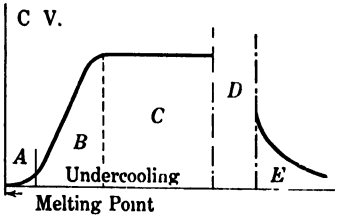


Fig. 112.

This typical behavior is represented in Fig. 112 for a temperature range extending from the melting point to temperatures at which the C. V. is negligible.

In the range *A*, 1—5° below the melting point, large crystals, rich in faces, grow from the places of inoculation in directions very different from that of the axis of the tube. Because of this, few consistent values for C. V. can be obtained. These values decrease rapidly towards the melting point. Thermal convection currents, or currents caused by slight admixtures of foreign substances in the melt, have great influence in this range upon the C. V., as well as upon the form of the crystal, tending to accelerate the process of crystallization. In a tube of 3 mm. diameter, crystallization of benzophenone takes place one degree below the melting point at a rate of about 10 cm. in 24 hours, whereas in a tube of 0.5 mm. diameter in which convection streams form less readily, about 72 hours are necessary. Finally, the admixture collects in the uppermost part of the tube (when the preparation

is inoculated at the lower end of the tube and crystallization proceeds upwards) causing the melting point to be lowered and the crystallization finally to come to a standstill.

In range *B*, about 5–30° below the melting point, a number of prisms form in the tube parallel to the axis of the tube, and grow mostly at the ends so that long crystal filaments are formed. At the beginning of range *B* the crystal filaments lie exclusively along the periphery of the liquid cylinder, for the heat of crystallization is more quickly removed from this than from the interior parts. With substances of large C. V., crystal filaments often grow spirally along the wall of the tube. Figure 113 represents the distribution of the crystal filaments in the tube for an average position in range *B*, and Fig. 114 for the beginning of range *C*.

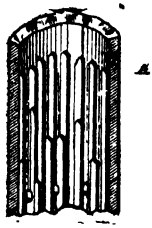


FIG. 113.

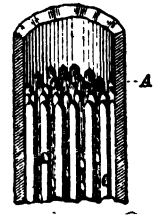


FIG. 114.

Whereas in the range *B* the crystal filaments grow chiefly along the tube walls, in range *C* they fill the tube. Between these crystal filaments at some distance from the visible limit of crystallization, *A*, hollow spaces are formed by the contraction of the substance during crystallization or by the separation of gas bubbles.

In the temperature range *D* stationary C. V. cannot be obtained under the conditions of crystallization as they exist in experiments carried out in glass tubes. In the range *E*, which is the falling part of the curve of C. V., it may be discovered by direct observation that the liquid crystallizes completely up to the limit *A*, no liquid remaining between the crystal filaments. The limit between the melt and the crystal filaments here is curved convexly to the melt, because the peripheral portion is colder than the central portion.

The change in the distribution of the crystals in the crystallization boundary and the change of the linear C. V. with undercooling leads to the following conclusions:

1. In range B crystallization is retarded by the heat of fusion evolved. The warming of the liquid layers immediately in front of the advancing crystal surfaces to the temperature of the melting point, together with the comparatively low temperature gradient which means slow removal of the heat of crystallization, results in a diminution of the C. V. With increasing undercooling, the temperature gradient at the limit of crystallization increases and with it increases the C. V., until the temperature gradient becomes so steep that crystallization can take place with the maximal velocity characteristic of it.

2. In the temperature range C the value of the C. V. is therefore independent of the bath-temperature, because a constant temperature prevails at the limit of crystallization, that of the melting point.[1] A sufficient quantity of heat is present for the production of this temperature in the heat of crystallization of the liquid between the ends of the crystal filaments, as shown by direct inspection of the limit of visible crystallization and by calculation. If t_0 designate the temperature of the melting point, c_m'' the mean specific heat of the crystal, r_0 the heat of fusion at the melting point, then the temperature t from which the temperature of the melt rises to the melting point, providing the liquid crystallizes without loss of heat, is given by the equation

$$t = t_0 - \frac{r_0}{c_m''}.$$

[1] Attempts have been made to measure the temperature of the boundary layer in order to test the conclusion that the temperature of the melting-point prevails in it. The wire of the thermoelement used was thicker than the liquid layer the temperature of which was to be measured, and although a rise in temperature was observed as the limit of crystallization passed the junction of the couple, this temperature never reached that of the melting-point. This is not to be taken to prove that a temperature other than that of the melting point prevails at the crystallization limit. Since the melting-point is assumed to be the temperature of the point of halt upon the cooling curve because this temperature is independent of the rate at which heat is removed from the melt, it follows that the equilibrium temperature is able to establish itself very quickly at the cost of the heat content of the melt. In order to test conclusively the proposal that the equilibrium temperature (melting point) prevails in the boundary liquid layer, it would be necessary to work with thermoelements of variable masses. It would then be found that with disappearing mass of the thermocouple the temperature registered would be that of the melting-point.

If the crystallization could be so conducted that no heat were lost from the limit of crystallization, the C. V. would then be forced to fall rapidly from its constant maximal velocity at the temperature *t*. In reality, however, two kinds of deviations are found because this condition is not met.

When the value of the C. V. is large—more than 100 mm. per minute—and when the tube is not very narrow, crystallization below the temperature *t* results in the heating of the layers near the limit of crystallization, and under these conditions no constant velocity obtains but the C. V. increases with time up to its maximal value notwithstanding the fact that the temperature of the melt was originally below *t* (range *D*).

When the C. V. is small—under 4 mm. per minute—the quantity of heat lost by conduction and radiation is probably so great that stationary velocities alone are possible, and under these conditions a decrease in the C. V. will be obtained only when the original temperature of the melt lies considerably higher than the temperature *t*.

This conception of the relation between the C. V. and the temperature leads to several conclusions that have been confirmed by experiment.

a. If the velocity of crystallization be retarded by defective removal of the heat of crystallization, the results of MOORE, indicating that the C. V. is independent of the diameter of the tube, cannot be universally true. According to our conception of the relation between the C. V. and the temperature, a decrease in the diameter of the tube will cause an increase in the C. V. in range *B* and a decrease in range *C*. This has been found by experiment. In addition, if the tube in which the melt crystallizes be made of a material of superior heat conductivity, the C. V. in the range *B* will be still further increased. The points *1*, *2*, and *3* in Fig. 115 represent the C. V. of benzophenone in tubes of inside diameter 6, 1 and 0.18 mm. in dependence upon the temperature of the bath. No difference in C. V. is noticeable in the tubes of 6 and 1 mm., but in the narrowest it is distinctly increased. Points *4* give the C. V. in dependence upon the bath-temperature in the annular space (Fig. 116) between a copper cylinder *AB* and a glass tube *DC* of 0.1 mm. wall thickness, connected by a rubber tube *FE*. Between 32 and 37° (Fig. 115) there is a large increase in the C. V. caused by the high heat conductivity of the copper. The same

results were obtained for other substances. Accordingly, it may be stated that there is no simple explanation for the C. V. measured in ranges *A* and *B*. The values obtained are equal to the constant maximal C. V. minus the decrease caused by the heat of crystallization, which in turn depends upon the conditions of external heat conduction. If these conditions of heat transference could be improved in any way, then crystal ization in a very fine filament of liquid would proceed with the maximal constant velocity characteristic of it at the temperature of the melting point. The values of the C. V. found in the ranges *A* and *B* have no significance

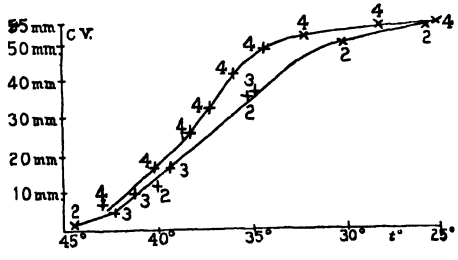


FIG. 115.



FIG. 116.

for the determination of the true temperature dependence of the C. V.

b. It also follows that with equal C. V. and with approximately equal conditions of external heat conduction, the extent of the ranges *A* and *B* must decrease with the heat of crystallization. For performing this comparison we have at disposal the C. V. of benzophenone I of m. p. 48.3. that of benzophenone III of m. p. 25.2, and the transition velocity of benzophenone III into benzophenone I which can be measured in a U-tube as an ordinary C. V. Figure 117 represents the C. V. of benzophenone I and III and the transition velocity of benzophenone III into I, in dependence upon the bath-temperature. The heat of fusion of benzophenone I is 23.4 cal., the heat of transition of III into I is 3.2 cal., therefore the heat of fusion of III amounts to 20.2 cal. Ranges *A* and *B*

extend over 20° for benzophenone I, and over 14° for benzophenone III. The range of constant maximal C. V. extends over 45°, whereas the range of the constant maximal transformation velocity, in accordance with the small value for the heat of transition extends over a range of only 3°.

c. The dependence upon the bath temperature for a small C. V. can likewise be derived from our conception of the conditioning factors. The quantity of heat set free in the U-tube during the unit of time decreases with decrease in the bath-temperature and in consequence the temperature range of the constant maximal C. V., namely, *C*, finally contracts to a point so that a maximum forms in the curve representing the C. V. in dependence upon the temperature of the bath

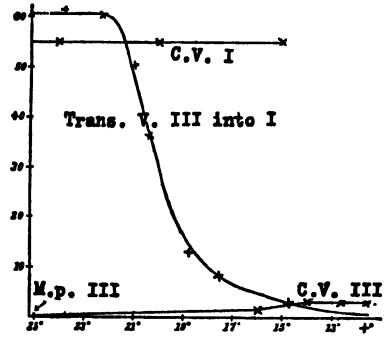


FIG. 117.

If increasing quantities of phthalide be added to liquid triphenylguanidine, the melting point of the latter will be depressed in increasing amounts. As a result of this, the maximal C. V. decreases, and since the maximal C. V. of pure triphenylguanidine is only 3.87 mm. per minute, the dependence of the C. V. upon the temperature can be substantially influenced by such a diminution in the maximal C. V. Figure 118 gives the values of C. V. obtained in this way by LAUTZ.[1]

The temperature of initial crystallization decreases with continued addition of phthalide, and with it decreases the maximal C. V., and also the temperature interval of the constant maximal C. V., until it has shrunk to a point in curve IV.

The flat maximum first occurs at a C. V. of 3 mm./min. and should lie at this value for all substances with equal heats of fusion and equal heat conductivity. If the C. V. be greater than 3 mm./min., a range of constant maximal C. V. is formed; if small, the maximum appears. When such a maximum appears the surface between the melt and the crystalline solid is curved concavely towards the melt in case the undercooling is less than

[1] *Z. phys. Chem.*, **82**, 626 (1913).

that of the maximal C. V., because the peripheral portions lose more heat than the central, causing the crystal filaments along the wall of the tube to grow more rapidly than those in the center. When the undercooling is greater than that of the maximum, the boundary surface is bent convexly toward the melt, for the reason that here the C. V. decreases with decrease in temperature.

The temperature of this maximum must approach the melting point of the substance with decrease in the diameter of the tube,

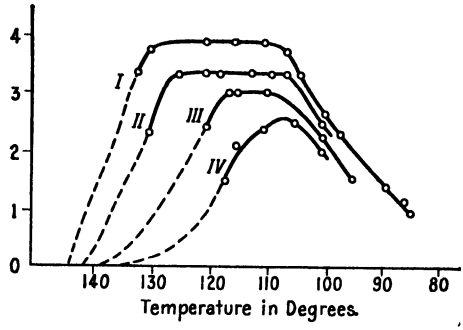


FIG. 118.

The linear C. V of the stable form of triphenylguanidine	M p
I. Pure triphenylguanidine	144 2
II Triphenylguanidine with 5 per cent phthalide.	141 2
III. Triphenylguanidine with 10 per cent phthalide	138 2
IV. Triphenylguanidine with 17 5 per cent phthalide	133 7

since with the resulting improvement in the abstraction of the heat of crystallization, the temperature at which everything in the layer undergoing crystallization becomes solid is increased. Figure 119 displays the dependence upon the bath-temperature for the C. V. of salipyrine I (m. p. 91.8°) and of salipyrine II (m. p. 86.3°), measured in glass tubes of different diameters. These diameters in millimeters are given by the numbers written above each of the curves. It may be seen that the maxima of these curves are actually displaced towards higher temperatures with decreasing diameter of the tube, in fact, from 60–72°. The maximal C. V. decreases with decrease in diameter in such a way that the temperature in the boundary layer appears no longer to reach that of the melting point, but decreases with the decrease in the diameter.

In the same way the temperature upon the falling branch of the C. V. curve, ranges *D* and *E*, does not correspond to the bath-

temperature but is the higher the greater the value for the C. V. With small C. V. (0.001 mm. per minute) the velocities of crystallization become nearly equal to each other in tubes of 0.03 and 0.01 mm. If the crystallization be allowed to take place upon a silver plate on which are scratched a few lines and on which the preparation is placed, warmed and pressed out into the thinnest possible layer, it will be noticed that after crystallization has proceeded for an hour at a velocity of 0.001 mm. per minute, the crystallization limit is somewhat advanced in the groove and in the neighboring thinner layers. It is evident from this that the heat of crystallization raises the temperature of the boundary

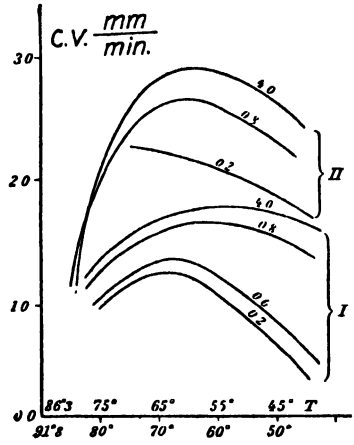


Fig. 119.

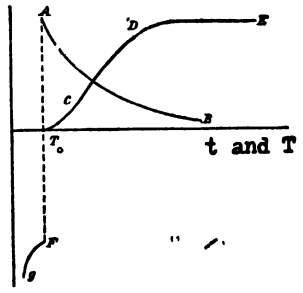


Fig. 120.

layer noticeably even in the case of such a small velocity as 0.001 mm. per minute. In consequence of this, the true temperature dependence of the C. V. is not determinable. Only one value of this function is approachable by measurement, namely, the constant maximal C. V. that refers to the temperature of the melting point.

If we consider, then, not the dependence of the C. V. upon the bath-temperature, t, as given by curve CDE (Fig. 120), but the true temperature dependence, which is the dependence upon the temperature prevailing at the limit of crystallization, the horizontal DE shrinks to the point A, and the C. V., freed from the influence of the heat of crystallization, decreases with falling

temperature in conformity with the behavior of all other transformation velocities. At the melting point the C. V. is equal to the velocity of melting, but opposite in sign. The velocity of melting grows with the temperature as indicated by the curve *GF*. According to the conception given in Fig. 120, in order to overheat a crystal it would be necessary to add heat so quickly as to exceed the melting velocity at the temperature concerned. It may be seen that such a rapid addition of heat even if a suitable heat transmitter were used would be possible only in the case of a very small maximal C. V. The great majority of crystallizing substances cannot therefore be overheated.

a. The Range of Variable C. V.

Substances of average C. V. exhibit on the falling branch of the C. V. curve, range *D*, high unchanging velocities only when the conditions for the removal of heat are good. With substances of great C. V. it is possible to measure only either very small constant velocities, or the maximal C. V. itself, for the reason that any velocity between these two extremes tends to accelerate under the conditions of heat removal, and finally to become the maximal C. V. The following example will make clear these relations. Benzophenone I crystallizes in tubes of various dimensions at the velocities given in Fig. 121, upon warming from the temperature of the carbon dioxide-alcohol mixture.

If the effect of the temperature upon the C. V. in any tube be followed it will be noted that at first a temperature change has but little effect. With constant bath temperature, crystallization proceeds at a rate that is independent of time, that is, with a constant velocity. A temperature is soon reached at which a sudden rise in the C. V. occurs. Up to this temperature the surface between crystal and melt is smooth, mirror-like, and arched towards the melt. At the moment when the C. V. makes it sudden increase it becomes jagged. Prior to the attainment of this critical temperature the liquid crystallizes completely; at the moment the critical temperature is reached an indefinite amount remains uncrystallized between the filaments formed.

At the temperature of the sudden rise in the C. V. the heat set free during the crystallization of the successive layers is still directly led away under the conditions of heat conductivity and

temperature gradient. Above this temperature, however, too much heat is set free under the limitation of the heat conductivity during crystallization, and the velocity therefore reaches a constant value. A rapid increase to the value of the constant maximal C. V. thus begins when the temperature in the boundary layer rises to the melting point.

A change in the diameter of the tube corresponds to a change in the amount of heat set free in the unit of length. The greater

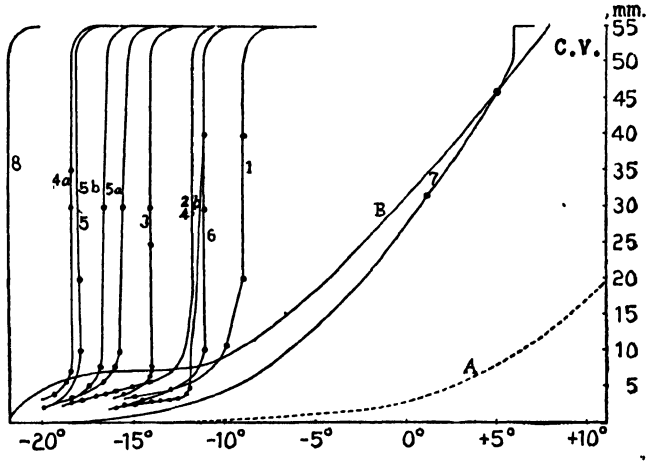


FIG. 121.

Tube 1, diameter, 0 7 mm.	Wall-thickness, 0 06 mm.
Tube 2, diameter, 0 6 mm	Wall-thickness, 0.08 mm.
Tube 3, diameter, 0.6 mm.	Wall-thickness, 0.7 mm.
Tube 4, diameter, 1 0 mm.	Wall-thickness, 1.5 mm.
Tube 5, diameter, 0 9 mm.	Wall-thickness, 1.1 mm.
Tube 6, diameter, 0 5 mm.	Wall-thickness, 1.0 mm.
Tube 7, diameter, 0.3 mm.	Wall-thickness, 1.0 mm.

the diameter of the tube, the lower will be the temperature at which the C. V. begins to accelerate. In tubes of 6 mm. inside diameter the acceleration begins at − 40° and at almost negligible C. V., attaining higher values with decreasing tube diameter and increasing temperature.

Curve *B* connects all of the points of velocity acceleration for tubes of different diameter, and gives the limit of stationary velocity for glass tubes in the alcohol-carbon dioxide bath. With better conducting tubes and a bath of higher conductivity, *B* would be displaced towards smaller C. V. Above *B* no stationary

velocities are possible under the prevailing conditions. The C. V. with momentarily complete heat-removal is represented by curve *A* which also represents the true dependence of the C. V. upon the bath-temperature when the temperature of the bath and that of the limit of crystallization are equal.

If the C. V. increase up to the neighborhood of curve *B*, the smallest changes in the conditions for the extraction of heat will be of greatest influence upon the C. V. The curves 4*a* and 4*b* were constructed from determinations made with the limit of crystallization moving downwards and upwards, respectively. At the same bath-temperature the stationary C. V. are very different. The C. V. of the downward motion is as great as that of the upward motion when the bath-temperature in the first case is 8° below that in the second, because conditions for the temperature rise at the limit of crystallization are more favorable with the downward motion on account of the lack of convection currents. The case was also observed in which the crystallization proceeded with accelerated velocity in the downward motion until the bend of the U-tube was reached, where, after transition into upward motion, the velocity again assumed small stationary values.

The transition of small linear velocities into maximal velocities also occurs in chemical reaction of explosive gas mixtures. In these cases the velocity of burning increases to the maximal, detonation velocity. These processes differ from those involving the linear C. V. in that the increase in pressure brought about by the explosion plays an important rôle.

b. The Temperature Dependence of the C. V. upon the Falling Branch of the C. V. Curve

The C. V. of most substances that permit considerable undercooling cannot ordinarily be followed over a wide temperature interval, for the reason that besides the crystal modification the C. V. of which is to be measured, other modifications of the crystallizing substance often appear at the limit of crystallization. In the case of o-benzile-carboxylic acid it has been possible to follow the C. V. over a temperature range of 140°. The melt of this substance becomes very viscous at 60° and quite vitreous at 30°.

The C. V. of o-benzile-carboxylic acid was measured over a temperature range of 135–55° in a U-tube of 0.2 mm. inside diameter and 1 mm. wall thickness. F. DREYER measured the C. V. at lower temperatures for a layer 0.1 mm. thick between two cover glasses. After crystallization centers had been formed and after the preparation had been exposed to a known temperature for a definite length of time, the distance of the limit of crystallization from a mark on the glass plate was determined by means of an ocular micrometer.

o-BENZILE-CARBOXYLIC ACID

C. V. $\frac{\text{mm.}}{\text{Min.}}$

t			t	
130 0°	2 32	±1 per cent	49 6°	$42\times10^{-4}\pm$ 4 per cent
115 0	3 20	±1	44 7	$15\times10^{-4}\pm$ 5
110 0	1.87	±1	39 6	$45\times10^{-5}\pm$ 8
85 0	0 66	±1	33.8	$31\times10^{-5}\pm10$
70.0	0 12	±3	28 7	$83\times10^{-6}\pm$ 3
55 0	0 0095	±4	24 1	$21\times10^{-6}\pm$ 3
50.7	0.0090	±2	18.0	$12\times10^{-7}\pm20$
			0.0	$< 1\times10^{-7}$

The equation

$$\rho_1 = \rho_0 e^{A\frac{T_1-T_0}{T_0T_1}},$$

fails to reproduce the observations at low temperatures, between 18° and 50°.
When

$$t_0 = 18°,\ \rho_0 = 0.0000012\ \frac{\text{mm.}}{\text{Min.}}$$

and a equals 24,384, up to 50° the equation gives values which are smaller than the observed, from which it is inferred that the C. V. observed are too large because of the increase in temperature at the crystallization boundary; but at temperatures over 55° the calculated values becomes very much greater than the observed (at 115°, 330 times), in which cases the opposite deviations would be expected, and the calculated curve would have given the value 3.24 mm./min. for the constant maximal C. V. at the temperature of the melting point.

As long as the C. V. rises with falling bath-temperature, or remains constant, admixtures diminish the C. V. Upon the falling branch of the C. V., small admixtures raise the C. V. of o-benzile-carboxylic acid, as the following table by F. DREYER shows:

o-BENZILE-CARBOXYLIC ACID WITH ADDITIONS OF BENZOIC ACID

C. V. $\times 10^{-5}$ $\frac{\text{mm.}}{\text{Min.}}$

$t°$	Addition				
	0 0%	0 1%	0 5%	1 0%	2 0%
51 0	1000	1410	1240	1150	970
49 6	420	678	602	482	432
44 6	149	268	223	196	164
33 8	31	32	29	27	23

c. The Maximal Vector of the C. V.

The constant maximal C. V. is a constant characteristic for each crystal-form, the determination of which is of importance in order to determine the relation between it and the other crystal properties. It is in high degree dependent upon the nature of the substance, and varies among polymorphic crystal-forms; that of the more stable form of higher melting point may be higher or may be lower than that of the less stable. Examples of this may be found in the following table (pages 266–267):

d. Crystal Growth in the Neighborhood of the Melting Point

In temperature range *A*, as we have seen, crystallization results in the slow formation of polyhedra having many faces. R. MACKEN [1] has made a special investigation of crystallization in this range. A copper rod with a hemispherical end was introduced into an undercooled melt of salol. At an undercooling of 1.5° the lower half of a polyhedron (Fig. 122*f*) formed around the end of the rod. When the undercooling was decreased to 0.5°,

[1] *N. Jahrb. f. Min.* 1915, II, page 133; and 1917, page 191.

MAXIMAL CONSTANT CRYSTALLIZATION VELOCITY

Name of Substance	Melting Point	Temperature of the Bath and Crystallization Velocity in Mm. per Minute				Crystal Form	Observer
Acetanilide	111 8°	85°	70°			rhombic	Bogojawlensky
		142 0±2	146.0±2				
α-Acetnaphthalide	160 0	140°	130°	120°	115°		Jendrychowski
		15 0±0.1	16.0±0.1	16.0±1	16 0±0.1		
β-Acetnaphthalide	132 0	114°					Jendrychowski
		23 4±0.1					
Acetyldiphenylamine	102.6	70°	60°	50°	40°	rhombic	Jendrychowski
		25.2±0.1	25.2±0.1	25.2±0.2	25.2±0.1		
Apiol I	30.0	10°	0°				T.
		7.09±0.08	7.13±0.07				
Apiol II	27 5	10°	0°	−10°			T.
		14.5±0.2	14.4±0.2	14.4±0.2			
Azobenzene	67.1	40°				monoclinic	Friedländer
		600±50					
Benzamide	127.3	90°					Bogojawlensky
		480±5					
Benzil	94 8	60°	40°	20°			Bogojawlensky
		433±2	433±2	433±2			
o-Benzile-carboxylic acid	141.2	120°	110°				Jendrychowski und T.
		3 22±0.02	3.19±0.02				
Benzoic acid anhydride	41.2	28 5°	15°				Friedländer
		30 0±0.3	30 0±0.5				
Benzoin	136.0	80°	75°			monoclinic	Bogojawlensky
		21 4±0.8	21 8±0 3				
Benzophenone I	48.0	25°	0°	−20°		rhombic	Friedländer und T.
		55 5±0 3	55.0±0.5	52.5±0 5			
Benzophenone II	25 0	5°—−5°				monoclinic	T.
		2 40±0.1					
m-Bromnitrobenzene	53.0	33°	28°	20°		rhombic	Jendrychowski
		698±11	680±10	669±10			

Bromparaacettoluene...	118.2	96°	90°	80°			Jendrychowski
		116.7±0.9	116.9±0.2	116.9±0.9			
Butylphenol.....	98.1	70°	60°	50°			Jendrychowski
		1117±26	1109±33	1085±45			
Cumenol.....	71.5	30°	20°				Jendrychowski
		120.6±1.2	119.1±1.6				
m-Dinitrobenzene.....	90.0	C. V. over 100 at 80° 1090				rhombic	Bogojawlensky
m-Dinitrobenzoic acid...	140.0	120°				monoclinic	Bogojawlensky
		31					
2.4-Dinitrophenol.....	113.5	40°	35°				Jendrychowski
		84 1±1.0	84.1±1.0				
Dinitrotoluene.....	70.0	at 40° very great C. V.				monoclinic	Bogojawlensky
Diphenylamine.....	52.6	36°	33°			monoclinic	Friedländer
		112.5±1	112.5±1				
Erythritol.....	118.0	60°	50°				Bogojawlensky
		26.5	26.6				
Guaiacol.....	28.4	0°	17°			hexagonal	T.
		5.6±0.3	5.6±0.1				
Hydrocinnamic acid ...	48.2	25–15°				monoclinic	Friedländer
		300±20					
Coumarin.....	67.1	C. V. over 0 at 35° 68.7				rhombic	Bogojawlensky
Mannite.....	165.0	130°	125°			rhombic	Bogojawlensky
		51.3±0.5	51.3±0.5				
Picric acid.....	122.0	85°	80°				Bogojawlensky
		858±24	858±24				
Salol I.....	42.0	20°	10°			rhombic	T.
		3 46±0.15	3 48±0.06				
Salol II.....	38.8	20°	10°				T.
		1.0	1.0				
Sulphonal.....	125.3	90°	80°	70°	60°		Bogojawlensky
		403 5	403 5	403.5	402.7±0.5		
Santonin.....	166.0	140°	130°	120°		rhombic	Bogojawlensky
		36.2	36.3	36.3			
Tolyl phenyl ketone....	55.5	30°	20°	10°	0°	monoclinic	Jendrychowski
		22 2±01	22 7±0.2	23 0±1	23 0±0.1		
Nitroglycerine.....	13.5 u.	+5°	0°	−5°	−17°		Naukhoff, *Z. angew. Chem.*, 1905
	−2.8	0.145	1.83	0 267	0 125		

the edges between the planes p and p slowly rounded off, as shown by Fig. 122*e*. In time this rounding-off encroached upon the other edges until finally a hemisphere remained, as shown by Figs. 122*c*, *b*, and *a*. During these changes the crystal was in the state of constant growth. With increased undercooling, and more rapid growth, the planes in Figs. 122*a*, *b*, *c*, *d*, and *e* form in succession. Completely analogous phenomena can be observed in the crystallization of benzophenone. With undercooling up to 2° in this substance, spherical forms are produced. Upon a slight increase in undercooling numerous planes begin to appear; with

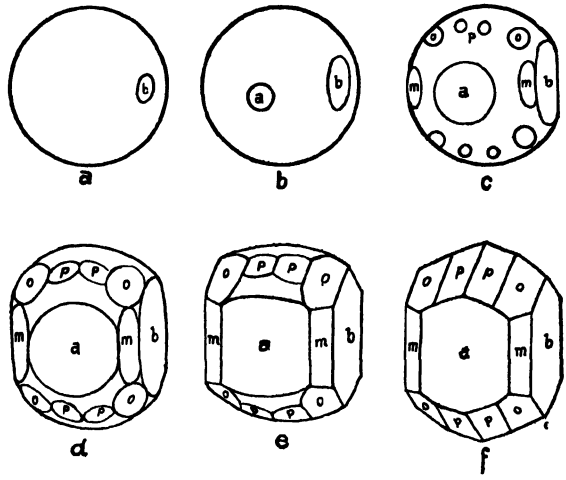


FIG. 122.

greater increase, in ranges B and C, crystal filaments are formed (Fig. 112, page 253), the ends of which, according to the nature of the substance, are bounded by the one or more planes which possess the maximal values of C. V.

It is concluded from these experiments that with very slight undercooling, that is, in the neighborhood of the melting point, the vectors of the C. V. all become equal, and that with increased undercooling differences in them appear which result in the formation of polyhedra with numerous sides. With still greater undercooling the formation of the planes corresponding to the smaller vectors is depressed, and filaments are formed, when the

crystallization is carried out in tubes, or spherulites, when crystallization takes place unrestricted from centers within a melt.

The formation of rounded crystallites is often observed with metallic substances. For example, copper separates from its solution in bismuth at a temperature of 1000–900° in the form of rounded crystallites, although at lower temperatures dendrites, with boundaries of corners and planes, are formed.[1] The explanation of the rounding in this case lies in the weakness of the copper crystals at the higher temperatures. These weak crystals are rounded by the force of surface tension and accordingly the transition from the polyhedric to the rounded form is accomplished gradually, in a wide temperature range. The rounding of salol crystals is wholly different, for here the transition is completed in a range of 0.5° in close proximity to the melting point. It is not likely that the solidity of salol crystals changes essentially in this small temperature range and we have additional evidence on this point in the fact that plates of salol show no tendency to shrivel during melting such as is shown by plates of copper and gold far under their melting points. In explanation of the phenomena observed with salol and benzophenone, therefore, there remains only the assumption that the vectors of the C. V. become equal at temperatures near to the melting point.

c. Abnormal Influence of Undercooling upon the C. V.

With substances possessing a C. V. greater than 3 mm. per minute, the C. V. ordinarily reaches a maximum at an undercooling of 20–30°, and remains constant at this value while the undercooling increases to 80° below the melting point. Substances have been known, however, the C. V. of which increases or decreases in the temperature range wherein it should be independent of the undercooling.

1. The C. V. of dinitrophenol (m. p. 112.8°) continues to increase at 40°. Although it should be independent of the degree of undercooling in the temperature range 80–40°, it has a value of 30.3 mm. per minute at 80° and 88.3 mm. per minute at 40°, increasing almost threefold. In addition to this substance, a distinct though weaker increase in the C. V. is observed in the

[1] Tammann, *Lehrb. d. Metallographie*, 3d Edition, page 22.

range of supposedly constant C. V. with acetanilide, antipyrene, and erythritol.[1]

2. A distinct almost linear decrease of the C. V. in range *C* is observed with *m*-bromnitrobenzene: 670 mm. at 30°, 561 mm. at 0°; as well as with *m*-chlornitrobenzene which has a C. V. of 905 mm. at 27° and 816 mm. at 10°.[2]

3. CH. LEONHARDT,[3] in a fundamental investigation upon the C. V. of salt hydrates, showed that the C. V. of $Na_2S_2O_3 \cdot 5H_2O$ which amounted to 118 mm. per minute, did not maintain a constant value over a definite temperature interval, but displayed a flat maximum at −2°. By the addition of water or of the anhydric salt the C. V. was depressed and independent of the undercooling.

4. A similar case was found in benzophenone. The measurements of V. PICKARDTS [4] upon an especially purified preparation gave a very flat maximum at 20° and a maximal value of 59.6 mm. per minute. A less carefully purified preparation gave a maximal value of 55 mm. between 23° and −15°.

5. Phthalide crystallizes in two forms with melting points of 72.8° and 65.0°. The C. V. of the unstable form is distinctly greater than that of the stable and in both cases, the C. V. increases at undercoolings greater than 20–30°.

The explanation of this abnormal dependence of the C. V. upon the undercooling is to be sought in the state of molecular aggregation of the particular liquid concerned. If a liquid consist of two or more kinds of molecules, polymers or isomers, and if the equilibrium between these molecules be dependent upon the temperature, the C. V. can then be independent of the temperature only in the case where the equilibrium characteristic to the melting point produces itself very rapidly, when the liquid is warmed to the temperature of the melting point. If this be not the case, the molecular aggregation will be dependent upon the undercooling, and since the equilibrium temperature with the crystals is dependent upon the state of molecular aggregation, the C. V. will therefore increase or decrease as the equilibrium temperature rises or falls.

[1] Bogojawlenski, *Z. phys. Chem.*, **27**, 599 (1898).

[2] Bogojawlenski. *Sitzungsber. der Naturforscherges. zu Dorpat*, **15**, 201 (1907).

[3] *Recherches sur la vitesse de cristallisation*, Paris, 1908. A. Kerrman.

[4] *Z. phys. Chem.*, **42**, 17 (1903).

If admixtures tend to accelerate the establishment of the equilibrium between the isomeric or polymeric molecules in the liquid a flat maximum may be found with a pure material, and a range of constant C. V., when impurities are present (LEONHARDT). If the explanation of the abnormal dependence of the C. V. upon temperature actually consist in this insufficiently rapid production of molecular equilibrium within the liquid upon warming to the melting point, and if several forms crystallize from the melt, these forms must all show an abnormal dependence upon the undercooling. This conclusion has been confirmed by H. LAUTZ [1] for phthalide.

The question of whether there exists in the liquid polymeric or isomeric molecules can be decided by the determination of the temperature coefficient of the molecular surface tension. If this show normal values, isomerism and not polymerism of the liquid molecules is concerned. Since the temperature coefficients of the molecular surface tension of liquids that show abnormal dependence of the C. V. upon undercooling have normal values, displacement of the equilibrium between isomeric molecules must be concerned in these cases.

A liquid, the molecules of which are slowly intertransformable, can show molecular compositions at one temperature differing according to whether the temperature of the liquid had risen or fallen in attaining this temperature; in consequence of this, its equilibrium temperature with the crystal is dependent upon the height of the heating and upon the velocity of the cooling. (See V, 6, page 110.) The variation of the C. V. with temperature will thus furnish evidence towards the proof of a slow production of inner equilibrium: an anomalous temperature dependence points to relatively slow production of the inner equilibrium; a normal dependence leaves open the question of whether the liquid consists of one or of several kinds of molecules, but demands that if the latter be the case, the transformation will take place very rapidly.

f. The Influence of Admixtures upon the Maximal C. V.

The equilibrium temperature of a crystal with its melt is lowered by the addition of non-isomorphous substances, and since

[1] *Z. phys. Chem.*, **84**, 628 (1913).

reaction velocity commonly decreases with falling temperature, a diminution in the C. V. is to be expected. Experiment has confirmed this, and has shown that the C. V. is independent of the time, which is of considerable importance. It is concluded from this that not only the temperature, but also the concentration in the range of constant maximal C. V. does not change at the crystallization limit and that therefore the melt constantly renews itself in the boundary layer.

Since equimolecular quantities of admixtures lower the equilibrium temperature of a crystal and its melt by equivalent amounts, an equivalent lowering of the C. V. by equimolecular quantities is to be expected, providing the substance added in no other way affects the C. V.

From the measurements of E. v. PICKARDT [1] it appears that the majority of substances (26) added to benzophenone in equimolecular quantities, actually lowered the maximal C. V. of this substance in nearly equal amounts, although five substances fell below this normal value and one, resorcinol, gave a value far above it.

If the temperature at the boundary between crystal and solution, T_1, be calculated according to the laws of the depression of the freezing point, and introduced into the equation:

$$CV_{T_1} = CV_{T_0} \cdot e^{A\frac{T_1 - T_0}{T_0 \cdot T_1}},$$

the C. V. for any value of T_1 may be calculated if the C. V. for T_0 be known.

For solutions of benzoic anhydride in benzophenone, $T_1 = 321.5 - 0.522n$ where n is the number of molecules of the substance dissolved in 100 moles benzophenone. If the values $T_0 = 311.06°K$ and $CV_{T_0} = 1.31$ mm. per minute be introduced into equation (1), a series of values for CV_{T_1} may be obtained.

The agreement between the calculated and the observed values is very satisfactory although it will not be so good in all cases, whereas the values calculated by v. PICKARDT'S interpolation formula do not agree with the observed. The chief factor which determines the influence of admixtures upon the maximal C. V. appears to be the lowering of the temperature at the boundary between crystal and melt.

[1] *Z. phys. Chem.*, **42**, 17 (1903).

n	CV_{T_1} Observed	T_1	CV_{T_1} Calculated According to Formula (1)	CV_{T_1} Calculated by PICKARDT
0 5	49 7	321 24	48 7	49 4
1 0	41 3	320.98	45 2	44 4
2 0	37 5	320 47	39 1	37 3
4 0	26 8	319 41	25 3	27 3
8 0	11 8	317 32	11 2	13 1
12 0	5.21	315 24	5 09	2 26
16 0	2 33	313 15	2 89	− 6 84
20 0	1 31	311 06	1.31	−15 0
25.0	0 476	308 45	0 482	−25 0

g. The Normal C. V. of Solid Solutions in Dependence upon Composition

Extensive investigations upon the C. V. of solid solutions have been made by BOGOJAWLENSKI[1] and M. HASSELBLATT.[2] If the solid solution component with the higher melting point have the greater C. V., the temperature at the crystallization limit determines the magnitude of the C. V. In this case the curves of the maximal C. V. in dependence upon concentration, and the curves which represent the mean of the melting intervals in dependence upon concentration, will be very similar to each other. If the former condition does not hold, then specific influences obtain, in addition to the influence of the temperature at the limit of crystallization.

h. The Dependence of the C. V. upon the Pressure

M. HASSELBLATT[3] has determined the dependence of the C. V. upon the pressure for a series of substances, and has found that the curve of the dependence of the C. V. upon the bath temperature does not change its type upon a rise of pressure from 1 to 1000 kg. The beginning of the range in which the C. V. is independent of the degree of undercooling lies at equal distances from the melting curve for the different pressures.

[1] *Sitzungsberichte der Naturforscherges. zu Dorpat*, **15**, 4 (1906).
[2] *Z. phys. Chem.*, **83**, 1 (1913).
[3] *Z. anorg. Chem.*, **119** (1921).

The maximal C. V. increases noticeably as a consequence of the increase in pressure only in the case of $Ca(NO_3)_2 \cdot 4H_2O$ (stable). With a few substances it does not change noticeably and with most it decreases. In the following table are given the quotients: maximal C. V. at 1000 kg. divided by the maximal C. V. at 1 kg., and also a few other quantities which change upon crystallization:

Substance and Modification	Ratio: $\frac{\text{Max. C. V. at 1000 kg. cm.}^2}{\text{Max. C. V. at 1 kg./cm.}^2}$	Difference of the Melting Points at 1000 and 1 kg./cm.^{2} $\text{M. P.}_{p=1000} - \text{M. P.}_{p=1}$	Molecular Entropy Increase upon Melting $\frac{\text{M. G.}}{T_s}$	Molecular Dilatation upon Melting $\text{M.}\Delta v$	Negative Temperature Coefficient of Molecular Surface Energy, $\frac{d\gamma(Mv)^{\frac{2}{3}}}{dT}$
$Ca(NO_3)_2 \cdot 4H_2O$, stable	1 43	10 0°	25 1	10 7	dissociates
$Cd(NO_3)_2 \cdot 4H_2O$	1 03	7 0°	24 4	8 4	dissociates
$Ca(NO_3)_2 \cdot 4H_2O$, unstable	1 01	>0	.....	small	dissociates
$Ca(NO_3)_2$, unstable	0 98	4 3°	.....	"	dissociates
Guaiacol	0 98	16 7°	.....	....	2.16
α-Chlorcinnamic aldehyde	0 89	12 7°	12 5	7 0	
Benzophenone III	0 85	.....	10 9	....	2.63
Benzophenone I	0 82	26 3°	13 4	16 1	2.63
Salol	0 81	27 4°			
Apiol I	0 76	.....	18 9		
Benzylaniline	0 75	22 3°	13 0	14 0	2 70
m-Iodonitrobenzene	0 71	.....	15–16 2		
Formanilide	0 70	28 8°	10 7	9 3	1 66
Apiol II	0 68				
Benzoic acid anhydride	0 53	18 8°			
Thymol	0 51	18 2°	12 8	10 6	2 15

Since the temperature at the limit of crystallization must rise along the melting curve, and since the C. V. rises rapidly with increasing pressure at this limit with rise in temperature, the pressure remaining constant, an increase in C. V. with pressure would be expected in case the temperature influence exceeds the pure pressure effect. This is not the case, however, since for the change of p and T upon the melting curve the pressure influence in most cases overbalances the temperature influence and the C. V. is

therefore diminished. This diminution of the C. V. depends in great degree upon the nature of the substance, for no connection can be seen between the change of the C. V. as a result of change in pressure and the change of the melting point likewise due to a change in pressure (second and third columns in the table). There is also no connection to be seen between the change in the C. V. due to pressure and the molecular entropy change, or the molecular volume change, upon melting.

5. Devitrification

When the temperature of an amorphous substance is raised into the temperature range where crystallization centers form devitrification will begin. This process may lead to the formation of crystallization centers of different polymorphic crystal-forms and all of these different crystal-forms may remain after devitrification, although it may also happen that only one remains.

The temperature of the mass undergoing devitrification will change according to the magnitude of the maximal crystallization velocity of the spontaneously forming crystals. This change in temperature is due to the heat of crystallization evolved during the process. The temperature rise Δt caused during devitrification by the operation of the maximal C. V. is determined by the heat of crystallization, r, and the specific heat of the crystals, c_p'':

$$\Delta t = \frac{r}{c_p''}.$$

A heat of crystallization of 50 cal. per gram and a specific heat of the crystalline solid of 0.25 cal. per gram, together with a high crystallization velocity could thus produce a temperature rise of 200° during devitrification.

If the temperature at which the formation of crystallization centers begins be 500° the rise in temperature of 200° as a result of devitrification will make itself evident through an incandescence of the mass. Conditions similar to these obtain for sodium metasilicate, Na_2SiO_3, the glowing of which is easy to demonstrate. This substance can be obtained as a clear glass by fusing equivalent quantities of sodium carbonate and silicic acid anhydride in a platinum dish, and quenching the crucible and its contents in cold

water. The silicate is obtained as a clear glass when the total quantity does not exceed two grams. Upon warming to a temperature somewhat greater than 500°, the formation of a few crystallization centers occurs, the C. V. becomes large, and the crystallizing glass soon begins to glow.

Figure 123 gives the temperature in vitreous sodium metasilicate in dependence upon the time. The silicate, in which was imbedded a thermocouple, was heated in a platinum crucible over a Bunsen flame. The section *cd* gives the rise in temperature brought about by the external addition of heat. Without devitrification the temperature could not have risen above 550°, whereas actually a temperature of 750° was obtained. The beginning of spontaneous crystallization is made evident by the sudden rise in temperature along the curve *ce*. A temperature decrease will occur at *e* if the temperature of the melting point be not reached with the devitrification; if the melting point be reached, the temperature will remain constant until everything is crystallized.

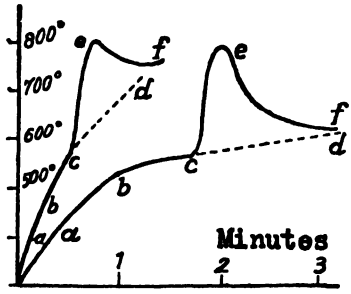


FIG. 123.

In the case of sodium metasilicate, the melting point (1055°) is not reached. The heat of crystallization at 20° is 29 cal. per gram, as obtained by the heats of solution at room temperature of the crystallized and the glassy substance. The specific heat of crystallized sodium metasilicate between 20° and 100° is 0.197. From these values it appears that devitrification at room temperature would cause a rise in temperature to 149°. A rise of about 160° was found at 520°.

The velocity at which the temperature of a glass is raised has no effect upon the temperature at which devitrification takes place.

The structure of the devitrified mass is determined by the number of crystallization centers and by the magnitude of the C. V. The relations obtaining in the devitrification of cupric metaborate, cobalt pyroborate and manganese biborate [1] are similar to those outlined above. The devitrification of amorphous

[1] W. Gürtler, *Z. anorg. Chem.*, **40**, 268 (1904).

zinc metaborate and of a silicate containing large amounts of alumina take place very slowly because of the fact that the nuclei number in these compounds is very small even in the temperature range in which it is maximal. In such cases it is advisable to produce a temperature gradient in a rod of the glassy substance and to discover in this way the temperature of the maximal tendency towards crystallization. In order safely to produce devitrification it is necessary to know the temperature at which this tendency is at its maximum, for at other temperatures the number of crystallization centers can be so small that a very long time may elapse before devitrification takes place. In connection with this it is to be noted that the temperature at which the C. V. reaches its maximal value is higher than that at which the nuclei number is greatest, and that the structure of the product of devitrification depends upon the number of nuclei and upon the magnitude of the C. V.

6. The Over-heating of Crystals and the Determination of the Equilibrium Temperature between Crystal and Melt for Small Values of C. V.

a. The Velocity of Melting and of Crystallization

Since the linear velocity of melting, like the linear velocity of crystallization, is vectorial in nature, we may consider melting as the displacement of crystal faces due to the subtraction of atom-planes from the surface of the crystal. For purposes of discussion, the melt is conceived to be in the state of lively motion in order to produce uniform conditions, and the displacement of a crystal-face during growth is conceived to take place parallel to itself. It is further assumed that etch-figures, which in fact have not been observed with the process of melting to the present line, do not form.

If θ represent the temperature of the melt, θ_0 the equilibrium temperature at the boundary between crystal and melt, δ the thickness of the layer which forms on the crystal-face, and s the displacement of the crystal-face during the time t, the following equation will obtain:

$$v_m = \frac{s}{t} = c_m \frac{\theta - \theta_0}{\delta}, \quad \ldots \ldots \quad (1)$$

v_m, the linear velocity of melting, is proportional to the temperature gradient in the boundary layer.

For the linear crystallization velocity, if θ be allowed to sink below θ_0, we have:

$$v_c = c_c \frac{\theta_0 - \theta}{\delta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The quantities c_m and c_c are the values of the linear melting and crystallization velocities when the temperature gradient in the boundary has the value 1. As long as θ is not removed too far from the melting temperature, the temperature of equilibrium, θ_0 is produced in the boundary layer, and the velocity of the surface of reaction will be determined only by the flow of heat. The heat consumed in the melting will then be equal to that transmitted through the boundary layer. If L designate the absolute heat conductivity in calories per unit of surface and unit of time, and ρ the heat of fusion of the crystal per unit of volume, then

$$v_m \rho = \frac{\theta - \theta_0}{\delta} L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and for the process of crystallization,

$$v_c \rho = \frac{\theta_0 - \theta}{\delta} L. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (1) and (3) as well as from (2) and (4), we may obtain,

$$c_m = c_c = \frac{L}{p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

With equal temperature gradients the flow of heat is the same, and for this reason the velocity of melting and that of crystallization are equal in the neighborhood of the melting point; when the temperature gradient is 1° this velocity is equal to the heat conductivity divided by the heat of fusion per unit of volume.

The temperature gradient at which the maximal value of the C. V. is reached may be represented by $\left(\frac{\theta_0 - \theta}{\delta}\right)_m$. If the temperature gradient $\left(\frac{\theta - \theta}{\delta}\right)_m$ be produced upon the melting crystal, and if we disregard the changes of L and ρ with temperature in the first approximation, then according to (3) and (4)

the velocity of melting and of crystallization will be equal to each other at equal distances from the melting point.

The value v_{cm} of the C. V. is the highest reached when everything crystallizes in the boundary layer. Therefore at the velocity v_{cm} the heat of fusion is completely led away during the displacement of the limit of crystallization under the temperature gradient $\left(\frac{\theta_0 - \theta}{\delta}\right)_m$. Conversely, if heat be led to the boundary of crystallization, the same temperature gradient would then have to be produced in order to drive back the crystallization limit at a velocity equal to v_{cm}. Under this temperature gradient the heat introduced would be completely consumed in melting,

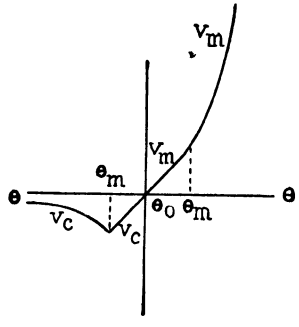


FIG. 124.

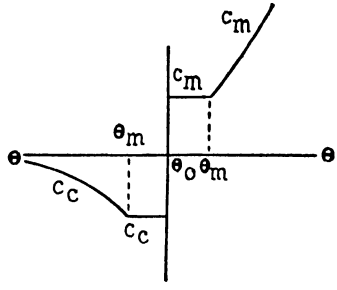


FIG. 125.

and the temperature of the melting point could still be accurately determined.

The velocity of melting, v_m, and the velocity of crystallization, v_c, depend upon the temperature in the manner indicated by Fig. 124. Both are zero at the melting point and both increase at the same rate with increasing distance from the melting point, for the flow of heat varies in the same way in both cases. However, the C. V. increases only to the value of the maximal C. V.. whereas the velocity of melting begins to accelerate at the value corresponding to that of the maximal C. V. The differential curve, Fig. 125, represents the equality of c_m and c_c at the melting point and also shows that these values increase by equal amounts in equal temperature intervals, the intrinsic velocities of the process not being of importance in this connection. In these temperature ranges the flow of heat is alone determinative for the processes of

melting and crystallization. The characteristic dependence of the velocities upon the nature of each process first makes itself manifest with the crossing of temperatures θ_m and each changes with temperature in accordance with the usual variation in rate of reaction with temperature, that is, c_c decreases with falling temperature, and c_m increases with rising temperature.

b. Conditions for the Overheating of a Crystal in its Melt

As stated before, the temperature gradient, the exceeding of which will cause the temperature of a crystal to rise above its melting point, can be calculated by equation (3).

If a cubic crystal of a substance with an absolute heat conductivity of 0.001 cal. per 1 cm.^{2} per second under a temperature gradient of 1° per centimeter, and with a heat of fusion of 30 cal. per cc. be placed in a large quantity of melt in the state of lively motion, δ may be estimated, according to the determinations of E. BRUNNER,[1] at about 0.002 cm. If the maximal C. V. of the crystal amount to 1 mm. per second, then, under the conditions outlined above, overheating of the crystal will occur when the temperature of the melt rises more than 6° above the melting point; a crystal of 6 cm. along the edge, however, under the above conditions would disappear in 30 seconds. With a maximal C. V. of 0.01 mm. per second, under similar conditions, a cubic crystal one centimeter along the edge would remain in the melt 8.3 minutes. It may therefore be seen that crystals with high maximal C. V. can remain only a very short time under conditions conducive to overheating, but that the smaller the maximal C. V. the longer a crystal may be overheated and the higher may be the temperature to which it is overheated.

The overheating of a crystal is possible only during its melting. To heat a crystal as such above its melting point without having the process of melting occur is impossible, as the widest experience in this respect has shown; melting always occurs with the greatest precision when the melting point is exceeded. In this way liquids that allow themselves to be undercooled differ essentially from their crystals. This difference may also be expressed by the statement that the number of centers of crystallization in a unit of volume in an undercooled liquid is extremely small in com-

[1] *Z. phys. Chem.*, **47**, 57 (1904).

parison to the number of points at which melting begins, for melting takes place on the surface of a crystal in a uniform manner, not in visibly distinct points, corresponding to centers of crystallization. The tendency to crystallize, of course, is much slighter than the tendency to melt, because it is necessarily easier to complete the transition from an ordered to an unordered arrangement than the reverse transition.

c. *Determination of the Melting Points of Crystals, the Temperature of which Can Rise Above the Melting Point upon Heating*

With good thermostatic control, the growth and the melting of crystals can be closely followed under the microscope, and the equilibrium temperature can be interpolated from the data obtained. Experiments with lævulose showed that the growth of crystals could be measured in this way, but that melting occurred too irregularly to be measured. During melting, the crystal-faces are not simply displaced parallel to each other, but edges and corners round off, so that, even if analogous directions be compared considerable differences will be found in the melting velocities obtained from different experiments.

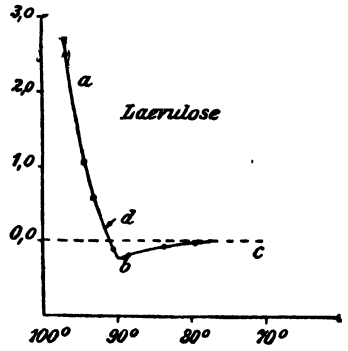


FIG. 126.

It is possible by means of a dilatometer to determine accurately the equilibrium temperature of a crystal with its melt by observing the volume changes in scale divisions at constant temperature per minute. Figure 126 represents these scale divisions in dependence upon temperature for lævulose. This curve may be derived from our knowledge of the linear C. V. Since the linear C. V. decreases with falling temperature when the undercooling has become very great (Range *E*), the volume diminutions will likewise decrease in this range, and since the linear C. V. has a maximum in dependence upon the undercooling, the volume diminutions must also have a maximum. For lævulose this maximum lies only 10° below the melting point. Beyond this maximum the volume diminutions

decrease with the C. V. with increasing temperature in order to reach a zero value at the melting-point, and then with further temperature increase the sign of the volume change is reversed and the change itself increases rapidly.

The exact determination of the equilibrium temperatures is now easy to perform: the point of intersection of the curve *ab* with the temperature axis *c*, is the temperature sought. The observations of one day, extending over a period of eight hours, gave a melting point of 91°. On the following day the determinations were repeated and it was found that the curve of volume change had shifted noticeably and the melting point fallen to 89.6°. In melted lævulose, therefore, some slow change takes place completing itself at about 90°. If the preparation be warmed to 95–100° for sixty hours, its C. V. decreases so greatly that crystallization can no longer be detected in the dilatometer.

For the accurate determination of the melting point of substances that melt with difficulty, substances of small C. V. such as feldspar, the crystals are first melted partially and their density determined at ordinary temperatures. Quantities of the substance are then heated to different temperatures in the neighborhood of the equilibrium temperature, again quenched and the density again determined. The volume changes brought about in this way in equal times must depend upon the temperature in the way indicated in Fig. 126, provided the equilibrium between crystal and melt is reversible.

BOWEN [1] determined the beginning and the end of fusion for solid solutions of anorthite and albite by determining microscopically the temperatures at which the first quantities of glass appeared, after quenching, and the temperatures at which the last residue of crystal disappeared. The uncertainty in this method lies in the fact that the equilibrium temperature is approached from only one side and it is therefore uncertain that actual equilibrium is obtained.

Among slow transformations the reversible can be distinguished from the irreversible by the method illustrated in Fig. 126. By the use of this method, MEISSNER [2] was able to show that the transformation of alpha- into beta-spodumene is not reversible.

[1] *Z. anorg. Chem.*, **82**, 283 (1913).
[2] *Z. anorg. Chem.*, **110**, 187 (1920).

X. LIQUID CRYSTALS

The group of substances known as liquid crystals has been the subject of a great deal of discussion and dispute. On the basis of the phenomena exhibited by this group of substances there has been assumed a special state of matter, the anisotropic liquid, and to this state an especial molecular structure has been assigned which differs essentially from that of the lattice structure. In the following paragraphs there is presented a critical review of the phenomena observed.

Substances that are supposed to occur in the state of liquid crystals are divided into three classes according to their chief properties. The first group consists of those substances that are turbid, mobile liquids in the temperature interval of the liquid-crystalline state. The substances of the second group are asserted to be liquid crystals because upon undercooling, their melts assume the colors of turbid media. There is no temperature range of stability for the substances in this class. The third group includes the easily deformable, weakly crystalline, substances. Credit is due to O. LEHMANN for having pointed out the existence of easily deformable anisotropic bodies, such as silver iodide in the neighborhood of its melting point, and for having established the fact that crystals do not necessarily have a considerable solidity.

1. THE GROUP OF p-AZOXYANISOLE

These substances do not melt to clear liquids, as is ordinarily the case, but give turbid melts which become clear at a sharply defined temperature. Upon cooling the reverse series of phenomena is completed, and the end-product is again transparently crystalline. Several of these substances with their melting- and clearing-temperatures are given in the following table:[1]

[1] D. Vorländer in his monograph, *Kristallinisch-flüssige Stoffe*, lists 170 substances many of which are in this group.

	Melting Point	Clearing Point
p-Azoxyanisole	116	134
p-azoxyphenetol	137.5	168
Anisaldazin	160	180
p-Azoxybenzoic ethyl ester	113.5	120 5
p-methoxycinnamic acid	170	185 7
p-Diacetoxylstilbene chloride	124	138

The substances of the group of azoxyanisole and the members of this group most suitable for investigation, namely, *p*-azoxyanisole and azoxyphenetol, deserve especial interest, because their turbid melts have been designated by all investigators as actually liquid and these assertions have been supported by viscosity measurements.

The chief question of debate with reference to these substances is this: Are these liquids chemically homogeneous (one-component systems), or are they to be considered as suspensions of isotropic or anisotropic particles in a solution saturated with respect to the particles? Microscopic investigation and the determination of the dependence of the various properties of the substances upon the temperature furnish evidence on this point.

A peculiarity of the two *p*-azoxy-bodies to which sufficient attention has not been given is the separation of black particles and filaments, which gather after turbidification on the bottom of the vessel during the cooling of a few grams of the clear yellow liquid. These particles and filaments are distinctly visible to the unaided eye. Even in the purest preparations (such as that of R. SCHENCK) this separation occurs, and although diminished in amount by repeated melting and cooling or by centrifuging, it is never wholly removed. The most careful microscopic examination on this point, which is probably that of G. WULF and H. DEISCHA,[1] where use was made of the cinematograph, has shown that in these turbid liquids occur large filaments and membranes, and also very small drops. According to these investigations the nuclei of the anisotropic liquid drops described by O. LEHMANN are not purely optical phenomena, but are structures

[1] *Z. Krystallographie*, **50**, 24 (1911).

with material extension which can be elongated into filaments by diminishing the thickness of the layer of liquid in which they occur (by pressing upon the cover glass) and which offer a resistance to the motion of the particles suspended in the liquid. The filaments, membranes, and particles disappear entirely upon crystallization, and clear crystals are formed. These structures are therefore more soluble in the crystal than in the melt, which is quite possible since crystals can decompose upon melting into two liquids, or, if they belong to a multi-component system, can decompose into two liquids and a new kind of crystal. Subsequent cooling will restore the clear crystal from these decomposition products. The contention that these two azoxy-bodies must be homogeneous, since no purer have been prepared, naturally cannot be credited.

The dark-colored separations probably form partly as a result of the reduction to the corresponding nitro-bodies, partly as a result of unknown reactions in the clear yellow liquid. Some such explanation must apply here, for it has not been possible by repeated warming and cooling under the clearing-point to bring about the disappearance of this deposit of dark particles, and although the deposit becomes smaller after repeating the operation ten times, it is restored in its original strength after recrystallization from alcohol.

In the light of these observations, the two *p*-azoxy-bodies cannot be considered chemically homogeneous, and accordingly attempts have been made to explain their optical behavior in a somewhat different manner, such as that of O. LEHMANN. These proposals will be reviewed in connection with the structure theory of O. LEHMANN.

If the *p*-azoxy-bodies be chemically homogeneous, some of their properties must change discontinuously on passing the temperature of clarification, as the properties of other chemically homogeneous bodies change at the melting point. R. SCHENCK,[1] who in particular has investigated this point, obtained results which seemed to indicate discontinuous property change, but these have since been corrected by the more accurate investigations of E. BOSE.[2] It has been found that the density as well as the heat content changes continuously at the point of clarification.

[1] R. Schenck, *Kristallinische Flüssigkeiten*, Leipzig, 1905.

[2] *Physik. Zeitschr.*, **8**, 347 (1907).

The dependence upon the temperature of the time of flow of a definite quantity of liquid is an especially characteristic function, as may be seen from the following discussion.

Figure 127 gives the dependence of the time of flow (F. T.) upon the temperature for an emulsion of two partially miscible liquids which becomes clear at the temperature T_1. At this temperature the curve of the F. T. has a peak. A distinct minimum lies at a lower temperature at which the liquid is completely turbid. Between these two temperatures two saturated solutions separate from the homogeneous mixture, one of which has a greater and the other a smaller F. T. than that of the homogeneous mixture. If the liquid with the smaller F. T. wet the walls of the capillary, a diminution in the F. T. is to be expected, and the F. T. will follow the solid portion of the curve upon which it will first decrease owing to the influence of the liquid of the smaller F. T., and then, in consequence of the temperature influence will begin to increase. If the liquid with F. T. greater than that of the homogeneous mixture wet the capillary, the F. T. will follow the dotted curve with decreasing temperature. A dependence of the F. T. upon the temperature as given by the fully drawn curve can also result if a solid separates from solution on passing temperature T_1. In this case it is of course necessary that the particles be very small so that the influence exerted by them upon the flow be as small as possible.

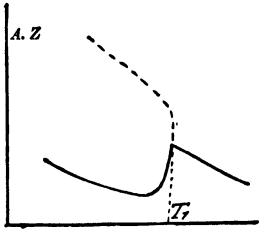


FIG. 127.

A dependence of the F. T. upon the temperature such as is represented by the fully drawn curve has been found for *p*-azoxyanisol by EICHWALD [1] and for anisaldazine by BÜHNER.[2] Figure 128 gives a series of values of F. T. measured in seconds, obtained by the author. The determinations were carried out with a slowly rising temperature which was arrested twenty minutes for each determination. The curve has a peak at 138°, at which point on cooling tiny turbid spheres separate, and at 136° the whole liquid is turbid. In the interval between 137° and 130° so much of the constituent which increases the F. T. separates

[1] *Dissertation*, Marburg, 1905.
[2] *Dissertation*, Marburg, 1906.

that the temperature effect is wholly masked and the influence of falling temperature does not become apparent until 130° is passed, whereupon the F. T. again increases. (The *p*-azoxyanisole used in this experiment was a preparation of bright yellow color especially purified by R. SCHENCK.)

The existence of membranes and filaments in the turbid melt of *p*-azoxyanisole is probably the reason for the fact that clarification cannot be brought about by centrifuging or cataphoresis.

According to O. LEHMANN the most important optical properties of the turbid melts of the two *p*-azoxy-bodies are the following. A thin crystalline layer of one of these substances, produced by melting a few crystallites upon a microscopic slide, covering the melt with a cover-glass, and crystallizing it, when viewed through crossed Nicol prisms during careful, repeated fusions, exhibits light and dark fields coincident with the peripheries of the newly melted solid crystals. This property of producing fields is not, however, a peculiarity of the turbid liquid, for the displacement of the cover-glass does not alter the fields essentially, although the liquid is thrown into lively motion. Evidently, particles have deposited from the melting crystals in very large quantities upon the object glass, which are oriented similarly in the same field but differently in different fields so that different fields have different directions of extinction. If a cover-glass be placed over crystals loosely upon a glass slide, and this then warmed while the turbid liquid is formed, the production of fields will no longer be observed and rotation of the analyzer does not cause a change in brightness in the field of vision. Indeed, with the experiment thus conducted, the separation of oriented particles is not to be expected.

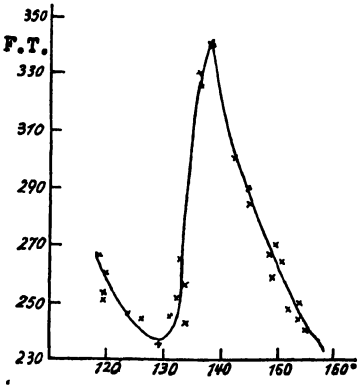


FIG. 128.

O. LEHMANN'S conception of the molecular structure of liquid crystals is supported by the following observations. If one of the *p*-azoxy-bodies be dispersed in a little oil and melted, small droplets

of the turbid liquid are formed. These may be divided into two classes according to their appearance.

The drops of the first class [1] show a dark point (LEHMANN'S nucleus point) surrounded by several concentric rings. The larger drops in the lower part of the photograph consist of several smaller drops and also show the dark spots of the original drops surrounded by regular streaks.[2] Between crossed Nicols a black cross appears upon these droplets, in which respect they behave similarly to spherulites formed between cover glass and slide. The occurrence of these crosses has been regarded as direct proof of the crystalline nature of the drops. It must not be forgotten, however, that bubbles of air in Canada balsam show similar crosses.

The drops of the second-class [3] exhibit, between crossed Nicols, two poles upon their peripheries from which, according to O. LEHMANN, a spindle-like body extends across the drop.

O. LEHMANN'S explanation of these phenomena is the following. The molecules in the drops are arranged in concentric layers with their longitudinal axes parallel to each other and tangential to the surface of the sphere. In this way a uniaxial structure is formed. In drops of the first class this axis is perpendicular to the object-glass, whereas in those of the second it is parallel. Thus the velocities of transmission of light differ according to whether the light passes in a direction perpendicular to the circles observed or parallel to them, and the refraction brought about in this manner causes the phenomena observed.

As we have seen, the optical nature of the nucleus-points has been a matter of dispute. They are probably material filaments, and this probability is supported by the persistence of the nucleus-point of each drop after its combination with others to form a larger drop. The spindle-like body of the second class, according to the observations of DIESCHA, consists in a membrane within the drop, stretched into a spindle-like structure.

It has been found possible to synthesize liquid crystals which show the properties of the *p*-azoxy-bodies. D. VORLANDER and GEHREN [4] arranged a series of pairs of substances which are

[1] O. Lehmann, *Flüssige Kristalle*, Leipzig, 1904, page 58, Figs. 95 and 96 and Plate X, Fig. 1.

[2] O. Lehmann, *Ibid.*, page 61.

[3] O. Lehmann, *Ibid.*, Plate XI, Fig. 3.

[4] *Berl. Ber.*, **40**, 1966 (1907).

wholly normal in the unmixed state, but of which the mixtures upon cooling, first become turbid and then crystallize. A mixture of 25 per cent piperinic acid with 75 per cent anisic acid becomes turbid upon cooling before crystallization occurs; under the microscope between crossed Nicols numerous bright droplets are to be seen and upon each of the drops a dark cross is evident. These phenomena are identical with those observed by O. LEHMANN for mixtures of *p*-azoxyanisol with oil.

It is also possible to reproduce the peculiarities of anisotropic liquids in suspensions of solid particles of vanadium pentoxide.[1] This suspension is optically isotropic when in a state of complete repose; but if currents occur in it, bright streaks may be seen. If a glass tube through which the suspension is streaming be brought between crossed Nicols, the familiar axial-cross may be seen, also a distinct reddish-yellowish-green dichromism. A magnetic field produced in the liquid causes an alinement of the suspended particles resulting in double refraction. The particles of vanadium pentoxide, in all probability rod-like in nature, arrange themselves parallel to the line of flow of the liquid, and can also be brought into alinement by magnetic and electric forces. A very small quantity of V_2O_5 is sufficient to bring about these phenomena, 0.8–0.08 per cent V_2O_5 in water producing the effect distinctly. A Fe_2O_3-sol behaves similarly.

Concerning the structures of anisotropic liquids, three different views have been advanced. The idea of O. LEHMANN, according to which the anisotropy is due to the alinement of the molecules, has already been explained. E. BOSE [2] sought to explain the observed anisotropy by postulating filamentous clusters of molecules (the " swarm hypothesis "). The formation of these is thought to be favored by the extended form of the molecules of the anisotropic liquids.

It is to be noted, however, that there are liquids such as the monocarboxylic acids and the normal hydrocarbons, the molecules of which, judging from their constitutional formulas, are at least as long as those of the *p*-azoxy-bodies, but which show neither a turbidity nor an anisotropism. Also, a sharply defined point of

[1] Disselhorst and Freundlich, *Physik. Zeit.*, **16**, 419; **17**, 117, also Elster and Geitel, *Festschrift*, page 453 (1915), as well as Freundlich, *Zeit. f. Elektrochem.*, **22**, 27 (1916).

[2] *Physik. Zeit.*, **9**, 708 (1908); **10**, 32, 230 (1909).

clarification would not be expected according to the swarm hypothesis. Rather it would be expected that the thread-like swarms would dissolve gradually with rising temperature, and that consequently the anisotropy would disappear little by little.

The third view[1] is the most conservative: in place of the molecules or the swarms of molecules there are postulated particles the presence and the alinement of which are the cause for the chief properties of the anisotropic liquids. These particles are probably droplets as well as crystallites. It appears that in the long dispute with respect to the structure of the anisotropic liquids, the facts speak most distinctly for this, the most conservative of the three explanations.

2. The Esters of Cholesterol and Phytosterol

These esters, as well as the original cholesterol and phytosterol crystallize from suitable solvents in large, well-formed crystals with definite melting points. Crystallization from melts is not so easy, however—numerous crystallization centers form, but these develop only slowly to spherulites. The maximal C. V. of these spherulites is very low and in consequence very small spherulites remain in the melt for a long time during cooling. Their size determines the color of the liquid in which they are suspended. These colors can be very lively and, with different substances in the group, very different. Between crossed Nicols the liquid in which these spherulites occur appears bright, but the layers in which the spherulites disappear on melting become black, while the other layers remain bright, and it appears as if there were two liquids, one isotropic and one anisotropic, which occur in streaming motion in streaks or other forms. It is not difficult, however, to convince oneself that actually there are not two liquids but only one, in which at one time numerous spherulites are suspended and at another, none.

The cooling of melts of cholesterol laurate and of cholesterol nonylate, and that of photesterol butyrate as well as its isobutyrate, produce a color which disappears with the growth of the spherulites which caused it; and upon further cooling a second kind of spherulite appears, which in turn gives rise to a color. In this case, as in others, there is no ground for assuming the formation of

[1] G. Tammann, *Ann. d. Phys.*, **4**, 524 (1901); **8**, 103 (1902); **19**, 421 (1906).

a second liquid anisotropic phase; there occurs only the formation of nuclei of the second kind of crystal which may be observed independently of this, though the number of nuclei be very large and its C. V. unusually small.

3. Soft Crystals

To this class belong divers substances which have the property in common of becoming very plastic under particular conditions, but which, unlike liquids, are not deformable by infinitesimal forces. To O. Lehmann belongs the credit for having called attention to the plasticity of silver iodide in the neighborhood of its melting point. Many metals and intermetallic compounds are so plastic at high temperatures that they are deformed under the influence of their surface tension and then exhibit spherical or ellipsoidal structures in preference to the usual polyhedral structure. On the other hand, the polyhedral form of a crystal is always an indication that its solidity cannot be overcome by its surface tension. If with rising temperature the surface tension become greater than the solidity, a rounding of the corners will first take place and finally the crystal will assume a completely spherical or ellipsoidal form.

In order to avoid misunderstanding in the discussion of liquid crystals it is necessary that there be no disagreement over the meaning of the word liquid. The word is here applied to these states in which the substance concerned can be deformed by infinitesimal forces. Accordingly, a substance which will not assume an even surface when a layer of it is placed upon a plane is not designated as liquid. The question will be raised as to the lower limit of the force which is able to effect deformation. For an isotropic substance this force will approach zero as the temperature of the substance rises through the softening range. For a non-isotropic, chemically homogeneous substance possessing a lattice structure, this force will have a finite end-value with rising temperature, since the crystalline forces which maintain the lattice structure to the temperature of the melting point, and therefore possess a finite value to this temperature, will require that a finite force be applied for the distortion of the lattice structure. It is evident, therefore, that a finite force is always

required for the deformation of an anisotropic substance, whereas an infinitesimal force suffices to deform an isotropic substance.

From this standpoint the clear anisotropic bodies produced by D. VORLANDER,[1] especially the esters of the type which have abnormally high rotatory power for the plane of polarized light, cannot be designated as liquid since they neither assume a plane surface when spread in a thin layer upon a glass plate (figure on page 2043). nor flow through glass capillaries under their own weight when brought to the temperature of the melting point.

In summary it may be said that the existence of liquid crystals, or anisotropic liquids, among chemically homogeneous substances has not been established up to the present time. The turbid anisotropic liquids of the *p*-azoxy-bodies are not chemically homogeneous, and their optical properties are conditioned by anisotropic and isotropic foreign bodies. The turbid liquid crystals of the esters of cholesterol are suspensions of spherulites in an isotropic liquid, and the clear bodies of VORLÄNDER with abnormally high rotatory power are not liquid crystals, but soft crystals.

[1] *Berl. Ber.*, **41**, 2033 (1908).

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