THE ELEMENTS OF METALLOGRAPHY

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OF
METALLOGRAPHY

BY

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PRIVATDOZENT AT THE UNIVERSITY OF GOETTINGEN

AUTHORIZED TRANSLATION

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Dedicated

TO

PROFESSOR Dr. G. TAMMANN

IN

GRATEFUL TOKEN OF ESTEEM

AUTHOR'S PREFACE.

Our knowledge of the constitution of metallic alloys has advanced surprisingly within the last few years. This has been brought about for the most part by careful study of solidification and transformation processes and by application of the doctrine of heterogeneous equilibrium to such processes. Thus, a recital of the methods by means of which these results have been obtained, must constantly rest on the basis of the above doctrine. However, the presentation which we have before us is not intended for the exclusive use of such readers as are thoroughly familiar with the principles of physical chemistry, but rather for anyone who is conversant with the fundamental facts of experimental chemistry and physics. It does not, therefore, presume knowledge of the doctrine of equilibrium.

For the above reason, I have deemed it necessary at the outset to repeatedly point out how the so-called fusion diagram originates in the collective arrangement of evidence furnished by the individual experiments, in order that its exclusive significance as a concise and lucid summary of the experimental results may be brought prominently into view. I have accordingly made no extended use of the phase rule. When this is adopted as a basis for the discussion, much abridgment is of course possible. On the other hand, there is on the part of the beginner a certain disinclination to use the phase rule — not without good reason in my opinion, for although it does, indeed, furnish a general view of possible equilibria and a means for their classification, it is less serviceable as a key to the understanding of individual cases. Finally, it did not appear advisable to consider the gas-phase, since this scarcely possesses any practical bearing upon the problems in hand.

It will, perhaps, seem to many that the space devoted to theoretical discussion is somewhat too great when compared with the actual material which it includes. I have desired, however, to avoid a possible contingency that the reader who manifests a lively interest in the topics which lie before us, fail to master eventual difficulties, and thus emerge imperfectly informed on the subject. Included material which is not essential to the preservation of continuity is distinguished by small print, or collected in the shape of supplementary matter at the close of certain chapters. I have presented only a limited number of examples, *i.e.*, such as seem of service in illustrating general developments. Those which are introduced at the beginning are subjected to rather detailed treatment, and are for the most part chosen from work which has been carried out in the *Institute for Inorganic Chemistry at Goettingen.*

In the practical part of the book, I have described at length only such experimental appointments as have been developed, or are in use at this Institute, and which, therefore, come within range of my own experience. Dimensions and sources of reference relative to such apparatus, etc., as are not generally familiar have been appended.

It is intended that this text shall place the reader in a position to intelligently follow the literature which pertains to the subject, and, in any specific instance, to use the methods which are depicted herein, and which are by no means restricted in their application to METALLOGRAPHY, in the solution of chemical problems. Two works of similar title exist at present in the German language. E. HEYN'S "*Die Metallographie im Dienst der Hüttenkunde*" particularly conforms to the purpose of awakening interest in, and furthering the understanding of, the subject in metallurgical circles. The aim of the other work "*Einfuhrung in die Metallographie*"[1] by Paul Goerens probably corresponds closely to that of the present text, although this author embodies a somewhat different course of procedure. I venture to hope that my presentation as well may win a certain friendly appreciation.

My entry into this field of activity has been chiefly furthered by Professor Tammann, and in the preparation of this text I have been fortunate in the possession of much valuable advice from this source. I take the liberty at this time of giving expression to my feeling of gratitude for his ever willing assistance in terms of the preceding dedication.

Dr. Fr. Doerinckel has rendered valuable assistance in proofreading.

R. RUER.

GOETTINGEN, *July*, 1907.

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[1] English translation by F. IBBOTSON (Longmans, 1908).

TRANSLATOR'S NOTE.

PROBABLY by far the greater number of those who are accustomed to deal with metal and alloy problems have devoted little or no attention to physical chemistry and, while scarcely able to repress some degree of interest in recent scientific developments under the head of METALLOGRAPHY, have felt disinclined to undertake a serious study of these new ideas and methods owing to unfamiliarity with the principles of physical chemistry which are involved. Dr. Ruer's book should prove serviceable to this class of workers, largely because he has made a worthy effort to render a detailed and clear explanation of the most essential scientific principles underlying the subject.

The student of metallurgy or of engineering stands in very much the same position. No great amount of time can be spent in acquiring a theoretical foundation for this class of work, and yet some knowledge of general deductions, *i.e.*, of the structural relations in alloy mixtures, is highly desirable. There can be no doubt that any careful reader who is reasonably well informed on general chemistry and physics will readily follow the discussion in this book and gain a reliable conception of the various conditions which may be encountered when metals are alloyed with one another.

While the author intended that this book should serve as an introduction to the subject and in no sense as a handbook, it is certainly true that many readers, after becoming generally familiar with the text, will particularly desire the presence of some reference material, so that their own special interests may be served. An elaborate addition in the shape of a catalogue to all investigations in this field would require much space and would interfere somewhat with the author's plan, but I have appended a complete list of references to binary fusion diagrams of all investigated systems composed of twenty-three chosen metals.

These include all of the metals which have been somewhat extensively studied in the present connection. The references are arranged in an order based upon the periodic system — from sodium to palladium. All possible binary combinations embracing these twenty-three metals are listed, but those which have not yet been investigated are placed in brackets. The reference for any chosen pair will be found under the metal listed first.

C. H. Mathewson.

New Haven, *June, 1909.*

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INTRODUCTION.

GENERAL CONCEPTION AND PURPOSE OF THERMAL ANALYSIS.

METALLOGRAPHY deals with the constitution of metallic alloys and with the methods which are employed in the investigation of such constitution.

Solidified metals and alloys are crystalline in their general make-up. The crystallization of an aqueous solution and the solidification of a molten alloy are completely analogous processes. Nevertheless, owing to the widely different temperatures at which these respective processes are realized, it is not feasible to extend the well-known methods of investigating crystallization processes in aqueous solution to analogous processes in alloy mixtures. Direct observations on the deposition of crystals, and separation of these crystals from the mother liquor for purposes of chemical analysis, constitute operations which are incapable (or only with extreme difficulty capable) of realization in a metallic alloy —presumably in a condition of red heat at its freezing point. We are, then, led first of all to investigate the completely solidified alloy. However, information developed on these grounds must, from the very nature of things, be incomplete. For this reason, much energy has been expended in searching for methods by means of which the same degree of accuracy can be obtained in interpreting crystallization processes in a white-hot molten material and ascertaining the composition of crystals and residual mother liquor, as has long been possible with the older methods in the case of aqueous solutions.

The desired end has been attained by systematically analyzing certain phenomena which attend crystallization. As such, we may cite the volume change to which a melt is subject during crystallization. Again, the change in heat content which is associated with change in state of aggregation may serve the same purpose. This latter method is particularly suited to the matter in hand, since, in the observation of rate of cooling or rate of heating of a substance, we possess a very convenient means of securing an approximate estimate of the differences in its heat content at various temperatures. The method under consideration, which has been designated "*thermal analysis*" by TAMMANN, will be presented in detail in the following pages.

It follows from the above that the application of this method is not restricted to the investigation of metallic alloys, but that the selfsame method serves as well in the general study of crystallization processes in a melt of any kind.[1] Thus, it is of importance to inorganic chemistry. It finds further application in the fields of mineralogy and geology, as regards the constitution of rocks and minerals which have been formed on crystallization from the molten magma. In this connection, the investigations of DOELTER,[2] VOGT,[3] DAY AND ALLEN,[4] and RINNE[5] may be mentioned. Nevertheless, metallic alloys, on account of their good heat conductivity and their particular capacity for crystallization, offer the least experimental difficulty in the application of this method, and are, therefore, excellent objects to serve by way of its further development.

[1] *Cf.*, *e.g.*, HEYN, Copper and Cuprous Oxide, Contributions from the Royal Technical Experiment Station, Berlin, 315 (1900); RUER, Lead Oxychlorides, Z. anorg. Chem., 49, 365 (1906); PLATO, Z. phys. Chem., 58, 350 (1907).

[2] *Cf.* here, DOELTER, Physico-chemical Mineralogy, Leipzig (1905).

[3] VOGT, Fused Silicate Solutions, Christiania (1903).

[4] DAY and ALLEN, Z. phys. Chem., 54, 1 (1906).

[5] RINNE, New Year Book of Mineralogy (1905), I, 122.

PART I.

THEORY.

THE ELEMENTS OF METALLOGRAPHY.

CHAPTER I.

ONE COMPONENT SYSTEMS.

§ 1. Graphical Representation.

Assumed that a body continually changes in temperature as a result of varying addition and abstraction of heat. We will proceed to follow the course of this change by making successive temperature observations at the end of small time intervals — every ten seconds, for example.

TABLE I.

Elapsed time in seconds.	Temperature in degrees.	Elapsed time in seconds.	Temperature in degrees.	Elapsed time in seconds.	Temperature in degrees.
0	10	70	132	140	186
10	30	80	145	150	187
20	50	90	153	160	183
30	70	100	162	170	175
40	90	110	170	180	162
50	105	120	175	190	138
60	120	130	181	200	110

The results of these measurements may be recorded in a table (see Table 1). The time, in seconds, which has elapsed since the beginning of observation is entered in the first column of this table, and the temperature in degrees corresponding to each time measurement, in the second column. We are in a position to conclude from this table that the temperature of the body rises at first rapidly, then more slowly, and thereupon falls at a rate which is at first moderate and subsequently becomes rapid. If the observations have been made at the end of vanishingly small time intervals, the temperature of the body may be calculated for any time between two of these intervals. Such calculation rests upon an assumption that the temperature varies uniformly at all points between two successive intervals.

Although a table of this sort furnishes complete information with regard to the temperature condition of the body during the period of observation, it is devoid of all pictorial effect. Graphical representation, wherein a geometrical picture is substituted for the table, is not open to this objection. For this purpose, we choose a right angled coordinate system, *i.e.*, we draw two straight lines *OM* and *ON* (Fig. 1) in the plane of the paper (which latter may be the common form of coordinate paper found on the market) meeting at right angles in the point *O*. This point is called the origin, while the two lines are named the axes of the system: *OM*, the axis of abscissas, and *ON*, the axis of ordinates. Starting from the point *O*, we lay off a number of equal spaces upon the axis of abscissas *OM* to represent the lapsed time in units of ten seconds. The temperature in degrees centigrade is represented in analogous manner along the axis of ordinates. To any point *X* in the coordinate system, there corresponds a certain time, measured by the distance *OA* (called abscissa), and a certain temperature, measured by the distance *OB* (ordinate). These distances *OA* and *OB* are obtained by dropping perpendiculars from the point *X* to the axes *OM* and *ON* respectively. In the present example, the point *X* corresponds to a time of 21 seconds and a temperature of 31 degrees.

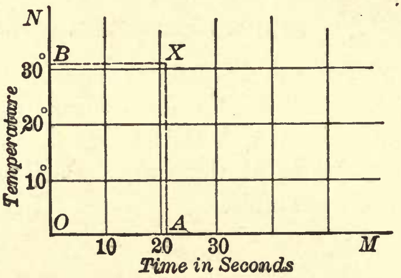

FIG. 1.

The figures of Table 1 are represented graphically in the above manner in Fig. 2. Now imagine that verticals be erected upon the axis of abscissas at ten-second intervals and at lengths which are proportional to the temperatures observed at the respective time values. The end points of such imaginary verticals are denoted by crosses. On passing a continuous curve through these end points, we are in a position to at once read off the temperature which the body possessed at any time between two values for which actual observations were made. The distance of any point upon the curve from the time axis represents the temperature, while that portion of the axis of abscissas marked off by a vertical dropped from this point, represents the corresponding time value. This method of ascertaining temperatures which have not been observed directly is more accurate in principle than the above-mentioned process of calculation, which rests upon the assumption that change in temperature be *uniform* throughout a definite time interval; a condition represented geometrically by a straight line, instead of a curve, from one point to the other. Obviously, the results which appear in such a continuous curve may be duplicated by the use of a suitable method of calculation, although the operation is not equally simple.

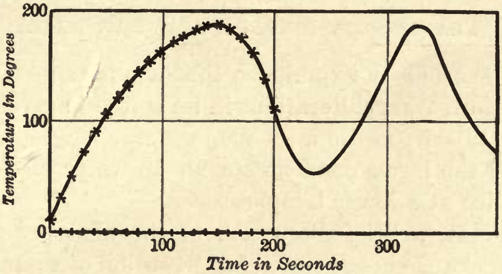

FIG. 2.

The chief advantage to be ascribed to graphical representation consists in its quality of rendering the prevailing conditions broadly apparent at a glance. Where the scale may be chosen at will, experimental results can be reproduced as accurately in this manner as through the figures of a table. In general, the choice of a scale is subject to certain restriction on the ground of practicability. For this reason, both methods of representation, tabular and graphical, are ordinarily used; the former in accurately reproducing experimental results, and the latter in securing a general systematic view of the whole field.

We shall give preference to graphical representation in the following pages and in general imagine the results, which are presumed to represent observations at sufficiently short intervals, continuously joined by a curve, without notation of the separate determinations. This has been done in the last half of Fig. 2.

§ 2. TRANSFORMATIONS OF A PURE SUBSTANCE.

We have learned by experience that a pure substance may in general sustain various alterations in its state of aggregation without change in composition. Thus, water changes to steam on heating, and the latter condenses again to water on cooling — or solidifies to ice at a lower temperature.

At this point, a brief discussion of the heat processes which occur during change in the state of aggregation of a pure substance, particularly during change from the crystalline into the liquid state and conversely, seems essential.

In common with TAMMANN[1] we shall avoid the term "solid" in defining a state of aggregation, since its meaning is not sufficiently well defined for purposes of classification. This term has been commonly applied to the crystalline as well as to the amorphous state of a substance, and in this connection implies that the individual particles of substance when assembled in either of these states offer considerable resistance to mutual displacement. Now, a crystalline material is especially characterized by properties which are partly directional in nature, *i.e.*, different in different directions. On the other hand, amorphous or glassy substances possess properties which are identical in all directions; such substances are isotropic, after the manner of liquids and gases,[2] and are consequently more closely related to the latter forms than to crystalline bodies. We are at liberty to consider amorphous bodies as liquids of high viscosity. In corroboration of this view, we find that an amorphous body changes its viscosity continuously on heating, passing without discontinuity from a glassy liquid to a mobile one, while transformation of a crystalline body to an isotropic liquid is discon-

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[1] *Cf.* TAMMANN, Krystallisieren und Schmelzen, Leipzig, 1903.

[2] "Liquid crystals" are disregarded above. Admitting their existence as proven, we should be obliged to distinguish between isotropic and crystalline liquids. The term liquid is used here in the isotropic sense alone.

tinuous, *i.e.*, characterized by sudden change in all of its significant properties. Continuous transformation in the latter case has never been observed, and is, according to TAMMANN, inconceivable.

A considerable number of pure substances are capable of being transformed from the crystalline to the liquid state without sustaining chemical alteration: they melt without decomposition. Other substances are not fusible without decomposition. In due course of time we shall become acquainted with instances wherein a crystalline substance when heated decomposes to melt and a new crystalline variety. For the present, no attention will be devoted to such substances as fuse with decomposition.

When a pure substance melts, the process occurs at a definite temperature which we call the melting point. Strictly speaking, the melting point depends upon the external pressure, and, in general, increases with the pressure; two substances only whose melting points are lowered by pressure are known. These are water (H_2O) and bismuth (Bi). The change in melting point with pressure is, however, very inconsiderable; in no known case exceeding 0.03° per atmosphere. In metallographical investigations, all determinations are usually carried out under a pressure of one atmosphere, *viz.*, in vessels which communicate freely with the atmosphere, and such changes in melting point as are due to variations in atmospheric pressure can hardly reach a thousandth of a degree, being of far lesser consequence than the errors which are associated with ordinary temperature determination. We shall, therefore, disregard all such changes.[1]

In order to transform a unit weight of a substance, 1 gram for example, from the crystalline state to the liquid state, it is necessary to add a definite quantity of heat. This heat quantity is called the latent heat of fusion (per gram) of the respective substance, and is measured in calories (cal.), *i.e.*, that quantity of heat which is required to elevate the temperature of 1 gram of water 1 degree.[2] When, on the other hand, a substance is changed from the liquid state to the crystalline state, this occurs

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[1] Atmospheric pressure is regarded in the present sense as mechanical pressure operating upon the melt from without.

[2] *Cf.* here NERNST, Theoretische Chemie, IV Ed., p. 11.

at a temperature which is identical with the melting point (in the absence of supercooling), and which is called the freezing point, while during the process a definite quantity of heat, equal to the latent heat of fusion, is liberated. This heat of crystallization, or of solidification, must be removed from the body in proportion as it is liberated, in order that the process of crystallization may continue. If heat addition or heat abstraction is suspended, the previously started fusion or solidification cannot proceed, *i.e.*, crystal and melt are capable of coexistence for any length of time at the temperature of the melting point: they are both "stable" at this temperature.

When heat from without is added to a crystalline substance of an integral nature, and one which melts without decomposition, its behavior may be detailed as follows, in line with previous explanations. First of all, the temperature of the body rises slowly until its melting point is reached. We know from experience that fusion begins at this temperature, and some portion of the added heat will of necessity be utilized in transforming the body from the crystalline state to the liquid state. Just what fraction of the supply this actually is, cannot be stated *a priori*. The process of fusion might require a certain finite length of time whereby the supply of heat could be more rapid than the ensuing fusion. On the other hand, the rate of fusion might be so rapid that the rate of heat supply, even though great, would be inappreciable in comparison. In the first case, we would have a more or less retarded temperature rise, depending upon the relation between both rates. A period of perfectly constant temperature during fusion could be expected in the latter case only. It is this latter condition which is experimentally realized. The rate of fusion at the melting point is so great that any rate of heat supply which may be attained in practice is negligible in comparison. Very recent observations by DAY and ALLEN[1] and by DOELTER[2] on feldspar and quartz seem, nevertheless, to indicate that superheating may be associated with these particular substances. Still we are abundantly justified in disregarding this evidence when considering the special subject of metals and alloys, in view of the fact that no indication

[1] DAY and ALLEN, Z. phys. Chem., 54, 1 (1906).

[2] DOELTER, Z. für Electrochemie, 12, 617 (1906).

of similar behavior has ever developed relative to these substances, nor is such to be expected on the basis of general experience. Thus, the temperature of our body will remain constant at its melting point until the last crystal has melted; then only can further heat addition be attended by temperature elevation. It is clear that heating experiments, as outlined above, are adapted to the determination of melting points.

A molten material will behave as follows on being allowed to cool (removal of heat) below its point of solidification (melting point). At first, a fall in temperature follows heat abstraction. Experience has shown that crystallization does not necessarily ensue when the melting point is reached. Many substances may be retained in a liquid or amorphous-glassy state at temperatures far below their melting points, and there is reason to suppose from the investigations of TAMMANN[1] that the greater number of substances could be obtained in the glassy condition by sufficiently rapid cooling. There are various ways of preventing the supercooling of a substance. In many cases, mere stirring is efficient in this respect. When this fails, however, the desired effect may almost invariably be secured by introducing a small crystalline fragment, and stirring at the same time if necessary.[2] It should, however, be noted that even this expedient cannot be depended upon to increase the rate of crystallization indefinitely. According to TAMMANN's investigations (l. c., from p. 131), the rate at which a liquid or an amorphous body becomes transformed to the crystalline state actually depends upon the following two factors:

(1) the number of crystallization centers (nuclei) which are formed within the liquid in a unit time, and which depends upon the temperature to a pronounced extent, and

(2) the linear rate of crystallization, *i.e.*, the rate, measured in millimeters per minute, or otherwise, at which crystalline growth proceeds after inception at some point, and under the assumption of sufficiently rapid heat abstraction. This is also essentially a function of temperature, and, in addition, varies enormously with the substance.

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[1] Kristallisieren und Schmelzen, p. 155.

[2] The efficacy of stirring is probably due to uniform distribution of small crystals which have formed in cooler portions of the melt — on the surface for example.

Now, by inoculation, we are able to increase the number of crystalline nuclei only; the linear rate of crystallization is thereby unchanged. If the linear rate of crystallization in the vicinity of the melting point is very small, the actual rate of crystallization may remain less than the rate of heat outflow as determined by experimental conditions, in spite of the large number of crystalline nuclei produced by inoculation and stirring. In such case, a more or less retarded fall in temperature, instead of a period of constant temperature, will be observed during solidification.

The rate of crystallization is extremely small for many silicates. (We have noted that these substances give evidence of possible superheating.) This condition seriously hinders the study of their constitution. Metals and alloys appear more favorably in this respect. It is true that marked supercooling of metallic melts not infrequently occurs, but inoculation and stirring invariably suffice to relieve this abnormality, since the linear rate of crystallization in the vicinity of the melting point has always been found sufficiently rapid in these cases to render any rate of heat outflow which may ordinarily be attained experimentally, negligible in comparison, viz., incapable of the above disturbing effect. Here, as well as in the rest of the theoretical discussion, we shall neglect the possibility of appearance of supercooling, and shall proceed under the assumption that crystallization begins as soon as the melt has cooled to the melting temperature, and progresses at a rate which is considerable in comparison with the rate of heat outflow. It is commonly said in such a case that the reaction is "regulated by the flow of heat" alone. Under these conditions, the heat liberated during crystallization will cause the temperature to remain constant at the melting point until the last drop of liquid has crystallized.

Fusion is not the only transformation which a crystalline substance may sustain without change in its composition. We refer here to polymorphism, *i.e.*, the capability of a substance to exist in various crystalline forms. It has been demonstrated through investigations by O. LEHMANN, H. LECHATELIER and G. TAMMANN that polymorphism is a widespread property of substances in general. Our attention shall be confined to such transformations as are reversible (enantiotropic, according to O. LEHMANN). The term reversible is applied to those transformations which, as in the case of fusion and crystallization, proceed in the one direction when heat is added, and in the other (reverse) direction when heat is abstracted. Thus, they are completely analogous to the fusion and crystallization of a pure substance. In these cases, which, as a matter of fact, constitute the smaller part of observed cases of polymorphism, there exists a perfectly definite temperature under atmospheric pressure, the so-called transformation, or transition, temperature, above which the one form is capable of existence, and below which the other form becomes stable. Both forms may exist side by side at the transformation temperature only. The crystalline form which is stable at the lower temperature is always designated as the α form; the crystalline form stable at the higher temperature as the β form. One stable at a still higher temperature would be called a γ form, etc. Addition of a definite quantity of heat is necessary in order to effect transformation of a unit mass of material from the α form into the β form. This is called the heat of transformation. Conversely, the same quantity of heat would be liberated during transformation of the β form into the α form (on cooling). The heat of transformation is usually less than the heat of fusion, although cases are known in which the reverse is true. The most conspicuous example of this is lithium sulphate. According to HÜTTNER and TAMMANN,[1] the heat of transformation is here five times as great as the heat of fusion.

A period of constant temperature will be observed at the transformation point (transition point) on heating and cooling a substance which undergoes reversible transformation, just as in the case of fusion and solidification, and this characteristic temperature may be determined in the same manner, *i.e.*, by cooling and heating experiments.

§ 3. COOLING- AND HEATING-CURVES OF PURE SUBSTANCES IN THE ABSENCE OF TRANSFORMATIONS.

We have seen that transformations, wherein we shall understand changes in state of aggregation as well as (reversible) polymorphous transformations, are made evident through certain heat effects, and may therefore be detected by observation of the behavior of a body on heating and cooling.

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[1] HÜTTNER and TAMMANN, Z. anorg. Chem., 43, 220 (1905).

We shall first endeavor to become familiar with the process of cooling for a pure substance in the absence of transformations. Suppose we are dealing with a solid body, a piece of platinum for example, at a higher temperature than its surroundings. It is assumed that the heat conductivity of the substance is so large that measurable temperature differences between the interior and the surface of the metal cannot develop. Let the body be situated in an evacuated chamber, in order that outflow of heat by means of air currents be avoided. Moreover, let the temperature of its surroundings be constant. According to NEWTON'S Law of Cooling, which is in accord with experimental results provided temperature differences are not too great, and which we may therefore adopt as the basis of our considerations, the quantity of heat given off in a unit time is proportional to the prevailing excess of the temperature of the body over that of its surroundings.

If the temperature of the body at a certain time is T, and that of the surroundings is constantly T_0, then the quantity of heat given off during the small interval of time z, within which the temperature T does not fall appreciably, is

$$w = kz\,(T - T_0), \tag{1}$$

where k represents a proportionality factor dependent upon the surface configuration of the body.

We may define w in another manner. In effect, addition or abstraction of a definite quantity of heat from various bodies causes their temperature to rise or fall, respectively, to a varying degree. As is well known, we designate that quantity of heat in calories which must be added to 1 gram of a body in order to elevate its temperature 1 degree as the specific heat of the body. When a body of the mass m and the specific heat c has cooled t degrees, it will have given off the heat quantity,

$$w = mct. \tag{2}$$

By equating both values we obtain

$$mct = kz\,(T - T_0),$$

or

$$\frac{t}{z} = \frac{k}{mc}\,(T - T_0). \tag{3}$$

Thus, t is the fall in temperature of the body during the small interval of time z, whence the quotient $\frac{t}{z} = v$ signifies the rate of cooling. We may, therefore, write equation (3) in the form

$$v = \frac{k}{mc}(T - T_0). \tag{3a}$$

Now, the mass m and the surface configuration, defined by k, are constant for the same body, while the specific heat of a solid body may be considered very nearly independent of the temperature. Thus, we replace the expression $\frac{k}{mc}$ by a single constant K and obtain

$$v = K\,(T - T_0), \tag{3b}$$

i.e., the rate of cooling is at any instant proportional to the prevailing excess of the temperature of the body over that of its surroundings.

The body therefore cools most rapidly at first, when its temperature is highest; the temperature falls throughout the same interval of time less rapidly in proportion as the actual temperature of the body becomes less, and approaches the temperature of the surroundings asymptotically (theoretically, at least), *i.e.*, it continually approaches the latter without actually reaching it. Obviously, the temperature excess of the body over its surroundings will have become so small after a certain time as to be incapable of detection with our measuring instruments.

Fig. 3, Curve 1 gives the theoretical cooling curve of a body according to Newton's Law. Time values are entered along the axis of abscissas, and temperature values along the axis of ordinates, as explained in § 1. The initial temperature is placed at 1000 degrees; the temperature of the surroundings, also called the convergence temperature, at 0 degrees. The form of the curve is determined by the factor K, according to equation (3b). Since the rate of cooling for a temperature excess of 1000 degrees is assumed to be 50 degrees in 10 seconds, K becomes (using *degrees centigrade* and 10-*second intervals* in a unit significance) $\frac{1}{20}$. Observing that $T_0 = 0$, we have

$$v = \tfrac{1}{20}\,T.$$

Thus, the body cools 50 degrees in 10 seconds at 1000 degrees, 40 degrees at 800 degrees, 10 degrees at 200 degrees, etc., as may be seen from Curve 1. Such a curve is known as a logarithmic curve.

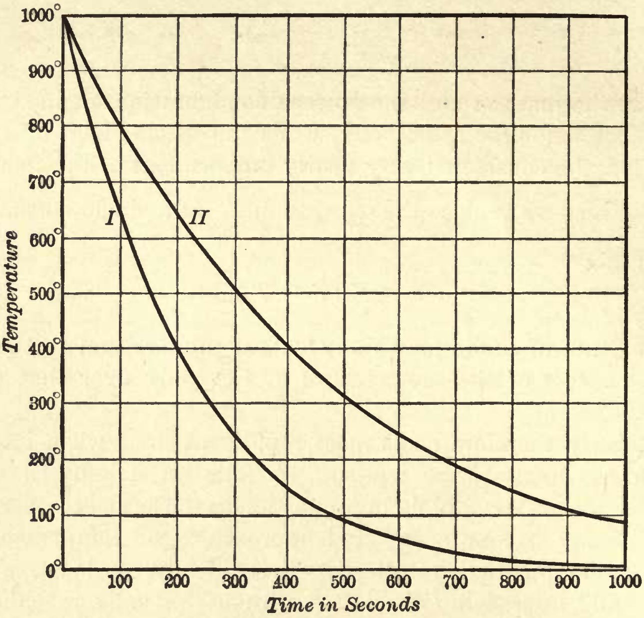

FIG. 3.

Turning once again to the first form of equation for the rate of cooling, viz., (3a),

$$v = \frac{k}{mc}(T - T_0),$$

we shall be able to draw certain conclusions relative to the rates of cooling of two bodies of different nature. For this purpose, all consideration of the surface configuration of the materials — determining the factor k — may be eliminated by placing each substance in a similar vessel of thin, polished platinum foil, so that each attains the same surface. Moreover, we shall assume the use of equal weights of the different substances for these comparative experiments, whence m and k as well, become constant. Let the specific heats of the two substances, again regarded as independent of the temperature, be c_1 and c_2. Now, if $T - T_0$ also be chosen equal for both bodies, we obtain

$$\frac{v_1}{v_2} = \frac{c_2}{c_1}. \tag{4}$$

This expression signifies that the rates of cooling of equal weights of two bodies are inversely proportional to their specific heats where the bodies possess the same surface configuration and the same temperature excess above their surroundings.

It is clear that the periods of cooling are determined by the rates of cooling. We readily see that a body which moves at twice the rate of another body in every point of its path will traverse a given distance in half the time required by the second body. In analogous manner, it may be said here that a body which possesses twice the rate of cooling of another body at every temperature will require only half as much time as the latter to cool through the same temperature interval. Thus, if we designate the periods which two bodies with the respective rates of cooling v_1 and v_2 require to cool off to the same extent, by Z_1 and Z_2, we obtain the relation

$$\frac{v_1}{v_2} = \frac{Z_2}{Z_1} = \frac{c_2}{c_1}, \tag{5}$$

i.e., the periods during which two bodies of the same mass and the same surface configuration will cool off to the same extent, where their temperature excess above the external temperature is the same, are directly proportional to their specific heats.

This result is, in the main, apparent without extended discussion; that body which possesses the greatest specific heat, *i.e.*, which possesses the greatest heat supply per unit mass, will require the most time to give up this heat supply to its surroundings, all other conditions being equal.

Curve II, Fig. 3, gives the theoretical cooling relations for a body of twice the specific heat represented in Curve I, the initial and convergence temperatures, as well as the quantity of material and surface configuration being the same in both cases. We observe that Curve II is much flatter than Curve I, and that the periods required for traversing the same temperature interval are twice as long upon Curve II as upon Curve I.

DULONG and PETIT used the relation given in equation (5) in their determination of specific heat and discovery of the well-known law relative to atomic heats which bears their names. According to the experiments of REGNAULT, however, the accuracy of this method is not very great, principally for the reason that the fundamental requirement of sufficient heat conductivity to preclude the occurrence of measurable temperature difference in the material at hand is not even approximately realized in practice, except where good conducting solid bodies and liquids are in question.

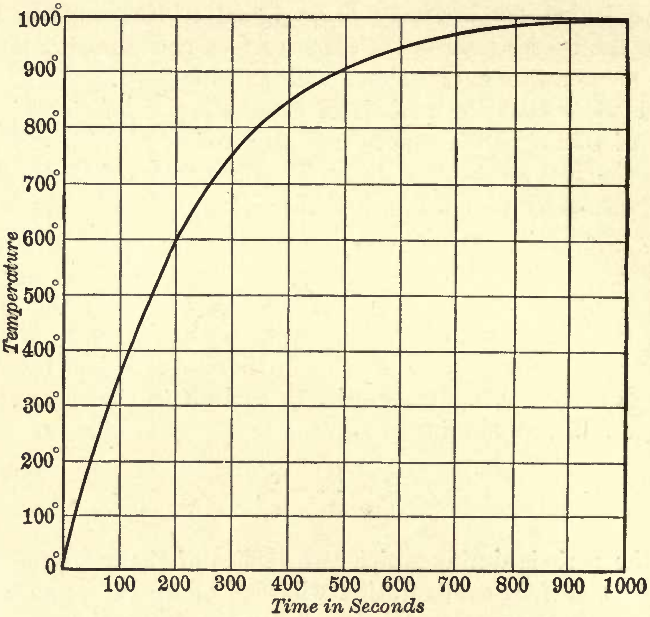

FIG. 4.

When a body possessing no transformation point is heated, conditions which are completely analogous to those just discussed are encountered. The temperature rises rapidly at first, then more slowly, and finally approaches an upper convergence temperature asymptotically. The value of this upper convergence temperature depends upon the temperature of the external source of heat, as well as upon the nature of heat insulation embodied in the experimental arrangement. Fig. 4 gives a heating curve constructed after the manner of the cooling curves already discussed.

§ 4. COOLING- AND HEATING-CURVES OF PURE SUBSTANCES IN THE PRESENCE OF TRANSFORMATIONS.

Attention is now directed to cooling and heating curves of a pure substance when transformation points occur within the temperature range under investigation. First of all, we shall consider a single transformation, viz., transformation from the liquid to the crystalline state. Suppose we are dealing with a body in the liquid condition at 1000 degrees, which solidifies to a crystalline variety at a definite temperature, *e.g.*, at 650 degrees. Let the heat conductivity of the body be so large that no measurable differences in temperature can occur within the body itself. Let there be no question of supercooling. Let the vessel containing the body be so thin that its mass, and therefore its heat capacity, may be neglected in comparison with the heat capacity of the body. Moreover, let the vessel be situated in an evacuated chamber. As in the preceding examples, let the exterior temperature (convergence temperature) be 0 degrees. Finally, we make an assumption that our experimental apparatus is so constructed that the rate of cooling at the beginning of the experiment (at 1000 degrees) is precisely that previously shown in Curve I, viz., 50 degrees in 10 seconds. If no transformation should occur, the complete course of the curve would then be determined by the formula $v = K\ (T - T_0)$; it would be identical with that given by Curve I, Fig. 3. Crystallization begins at 650 degrees, and we may assign such a value to the heat of crystallization which is liberated at this point, that it compensates the loss of heat from the body to its surroundings for 200 seconds. Suppose that the last drop of liquid has crystallized at the end of this interval, *i.e.*, that this source of heat is then exhausted. The temperature of the body now falls again according to Newton's Law of Cooling.

According to the above, the portion *ab* of the curve (Fig. 5) must be identical with the corresponding portion of Curve I, Fig. 3.

But from the point *b* the temperature does not continue to fall in accordance with the dotted continuation of *ab*; it remains constant for 200 seconds. The horizontal portion *bc* of the cooling curve corresponds to this period of constant temperature. A period of this sort is called a halting point. At this juncture, it would be simplest to assume that further cooling below *c* proceeds just as though no transformation had taken place. Representing this idea geometrically, we would displace the dotted prolongation *bb′* across the portion *bc*, causing it to continue on from the end point of solidification at *c* parallel to its previous course. In so doing, however, we should be making an assumption the qualifications of which cannot be settled *a priori*, as we shall proceed to point out. Formula (3a) for the rate of cooling (p. 13) reads

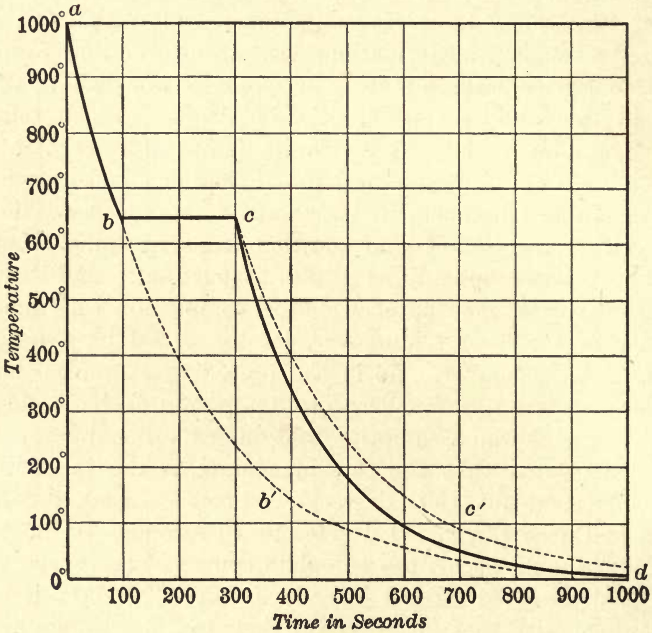

FIG. 5.

$$v = \frac{k}{mc}(T - T_0).$$

That portion of the expression which determines the rate of cooling for a given temperature excess above the surrounding is seen to be

$$\frac{k}{mc}.$$

Now, the mass has obviously remained constant, and the same is true of the factor k, which is determined by the surface configuration, since we have conducted the cooling in one and the same vessel. But the specific heat may have changed. If an assumption that the dotted curve $cc' \| bb'$ represents the temperature condition of the body from c onwards were correct, it would signify that the specific heat of the molten body had not changed during transformation into the crystalline state. This is contradicted, however, by common experience. It is quite generally true that the specific heat of a body when in the liquid state is greater than when in the crystalline state.

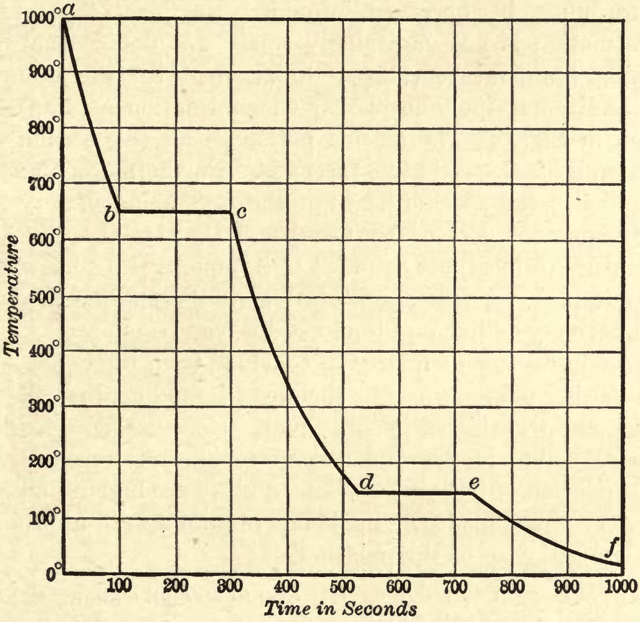

FIG. 6.

Thus, the specific heat after solidification is here greater than before. Hence the expression $\frac{k}{mc}$, signifying the rate of cooling for a given temperature difference, is greater than would correspond to a parallel displacement of the curve branch *bb'*, as described. The full branch *cd*, which is intended to represent the true course of cooling, gives expression to this decrease in specific heat, in that it falls off more steeply than *cc'*. A 25 per cent decrease in specific heat is assumed in its construction.

If, in addition to the fusion, polymorphous transformation occurs within the observed temperature interval, whereby a second crystalline variety is formed, a second period of constant temperature must be observed, provided the heat effect of this transformation is not vanishingly small. A modification of the preceding temperature changes to accord with the occurrence of an additional (polymorphous) transformation at 150 degrees is given in Fig. 6. The halting period *de* for this second transformation is also placed at 200 seconds. Furthermore, on account of simplicity, the specific heats of the crystalline variety stable at the higher temperature (β form) and that stable at the lower temperature (α form) are assumed to be equal. No generalization in this respect, as was cited relative to the specific heats of a body in the crystalline and liquid states, can be offered.

We are in no wise at liberty to conclude from the equal lengths of the halting points, viz., the distances *bc* and *de*, that the heats of fusion and transformation are equal. However, it is possible to use these values in drawing certain conclusions relative to the mutual relation of both heat effects, and we are hereby[1] possessed of a very convenient method for obtaining an approximate numerical estimate of this relation.

This may be seen as follows. The rate of cooling signifies the fall in temperature during a unit time:

$$v = \frac{t}{z} \cdot$$

According to equation (2), p. 12, the heat quantity given off throughout the temperature fall t is $w = mct$, where m represents the mass of the material and c its specific heat. Eliminating t by using the above equation for the rate of cooling, we obtain the expression

$$w = mcvz.$$

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[1] Hüttner and Tammann, Z. anorg. Chem., 43, 218 (1905).

Thus, w is the quantity of heat which the body gives up to the surroundings at the temperature in question, during the fraction of time z. This would cause a slight fall in temperature t. Now, if a fall in temperature is prevented through the agency of the internal heat source, which yields heat in the form of heat of fusion or of transformation, then the quantity of heat given up to the surroundings during every fraction of time z must have been compensated from this internal source. If, then, the heat quantity W, which has been liberated during the time Z, has served to maintain the temperature constant, it must amount to

$$W = mcvZ.$$

We are therefore in a position to determine the relation between any two liberated heat quantities W_1 and W_2 by using the cooling curves in connection with information concerning the masses and specific heats of the substances in question:

$$\frac{W_1}{W_2} = \frac{m_1c_1v_1Z_1}{m_2c_2v_2Z_2}. \tag{1}$$

Obviously, if the actual value of one heat quantity, *e.g.*, of W_1, is known, the value of the other, W_2, may be calculated at once.

No assumptions relative to the relation between rate of cooling and temperature were made during the above discussion. Formula (1) does not therefore presume validity of Newton's Law of Cooling.

When two liberated heat quantities are compared upon the same cooling curve, as in the present instance, the values m_1 and m_2 cancel from the formula, and we have

$$\frac{W_1}{W_2} = \frac{c_1v_1Z_1}{c_2v_2Z_2}. \tag{2}$$

This formula appears vague in one respect. We have seen that the specific heat of a substance depends upon the state of aggregation. In the construction of the curve given in Fig. 6, for example, we assumed a falling off in specific heat of 25 per cent on solidification. Some doubt might accordingly arise as to which specific heat were implied by the subscript 1 where the letters bearing this subscript refer to values associated with solidification. The question is, whether the specific heat of the body in the liquid or in the crystalline state should be substituted in the formula. As a matter of fact, it makes no difference which is chosen, as long as the corresponding rate of cooling is used at the same time. According to equation (4), p. 15, the rates of cooling are inversely proportional to the specific heats, for the same temperature excess above the surroundings, and similarity of other conditions (*i.e.*, the same mass and the same surface configuration). Differentiating between values which apply to the liquid and crystalline states by the indices (′) and (″), respectively we write,

$$\frac{v_1'}{v_1''} = \frac{c_1''}{c_1'}, \text{ or } v_1'c_1' = v_1''c_1'',$$

i.e., the product of specific heat and (corresponding) rate of cooling is constant. We may thus refer both values v_1 and c_1 at will to either the liquid or crystalline state when using them in formula (2), as follows:

$$\frac{W_1}{W_2} = \frac{c_1'v_1'Z_1'}{c_2v_2Z_2}, \tag{2a}$$

or,

$$\frac{W_1}{W_2} = \frac{c_1''v_1''Z_1''}{c_2v_2Z_2}. \tag{2b}$$

Now, at this point we observe that the specific heats of solid bodies are independent of the temperature within rather wide limits, provided no polymorphous transformations occur. Therefore, choosing formula (2b), in which the rate of cooling v_1'' and the specific heat c_1'' refer to the material after solidification (along *bc*, Fig. 6, in the present case) we reflect that c_1'' at 650 degrees must invariably approximate the specific heat of the body at 150 degrees, before transformation, and make the change,

$$\frac{W_1}{W_2} = \frac{v_1''Z_1}{v_2Z_2},$$

or, considering the possibility of change in specific heat during polymorphous transformation,

$$\frac{W_1}{W_2} = \frac{v_1''Z_1}{v_2'Z_2}. \tag{3}$$

In this formula, W_1 represents the heat of fusion, W_2 the heat of transformation, Z_1 and Z_2 the duration of the respective halting points, v_1'' the rate of cooling at the melting temperature after crystallization, and v_2' the rate of cooling at the temperature of polymorphous transformation before the change.

Only such values are contained in formula (3) as may be read directly from the cooling curves — knowledge of specific heats is not required in its use.

In the previous example, (Fig. 6), $Z_1 = Z_2 = 200$ seconds, $v_1'' = 43$ degrees in 10 seconds, and $v_2' = 10$ degrees in 10 seconds, whence the relation $\frac{W_1}{W_2}$ gives the value 4.3, *i.e.*, the heat of fusion is 4.3 times the heat of polymorphous transformation.

For the purpose of simplifying the above considerations, we assumed perfect heat conductivity of the substances, non-appearance of supercooling, and cooling in an evacuated chamber towards an invariable convergence temperature. These assumptions are not perfectly realized in practice. It will be shown in Part II, Practice, that v is not constant along the halting points of cooling curves obtained under usual conditions. Moreover, it is scarcely possible to exceed an accuracy of 10 per cent in the determination of halting-point periods, since a difference as large as this frequently characterizes the results from two experiments carried out under precisely the same conditions. Consequently, this method amounts to little more than an extremely convenient and simple means of estimating results.[1]

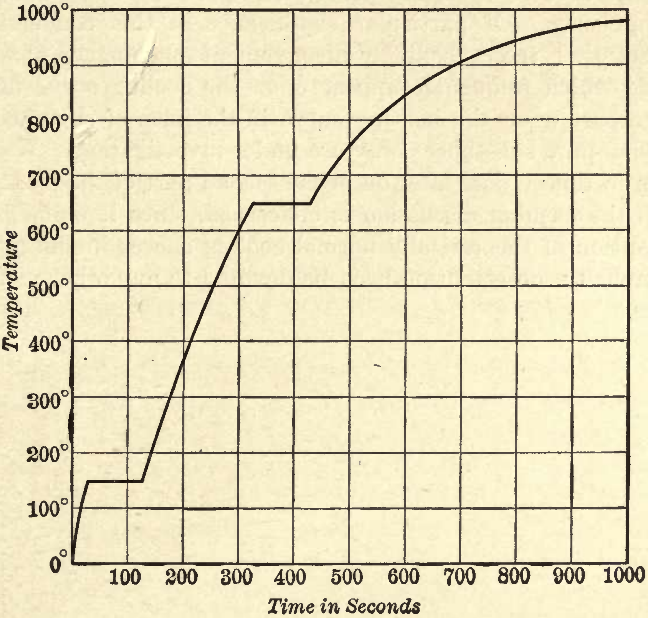

FIG. 7.

When a source of uniform heat supply is used in elevating the temperature of a body, the resulting heating curve reveals any transformation points which may exist, after the manner of a cooling curve. The temperature rises continuously (Fig. 7) up to the transformation point in question, when a period of constant

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[1] Compare PLATO relative to changes in cooling conditions, Z. Phys. Chem., 55, 721 (1906).

temperature is observed. After transformation has become complete, a second rise of temperature ensues. This culminates in the second transformation point, here the melting point, where a second period of constant temperature is observed. After complete fusion, the temperature rises for a third time, in this case, assymptotically towards 1000 degrees as an upper limit. The heating curve is of certain practical importance in checking the cooling curve. Of particular significance in this connection is the fact that the exceedingly inconvenient phenomena of supercooling which frequently appear upon the cooling curve find no counterpart upon the heating curve in the form of superheating, provided pure substances only are under investigation. We shall return to this subject later on in the second part of the book. As far as the ensuing discussion is concerned, since it embodies an assumption of theoretically normal cooling curves in the interest of simplicity, no attention need be devoted to any other modified curves.

CHAPTER II.

HETEROGENEOUS EQUILIBRIUM.

In this chapter we shall discuss certain laws of chemical statics, familiarity with which will be of value in furthering a satisfactory understanding of what is to follow.

In every investigation it is essential that the object under examination be protected from uncontrollable influences on the part of its surroundings. We shall designate those objects of investigation which may be considered immune from certain external influences, such as a flow of energy in either direction, and which may, therefore, be regarded as isolated in this sense, as *closed systems*, or, in a word, *systems*.

We differentiate between such systems as are homogeneous and such as are heterogeneous. A system is said to be homogeneous when it possesses the same physical and chemical properties in its every part, as far as any division may be affected by *mechanical* means; otherwise it is said to be heterogeneous. Thus, a gas, a liquid, or a single crystalline variety constitutes a homogeneous system, while a system composed of a gas and a liquid, or of two immiscible liquids, or of two or more crystalline varieties, etc., must be characterized as heterogeneous. Hence it appears that a heterogeneous system may be regarded as composed of two or more homogeneous systems. According to Willard Gibbs[1] the originator of the doctrine of heterogeneous equilibrium, the homogeneous systems which compose an heterogeneous system are called phases. Thus, an homogeneous system is composed of a single phase, while an heterogeneous system is composed of at least two phases.

If a system sustains no alteration on being left to itself for an *indefinite length of time*, we say that it is in equilibrium. Theoretically this is an adequate criterion, but practically it may lead to error in certain instances, namely, when the reaction velocity

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[1] Willard Gibbs, Studies in Thermodynamics, Trans. Conn. Acad., iii, 1875–8.

of the substances concerned is exceedingly small. By way of example, the well-known case of hydrogen and oxygen may be cited. A mixture of these substances may be kept for years at ordinary temperature without change. But it is merely necessary to heat the mixture sufficiently high at a single point for an instant — viz., by means of an electric spark — in order to bring about an unusually violent combination of the two gases in any quantity, provided the proper proportions are observed in the mixture. On the other hand, we are well aware that it is impossible to induce an automatically progressive decomposition of water into hydrogen and oxygen by momentarily subjecting water or steam to a high temperature. Hence, we conclude that a mixture of hydrogen and oxygen is not in a condition of equilibrium, and our experience relative to reaction velocity in general justifies the assumption that water is formed from the mixture even at ordinary temperature; so slowly, however, that the quantity produced in years cannot be detected with our available measuring instruments.

Now, there can be no doubt that equilibrium obtains wherever a process is reversible. Thus, if we observe that a closed system composed of a single crystalline variety and its melt suffers no change in the quantity of either constituent, we may convince ourselves in a very simple manner, owing to the reversibility of the process (crystallization and fusion) that equilibrium is actually at hand. For, if, on supplying heat to the system, a decrease in the quantity of crystals, and, on abstracting heat, an increase in the quantity of crystals, is observed, the invariability of our system could not have been due to a too trifling rate of reaction. The system is rather in a condition of *actual* equilibrium. We shall continue to disregard the former condition of *apparent* equilibrium, due to insufficient reaction velocity.

Since we have learned by experience that existent differences of temperature and pressure tend spontaneously towards equalization, we conclude that *the same temperature and the same pressure prevail in every part of a system which is in equilibrium.* (Obviously, all effects of gravitation, capillarity, etc., are excluded from present consideration.)

Furthermore, it is at once clear that an heterogeneous system cannot be in equilibrium unless *equilibrium prevails in each of* *the homogeneous systems or phases of which it is composed.* Hence, different parts of the same phase cannot differ in composition; equalization would be effected by diffusion.

As a further condition governing heterogeneous equilibrium, we now add that the phases must be in equilibrium among themselves. The following general principle holds relative to the effect of the quantity of each phase present:

The equilibrium is independent of the quantity of the phases.

We shall regard this as an empirical principle which has thus far stood every experimental test. (This principle is also substantiated from a molecular-theoretical point of view.[1]) Some of the simpler facts which may be provisionally introduced by way of confirming the above principle are as follows: At the temperature where 1 kilogram of ice and 1 milligram of water are capable of indefinite existence in the presence of one another, 1 kilogram of ice and 1 milligram of water are also capable of indefinite coexistence. At the temperature where a saturated solution fails to dissolve any portion of 1 milligram of the substance with which it is saturated, the solution will be just as incapable of dissolving more material when 1 kilogram is open to treatment. Thus,.the equilibrium between a crystalline variety and melt is not altered when the quantity of crystalline material is either increased or decreased. Hence, it follows that the condition of equilibrium is uninfluenced by the manner in which the crystals are distributed throughout the melt — whether in the form of one large crystal, or of many small ones. Since, according to the above principle, a single crystalline splinter suffices to determine the condition of equilibrium, no effect can attend the introduction of a further quantity of the same crystalline variety, irrespective of the manner in which the new quantity is disposed throughout the liquid. It is then evident that when a system is to be characterized by the number of its phases, each crystalline variety must be counted as a single phase only, however it may be distributed.

This latter observation may be generalized in the form of a second principle:

The equilibrium is independent of the arrangement of the separate phases.

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[1] Nernst, Theoretische Chemie, 4th ed., 1903, p. 459.

On this basis, it is immaterial which of the phases are in direct contact. If two phases *B* and *C* are both in equilibrium with the same third phase *A*, then they are also in equilibrium with one another. The proof of this self-evident principle is simple and is founded upon the experimental fact that when two substances which can react with one another are brought in contact, such reaction finally ceases. That is, a condition of equilibrium occurs sooner or later in every system, and when the latter is thereafter protected from changes of temperature and pressure a condition of rest persists. Now, our contention is that when this condition of equilibrium has once resulted in a system whose phases are arranged as in Fig. 8a, it will continue if the two phases *B* and *C* are brought into direct contact. To prove this, let the phases be arranged in a ring as shown in Fig. 8b, *B* and *C* touching one another. Let the ring be entirely closed and possessed of rigid walls, so that changes in atmospheric pressure can have no effect upon the system. To guard against temperature changes, let it be immersed in a large bath of some liquid which may be maintained at constant temperature. Now, if *B* and *C* were not in equilibrium, they would react with one another and sustain mutual alteration. Then, as soon as these two phases had reached equilibrium with one another, they would no longer be in equilibrium with *A*. On regaining equilibrium with *A*, they would again cease to be in equilibrium with one another. Thus it appears that such a system would never come to rest, a result entirely at variance with actual experience (impossibility of perpetual motion of the second kind). Hence, *B* and *C* must be in equilibrium when in contact.

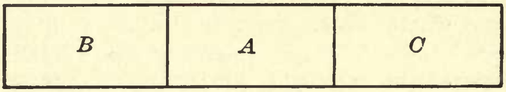

FIG. 8A.

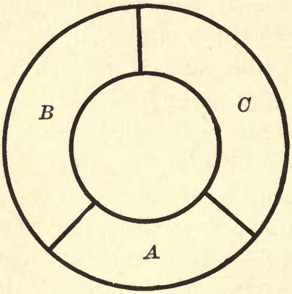

FIG. 8B.

The above argument implies a certain qualification to the effect that division of any phase shall not be carried far enough to bring the question of surface energy into prominence. As a matter of fact, the solubility of a substance depends somewhat upon its state of division; large crystals are less soluble than small ones. It is possible for such differences in solubility to become considerable when the fineness of division exceeds a certain limit. We shall omit all consideration of such cases as unimportant in the present connection.

The two foregoing principles are of particular significance in that they serve by way of differentiation between the various types of heterogeneous equilibrium which we shall encounter. In the above terms, a system is completely characterized as regards its state of equilibrium by the following classes of data:

(1) Data concerning the pressure under which the system is existent. This pressure must be uniform in all parts of the system, and we shall invariably assume the same to equal one atmosphere — regarded as mechanical pressure operating upon the system.

(2) Data concerning the temperature of the system, which must also be uniform throughout.

(3) Data concerning the number of phases composing the system.

(4) Data concerning the composition of each and every phase, and its state of aggregation; where polymorphism occurs, such data to define the modification in question.

Data relative to the quantity of material represented by the separate phases, as well as to the arrangement of phases, is superfluous in this connection.

The system may undergo change in temperature or pressure (the latter excluded under present conditions) as a result of heat addition or abstraction, etc. Again, new phases may appear, or current phases disappear. Finally, the composition of one or more phases may change. If heat addition or abstraction causes no change in the number or composition of at least one phase, but merely alters the quantity of material in any of the phases, the current condition of equilibrium remains unaffected; there is no attendant temperature change.

We shall proceed to elucidate these general relations by way of several simple examples, turning first of all to the reversible process of fusion and crystallization. Suppose that a pure substance which melts without decomposition has been heated to such an extent that a portion is in the molten condition. If the system is now protected from any flow of heat in either direction, no further change takes place; the quantity of melt and of crystalline material each remains constant for an indefinite length of time; the system is in a condition of equilibrium. Such equilibrium is characterized by the pressure exerted upon the system by the atmosphere — assumed to be invariable — by the temperature and by the number (two) of phases. The latter are described by the terms crystalline and liquid, and both possess the same percentage composition. If we proceed to supply the system with heat, transformation of a definite quantity of these crystals into liquid results. Does an elevation of temperature attend this change? Such is not possible while the crystalline phase remains at all represented in the system. For we know that the condition of equilibrium is not qualified by the quantity of material representing any phase of the system. It is merely a decrease in the quantity of crystals and an increase in the quantity of melt which we effect by heat addition; no change in the composition of either phase is brought about. Therefore the temperature must remain constant. Moreover, it cannot change until the last crystalline splinter has melted. At this point, the process of fusion becomes complete owing to exhaustion of one phase, and addition of heat is thereupon attended by elevation of temperature.

A similar line of reasoning may be employed when we are dealing with abstraction of heat from the system. The solidification process continues until the last drop of liquid is exhausted, whereupon further heat abstraction effects a fall in temperature. Thus it appears that the fusion of pure substances at definite and invariable temperature under atmospheric pressure (where no decomposition ensues) and their complementary solidification at the same temperature constitute a special case under the general principle that the equilibrium of a heterogeneous system bears no relation to the quantity of material appearing in each of the phases which make up the system.

The occurrence of polymorphous transformation at definite temperature also appears in the same light.

We shall now take up a special case which will serve to illustrate a type of phenomenon frequently observed in the alloy field, for the explanation of which we are indebted to TAMMANN.[1] It often happens that a pure inter-metallic compound fails to melt unchanged, but undergoes partial liquefaction only, when heated to the proper temperature. At the same time, a crystalline variety of different composition is separated. The reverse process occurs on cooling the mixture. Thus, VOGEL[2] observed that a gold-lead compound of the formula Au_2Pb decomposes, on heating, to melt and a new crystalline variety, viz., pure gold. In order to bring about fusion of the gold, and thus obtain a homogeneous melt, further elevation of temperature is necessary. Conversely, the first crystals which separate on cooling a melt of the composition Au_2Pb consist of pure gold, and these react with the remaining melt at some lower temperature to form the compound Au_2Pb. The stoichiometrical relations for this process are given in the following equation, which at first sight appears somewhat unusual in form:

$$Au_2Pb \rightleftarrows 0.722\ Au + \text{Melt}\ (1.278\ Au + 1\ Pb).$$

Verbally, this indicates that 1 gram molecule of the compound Au_2Pb yields when heated 0.722 gram atoms of gold and a quantity of melt. The composition of this melt in gram molecules or gram atoms, respectively, is of course given by the difference between 1 gram molecule of the compound Au_2Pb and the quantity of separated gold, *i.e.*, $(2\ Au + 1Pb) - 0.722\ Au = 1.278\ Au + 1\ Pb$.

The composition of this melt expressed in percentage form is 45 per cent Pb + 55 per cent Au.

The arrows indicate reversibility of the process, whereby the reaction may proceed towards the right or left, according as addition or abstraction of heat is brought about.

We again raise the question as to whether decomposition of the pure compound and the associated recombination of its dissociation products does or does not proceed at constant temperature. In answering this question we need only consider what takes place on cooling after the compound has once been

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[1] TAMMANN, Z. anorg. Chem., 37, 303 (1903).

[2] VOGEL, Z. anorg. Chem., 45, 11 (1905).

heated to the point where partial decomposition into pure gold and melt will have resulted. When heating has been carried thus far, and the system is isolated as regards flow of heat in either direction, we have equilibrium between the following phases:

(1) A crystalline variety composed of the pure compound Au_2Pb,

(2) A crystalline variety composed of pure gold,

(3) Melt of the composition $1.278\ Au + 1\ Pb$.

Our authority for such assertion of equilibrium lies in the observation that no change takes place within the closed system. Neither the quantity of crystals (of either variety) nor of melt changes, while the temperature remains constant under constant pressure. Now, when the system is supplied with an additional quantity of heat, further decomposition of the compound Au_2Pb into pure gold and melt ensues. In this way the quantity of "Au_2Pb" crystals decreases, while the quantity of "pure gold" crystals and that of melt increase. But, obviously, the melt formed at first possesses the same composition as that formed subsequently. The composition of each and every phase remains unchanged; the quantity alone changes. Therefore, there can be no change of temperature until the last crystal of Au_2Pb has decomposed into pure gold and melt, and it appears that a compound which melts under decomposition, as above, is as well characterized by a constant point of decomposition and of formation as is a compound which melts unchanged by a constant melting point and freezing point. We shall not hesitate to apply the more concise term, melting point, to a temperature of decomposition, for obvious reasons.

We may summarize previous developments as follows:

When in a reversible process the quantity but not the composition of the separate phases sustains alteration, owing to addition or abstraction of heat, the temperature remains constant, for constant pressure, until some phase becomes completely exhausted.

And conversely:

When, on adding heat to or abstracting heat from a system, it is observed that the temperature remains unchanged under constant pressure, it follows that the quantity but not the composition or number of the separate phases has sustained alteration.

These considerations are based upon the principle that in any system the condition of equilibrium is unaffected by variation in the quantity of any phase, or phases. Hence, they appear justifiable only in the event that the system remain continually in the equilibrium condition during addition or abstraction of heat. In other words, the process must be not only theoretically reversible, but it must be actually carried out reversibly. Thus, the reaction velocity of the process in question must in every instance be great enough to exceed the rate of addition and abstraction of heat: the process must be regulated by the flow of heat alone. When this is not the case, abnormalities, such as supercooling, etc., will develop, and the above principle become invalid.

Adopting Roozeboom's phraseology, we shall characterize that form of equilibrium in heterogeneous systems, wherein change in the quantity of separate phases, but not in their composition, is effected by addition or abstraction of heat under constant pressure, as *complete heterogeneous equilibrium*, or in a word, *complete* equilibrium.

In contradistinction to *complete equilibrium* we have *incomplete (heterogeneous) equilibrium*, wherein not only the quantity of separate phases, but the composition of at least one phase as well, is altered during the reversible process attending addition of heat to or abstraction of heat from the system. This type of heterogeneous equilibrium is well illustrated by the solidification of salt solutions. We are well aware that water may be frozen by abstraction of heat, and that ice may be melted by addition of heat. The process is therefore reversible, and may be represented by the expression

$$H_2O_{\text{solid}} \rightleftarrows H_2O_{\text{liquid}},$$

in which the arrows indicate reversibility, as on the previous occasion. When pure liquid water and ice are in equilibrium, addition of heat to or abstraction of heat from the system causes change in the quantity of each phase, but no change in its composition: the process takes place at constant temperature (at 0 degrees) under constant pressure, and we are dealing with complete equilibrium.

If we dissolve a second substance, *e.g.*, common salt, in pure water and abstract heat from the solution, it is found that pure ice separates, at least from solutions which are not too concentrated. Thus, we now have pure ice in equilibrium with a solution of common salt. Obviously, the equilibrium temperature of this system need not be the same as that of the former system (ice-water), and, indeed, we know that it is not the same. If we continue to abstract heat from the system, the quantity of ice increases and the quantity of liquid decreases. Since, however, a single constituent is removed from the liquid phase, namely, pure water, this phase becomes richer in its other constituent, namely, common salt. Hence, one phase changes in composition during this process, *i.e.*, we are dealing with incomplete equilibrium. The temperature must change as ice freezes out, and experience shows that the temperature of a freezing salt solution falls continuously (down to a certain point). If, contrary to the actual state of affairs, the composition of this solid phase were identical with that of the solution, we should look for no change in temperature during solidification.

Apart from the above classification of systems into such as show complete or incomplete equilibrium, we are called upon to consider another type of distinction between systems which are in heterogeneous equilibrium: one which is generally brought into requisition, and which will be used extensively in this text. We refer to classification according to the number of independently variable constituents or, briefly, components of the system. We have on this basis, one component systems, two component or binary systems, three component or ternary systems, etc. In the case of metallic alloys, the number of independent constituents is equal to the number of metals present, at any rate as far as the investigation deals with all possible combinations of the respective metals with one another.

Accurately speaking, a system possesses as many independent constituents, or components, as the number of different substances which are necessary, and will suffice, for construction of each and every phase in question. Consequently, this number cannot be given until the composition of each and every phase of the system under investigation is known. Moreover, it depends upon the precise nature of change considered in the system, and hence may not be placed unqualifiedly equal to the number of elements which appear in the system. A few examples will serve to make this clear. We are well aware that ice does not change in percentage composition on transformation into the liquid state. The information that ice contains *a* grams H_2O and liquid water, *b* grams H_2O per cubic centimeter is, therefore, ample for the purpose of defining the composition of each and every phase in the system, *Ice-Liquid* water. Hence, this must be regarded as a one competent system under the present specification. The same is obviously true in relation to any pure substance melting without decomposition, provided we confine our investigation to the configuration, *Crystalline-Melt.*

If, however, a substance which melts under decomposition is investigated — the compound Au_2Pb (discussed on p. 31), for example — it is found that the composition of the different phases cannot be defined in terms of Au_2Pb (*a*, *b* or *c* grams of the compound per cubic centimeter). For, one of the phases derived from the compound is lead-free, as we have seen (pure gold), and the other, viz., melt, consists of gold and lead in some proportion other than that which corresponds to the above formula. Accordingly, two substances must be used (and only two need be used) in defining the percentage composition of each and every phase. Hence, we regard this as a two component system. The choice of components is left more or less to our discretion. We choose gold as one, since one phase is composed of pure gold. When lead is chosen as the other, the atomistic composition of the three phases becomes, Au, 2 Au + 1 Pb, and 1.278 Au + 1 Pb, as explained on p. 31. But when the gold lead compound $AuPb_2$[1] is chosen as the second independent constituent, the composition of the three phases must be expressed as follows:

(1) The crystalline variety pure gold by Au,
(2) The crystalline variety Au_2Pb by $AuPb_2 + 3\ Au$,
(3) The melt $1.278\ Au + 1\ Pb$ by $AuPb_2 + 1.556\ Au$.

Either assumption is permissible, inasmuch as it is actually possible to build up the particular system by using the substances herein chosen as components. Hence it follows that in classifying systems we are free to use the number of independent constituents, but are not justified in imposing any specification as to their nature, viz., whether elements or compounds; this is more or less optional.

Suppose that the compound Au_2Pb were to undergo polymorphous transformation at some point below its decomposition temperature. Then, in studying the equilibrium between these two crystalline varieties of the same composition we should be dealing with a one component system in which Au_2Pb is the component.

Turning to a system produced by fusion of mixed PbO and $PbCl_2$[2], we note the following: As long as the correct proportions of lead, oxygen, and chlorine in each and every phase may be given in the form, *a* grams PbO + *b* grams $PbCl_2$ per cubic centimeter, the system is to be regarded

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[1] Vogel, l. c., p. 31.

[2] Ruer, Z. anorg. Chem., 49, 365 (1906).

as constructed from two independent constituents. When our investigation is restricted to the fusion and solidification process associated with the compound $PbCl_2 + 2\,PbO$ (at 693 degrees), we are dealing with a one component system, although three elements are concerned in the change. If, however, the compound $PbCl_2$ should undergo decomposition during any alteration in the system — whereby it would be necessary to indicate the composition of one phase after the manner, $a\,PbO + b\,PbCl$, and that of the other after the manner, $c\,PbO + d\,PbCl_3$ — we should be obliged to regard the system as embracing three components with respect to this particular change.

A system embracing hydrogen, oxygen and water at ordinary temperature, where no appreciable combination of hydrogen and oxygen occurs, must be regarded as a three component system, notwithstanding the fact that only two elements are present. At some higher temperature, where the above combination is sufficiently rapid, the two elements alone would appear as components. The same effect might be secured through the action of a catalysing agent, platinum sponge, for example. However, all cases of this sort do not properly belong here, since we have made an assumption of actual equilibrium in every phase to the exclusion of all apparent equilibria.

The conception of independent constituents of a phase system plays an important rôle in the doctrine of heterogeneous equilibrium, owing to the fact that an exceedingly simple relation exists between the number of phases which are in complete heterogeneous equilibrium and the number of independent constituents of the system. This was developed by WILLARD GIBBS[1] and forms what is known as the phase rule. (Cf. remarks upon this subject supplementing Chapter IV.) We shall, however, make little use of this rule in our general presentation of the subject.

In this chapter, we have dealt with those transformations which a pure substance undergoes without changing its composition, and have, therefore, made the chapter heading, ONE COMPONENT SYSTEMS. As is well known, metallic alloys are prepared by fusing two or more metals together, whence our attention is transferred to TWO COMPONENT SYSTEMS as a subject for the next chapter, and to THREE COMPONENT SYSTEMS for subsequent treatment. The investigations of the last few years have, nevertheless, been almost exclusively confined to two component systems. There have been very few systematic investigations dealing with ternary alloys, and none at all dealing with quaternary alloys.

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[1] loc. cit., p. 25.

CHAPTER III.

TWO COMPONENT SYSTEMS.

MUTUAL SOLUBILITY AND STATE OF AGGREGATION.

THE susceptibility of two substances to mutual mixture is dependent to a marked degree on their state of aggregation.

It is well known that gases are miscible with one another in all proportions. We must differentiate between two cases of miscibility in the liquid state; two liquids are either completely miscible with one another, as are alcohol and water and the greater number of molten metals, or they are miscible with one another (dissolve one another) to a limited extent only. In the latter case, the two liquids, owing to their difference in density, become separated from one another and appear in two layers after standing for a time. When the liquids are in a condition of equilibrium, each has of course dissolved the other to the point of saturation. The saturation concentration varies to an exceptional degree with different liquids, and is, moreover, highly dependent on the temperature. Water-ether and, of the metals (which may be characterized as comparatively prominent in showing this condition), lead-zinc, may serve as examples of limited solubility in one another. The extraction of silver from lead by the *Parkes Process* is founded upon the latter case of limited miscibility.

The capability of substances to mix with one another is further reduced in the crystalline state. Nevertheless, many pairs, etc., of substances which mutually dissolve in the crystalline condition in all proportions, or which, as is commonly said, form complete series of mixed crystals, are known. By way of example, we may cite silver-gold. Limited miscibility in the crystalline state is illustrated by the gold-nickel series. On account of the generally limited miscibility of substances when in the crystalline state, we frequently observe that a mixture which is homogeneous in the liquid state, separates on crystallization. Investigation of crystals which have been removed from a partially solidified mixture and freed from adherent mother liquor frequently shows that these represent one component alone, or at any rate a practically pure component. Crystallization from aqueous and other solutions, which are so commonly carried out in the chemical laboratory, afford excellent illustration of such immiscibility in the crystalline condition. The gold-thallium series will serve in this connection as an example taken from the alloy field. Thus, from a purely practical standpoint we are in a position to speak of immiscibility in the crystalline state, although this case must be theoretically regarded as an extreme condition of limited miscibility.

The varying degree of miscibility in the liquid and crystalline states serves in connection with the possible existence or non-existence of chemical compounds as a criterion for the classification of two component systems.

§ 1. The Liquid State is Characterized by Complete Miscibility; the Crystalline State by Complete Immiscibility.

The following statement summarizing a general result of practical experience will be adopted as a broad basis for subsequent developments:

When two pure substances are miscible in the liquid state and immiscible in the crystalline state, the temperature of solidification of each substance will be lowered by addition of the other.

This generalization is commonly known as the LAW OF FREEZING POINT OR MELTING POINT LOWERING. By the term, temperature of solidification, is meant the temperature at which crystallization begins.

As we have seen above, this preassumed immiscibility in the crystalline state implies that each of the two substances separates from the melt in the pure condition. If such is not the case, the law of freezing point lowering loses its validity.

A. *Polymorphous Transformations do not Occur. The Components do not Unite to Form a Chemical Compound.*

1. The Crystallization of Aqueous Solutions of Common Salt. — We will again take up the subject of crystallization of an aqueous solution of common salt, with due regard to the law of

freezing point lowering and to the views which we have acquired through previous consideration of heterogeneous equilibrium.[1] A solution of this sort represents a two component system in which the components are water and salt, and the fact that water, in the form of pure ice, separates first of all on cooling the dilute solution, while salt, likewise in the pure condition, first separates on cooling a concentrated salt solution (for example, a solution which is saturated at 100 degrees), certifies that our required condition of immiscibility in the crystalline state actually obtains. Pursuant to general usage covering such cases, we shall designate water as the solvent and common salt as the dissolved substance.

We will now assume that a dilute salt solution, containing some two and a half per cent of salt, is allowed to freeze completely, during which process continual observation of temperature is made. Owing to the freezing point lowering of water following the addition of salt, no freezing occurs at 0 degrees, the true freezing point of pure water. Separation of ice crystals is first observed at about −1.5 degrees. By reason of this separation of ice, the residual solution becomes richer in common salt; a condition of incomplete equilibrium is then at hand and we shall not expect complete solidification of the solution to occur at the above temperature, −1.5 degrees. If, then, complete solidification does not occur at −1.5 degrees, as is actually the case, it is self-evident that the freezing point of the enriched salt solution lies at a lower temperature; it could not lie higher, for then the solution would not be in equilibrium at −1.5 degrees, but would be existent below its true freezing point, or, in other words, it would be supercooled and therefore in a labile condition. We may, thus, make the general statement:

If a solution does not crystallize at constant temperature, its freezing point must fall as freezing progresses.

To secure further separation of ice, we must, then, cause the temperature to fall, *i.e.*, the freezing point of the salt solution falls, in proportion as the latter becomes more concentrated. When half of the water has frozen to ice, the remaining salt solu-

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[1] Complications due to separation of the hydrate $NaCl \cdot 2H_2O$ (Landolt & Börnstein; Phys. Chem. Tables, 3d ed. p. 556) will not be taken into account during this discussion.

tion contains 5 per cent salt, and we observe a freezing temperature of —3.1 degrees. When the solution has attained a salt content of 10 per cent, or 15 per cent, respectively, its freezing point will have fallen to —6.7 degrees, or —12.2 degrees.

Now, an unlimited depression of the freezing point of the salt solution is not possible — first of all we need consider none other than purely experimental evidence in reaching this conclusion. A solution of minimum freezing point will accordingly result sooner or later, and such a solution must obviously freeze completely at this temperature, for the very reason that it can have no lower freezing temperature. For an aqueous solution of common salt this temperature is —22.4 degrees. Thus, we observe, on allowing the freezing process to continue progressively, that the temperature sinks continuously until —22.4 degrees is reached, when further abstraction of heat is not attended by temperature fall for the time being. The thermometer indicates this very temperature until the last residue of liquid has become transformed into crystalline material. Not until then does the temperature fall below this point. It thereupon proceeds to converge towards the temperature of the surroundings.

We learn by analysis of the solution which solidifies at —22.4 degrees that it contains 23 per cent of common salt and 77 per cent of water. A solution of this concentration solidifies at constant temperature, after the manner of a pure substance. But such a period of constant temperature during abstraction of heat from the system is our criterion for the existence of complete heterogeneous equilibrium. In effect, throughout this period the composition and the number of phases can sustain no alteration. That is to say, the frozen material must possess the same composition as the solution. This conclusion is apparently substantiated by experiment, for, when a partially frozen aqueous solution of common salt is viewed under the microscope, two different crystalline varieties, viz., ice crystals and common salt crystals, may be plainly recognized.

The mechanism of the process is clear in the light of the above observation. Further concentration of the solidifying 23 per cent salt solution is prevented in that not only ice crystals but salt crystals as well separate from it on continued abstraction of heat. Moreover, these two crystalline varieties separate from the solu-

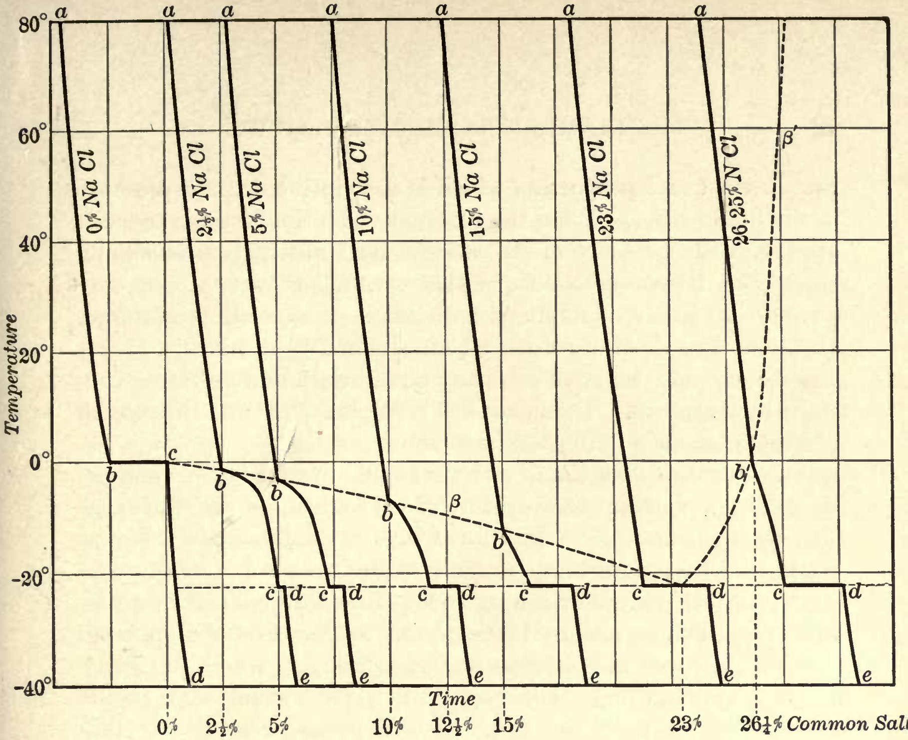

FIG. 9a.

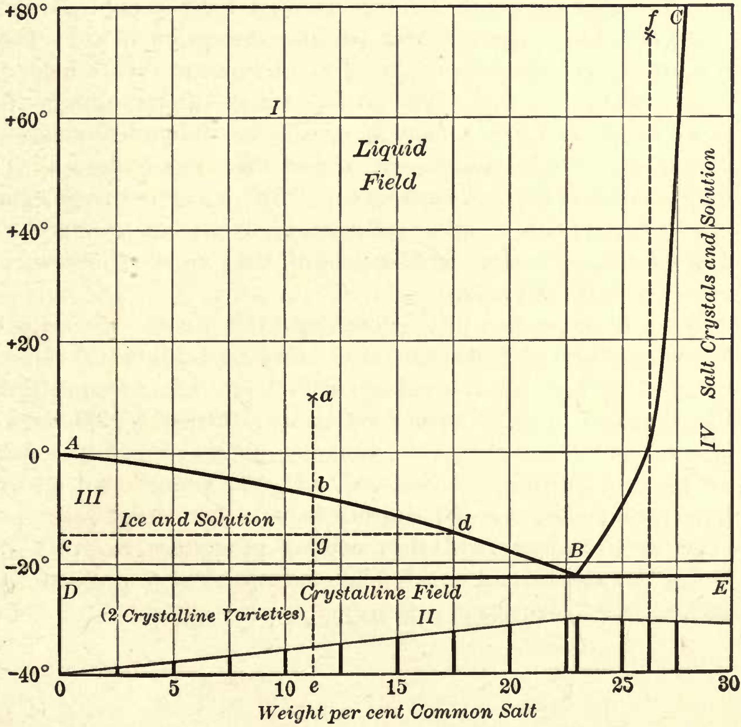

FIG. 9b. Fusion Diagram of the System Water-Common Salt. (41)

tion in the exact proportion which is descriptive of their presence in the liquid state. From the moment when the first salt crystals appear in the presence of ice crystals, heat abstraction effects no change in the composition of either crystalline variety, but only an increase in the amount of both kinds of crystalline material. Until the last drop of solution has solidified to a mixture of salt and ice crystals, we have complete equilibrium and therefore constant temperature. Then only is it possible for further abstraction of heat to cause a fall in temperature.

A 23 per cent solution of common salt in water is thus characterized by a constant temperature of crystallization and fusion, as is a pure substance. A mixture which crystallizes and fuses as above at a minimum temperature is called an *eutectic mixture*, or, simply an *eutectic*. For a long time, such solutions and mixtures were regarded as chemical compounds owing to their constant melting points — notwithstanding the difficulty which is experienced in representing their composition by formulas in proper correspondence with the law of multiple proportions. It is a noteworthy fact that GUTHRIE,[1] who proposed the term eutectic mixture, and to whom we are indebted for the explanation of these conditions (particularly for our perception of the general conformity in behavior of solutions and alloys in this connection), maintained in his first paper dealing with aqueous solutions that those substances which melt at constant (minimum)temperature were chemical compounds, and named them cryohydrates. This too, in spite of the fact that he correctly interpreted the mechanism of the process in all of its details. The term cryohydrate is applied now and then at the present time to such eutectica as consist in part of water.

We will proceed to further elucidate the process of cooling for water and variously concentrated aqueous solutions of common salt by making use of cooling curves — it being assumed that the cooling converges towards a temperature of −100 degrees. We will at the outset suppose that the quantity of solution taken for every experiment is identical, *e.g.*, 100 grams; that all solutions are heated to 100 degrees before the actual registry of experimental data; and that cooling progresses in every case under the same conditions. The curve marked *0 per cent NaCl*

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[1] GUTHRIE, Phil. Mag., v, 17, 462 (1884).

in Fig. 9a (p. 41) represents the cooling of pure water whose freezing point lies at *0 degrees C.* Such values may be conveniently assigned to the time units, which are entered upon the abscissa axis, as will bring the period of constant temperature for pure water, represented by the portion *bc*, up to 10 minutes. The scale of temperatures along the axis of ordinates is shown in the figure. The above mentioned cooling curve is made up of the three parts *ab*, *bc*, and *cd*, of which *ab* corresponds to the cooling of liquid water, *bc* (halting point) to crystallization, and *cd* to the cooling of ice towards the temperature of convergence.

The curve marked *2½ per cent NaCl* (Fig. 9a) represents the cooling of a 2½ per cent solution of common salt in water — which process has been described previously at some length. Ice crystals first separate at the point *b*, corresponding to −1.5° C. Owing to the heat liberated during crystallization, a decrease in the rate of cooling begins at this point, which condition is shown on the cooling curve by a break at *b*. At first, as ice begins to separate, the temperature sinks very slowly — when the substance has become half crystallized, *i.e.*, when the residual liquid has become a 5 per cent solution (NaCl in H_2O), the temperature has fallen only 1.6 degrees, having reached the value −3.1° C. Since the amount of solution (yielding heat on crystallization) continually becomes less, the fall in temperature along the branch *bc* of the curve becomes more rapid with lapse of time. When the temperature has fallen to −22.4° C, its value at the point *c*, the solution contains 23 per cent of common salt, and a period of constant temperature, given by the branch *cd*, and corresponding to crystallization of the eutectic, ensues. This halting point must be of comparatively short duration, for the 2½ grams of common salt which were present in our original solution suffice to form 10.87 grams only of 23 per cent salt solution. After the last residue of solution has crystallized, normal cooling ensues along the branch *de*, the temperature converging towards −100 degrees. To summarize, then, the cooling curve of our solution consists of the four branches *ab*, *bc*, *cd* and *de*.

The cooling curve of a 5 per cent solution presents a similar appearance (see the curve marked *5 per cent NaCl* in Fig. 9a). However, separation of ice commences here at the somewhat lower point *b* (= —3.1 degrees). When half the substance has crystallized, the solution contains 10 per cent common salt, and the temperature has reached —6.7 degrees; it has fallen 3.6 degrees. Notwithstanding the fact that the freezing point lowering is very closely proportional to the salt content of the solution up to a content of 10 per cent, the fall in temperature along *bc*, which accompanies crystallization of ice, is more rapid from the start in concentrated solutions than it is in dilute solutions. This is obviously due to the far greater percentage change in salt content sustained by a concentrated solution than by a dilute solution, when equal amounts of ice are frozen out. The temperature falls at a continually increasing rate until the point *c* is reached, when the period of eutectic crystallization at —22.4 degrees (along *cd*) ensues. This period will be exactly twice as long as was the case in the 2½ per cent solution, for obviously the 5 grams of common salt present in 100 grams of the solution with which we are now dealing furnish twice the quantity of 23 per cent salt solution as did the 2½ grams of salt present in former solution, and consequently, twice the quantity of heat at the halting point. After the period of eutectic crystallization has transpired, *i.e.*, after all the material has crystallized, the temperature falls normally as shown by the branch *de*.

There is no fundamental difference between the cooling curves of 10 and 15 per cent salt solutions, respectively (Fig. 9a), and those just considered. They also consist of four branches; *ab*, which represents cooling of the liquid mixture; *bc*, the branch of retarded fall in temperature along which separation of ice occurs, *i.e.*, the branch which, as was previously shown, represents incomplete equilibrium between ice and solution of progressively increasing concentration; *cd*, a horizontal branch representing the eutectic halting point, along which ice and crystals of common salt are in complete equilibrium with solution of continually decreasing quantity but invariable composition; and finally *de*, along which the completely solidified mixture cools convergently towards —100 degrees. We note, however, that the first separation of ice occurs at successively lower temperatures in the several mixtures, viewed in the order of increasing concentration. (The order of their presentation and discussion.) For the 10 and 15 per cent solutions these temperatures are —6.7 degrees and −12.2 degrees, respectively. Furthermore, it is evident that the branch *bc* joins the branch *ab* at a wider angle (approaching 180 degrees) as we pass from concentration to concentration (whereby the break *b* becomes more and more indistinct), and that the period of crystallization at the eutectic halting point, which occurs at the same temperature in all cases, increases in proportion to the original salt content of the solution; in the 10 per cent concentration it is four times, and in the 15 per cent solution six times as long as in the 2½ per cent concentration.

If a solution possesses the same salt content as the eutectic mixture, the break *b* is of course lacking on its cooling curve. In such a case, when the temperature of eutectic crystallization has been attained, ice and salt crystals separate simultaneously in the exact proportions which defined their previous existence in the solution, but at no time does there occur any individual crystallization of either component. During the whole crystallization process, the temperature remains constant, thereafter falling in the regular manner towards its lower limit. The cooling curve of a 23 per cent aqueous solution of common salt (Fig. 9a) consists, then, of three branches, as does that of a pure substance; *ac*, which corresponds to cooling of the liquid; *cd*, a halting point, which corresponds to eutectic crystallization at −22.4 degrees; and *de*, which corresponds to cooling of the completely solidified mixture. The period of eutectic crystallization amounts in this case to 9.2 times that observed in a 2½ per cent solution, as follows from a simple calculation: it has attained its maximum value here, since the whole of the original mixture crystallizes at this temperature.

The 23 per cent solution is the only one which can exist at −22.4 degrees (provided we confine ourselves, as is continually presumed, to discussion of equilibrium conditions, and abandon all consideration of supercooling). Here, we have complete equilibrium between ice, solid salt and a 23 per cent solution, as has been repeatedly noted, and an increase in the amount of ice or salt can have no effect on the condition of equilibrium, *i.e.*, on the composition of the solution. This particular solution may be regarded as a saturated solution of salt at this temperature, owing to the participation of solid salt in the equilibrium. Since, then, the salt content of a solution, saturated at −22.4 degrees, amounts to 23 per cent, that of any solution which had originally been more concentrated must have fallen to 23 per cent, on cooling to −22.4 degrees. Therefore, such a solution must become less concentrated as freezing progresses, exactly the reverse of the cooling effect on previously considered solutions. This general conclusion is confirmed by the experimental results. The first separation of crystals is indicated on the cooling curve of a 26.25 per cent aqueous solution of common salt (Fig. 9a) by the first appearance of a period of retarded fall in temperature and the attendant break (which is none too well marked, and has therefore been exaggerated in the figure) at *b* (= 0° C.). The crystalline variety which separates along *bc* is not ice, however, but pure salt. Separation of crystals continues until the temperature has fallen to −22.4 degrees; the salt content to 23 per cent. Then eutectic crystallization sets in along the horizontal *cd*, and continues throughout a period which is some 4 per cent shorter than that corresponding to the 23 per cent solution, on account of the proportionately lesser amount of eutectic furnished by the solution in hand. After completion of the eutectic crystallization, a normal fall in temperature along the branch *de* ensues. On further increase in the salt content of the mixtures, the temperature of initial crystallization rises rapidly, in correspondence with the well-known fact that the solubility of common salt in water changes only slightly with the temperature. For example, the first separation of crystals from a 28.1 per cent solution occurs at the comparatively high temperature of 100 degrees, while the quantity of eutectic mixture which is left to solidify at −22.4 degrees is 93 per cent of the whole original mixture.

It is evident from the above example that, in a strict sense, we are not entitled to follow general usage and certify to a difference between the two components of our system by invariably calling one solvent and the other dissolved substance. On consideration of a sufficient number of different concentrations, we cannot fail to observe that both substances behave in an analogous manner. When the salt content is less than 23 per cent, the component, water, separates first in the form of crystals; when it is more than 23 per cent, the other component, salt, separates first.

In Fig. 9a, cooling curves of the separate solutions are so arranged that the distances of their respective *b* points (first break in the curves) from the point *c* on the curve for pure water (first curve at the left) are proportional to the initial salt contents of the original solutions. If we now pass a (dotted) curve through all of these points, we shall be in a position to locate the temperatures of initial crystallization for concentrations which have not been investigated directly. We see at once from the figure that the first separation of crystals from a 12½ per cent salt solution occurs at −9.5° C. (This temperature corresponds to the point of intersection β of the dotted line with a line drawn parallel to the temperature axis through a point 12½ concentration units distant from the point *c* of the curve for pure water.) The dotted horizontal line joining the eutectic halting points signifies in this particular instance (typical of its general signification) that a halting point must appear at −22.4 degrees and continue (provided the cooling refers to 100 grams of solution) throughout a period of time which is the arithmetical mean of the periods actually observed in the preceding (10 per cent) and following (15 per cent) solutions. In the selfsame manner, we learn that the first salt crystals will separate from a 27½ per cent salt solution at +60 degrees, corresponding to the point β', and that eutectic crystallization will also occur at −22.4 degrees. The steep ascent of the curve $b\beta'$ indicates that the solubility of common salt in water increases only slightly from 0 to 100° C.

Thus, the answer to any question which may be proposed relative to the process of solidification in an aqueous solution of common salt of any concentration lies in Fig. 9a, provided such concentration is within the range investigated. To reiterate, this result was secured by arranging the cooling curves in such a manner that the distances between their first breaks are proportional to the concentration differences between the respective mixtures. But we may proceed to simplify this representation by omitting the cooling curves entirely, and retaining only the dotted curves and the eutectic horizontal in our figure. Fig. 9b represents a modification of this sort. In this figure, which is known as a *fusion diagram,* the time axis is lacking; the axis of abscissas, which was previously used in this connection, has now become the *concentration axis,* along which the percentage salt content of the solution is entered. The axis of ordinates continues as temperature axis. Thus, every point in our present co-ordinate system corresponds to a mixture of common salt and water of definite concentration, and at definite temperature; the point *a* for example, corresponding to a mixture of concentration $0e = 11.25$ per cent NaCl, at the temperature $ae = +10$ degrees. The curve branches *AB* and *BC*, which correspond to the dotted curve branches of Fig. 9a, were obtained by entering the breaks *b* from the cooling curves (corresponding to the temperature of separation of a single crystalline variety) every observed concentration in the co-ordinate system, and for joining these points by a continuous curve. The eutectic horizontal was obtained in like manner, by joining the several eutectic halting points, all of which lie at one temperature (-22.4 degrees).

This simplified diagram is equally capable of furnishing those who are well versed in its interpretation with complete information on any question concerning the state of aggregation of a salt solution of any concentration at any temperature. The beginner usually experiences some difficulty in becoming accustomed to this method of representation, but those who have overcome these incipient, moreover trivial, difficulties, can scarcely fail to recognize its inherent desirability — we may even say its necessity. When conditions are complicated, we may rest assured, from the very nature of affairs, that a detailed description, covering many pages, will fail to render a clear perception of points which are at once plainly apparent on glancing at a diagram of this sort. It therefore appears advisable to discuss the simple examples which we shall consider first in great detail, even though some repetition of earlier statements may be unavoidable.

The whole area bounded by the co-ordinate axes (Fig. 9b) is known as the concentration-temperature plane. It is divided into separate "fields of condition" (of the material which is existent within the prescribed limits), or simply fields (called variously, areas, regions, etc.), by the curve *ABC* and the line *DE*. Four fields are to be differentiated as follows:

Field I — above the curve branches *AB* and *BC* — is known as the liquid field, since every mixture of common salt and water which exists under some condition of concentration and temperature given by a point located within this field is a homogeneous liquid, when in a condition of equilibrium. For example, this is true of the above-mentioned 11.25 per cent salt solution, corresponding to the point *a* (temperature 10° C.).

Field II — below the eutectic line *DE* — is known as the crystalline field. Any common salt-water mixture, the concentration and temperature of which correspond to a point situated within this field, is entirely solid, consisting of two crystalline varieties (ice and salt). Liquid mixtures are incapable of existence below the eutectic horizontal (provided a condition of equilibrium obtains).

Field III — within the triangle *ABD* — answers to the characterization, ice + solution. Obviously, any mixture located within this field (abbreviated phraseology which will henceforth be adopted to signify mixtures which correspond in concentration and temperature to a point within the field) can neither exist as homogeneous liquid, nor as homogeneous crystalline material, but rather as ice and solution. (The original mixture, which was homogeneous liquid at higher temperatures, has separated on crossing the boundary into this field.)

Field IV bears close analogy to Field III — included mixtures consist of salt crystals and solution.

Making use of our diagram, the following assertions may now be made relative to the changes which will occur on continued cooling of a solution corresponding to the point *a*, for example (11.25 per cent NaCl, 10° C.). The mixture will remain liquid until fall in temperature brings it into Field III. This occurs on passing the branch *AB*, *i.e.*, at a temperature of −8° C. (point *b*, where the crystallization of ice begins), and our mixture now consists of pure ice and a salt solution which becomes more concentrated as the temperature falls, until this solution has reached the limiting concentration of 23 per cent salt, at −22.4 degrees. We have now reached the eutectic horizontal *DE*, where the mixture must be composed of ice crystals, salt crystals, and solution. On passing *DE*, the crystalline field is reached, wherein our mixture must consist purely of ice and salt crystals.

The salt solution represented by the point *f* (26.25 per cent NaCl, 75° C.) is also situated within the liquid field. On cooling, it remains liquid until the branch *BC* is crossed and Field IV entered. Beginning here, the mixture is composed of salt crystals and solution, which latter becomes *less concentrated* as the temperature falls, until it has reached the limiting concentration of 23 per cent salt, and the temperature has reached that of the eutectic horizontal (just as in the above case), whereupon ice appears as a new phase. After crossing the eutectic horizontal, no liquid remains, and the mixture is composed entirely of salt and ice crystals.

The curve *ABC*, composed of the two branches[1] *AB* and *BC*, is called the *fusion curve*; it joins the points of initial separation of a crystalline variety from the melts, and is a curve of incomplete equilibrium. The branch *AB* corresponds to incomplete equilibrium between ice and salt solution. It gives the temperature at which the first separation of ice occurs in any concentration between 0 and 23 per cent common salt, and conversely the salt content of the solution which is in *incomplete* equilibrium with ice at any freezing temperature. The equilibrium represented by this branch is called incomplete, for the reason that the concentration of a phase, the solution, in this case, varies continuously as the reaction proceeds. The continuous fall in temperature which ensues, follows this branch, and may therefore be read from it. This may be made clear by a few moments consideration of our 11.25 per cent salt solution. When the temperature has fallen to $b = -8$ degrees, the point of intersection of a vertical drawn (as a dotted line) at right angles to the concentration axis through *a*, with the branch *AB*, we have, corresponding to *b* in our co-ordinate system, a mixture of salt and water of concentration 11.25 at a temperature of -8 degrees. The first separation of ice from the previously homogeneous solution occurs at this temperature. If we should now, the first trace of ice having appeared, permit no change in the temperature of our system, no further crystallization could occur, since, on separation of ice, the solution becomes more concentrated, and its freezing point falls.

This is, perhaps, the place for again pointing out the difference between complete and incomplete equilibrium. If we are deal-

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[1] Sections of the curve which are distinguished from one another by a point (in this case at *B*) where the direction of the curve is suddenly changed are termed branches, in this connection.

ing with *complete equilibrium,* replacing the salt solution by pure water, for example, we may bring the whole system at will into the liquid or crystalline condition while the temperature remains at 0° C., or, as is commonly said, we may conduct the process isothermally. For example, in order to completely freeze the system, we have only to bring it into a chamber where the temperature is 0 degrees, and provide for removal of the heat which will be liberated during the ensuing crystallization. Conversely, pure ice may be completely melted at 0 degrees, by in some manner supplying it with the heat which must be absorbed (bound) during fusion. In fact, we are quite unable to impart either a higher or lower temperature than 0 degrees to a system composed of pure ice and pure liquid water; all the ice must first be melted, or all the water frozen before these respective effects can be brought about. When a system is in *incomplete equilibrium,* it is, on the contrary, impossible to bring about reaction in either direction at constant temperature, under constant pressure. We are thus unable to completely freeze the 11.25 per cent salt solution at −8 degrees, even though care be taken to remove the heat liberated during crystallization: the more concentrated solution which remains after the first crystal of ice has separated will crystallize no further until some temperature lower than −8 degrees is reached.

Now, complete information relative to the manner of crystallization of the 11.25 per cent salt solution is supplied by the branch *AB* of the fusion curve. We see, on considering its course, that the freezing temperature of a solution will have fallen to −9.5 degrees, or to −12.2 degrees when this solution has reached the concentration value of 12½ per cent, or of 15 per cent, respectively, owing to the freezing out of ice. The point *B* (= 23 per cent NaCl, and −22.4° C.) is the end point of this particular curve of incomplete equilibrium, and lies upon the eutectic horizontal *DE*, at which location complete equilibrium characterizes the initial appearance of salt crystals.

We may also infer, from the general discussion above, that our diagram must supply information concerning the quantitative relations as well. It is at once apparent that questions of this nature will pertain to Fields III and IV only, since the material in Fields I and II is completely molten or crystalline, respectively.

We will continue to abide by the 11.25 per cent salt solution as an example, and propose the question, What amount of ice has separated from the solution when a given temperature, say −15 degrees, has been reached? We see from the diagram that the concentration of a solution, and indeed the only solution, which is in equilibrium with ice at −15 degrees, amounts to 18 per cent NaCl — a line *cd* drawn parallel to the concentration axis at −15 degrees cuts the branch *AB* at the point *d*, corresponding to a concentration of 18 per cent NaCl. Therefore, our original 11.25 per cent solution has become concentrated up to 18 per cent at − 15 degrees, and in answering the above question we need only calculate how much water must be removed from an 11.25 per cent solution to make it an 18 per cent solution.

Placing the initial amount of solution at 100 parts by weight, we have 11.25 component parts of salt, from which 62.5 parts of 18 per cent solution may be made, as is seen from the following proportion:

$$11.25 : x = 18 : 100$$

$$x = \frac{1125}{18} = 62.5.$$

To do this, 37.5 parts of water must be removed in the form of ice. Our 11.25 per cent solution has therefore separated at −15 degrees to 37.5 per cent ice and 62.5 per cent salt solution of concentration, 18 per cent NaCl.

Thus, the fusion diagram, although it does not show cooling curves, renders information concerning all questions which pertain to the state of aggregation of a salt-water mixture of any concentration, at any temperature (atmospheric pressure being assumed). Herein is included the condition of a mixture of given concentration at all stages of cooling (represented by the points of a line drawn parallel to the temperature axis at the corresponding concentration value). The relative quantities of eutectic[1] in the completely solidified mixtures of each and every concentration may also be deduced from the diagram. At concentration B (= 23 per cent), where the whole alloy is crystallized as eutectic, this quantity is unity (1). It is clear that the same amount of solution of concentration $\frac{B}{2}$ (= 11.50 per cent) can

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[1] By relative quantity, or simply quantity, of eutectic is meant a quantity referred to unit weight of substance, or the actual quantity of eutectic divided by the total weight of substance.

yield only half as much of a 23 per cent solution, *i.e.*, that the quantity of eutectic in a mixture of this sort amounts to one-half. In general, the relative quantity of eutectic for any concentration $\frac{m}{n}B$, between 0 and B, is equal to $\frac{m}{n}$, where $\frac{m}{n} < 1$ by assumption (viz., the respective concentration must actually lie between 0 and B). In accord with this generalization, the quantity of eutectic at the concentration 0 (pure water) is also 0. A relation of this sort is said to be linear, and we make the general assertion: the relative quantity of eutectic is a linear function of the concentration for all concentrations between 0 and 23 per cent. This condition of affairs is brought into prominence in the diagram by the erection of verticals upon the concentration axis as base, at lengths which are made proportional to the relative quantities of eutectic in the different concentrations. A line joining the end points of these verticals is straight (hence the term linear) and cuts the base, or concentration axis, at 0 per cent (pure water). An analogous relationship must hold for the concentrations which are beyond B: in this region as well, the quantity of eutectic must decrease lineally from a maximum of 1 at B, to 0 at concentration 100 (pure salt).

If the experiments are conducted with uniform amounts of substance throughout the whole range, the heat quantities liberated during eutectic crystallization and the lengths of the eutectic halting periods upon the cooling curves as well (assuming uniformly ideal cooling conditions — see p. 17) must actually appear as linear functions of the concentration.

It would seem superfluous to make such special entry in the diagram of the quantities of eutectic pertaining to the several concentrations, since these quantities are given by the diagram in any case. Direct observation of the lengths of the eutectic halting points is, however, of the greatest assistance in perfecting the fusion diagram, as was first shown by TAMMANN[1], and we shall, therefore, consistently follow this plan.

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[1] TAMMANN, Über die Ermittelung der Zusammensetzung chemischer Verbindungen ohne Hilfe der Analyse, Z. anorg. Chem., 37, 303 (1903); Die Anwendung der thermischen Analyse in abnormen Fallen, Z. anorg. Chem., 45, 24 (1905); Über die Anwendung der thermischen Analyse III, Z. anorg. Chem., 47, 289 (1905).

Our fusion diagram of the system salt-water is incomplete, inasmuch as it does not extend beyond the concentration, 30 per cent NaCl. This is due to the fact that it is not possible, in view of the low boiling point of water, to investigate higher concentration under atmospheric pressure.

2. Quantitative Relations on Disintegration into Two Phases. (The Lever Relation.) — From our knowledge of the concentrations *c* and *d* of the two phases composing a salt-water mixture *g* in the equilibrium condition, which information was obtained directly from the fusion diagram, Fig. 9b, we were able to draw an accurate conclusion concerning the quantitative relationship between these two phases. We will now proceed to discuss the general case. Let the system be composed of the two substances *A* and *B*, and let all concentrations be expressed in weight per cent *B*. A mixture of concentration *b* will then contain *b* grams of the substance *B* in 100 grams total weight. Suppose that such a mixture is incapable of existence in a homogeneous condition at the temperature *t*, but be separated into two phases of the respective concentrations *a* and *c*. Our problem is to ascertain the ratio $\frac{Q_a}{Q_c}$ of the quantities of these two phases.

We make use of the graphical method recently discussed in depicting this relationship — Fig. 10. The axis of abscissas serves as concentration axis; along this axis we enter the percentage content of the mixture in *B* progressively from left to right. The percentage content in *A* is of course fixed at the same time. The concentration 0 signifies pure *A*, and the concentration 100, pure *B*. The axis of ordinates is again chosen as temperature axis, centigrade temperatures being entered progressively from bottom to top. (For the sake of clearness, temperature axes are usually erected at both end points of the concentration axis.)

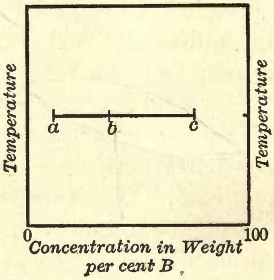

Fig. 10.

Let the total quantity of mixture be 100 grams. If, then, *x* grams of the phase of concentration a are present in a condition of equilibrium, the quantity of the complimentary phase of concentration c is $(100 - x)$ grams.

Now, the x grams of the phase of concentration a contain

$$\frac{x}{100}a \text{ grams of the substance } B,$$

and the $(100 - x)$ grams of the phase of concentration c contain

$$\frac{100 - x}{100} c \text{ grams of the substance } B.$$

But the total quantity of the substance B is given by the percentage content b of the original (inhomogeneous) mixture, multiplied by the total weight of the latter, which was assumed to be 100 grams (b per cent of $100 = b$). Whence we write,

$$\frac{x}{100}a + \frac{100 - x}{100}c = b.$$

From this, we obtain for the quantity x of the phase a, in grams per 100, viz., the percentage quantity of phase a,

$$x = 100\frac{c - b}{c - a} = Q_a,$$

and for the percentage quantity $100 - x$ of the phase c,

$$100 - x = 100\frac{b - a}{c - a} = Q_c.$$

These two equations yield the relation,

$$\frac{Q_a}{Q_c} = \frac{c - b}{b - a} = \frac{bc}{ab},$$

which signifies that the concentration difference $c - b$ is equivalent to the distance bc in the diagram, and the difference $b - a$ equivalent to the distance ab.

Considering abc as a lever with its fulcrum at b, and imagining masses equivalent to Q_a and Q_c suspended at the end points a and b respectively, we have the well-known equilibrium condition,

$$Q_a \cdot ab = Q_c \cdot bc.$$

Separation of the mixture *b* has, then, progressed in accordance with the above proportion. We shall make extended use of this simple relation in the following pages under the name "lever relation."

3. General Case. — Let it be granted that we are dealing with two substances *A* and *B*, and for the sake of simplicity let these be considered as elements. Moreover, let *A* and *B* denote their respective melting points in degrees centigrade as well. We shall proceed under the primary assumptions: (1) that the two elements are completely miscible in the liquid state, but completely immiscible in the crystalline state; (2) that they show no polymorphous transformations; and (3) that they form no chemical compounds with one another. It is our present object to become familiar with the fusion diagram representing this case. Concentrations, in weights per cent *B*, and temperatures, in degrees centigrade, are entered in Fig. 11a, in the usual manner.

When a small quantity of *B* is dissolved in a large quantity of *A*, and the mixture allowed to crystallize, it is *A* which first crystallizes — pure *A*, in accordance with our previous assumption of immiscibility in the crystalline state. According to the law of freezing-point depression, this separation commences at some temperature below the melting point of pure *A*. Moreover, it does not proceed at constant temperature, since we are here dealing with a condition of incomplete equilibrium. On the contrary, in order that *A* may continue to crystallize, it is necessary for the temperature to drop continuously. During the process, the melt which remains in equilibrium with pure *A* crystals becomes continually richer in *B*. This condition has already been discussed at length, relative to crystallization of an aqueous solution of common salt, and leads to the conclusion that the first separation of *A* must take place at a temperature, the value of which decreases in proportion as the addition of *B* increases. Thus, when we enter the temperatures of initial separation of *A* from melts of varying concentrations in our co-ordinate system and join these points continuously, we obtain a curve which drops to lower temperatures as the *B* concentration increases. Let this curve be represented by *AX* in the figure (11a).

A and *B* are the two independent constituents of our system, and, as such, are on a plane of equality. The melting point of *B*

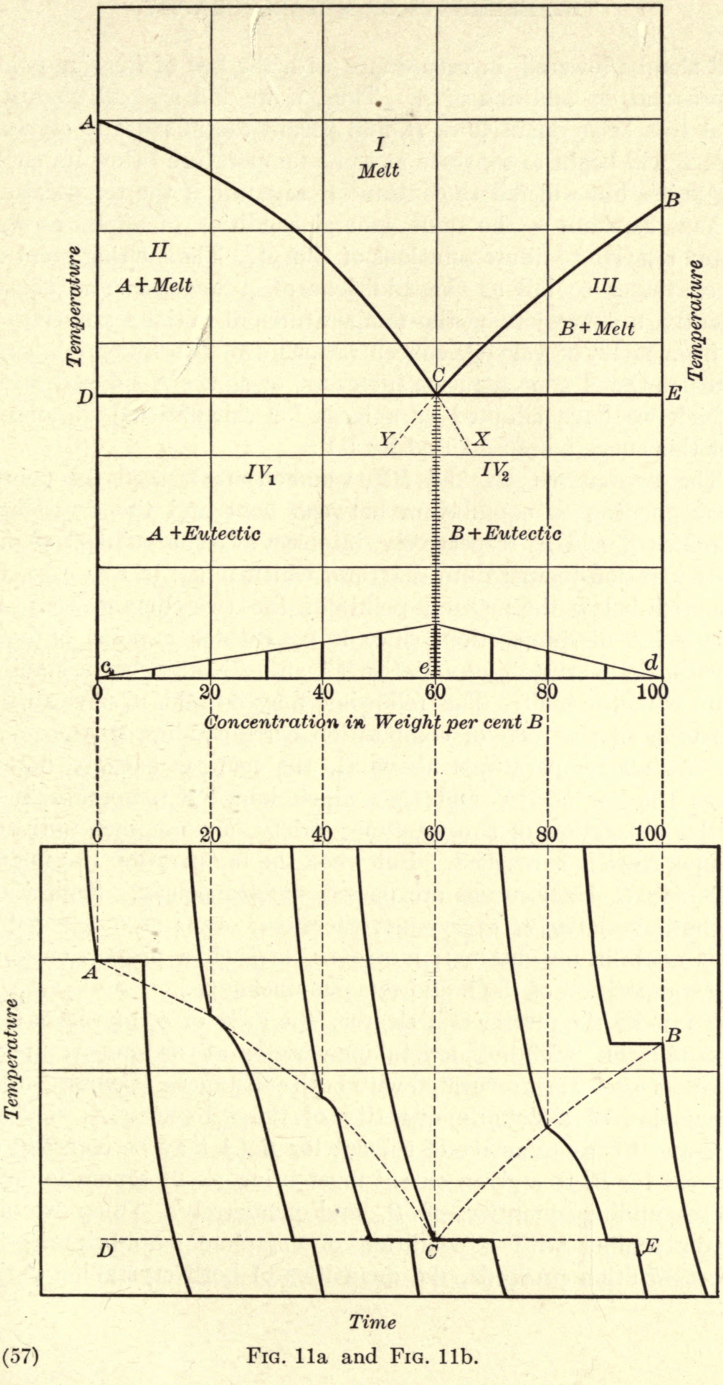

FIG. 11a and FIG. 11b.

will also be lowered, in accordance with the law of freezing-point depression, on addition of *A*. Thus, if we add a small quantity of *A* to a large quantity of *B*, and permit the mixture to crystallize, *B* will begin to separate at some temperature below its melting point, but will fail to continue to separate if the temperature is kept constant — the same general condition of affairs as was noted relative to dilute solutions of *B* in *A*. The melting point of *B* continues to fall as the additions of *A* increase, and consequently, a curve joining the temperatures of initial separation of *B* from melts of varying concentrations drops to lower temperatures as the *A* concentration increases, or as the *B* concentration (which we have adopted as a basis for calculations) decreases. Let this curve be represented by *BY*.

The two curves *AX* and *BY*, whereon are located the points corresponding to equilibrium between melt and the crystalline varieties *A* and *B*, respectively, intersect at some point *C* of our concentration-temperature diagram, which must, in any case, be situated below the melting points of the two components. At this point of intersection, since it constitutes a point of both curves, both crystalline varieties (*A* and *B*) must be in equilibrium with the melt. The following may be said relative to the behavior of the melt of composition corresponding to the point *C*: At all temperatures above *C*, the melt is entirely liquid, since the curves *AX* and *BY*, which join the temperatures of initial separation of a crystalline variety, are not met until the temperature *C* is reached. But when the temperature has finally fallen to *C*, both curves are passed simultaneously. Separation of both varieties *at once* must, therefore, occur at *C* (assuming that equilibrium obtains); moreover, in such a proportion that the composition of the liquid remains unchanged.

To make the matter still clearer: the melt of composition *C* is in equilibrium with both crystalline varieties at the temperature *C*, in other words, it is saturated with both substances. Consequently, separation of a definite quantity of the substance *A*, that is, decrease in the quantity of solvent for *B* (*A* may be regarded as solvent for *B*) to a given extent must bring about separation of a corresponding quantity of *B*, and conversely. Thus, we are again dealing with a condition of complete equilibrium, — as crystallization proceeds, the quantities of both crystalline varieties increase and the quantity of melt decreases, but no one of the phases changes its composition. In effect, the melt of composition corresponding to *C* solidifies at the temperature corresponding to *C*, after the manner of a pure substance. It is now plainly evident that the point *C* represents the eutectic mixture of *A* and *B*.

The fact that the melting point of a pure substance may not be lowered beyond a certain limit by addition of a second substance (which we were content to regard on p. 40 in a purely experimental light) now appears as an inevitable consequence of the melting-point depression of both components. Presupposing a condition of equilibrium, the existence of a liquid (or even partially liquid) mixture of *A* and *B* at a lower temperature than that corresponding to *C* is not possible. Nevertheless, the dotted continuation of both curves beyond *C* is of a certain practical significance. It is not infrequently observed on cooling curves that separation of the second crystalline variety, which should commence at *C*, is subject to retardation, whereby such continuation of one, or even both, of the curves becomes descriptive of actual conditions. All such systems, however, constitute supercooled or unbalanced systems, which will, after a time, undergo spontaneous transformation into the stable condition, with attendant rise in temperature. We shall continue to disregard these phenomena of supercooling.

To summarize, then, our diagram supplies the following information:

(1) All melts of concentrations between 0 and *C*, on solidification, first separate pure *A*, becoming progressively richer in *B* with falling temperature, until what remains of them has attained the eutectic composition *C*. These residual amounts then crystallize at the constant temperature *C*.

(2) All melts of concentrations between *C* and 100, on solidification, first separate pure *B*, becoming progressively richer in *B* with falling temperature, until what is left has likewise attained the eutectic composition *C*; whereupon crystallization ensues at constant temperature, as before.

(3) A melt of concentration *C* crystallizes at constant temperature, yielding *A* and *B* simultaneously, in the proportion given by *C*. The eutectic horizontal *DE* passing through the eutec-

tic point *C*, and extending throughout the whole concentration range, signifies that eutectic crystallization occurs in all mixtures of *A* and *B*. As to the relative quantities of eutectic, a maximum (unit quantity) obtains at the concentration *C*, since the whole melt crystallizes eutectically at this concentration, and zero values obtain at the concentrations 0 and 100, since the eutectic is of necessity a mixture. For concentrations between 0 and *C*, this quantity (of eutectic) is proportional to the *B*-content, and for concentrations between *C* and 100, it is proportional to the *A*-content since, in the first case, where *A* is the first substance to crystallize, the whole initial quantity of *B*, and in the second case, where *B* is the first substance to crystallize, the whole initial quantity of *A*, remains in the liquid condition up to the eutectic point, and is therefore utilized in the formation of eutectic. The quantity of eutectic must, then, decrease lineally from concentration *C* to concentration 0 (pure *A*), and in like manner from concentration *C* to concentration 100 (pure *B*). This is shown in the diagram, according to the method previously described: Verticals are erected upon the concentration axis as base, in such manner that their lengths, for the various concentrations, are proportional to the quantities of eutectic in these respective concentrations. As is apparent, these quantities reach a maximum value at *C*. On joining the end points of these verticals, two straight lines are obtained, one intersecting the concentration axis at 0 per cent, and the other, at 100 per cent.

When equal amounts of substance are used in determining each of the cooling curves, the heat quantities liberated during eutectic crystallization are proportional to the lengths of these verticals. Furthermore, if cooling is conducted in all cases in uniform manner — based upon the cooling conditions which we have assumed to be ideal — the lengths of the eutectic halting points which appear on the cooling curves will also be proportional to the lengths of these verticals.

(4) The attainment of a zero value for the eutectic at concentrations 0 and 100 constitutes in itself an expression of the fact that the pure substances *A* and *B* crystallize at constant temperature.

It is clear that the inverse process of constructing cooling curves from our diagram may be carried out, provided we know the melting points of both components *A* and *B*, as well as their heat of mixture. For this purpose, information relative to conditions of cooling, temperature of convergence, etc., must also be at hand. In Fig. 11b, an approximate picture of cooling curves of the two pure substances and of four intermediate concentrations is given under the assumption that the latent heat of fusion is approximately the same for both substances, and that the heat of mixture is negligible. The cooling curves are again arranged in such manner that the distances of the initial breaks from one another are proportional to the concentration differences for the respective curves. Conversely, it may of course be seen from this example in what manner the fusion diagram is built up from the individual cooling curves, which are directly obtained by experiment.

The fusion curve *ACB*, (Fig. 11a), which joins the temperatures of initial separation of a single crystalline variety, is, as we are well aware, a curve of incomplete equilibrium. The variety *A* separates along the branch *AC*. From the course of the curve, we deduce the particular temperature at which a melt of given concentration is in equilibrium with crystalline *A*, and similarly, the concentration of the particular melt which is in equilibrium with crystalline *A* at a given temperature; in other words, the concentration of a melt which will begin to crystallize at this temperature. Analogous relations hold for the branch *BC*, along which the variety *B* separates. Complete equilibrium between the two crystalline varieties *A* and *B* and the melt of composition *C*, prevails along the eutectic horizontal *DE*.

The concentration-temperature diagram is divided into four fields of condition by the fusion curve and the eutectic horizontal:

Field I, above the fusion curve *ACB*, is the field of homogeneous liquid material, or simply, of melt.

In Field II, represented by the triangle *ACD*, the separated crystalline variety *A* is found in equilibrium with melt along the branch *AC*. (This phraseology is intended to suggest, in as few words as possible, the concentration changes of the melt for falling temperature.) Questions concerning the quantity of separated *A* and the quantity of melt, which are together in equilibrium at any chosen point within the field, are answered by application of the lever relation (see p. 54).

In Field III, represented by the triangle *BCE*, the crystalline variety *B*, separating along the branch *BC* is found in equilibrium with melt.

Field IV, below the eutectic horizontal *DE*, is the field of homogeneous crystalline material, and includes the two crystalline varieties *A* and *B*. This field is divided into two sections, IV_1 and IV_2, by a line *Ce* drawn through *C* (rendered prominent by means of cross dashes) parallel to the temperature axis. Such division corresponds to differences in structure which are apparent on microscopical examination of the completely solidified alloys, viz., those located below *DE*, or in Field IV of our diagram. Discussion of microscopical investigation, which for experimental reasons is adapted to the completely solidified alloys alone (in measure dependent on their individual nature), is reserved for subsequent pages.

In effect, then, the eutectic is regarded as an individual structure element in all metallographical investigations. When not too highly magnified, it is generally homogeneous in actual appearance. Only when higher powers are used, does it become apparent that two different crystalline varieties are concerned in its make-up. It is noticeable that these individual constituents of the eutectic are very often arranged side by side in a finely lamellar form, or in the form of irregular grains. The reason for this apparent homogeneity is not difficult to discover when we inquire closely into the manner of crystallization of the eutectic. For, as soon as the least quantity of *A* has separated, the melt is supersaturated with respect to *B*, and therefore permits immediate separation of a corresponding quantity of *B*. *A* and *B* thus occur side by side in minute crystals.

Now, on the *A*-rich side, *i.e.*, in concentrations intermediate between *O* and *C*, pure *A* has first separated and has continued to separate up to the point where the melt has become enriched sufficiently in *B* to correspond with concentration *C*. At this point, complete eutectic crystallization takes place. Consequently, there must be present in the solidified alloys of Field IV_1, primarily separated crystals of *A*, imbedded in the eutectic which has subsequently crystallized. Thus Field IV_1 is to be designated as the field of Crystalline A and Eutectic when we regard the latter as a separate and distinct structure element. In analogous manner, Field IV_2 (situated at the right of the line Ce), in which primarily separated B crystals surrounded by eutectic must occur, is characterized as the field of Crystalline B and eutectic.

Proceeding from several general experimental facts, we have in the last few paragraphs derived the form of the fusion curve for a two component system, where the two substances sustain no polymorphous transformation, unite to form no chemical compound, and show no miscibility with one another in the crystalline state. The characteristic properties of such a diagram may be summarized as follows:

(1) The fusion curves consist of two branches only, AC and BC.

(2) One eutectic horizontal, passing through the point of intersection C of the two branches of the fusion curve, occurs.

(3) The eutectic horizontal traverses the whole diagram. If, upon the concentration axis as base, verticals are erected throughout the various concentrations, at lengths which are proportional to the relative quantities of eutectic in these respective concentrations, and the end points of these verticals joined, two straight lines, which intersect with one another at C, and with the concentration axis at concentrations 0 and 100, are obtained.

We shall see, on considering other cases describing the mutual relations of the elements, that a fusion diagram of this type is valid for a two component system only when the above assumptions are actually realized.

Now, if we have investigated the mutual relations of two elements by the method of thermal analysis, viz., by taking cooling curves of the pure elements and of a series of mixtures, say from 10 to 10 per cent progressively, and if we find that the fusion diagram deduced from these cooling curves reproduces the characteristic properties of the diagram which we are now considering, the following inverse conclusions may be drawn:

(1) The elements exhibit complete miscibility in the liquid state, and no miscibility in the crystalline state.

(2) They undergo no polymorphous transformation, at least none which is accompanied by a sufficient heat effect to render it apparent under the given conditions.

(3) They form no chemical compounds with one another; more accurately, they fail to unite with one another under the conditions of experiment (namely, on being fused in conjunction at the respective temperature) to an extent which may be ascertained thermally. The above qualification is essential. For, in case we had undertaken to work up the fusion diagram for liquid hydrogen and oxygen, we would have been forced to a conclusion on the basis of our cooling curves, that no compound of these two elements exists. In reality, non-appearance of the compound under these conditions is merely due to the fact that the reaction velocity at this low temperature, and even at ordinary temperature (far above the boiling points of these two elements), is so trifling that appreciable quantities of water fail to be formed. Obviously, the metals are not exempt from entering into relations of this sort. TAMMANN[1] is inclined to the opinion that the aluminium-antimony alloys belong in this category. It is also possible for two elements to form a compound which can exist only at temperatures even lower than that of the eutectic point (see Fig. 45, p. 145).

If, then, we confine our reasoning to the temperature region throughout which our investigation is extended, the conclusions drawn from the fusion diagram are binding. It may be noted, in this connection, that every experimental result which is followed by a negative conclusion of some sort (*e.g.*, in the above instance, affirmation of non-existence of a compound) implies certain limitations of this general nature. On the other hand, positive conclusions (*e.g.*, relative to the existence of a compound) are subject to no such limitations.

In any case, however, it appears desirable to test the evidence of the fusion diagram, however unimpeachable it may seem, by some independent method. The most valuable method available for this purpose is direct investigation of the structure of the solidified alloys. Great importance is therefore attached to this method. The structure of the alloys often serves as a key to the solution of all questions, particularly when the results of thermal investigation are not sufficiently detailed to permit construction of a diagram which shall be free from all objection. For investigation of this sort, the solidified reguli are ground and polished to

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[1] TAMMANN, Z. anorg. Chem., 48, 53 (1905).

a mirror-like surface. At times, conclusions may be drawn on examination of the polished sections before they have been subjected to any additional treatment, as is the case when the separate constituents differ in color. In general, after polishing, it is necessary to apply some further treatment depending upon the different chemical behavior of individual constituents, such as variable resistance to the action of certain reagents (etching), variable susceptibility to oxidation in the air at ordinary temperature or on heating (causing them to tarnish), etc. The naked eye does not often suffice in making these observations. Usually a suitable microscope must be brought into requisition.

We will here assume the choice of two metals *A* and *B* which behave differently towards a certain etching agent, *A* withstanding its action, and *B* vigorously attacked by it. The alloy sections of various concentrations, after polishing and etching, are illuminated by a beam of light which is made to fall normally upon their polished surface. This may be attained by using a vertical illuminator, as we shall see later. The portions of the section which have not been attacked by the etching agent will have retained their mirrored surface, and will, therefore, completely reflect the incident light, while the affected portions, having attained a rough surface, will fail to reflect the light to any extent. If, then, we examine the section through a microscope, the axis of which is at right angles to the surface of the section, the reflecting portions must appear light, and the non-reflecting portions dark.

Fig. 12a is intended to represent a section composed of pure *A* which has been manipulated in the above manner. The structure of a section composed of a single structure element is very often difficult to develop. Still, it is in general possible by choice of a suitable etching agent and proper treatment to bring out the boundaries between the separate polyhedrons which have been formed on crystallization of the melt. This polyhedral configuration obviously affords a polygonal structure at the plane surface of the section. In general, the sharp appearance of polygonal structure is traceable to small quantities of some relatively non-resistant impurity, which crystallizes last of all, and therefore collects between the individual polygons, where it is affected by the etching agent. Thus we see a network of dark lines all over

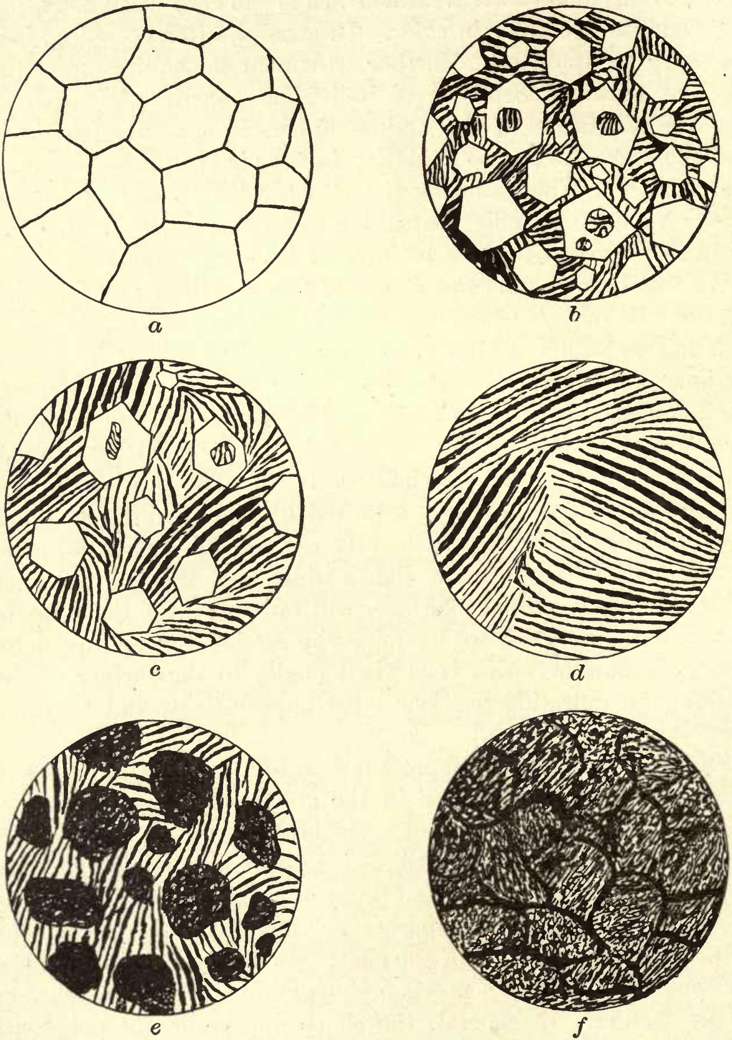

FIG. 12.

the surface of our section, and these form acute angular boundaries of the bright unattacked crystalline polygons. These polygonal cross sections through the crystals are, as a rule, six-sided. Fig. 12f represents a section of pure *B*, etched in the same manner. In accordance with the preassumed slight resistance of *B* to the action of the etching agent, this section appears etched to a dark color. It is quite possible to discern its structure, and we note the appearance of irregular crystalline polygons with rounded corners.

The action of the etching agent is sometimes particularly marked at certain spots, giving rise to the formation of local indentations (Aetznäpfchen).[1] Fig. 12d represents a section composed of 60 per cent *B* and 40 per cent *A*. The alloy of this concentration solidifies completely at the eutectic temperature, as may be seen from the diagram, Fig. 11a. Accordingly, we now have what is commonly called the pure eutectic under consideration, and we will suppose that it shows the previously mentioned characteristic lamellar structure. Interposed light and dark striations (the former corresponding to unetched particles — consisting of *A*; the latter to etched particles — consisting of *B*) are, therefore, to be seen. We are unable to advance any reason for the development of this remarkable lamellar structure. Slow cooling appears to favor its appearance. However, the eutectic frequently shows a more or less finely granular structure, which in many cases occurs alone, but, on the other hand, often accompanies the lamellar structure.

Fig. 12b represents a section composed of 20 per cent *B* and 80 per cent *A*. A glance at the diagram serves to inform us that here the crystalline variety *A* has first separated. Accordingly, we recognize bright angular *A* crystals imbedded (like islands) in the lamellar eutectic, which has solidified at a later period. The primarily separated *A* crystals show included eutectic in places, a condition which frequently occurs in practice and which, under certain circumstances, renders it difficult to distinguish between primarily and secondarily separated material.

Fig. 12c, which is intended to represent a section consisting of 40 per cent *B* and 60 per cent *A*, must offer essentially the same

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[1] These might be called in English, etch-holes, or etch-hollows (Translator).

picture as Fig. 12b, since, according to the diagrammatic evidence, the crystalline variety *A* has also separated first in this case. But, while the *A* crystals make up two-thirds, and the eutectic one-third, of the total quantity of the first alloy, this proportion has become reversed in the present alloy, which fact also follows from the diagram. Consequently, a corresponding decrease in the quantity of *A* crystals and increase in the quantity of eutectic is to be seen in Fig. 12c (compared with Fig. 12b).

Fig. 12e represents a section containing 80 per cent *B*. Here *B* has separated first (as shown by the diagram), and we find the rounded *B* crystals, which have been vigorously attacked by the etching agent, disposed throughout the entire eutectic. This eutectic in no wise differs from that which has crystallized in the other concentrations. The diagrammatic evidence that half of the alloy of concentration 80 per cent *B* solidifies eutectically is corroborated by the appearance of the microscopic picture shown in the drawing, Fig. 12e.

We may now offer a brief summary of the respective pictures which must be presented by the sections, provided their structure is in accord with the specifications of the diagram:

(1) The quantity of eutectic must increase steadily from concentration 0 per cent *B*, where its value is zero, up to concentration *C* per cent *B*, where its value is unity, and it must decrease from this latter concentration towards concentration 100 per cent *B*, where its value is again zero. The structure of the eutectic must in all cases be identical.

(2) The crystals which have separated primarily between concentrations 0 and *C* must be alike among themselves, but must differ from those which have separated primarily between concentrations *C* and 100, and which are also alike among themselves. That the crystals have separated primarily is apparent from their being embedded in the coherent eutectic. The quantity of a crystalline variety which has separated primarily obviously decreases in proportion as the quantity of eutectic increases. (It is possible for both crystalline varieties to be present in the vicinity of the eutectic point *C* as primary elements when supercooling occurs.)[1]

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[1] LEVIN, Z. anorg. Chem., 45, 31 (1905).

(3) No structure element aside from the three which have been discussed, namely, the crystalline varieties *A* and *B* and the eutectic, can appear in the sections.

In one respect, investigation of the sections carries us further than thermal investigation. It is clear that the eutectic horizontal *DCE* (Fig. 11a) extends throughout the whole diagram, in other words, that the quantity of eutectic becomes equal to zero at the precise concentrations 0 and 100 (the pure substances) only when there is absolutely no miscibility in the crystalline state. If *A* is capable of dissolving a certain quantity of *B*, pure *A* crystals will not separate on the *A*-rich side, but, rather, *A* crystals, which have dissolved a quantity of *B*. The result will be that no eutectic can appear until more *B* than the *A* crystals can dissolve is present in the mixture. Analogous relations hold for the *B*-rich side, provided the *B* crystals are possessed of a certain tendency to dissolve *A*. In such cases, then, the eutectic horizontal fails to extend throughout the whole diagram, but ends on the *A*-rich (left) side at some point between *D* and *C*, and on the *B*-rich (right) side at some point between *C* and *E*. These relations will be discussed in greater detail later, when miscibility in the crystalline state is taken up. At present, the only question at issue is: What are the limits within which our assumption of immiscibility in the crystalline state is realized? Thermal investigation is not adapted to the task in hand. That is to say, when the quantity of eutectic has become very small, the period of constant temperature during solidification of the eutectic will have become so short as to escape observation on the cooling curves. Graphical deduction of the end points of the eutectic horizontal, with the aid of the eutectic periods throughout an extended concentration range, also admits of uncertainty, not infrequently amounting to several per cent. Microscopical investigation of the prepared sections carries us much further in this respect. *If there is actually no miscibility in the crystalline state, the eutectic cannot fail to appear on very slight additions (amounting to less than one per cent) of B to A and of A to B. The eutectic may, in general, be recognized without difficulty by its characteristic lamellar or finely granular structure.* Investigation of electrical conductivity — to be discussed later — may perhaps be even better suited to the object in view.

In concluding this section, a few remarks relative to the general course of the fusion curve *ACB*, and to the position of the eutectic point *C*, may be offered. As long as the quantity of one component is small in comparison with that of the other, viz., as long as we are dealing with so-called dilute solutions, the freezing point depression which a pure substance *A* sustains on addition of a given quantity of a second substance *B*, when complete miscibility occurs in the liquid state and complete immiscibility in the crystalline state, is subject to simple laws. According to van't Hoff, the depression depends, on the one hand, on the properties of the substance *A* which plays the part of solvent; it increases in proportion as the melting point of the solvent becomes higher, and as the latent of fusion becomes less. On the other hand, it depends upon the added substance *B* (dissolved), according to the simple law: The freezing point depression is proportional to the ratio of the number of dissolved molecules to the total number of molecules. Now, investigations by RAMSAY, TAMMANN and HEYCOCK and NEVILLE have shown that the greater number of metals dissolve in a monatomic condition. Thus, the freezing point depression caused by metals in their capacity as dissolved substances is inversely proportional to their atomic weights. This relationship between freezing point depression and atomic weight may readily be shown, as is done in Fig. 13, by entering the composition of the alloy in atomic per cent, instead of weight per cent, on the axis of abscissas.[1]

The curve branches *AX* and *BY* must appear as straight lines, as long as the laws of dilute solutions hold (in practice up to additions of 5 to 10 atomic per cent). The subsequent course of these two branches is subject to great diversity. Very often (N.B. If atomic per cents are entered as abscissas) the whole course remains rectilinear. They may be concave, convex, or partly concave and partly convex, with respect to the concentration axis. However, these branches do not deviate in their form from a straight line to such an extent as to render it impossible to

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[1] If an alloy is composed of p weight per cent of the element A, of atomic weight A, and q weight per cent of the element B, of atomic weight B, then its A-content in atomic per cent is $\dfrac{100\,p}{p+q\left(\frac{A}{B}\right)}$, and its B-content, $\dfrac{100\,q\left(\frac{A}{B}\right)}{p+q\left(\frac{A}{B}\right)}$.

draw conclusions concerning the position of their intersection. Relative to the position of the point of intersection C of the two branches AX and BY, we may say that it approaches the central point between A and B and also becomes lower *ceteris paribus* in proportion as the melting points A and B approach one another. If, however, the two components A and B_1 (Fig. 13) differ considerably in melting point, the point of intersection C_1 of the two branches AX and B_1Y_1 assumes a position towards the side of the less fusible component — the A side. This conclusion is generally in accord with the experimental results.

We see from the position of the point of intersection C_2 of the branches AX and B_2Y_2, also shown in Fig. 13, that this approach to A can be indefinitely close, whereby we are confronted by the possibility that C and A practically coincide. In such a case, which is shown in Fig. 14, the eutectic must be practically identical with the less fusible pure substance A. Accordingly, the following relations are to be expected on crystallization of a molten mixture of A and B: The less fusible crystalline variety

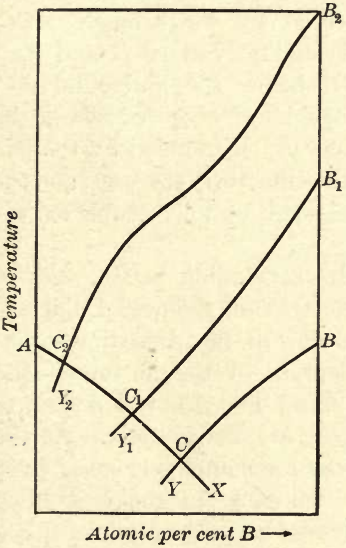

FIG. 13.

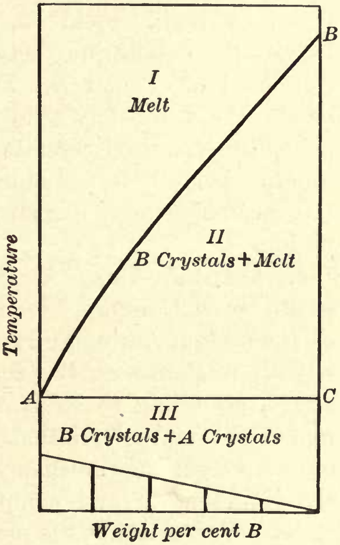

FIG. 14.

B separates first on cooling any liquid mixture of *A* and *B* (any solution of *A* and *B* in one another). The temperature falls along the curve of incomplete equilibrium *BA* until all *B* has crystallized. At this point, the melt consists entirely of pure *A*, which now crystallizes at its own constant melting temperature. No melting point depression occurs, then, on adding *B* to *A*, because melts of all concentrations first of all separate *B*. The (eutectic) horizontal extends to pure *B*, since, under our preassumed condition of immiscibility in the crystalline state in all concentrations between 0 and 100 per cent *B*, liquid *A* must be present up to the very last. The time duration of this "eutectic crystallization" is a linear function of the quantity of *A* in weight per cent, provided the same total quantity of substance is used in all cases, and the same ideal cooling conditions obtain. The concentration-temperature diagram is divided into three fields of condition. Field *I*, above the curve *BA*, is the field of liquid or melt. Field *II*, represented by the triangle *ABC*, locates the equilibrium between crystalline variety *B* and melt composed of *A* and *B*. Field *III*, below the horizontal *AC*, locates the completely solidified alloys, all of which consist of the primarily separated crystalline variety *B*, surrounded by the last separated variety *A*. *A* represents the eutectic in this case, and the latter can show only one structure element on microscopic examination.

4. ANTIMONY-LEAD ALLOYS. — In concluding section *A* (*cf.* p. 38) we will discuss, by way of illustration, the actual diagram of the system Antimony-Lead. In view of the preceding explanation, a glance at the fusion diagram of the antimony-lead alloys, according to ROLAND-GOSSELIN,[1] Fig. 15, will suffice to render the mutual relations of these two metals clear. At the outset, we see that antimony and lead are completely miscible in the liquid state and completely immiscible in the crystalline state. We learn that the metals undergo no polymorphous transformations within the temperature range investigated, at least none which are accompanied by noticeable heat effects, and, finally, we perceive that the metals form no compounds with one another, on being fused in conjunction. As to details, we see

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[1] ROLAND-GOSSELIN, Contribution à l'étude des alliages, Paris (1901), p. 104.

that the melting point of lead was found to be 326 degrees, and that of antimony, 632 degrees. Again, the composition of the eutectic appears as 13 weight per cent antimony + 87 weight per cent lead; its melting point as 228 degrees.

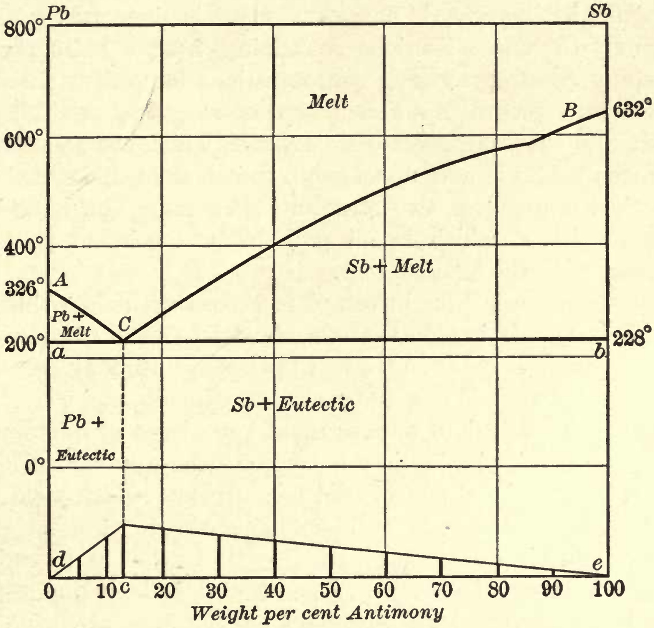

FIG. 15. Fusion Diagram of Antimony-Lead Alloys.

It should be noted, in this connection, that the diagram was not made as complete by the author as is shown in our figure. He gives only the course of the fusion curve *ACB*; no indication relative to the extreme concentrations at which the presence of eutectic is revealed by the cooling curves is to be found in his paper. On this score, then, we are not justified in assuming complete immiscibility in the crystalline state. The extension of the eutectic horizontal throughout the whole diagram, and the erection of verticals on the concentration axis proportional to the relative quantities of eutectic, would appear, thus far, to be a wholly arbitrary proceeding. This is justified, however, by the results of a microscopical investigation of prepared sections of the reguli by CHARPY.[1] Charpy certifies to the following: Sections containing from 13 to 100 per cent antimony show, after polishing, primarily separated, hard, cubical crystals of antimony, surrounded by eutectic, both constituents of which may be rendered perceptible by weak etching with nitric acid. The quantity of primarily separated antimony crystals increases with the antimony content. Sections containing from 0 to 13 per cent antimony (those possessing concentrations located at the left of the eutectic) present a different appearance; they are difficult to polish, and show large dendritic crystals, which are blackened by hydrogen sulphide and dissolved by nitric acid, imbedded in an eutectic composed of two structure elements. The quantity of these dendrites, which in all probability consist of pure lead, increases with the lead content.

The structure is thus in complete accord with the evidence of our diagram. It is true that Charpy fails to state in particular that the eutectic between 0 and 13 per cent antimony is identical with that between 13 and 100 per cent antimony, and yet he could scarcely have failed to remark upon any observed differences in this respect. Again, he does not specify the minimum additions of antimony to lead, and of lead to antimony, which yield alloys wherein the eutectic is still distinguishable. Nevertheless, we gather from his statements in their entirety that he investigated a large number of concentrations, doubtless including those of very low and very high antimony content, and we may affect some assurance that our elaboration of the diagram has been based upon inferences which are in the main correct.

The fields of condition are accordingly characterized as follows: Above *ACB*, the alloys of all concentrations exist in the liquid condition alone. In the regions bounded by the fusion curve and the eutectic horizontal, a single crystalline variety, more specifically in the triangular field *ACa*, pure lead, and in the triangular field *BCb*, pure antimony, is found in equilibrium with melt. Below the eutectic horizontal *aCb*, the alloys are completely solidified, and are composed of the two crystalline varieties, lead and antimony. In that we regard the eutectic as an individual structure element, we have, at the left of the dotted line *Cc*, a field of primarily separated lead crystals and eutectic,

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[1] CHARPY, Contribution, p. 131.

and, at the right of this line, a field of primarily separated antimony crystals and eutectic.

A few additional examples of systems embracing two metals in which the components presumably exhibit the same mutual behavior as do antimony and lead are to be found in the literature. Unfortunately nearly all of the respective investigations are impaired by a lack of determinations which would fix the extent of the eutectic, or by a lack of data relative to such work. Accordingly, more or less uncertainty attaches itself to all conclusions based upon the material which is generally available, and we will therefore rest content with the above choice of an example which is itself not free from this objection.[1]

B. *Polymorphous Transformations do not Occur. The Components when Fused in Conjunction Unite to Form One or More Chemical Compounds which Melt without Decomposition.*

1. General Case. — We will again choose two elements for the components of our system, denoting them, as well as their melting points, by A and B. For simplicity, we will assume only one compound, possessing the formula A_mB_n, to exist between them. In this formula, m and n are simple integers, according to the law of multiple proportions. To secure better definition at the start, let us suppose that the compound contains 40 per cent A and 60 per cent B. We assume that it melts without decomposition, and that its melting point is C. Our general assumption of complete miscibility in the liquid state and complete immiscibility in the crystalline state applies to the compound as well as to the components.

First of all, let us confine our attention to that part of the concentration-temperature diagram which is located between 0 and 60 per cent B (concentration of the compound A_mB_n). In view of previous explanations, we are in a position to adequately define the general character of this part of the fusion diagram. In effect, we have a two component system, one component being A and the other B. Under our primary assumptions,

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[1] A thorough thermal and microscopical study of these alloys by Gontermann, published about a month after this book left the hands of the author, shows conclusively that the above interpretation is correct. Z. anorg. Chem., 55, 419 (1907). — *Translator.*

complete miscibility in the liquid state, and complete immiscibility in the crystalline state, obtain, polymorphous transformations are excluded, and the two components give no compound with each other, since A_mB_n is the only compound which occurs. Thus, we are dealing with the very case discussed under A (from p. 38). Accordingly, the melting point of A will be lowered by addition of A_mB_n, and, likewise, the melting point of the pure compound by addition of A. Two curve branches of incomplete equilibrium, AX and BY (Fig. 16a), are, therefore, to be expected,

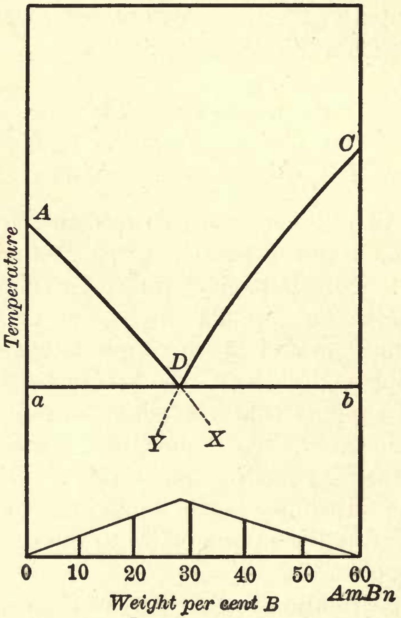

FIG. 16a.

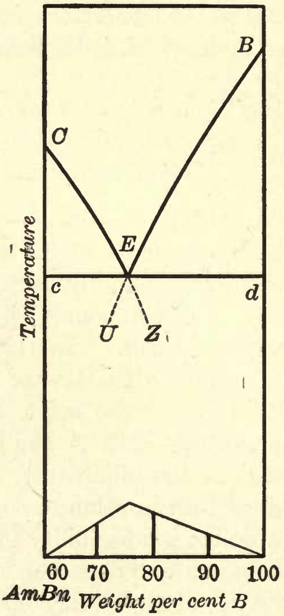

FIG. 16b.

each of them maintaining a rectilinear course from the start, as long as the laws of dilute solutions hold. The crystalline variety A separates along AX, the variety A_mB_n along AY. The two branches intersect at the eutectic point D. An eutectic horizontal aDb passes through this point, reaching, on the one hand, up to the concentration 0 (pure A), and, on the other hand, up to the concentration 60 (pure compound A_mB_n). The relative quantity of eutectic is at its maximum value 1 at the concentration *D*, in that, here, the whole alloy crystallizes eutectically, and decreases lineally toward both sides, reaching the zero value at concentrations 0 and 60, respectively. This is indicated in the usual manner by erecting verticals on the concentration axis, at lengths which are proportional to the relative quantities of eutectic.

We may also consider that part of the diagram between concentrations 60 and 100 per cent *B* separately, in like manner (Fig. 16b). The melting point *C* of the compound A_mB_n is lowered by addition of *B*, and that of *B* by addition of A_mB_n. We have here a system composed of the two substances *B* and A_mB_n, which is completely analogous to the preceding system. Again, we observe two curve branches, namely, *CZ*, corresponding to primary separation of the crystalline variety A_mB_n, and *BU*, corresponding to primary separation of the variety *B*, which intersect at an eutectic point, namely *E*. The eutectic horizontal *cEd* passes through this point and ends at concentration 60 (pure compound) on one side, and at concentration 100 (pure *B*) on the other side. The relative quantity of eutectic is at its maximum value at the eutectic concentration *E*, and decreases lineally toward both sides, reaching the zero value at both end points of the eutectic horizontal. This is also represented in the figure (16b) in the usual manner.

Now, it would be purely a matter of chance if the temperature of eutectic crystallization along the line *aDb* were practically the same as the temperature of eutectic crystallization along the line *cEd*. (We use the words practically the same, since the possibility that two independent processes take place at *precisely* the same temperature may be disputed on the basis of the theory of probabilities.) In general, the eutectic horizontal *cEd* will lie at a different temperature than will the horizontal *aDb*.

At this point, we need only to combine the two single diagrams into one (Fig. 16c) in order to obtain the general form of fusion diagram for this case. The following trivial modification must be observed in this connection. According to our derivation, the fusion curve *ADCEB* is composed of the four branches *AD*, *CD*, *CE* and *BE*, all running rectilineally at the start, and any two successive ones intersecting in a sharp angle (at the respective points *D*, *C* and *E*). Such a trend of the fusion curve in the vicinity of C (Fig. 16c) is indicated by dotted branches. In reality, a sharp peak never occurs at C, but, rather, a more or less flattened maximum, as shown in the diagram by the full curve. Since it may be shown theoretically[1] that an upward peak, viz., a point elevated above its immediate surroundings, can never occur upon a fusion curve, it appears that whenever the experimental investigation seems to indicate the presence of a peak rather than a maximum, we are, in fact, dealing with a maximum, even though it be very little flattened.

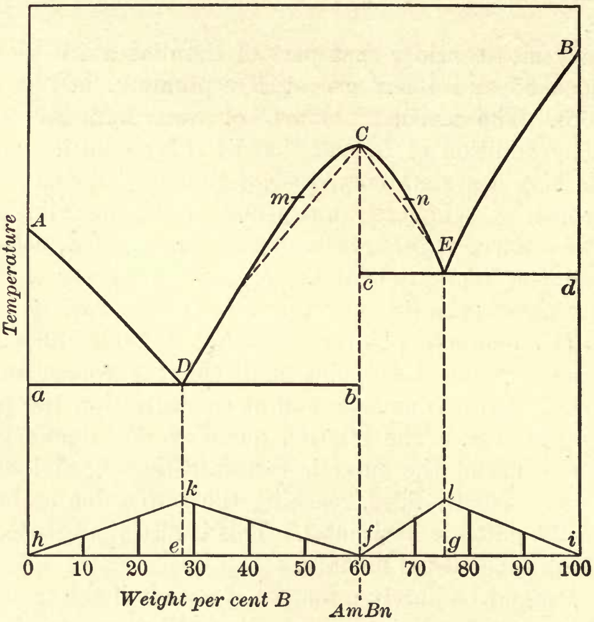

FIG. 16c.

The central portion DCE of the fusion curve therefore shows no discontinuity at C (it manifests no abrupt change in direction), and is to be regarded as a single curve branch. The only abrupt changes in direction throughout the entire course of the curve are at D and E. Accordingly, there are only three branches, namely, AD, DCE and BE (see p. 50, footnote).

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[1] *Cf.* H. A. LORENTZ, Z. phys. Chem., 10, 194 (1892); RUER, Z. phys. Chem., 59, 1 (1907).

The fact that a maximum instead of a peak appears at C may be regarded as a consequence of the partial dissociation of the compound, when in the liquid state, into its components. Assuming, for simplicity, that the formula of the compound is AB, the dissociation process accompanying fusion is represented by the equation,

$$AB \rightleftarrows A + B.$$

The massaction law yields the relation,

$$[A]\,[B] = k\,[AB],$$

wherein the concentrations of the several varieties of molecules are denoted by the use of brackets. As soon as some crystalline AB has separated, *i.e.*, as soon as the solution has become saturated with AB, $[AB]$ becomes constant at the *respective* temperature, and we obtain,

$$[A]\,[B] = \text{const.}$$

Addition of a *foreign* substance (we grant here that the leading assumptions of complete miscibility in the liquid state and of complete immiscibility in the crystalline state — which have applied to all of the recent discussion — are realized) determines a lowering of the melting point of AB, and, furthermore, this lowering is proportional to the number of dissolved molecules, as long as the addition is so slight that the laws of dilute solutions continue to hold. Now, the actual lowering caused by additions of A and B, respectively, is lower in comparison. For, on increasing the quantity of A in the melt, a decrease in the quantity of B must ensue, owing to the required constancy of the solubility product $[A]\,[B]$, *i.e.*, a certain quantity of the compound AB will be re-formed, and thereby free A, as well as free B, utilized. We see, then, that not all of the added quantity of A operates to lower the melting point, but only a certain percentage allowance, which, for unchanging dissociation, *decreases* as the addition of A is made *smaller*. Obviously, addition of B to the compound AB is responsible for an analogous effect, and it follows that the fusion curve in the vicinity of the point C cannot be made up of two straight lines intersecting in a sharp peak, but must, on the contrary, represent a more or less flattened maximum.

If the dissociation of the compound, in proximity to its melting point, is very slight, only a trifling portion of the A material, or B material, respectively, will be used in re-formation of the compound, and the fusion curve at C will approximately represent two intersecting straight lines; at all events it will show a well-marked maximum in this vicinity. If, however, the dissociation is very great, in which case the solubility product will possess a high value, the quantity of A and B, which serves for re-formation of the compound, and is therefore unavailable for lowering the melting point of AB, will be very considerable, particularly at the start. That is, the maximum will be flat. Both cases actually occur, and we are at liberty to conclude from the character of the maximum at C whether the fused compound is considerably, or only slightly, dissociated. In accordance with the above, the "true" melting points of compounds which are subject to such dissociation are never observed; lower values are invariably obtained.

In calculating the degree of dissociation of a compound from the course of its fusion curve, we are confronted by certain difficulties. In the first place, the change in value of the solubility product with the temperature is unknown, and, in the second place, a compound of the general formula A_mB_n may dissociate in various ways. Thus, the compound AB_2 may dissociate partially, *e.g.*, into A and B_2, or into AB and B, as well as completely *i.e.*, into A and $2B$. Nothing whatever is known concerning the extent to which these various dissociations may occur in the presence of one another.

According to the above, our fusion diagram shows the following characteristics:

(1) The fusion curve — the curve of incomplete equilibrium joining the temperatures of initial separation of a crystalline variety — is composed of the three branches AD, DCE and BE. A definite crystalline variety is in equilibrium with the melt along each one of these branches. Along the branches AD and BE, we have the pure substances A and B, respectively, while, along the fusion curve DCE, we have primary separation of the compound A_mB_n. The latter is especially characterized by its capacity for existence in a condition of equilibrium with either of two melts of different concentration at one and the same temperature. By way of illustration, m and n represent two such points on the branch DCE — they are equally distant from the concentration axis and therefore correspond to the same temperature. In this connection, we will regard the melt of concentration m as composed of molten A, saturated with the compound A_mB_n at this temperature, and the melt of concentration n as composed of molten B, likewise saturated with the compound at this temperature. This interpretation is confirmed by the fact that, in the first case, the eutectic is made up of the two structure elements A_mB_n and A, while, in the second case, it is made up of A_mB_n and B. (See below.)

(2) Of the three branches, one, namely *DCE*, possesses a maximum (at *C*) which corresponds to the compound A_mB_n.

(3) At length, there are in the diagram two eutectic horizontals, *aDb* and *cEd*, corresponding to two different complete equilibria. Along the horizontal *aDb*, we find the crystalline varieties *A* and A_mB_n in complete equilibrium with melt of invariable composition *D*. Along the horizontal *cEd*, the prevailing condition of complete equilibrium pertains to the two crystalline varieties A_mB_n and *B*, on the one hand, and melt of invariable composition *E*, on the other hand. *The temperatures of these two eutectic horizontals are different.* The relative quantities of eutectic for the various concentrations, and the eutectic halting periods on the cooling curves which are proportional to the same under the familiar assumptions, increase lineally along the eutectic horizontal *aDb* from the zero value at concentration 0 up to a maximum value at concentration *D*, and thereupon decrease lineally to a second zero value at the concentration *C* of the compound. Along the eutectic horizontal *cEd*, an analogous increase from zero to maximum between concentrations *C* and *E* occurs, as well as an analogous decrease from maximum to zero between concentrations *E* and 100.

The complete concentration-temperature diagram is divided by the curves and straight lines into nine fields of condition, provided we consider the eutectics as individual structure elements, in accordance with earlier explanations. Above the fusion curve *ADCEB*, all alloys exist in the liquid state; we have, here, the field of melt. Between the fusion curves and the eutectic horizontals, lie the fields in which a single crystalline variety is in equilibrium with melt. Four *"fields with one crystalline variety,"* as we shall call them, are in evidence. All are triangular in form, and two of them refer to the compound A_mB_n. Their characterization follows:

(1) The triangle *AaD*. In this field, the crystalline variety *A* occurs in equilibrium with melt. Separation of *A* takes place along the curve branch *AD*. During this process, the composition of the melt gradually approaches concentration *D*. The quantities of variety *A* and melt, into which any given mixture separated on attaining a position in this field, are given by the lever relation.

(2) The triangle *CbD*. This is a field of the crystalline variety A_mB_n and melt. On falling temperature, separation of A_mB_n proceeds along the branch *CD*, whereby the composition of the melt continually approaches concentration *D*.

(3) The triangle *CcE*. This is also characterized as a field of crystalline variety A_mB_n and melt. In fact, we have already noted that the compound A_mB_n may exist in equilibrium with two different melts at the same temperature. On falling temperature, crystallization of A_mB_n proceeds along the branch *CE*, and the composition of the melt continually approaches concentration *E*.

(4) The triangle *BdE*. This is the field of the crystalline variety *B* and melt. The composition of the latter continually approaches concentration *E* as the temperature falls.

The four fields of condition in which the alloys are entirely crystallized are situated below the eutectic horizontals *aDb* and *cEd*. Since two crystalline varieties are invariably present within these fields, we denote them as "*fields with two crystalline varieties.*" Each one of these fields is subjoined to a field with one crystalline variety (situated directly above it). (There are four of each.) Characterization follows:

(1) The field with two crystalline varieties *aDeh* corresponds to the superposed field with one crystalline variety *ADa*. After primary separation of *A* has ceased, the residual melt will have attained the composition *D*, and will henceforth crystallize at the constant temperature of the eutectic horizontal *aDb*. During this time, then, we find ourselves upon the limiting line *aD* which belongs to neither of the fields, since here two crystalline varieties and melt are in equilibrium. As soon as the whole melt has crystallized, however, we cross this limiting line and enter the field *aDeh*. We now have primarily separated *A* crystals, surrounded by eutectic of concentration *D*; the latter composed of the two crystalline varieties *A* and A_mB_n.

(2) The field with two crystalline varieties *Dbfe* is associated with the superposed field with one crystalline variety *CbD* in exactly the same manner. In this case, the structure elements are primarily separated compound A_mB_n, surrounded by eutectic *D*; the latter identical with the eutectic of the preceding field.

(3) Primarily separated A_mB_n is also present in the field with two crystalline varieties *Ecfg*. It is, however, surrounded by a different eutectic, namely, that of concentration E, composed of the two crystalline varieties A_mB_n and B.

(4) Field *Edig* contains the primarily separated crystalline variety B, surrounded by eutectic E; the latter identical with the eutectic of field 3.

In accordance with the above detailed characterization of the alloys in this series, we shall expect the following results on microscopical examination of prepared sections of the corresponding reguli:

(1) A section of concentration 0 will be homogeneous, showing the single crystalline variety A.

(2) Sections of concentrations between 0 and e will show primarily separated crystals of A, surrounded by eutectic D; the latter composed of the two varieties A and A_mB_n. The quantity of primarily separated crystals will decrease with increasing concentration, while that of eutectic will increase.

(3) A section of concentration e will show eutectic D alone; no primarily separated single crystalline variety.

(4) Sections of concentrations between e and f will show primarily separated crystals which must differ from those in sections 1 and 2. These will consist of compound A_mB_n, but the surrounding eutectic will be identical with that of the preceding sections. The quantity of A_mB_n crystals will increase with increasing concentration, while that of eutectic will decrease.

(5) A section of concentration $f = C$, corresponding in composition to the pure compound, can show only one crystalline variety, namely A_mB_n, and must therefore appear completely homogeneous.

(6) Sections of concentrations between f and g will show the same primary structure element as did sections 4 and 5, namely, the compound A_mB_n. However, a different eutectic E will appear here. This is composed of the two crystalline varieties A_mB_n and B. The quantity of primary crystalline variety will decrease with increasing concentration, while that of eutectic will increase.

The new eutectic possesses the crystalline variety A_mB_n in common with the previously observed eutectic, but contains the variety B as a substitute for the variety A of the latter. Therefore, we might look with some assurance for a corresponding difference in the appearance of the two eutectics. Microscopical investigation proves inadequate, however, in just this respect — eutectics of different composition frequently show the same lamellar, or finely granular, structure, with very little if any distinction, while, on the other hand, identical eutectics may differ more or less from one another in appearance (*cf.* p. 100). The temperature at which an eutectic crystallizes in general serves as the best criterion regarding its nature. On the contrary, the *presence* of eutectic in very close proximity to the concentration $f = C$ is usually detected to better effect by the microscopical method than by the thermal method.

(7) A section of the composition g will show eutectic E alone (same condition as in 3).

(8) Sections of concentrations between g and i (= 100 per cent B) will show a new crystalline variety B, as primary structure element, surrounded by the same eutectic E found in sections 6 and 7.

(9) A section of concentration 100 contains the crystalline variety B only, and will therefore appear completely homogeneous.

In summation, the characteristic properties of the fusion diagram, representing the mutual behavior of two substances according to the assumptions upon which our discussion has been based, are as follows:

(1) The fusion curve is made up of three branches, of which the central one possesses a maximum.

(2) *Two different* temperatures of eutectic crystallization exist. One eutectic horizontal begins at the pure substance A; the other at the pure substance B. Both end at the exact concentration of the maximum C of the central curve branch.

Conversely, if the diagram of a two component system is constructed on the basis of cooling curves of an adequate number of different concentrations and reveals the two above characteristics, we are at liberty to conclude that:

(1) Complete miscibility in the liquid state and complete immiscibility in the crystalline state obtain (the latter, owing to the fact that both eutectic horizontals begin at the pure substances A and B, respectively, and end at the same concentration).

(2) The two components, on being fused in conjunction, unite to form a single chemical compound (subject, of course, to the limitations discussed on p. 64).

(3) The compound fuses without decomposition.

In determining the composition of the compound, the following expedients,[1] based upon the preceding discussion, are brought into requisition:

(1) The composition of the compound corresponds to the maximum *C* of the central branch of the fusion curve.

(2) The eutectic horizontal *aDb* ends at the concentration of the pure compound. The periods of eutectic crystallization are used, in the familiar manner, in locating this end point. Thus, when verticals are erected upon the concentration axis at lengths which are proportional to the eutectic halting points on the cooling curves (assuming the use of equal quantities of substance in all experiments as well as equal and ideal conditions of cooling), one of the two straight lines joining the end points of these verticals, namely *kf*, must intersect the concentration axis at the concentration *f* of the pure compound.

(3) The same (2) holds for the eutectic horizontal *cEd*, in that this horizontal also ends at the exact concentration of the compound — the straight line *lf* cuts the concentration axis at the same point *f*.

These three criteria check one another. Two other criteria serve by way of further confirmation:

(4) An alloy of the exact concentration of the compound melts at the temperature *C* after the manner of a pure substance, and should show no eutectic in its prepared section.

(5) The composition of the compound must correspond to the law of multiple proportions.

Relative to the value of the individual criteria, we may say that Criterion 1 may be depended upon for accurate results only when the maximum is not too flat. For, even though the method of temperature measurement (discussion of such methods follows in Part II, Practice) be admirably developed, differences of some 5 degrees between individual temperature determinations, or of 10 degrees or even more at temperatures above 1200 degrees, are not exceptional. Unusual care in experimentation and fre-

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[1] Tammann, Z. anorg. Chem., 37, 303 (1903).

quent repetition of the separate determinations for the purpose of securing check must be observed if any considerable reduction of this error is to be secured. In effect, then, if the maximum is very flat, its position on the fusion curve is often uncertain by several per cent, particularly in cases where the melt is disposed toward supercooling, viz., where exact determination of the initial temperature of crystallization is subject to further difficulty. In dealing with what appears to be an extremely flat maximum, there may be considerable doubt as to whether it actually is or is not a maximum.[1]

Criteria 2 and 3 are in general much more valuable, as first pointed out by TAMMANN. It is indeed true that conditions may operate here to render the lines *hk*, *fl* and *li*, joining the end points of the verticals which represent periods of eutectic crystallization, curved instead of straight. We note particularly, in this connection, the effect of supercooling and the impossibility of completely realizing ideal cooling conditions in actual practice. But, on the one hand, these two sources of error are opposite in effect, and compensate one another in many cases, as will be shown later, while, on the other hand, when the lines are not straight, but are curved in some way, their prolongation almost invariably meets the concentration axis at the proper locality. Moreover, microscopic examination of the corresponding sections usually permits very accurate estimation of the concentrations at which the eutectics vanish.

Criterion 4 is, likewise, of especial value when the thermal investigation is confirmed by use of the microscope to show that the solidified alloy in question is actually homogeneous, containing no eutectic, or at most a negligible trace of eutectic.

Finally, Criterion 5 is of little value, since the inter-metallic compounds frequently correspond to formulas which, in the first place, are rather complicated, and, in the second place, fail to conform to the doctrine of valence — itself a development based upon the investigation of compounds between metals and non-metals. Thus, SCHÜLLER[2] describes the following sodium-mercury compounds:

$NaHg_4$, $NaHg_2$, $Na_{12}Hg_{13}$, $NaHg$, Na_3Hg_2, Na_5Hg_2, and Na_3Hg.

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[1] RUER, Z. anorg. Chem., 52, 350 (1907).

[2] SCHÜLLER, Z. anorg. Chem., 40, 385 (1904).

At this point, we will permit the limiting assumption that the two elements form only one compound to lapse. We will continue to assume, however, that each compound melts without decomposition. No difficulty will be met in handling this case, in view of the preceding explanations. Let us suppose that two, and only two, compounds exist. The two components of the system and their melting points are again denoted by A and B. The melting point of one compound A_mB_n is C, and that of the other compound, of composition A_oB_p, is D. If the whole diagram (Fig. 17) is now divided into three parts by the two dotted lines erected upon the concentration axis at the respective concentrations of the two compounds, each part corresponds to a two component system including no compound, and we may

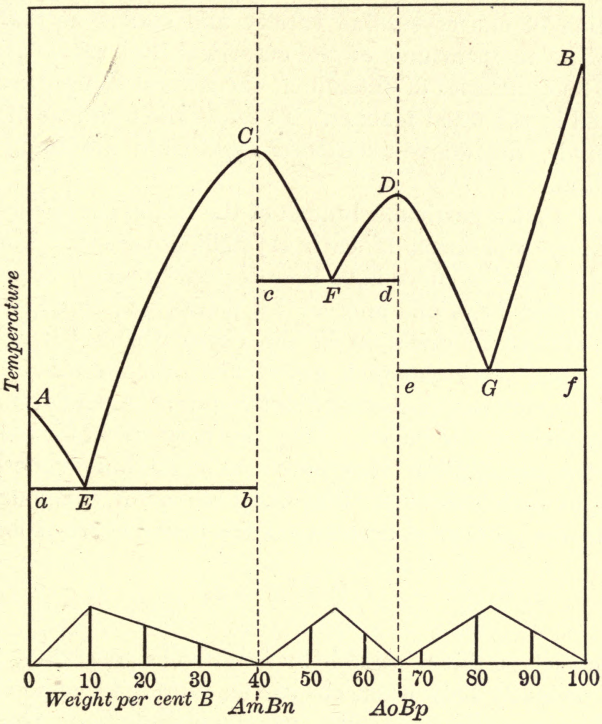

FIG. 17.

draw the same conclusions which led to the development of the fusion diagram including a single compound.

We deduce very simply that the fusion curve now consists of four branches, namely, *AE*, *ECF*, *FDG* and *GB*. The two central branches each possess a maximum at the concentration of the respective compound. Furthermore, we have the three eutectic horizontals *aEb*, *cFd* and *eGf*, each beginning at the concentration of one crystalline variety and ending at that of the next. The temperatures of the eutectical horizontals are different. The quantities of eutectic at the several concentrations are indicated in the usual manner. In fixing the formulas of the two compounds, the above-mentioned expedients are brought into requisition.

We see that a particular branch of the fusion curve corresponds to primary separation of each crystalline variety. These portions of the fusion curve have been termed branches because they are separated from one another by points (*E*, *F*, *G*) where an abrupt change in direction of the curve occurs. If, as in the current case, two compounds are existent, there are four separate crystalline varieties (including the two pure components) and also four branches of the curve. Thus, we may affirm for such cases, under the assumption that only one crystalline variety corresponds to each substance, that the number of compounds V is equal to the number of branches of the fusion curve A less 2:

$$V = A - 2.$$

Nevertheless, this relation is by no means a generality. It does not of necessity hold when one of the substances appears in two crystalline modifications, viz., when polymorphous transformations occur. Again, it requires that the assumption, "complete miscibility in the liquid state, complete immiscibility in the crystalline state," be realized. Even in these cases, this rule is frequently of no practical importance, since a branch of the fusion curve may be dwarfed beyond recognition (see Fig. 14, p. 71), or abrupt changes in direction along the curve may be imperceptible.

Since precisely two crystalline varieties are required in the formation of an eutectic, the following analogous rule may be composed: The number of compounds V is equal to the number of eutectic horizontals E less 1, under the assumption that no polymorphous transformations occur:

$$V = E - 1.$$

The validity of this rule is dependent upon the same assumptions, in general, as that of the first rule, and, in addition, upon an extension of our conception of an eutectic horizontal on the basis of criteria which presume very exact knowledge of the complete fusion diagram.

All such rules are of interest merely in the sense that they may serve the purposes of a preliminary survey. Knowledge of the complete fusion diagram is essential in formulating final answers to questions as to what and how many compounds are formed between two substances.

2. MAGNESIUM-TIN ALLOYS. — We will now proceed to the discussion of examples under the above general case, first directing attention to the fusion diagram of the magnesium-tin alloys, as constructed by GRUBE.[1] His summary of results obtained from cooling curves is given in Table 2.

TABLE 2.

Weight per cent tin.	Weight per cent magnesium.	Atomic per cent tin.	Atomic per cent magnesium.	Temp. of breaks.	Temp. of eutectic halting points.	Duration of eutectic crystallization in seconds.
0	100.00	0	100.00	M.P. 650.9°. Time of crystallization 125		
10.00	90.00	2.22	97.78	625.0°	565.0°	15
20.00	80.00	4.87	95.13	607.5	566.1	40
30.00	70.00	8.07	91.93	583.0	564.6	85
40.00	60.00	12.01	87.99	585.4	565.1	140
50.00	50.00	16.99	83.01	698.0	566.3	75
60.00	40.00	23.46	76.54	753.5	564.8	35
65.00	35.00	27.55	72.45	773.7	561.9	20
70.95	29.05	33.33	66.67	Separation of compound $SnMg_2$ at 783.4°. Time of crystallization 110		
75.00	25.00	38.05	61.95	754.1	204.5	40
80.00	20.00	44.55	55.45	720.0	211.2	90
85.00	15.00	53.70	46.30	666.1	210.3	145
90.00	10.00	64.82	35.18	550.0	210.3	200
95.00	5.00	79.55	20.45	330.5	210.5	240
97.50	2.50	88.87	11.13	217.4	209.3	275
99.00	1.00	95,29	4.71	220.0	209.4	125
100.00	0	100.00	0	M.P. 231.5°. Time of crystallization 250		

[1] GRUBE, Z. anorg. Chem., 46, 76 (1905).

We find in this table:

(1) The composition of such melts as were investigated, in both weight and atomic per cent.

(2) The temperatures at which primary separation of each crystalline variety begins. Since these temperatures are rendered perceptible upon the cooling curves by abrupt changes in direction, or breaks, they are entered as "breaks" in the table.

(3) The temperatures of eutectic halting points.

(4) The periods of duration of eutectic crystallization, in which connection all cooling experiments were conducted with the same total quantity of material (20 grams), and under as uniform conditions as were possible.

The breaks and halting points tabulated above are entered by the author in a co-ordinate system; concentrations appearing as abscissas, and temperatures as ordinates, in the well-known manner. Observed points are denoted by crosses. The concentration axis is graduated in *weight per cent* tin, from 10 to 10 per cent progressively. Thus, concentration 0 corresponds to pure magnesium, and concentration 100, to pure tin. The atomic per cents which correspond to these even decimal weight per cent units are entered upon a horizontal line immediately above the concentration axis. This diagram is reproduced in Fig. 18.

The fusion curve, or the curve giving the temperature of primary separation of one crystalline variety throughout the series, is made up of the three branches *AB*, *BCD* and *DE*. The branches *AB* and *DE* are approximately rectilinear, while the branch *BCD* possesses a well-marked maximum situated at the temperature 783.4 degrees (see Table). The branches *BCD* and *DE* intersect at the eutectic point *D* — concentration 97.5 weight per cent tin — while the branches *BCD* and *AB* intersect at the eutectic point *B* — concentration 38.7 weight per cent tin. The mean value for the eutectic temperature *B*, calculated from the several observed values given in the table, is 564.8 degrees, and for the eutectic temperature *D*, 209.4 degrees. Thus, the temperature difference between the two eutectic horizontals amounts to some 350 degrees. The first eutectic horizontal commences at pure magnesium and ends at the point *c*, located very nearly upon the vertical which bears the maximum *C*. The

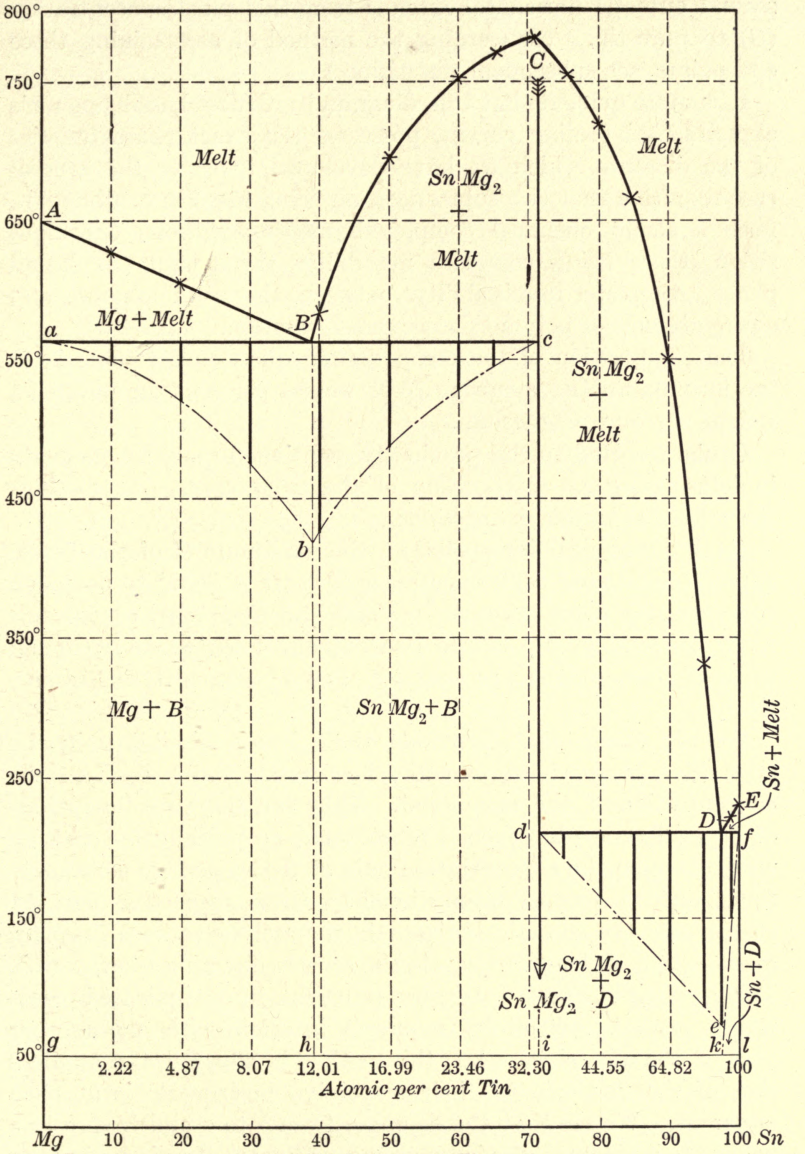

FIG. 18. Fusion Diagram of Magnesium-Tin Alloys according to Grube.

second eutectic horizontal extends from this exact concentration (C) to pure tin. (Concerning the method of ascertaining these end points, see subsequent discussion.)

It is quite evident that this diagram by Grube, based upon his experimental cooling curves, possesses the exact characteristics of the diagram which we have developed to cover the general case requiring that two substances, on being fused in conjunction, form a single chemical compound melting without decomposition, there being complete miscibility throughout the liquid phase, complete immiscibility between the solid phases, and entire absence of polymorphous transformation.

The composition of the compound in question corresponds to the formula $SnMg_2$, requiring 70.95 weight per cent tin and 29.05 weight per cent magnesium.

Grube resorted to the previously mentioned (p. 85) expedients in determining the composition of the compound. He specifies the following in this connection:

(1) By graphical interpolation, the maximum C of the fusion curve (constructed from experimental data) is found to possess a concentration value between 70.5 and 71.5 weight per cent tin.

(2) The end points of the two eutectic horizontals are found to lie at 70.8 weight per cent tin, and 71 per cent tin, respectively.

We are aware that, provided there is no miscibility in the crystalline state, both eutectic horizontals must end at the concentration of the compound. Thus far, the eutectic periods of crystallization have been represented graphically by erecting verticals upon the concentration axis at the respective concentrations, and at lengths proportional to these respective periods. Grube uses the eutectic horizontals themselves as base lines for construction of these verticals in the reverse direction (downward). This trifling alteration is very practical in complicated cases where several horizontals frequently interfere with one another part of the way, since, when this method is adopted, the application of the verticals to their respective horizontals is at once apparent. We see that the decrease from b to a and from b to c below the horizontal aBc is by no means linear. In discussing the general case, we referred to the frequent occurrence of such anomalies in the fusion diagram and to their forthcoming explanation (in Part II). It is, however, evident that prolongation of the curve joining the end points of the verticals results in its intersection with the eutectic horizontal at the point *a* of concentration 0 (at pure magnesium), on the one hand, and at the point *c* of concentration 70.8 on the other hand. The eutectic periods decrease lineally, within the limits of observation, along the eutectic horizontal *dDf.* The lines joining the end points of these verticals are therefore straight, and we have for points of intersection with the ground line (horizontal), *f* of concentration 100 (pure tin), on the one hand, and *d* of concentration 71, on the other hand.

In summation, then, the values for the composition of the compound, 70.8 per cent Sn and 71 per cent Sn, obtained with the aid of the eutectic periods, agree excellently with one another, and, within the limits of experimental error, with the concentration value found for the maximum of the fusion curve, namely, 70.5 – 71.5 per cent Sn.

By way of further check, Grube took the cooling curve of an alloy corresponding exactly to the compound $SnMg_2$ in composition (containing 70.95 per cent Sn). This cooling curve was that of a pure substance, showing a halting point at which the temperature remained constant during a long period of time (110 seconds). This halting point appeared at a higher temperature (783.4 degrees) than did the breaks upon cooling curves of neighboring concentrations (65 and 75 per cent Sn), and, hence, must actually correspond to a maximum (*cf.* Table 2). Accordingly, the melting point of the compound lies at 783.4 degrees. The melting point of the compound is considerably above the melting point of the less fusible component; a condition which is frequently realized. Grube makes no mention of having proved the unity of the alloy of the above concentration and the absence of an eutectic structure element by microscopical investigation. Presumably, the brittleness of the pure compound, which he mentions, precluded preparation of a serviceable section.

Finally, the simplicity of the above formula, added to the circumstance that it satisfies the requirements of the valence theory, may be regarded as further confirmation of the conclusions which have been drawn from the diagram.

The fields of condition of the diagram are as follows: Above the fusion curve *ABCDE*, the alloys of all concentrations are entirely liquid. In the three-cornered fields, bounded above by the fusion curve and below by the eutectic horizontals, we have one respective crystalline variety in equilibrium with melt. Below the eutectic horizontals, the alloys of all concentrations are entirely solid, and are invariably made up of two crystalline varieties. Table 3 gives a summary of the fields.

TABLE 3.

Fields of condition			
with one crystalline variety.		with two crystalline varieties.	
ABa	Mg	*aBhg*	Mg + Eutectic B [Mg + $SnMg_2$]
CBc	$SnMg_2$	*Bcih*	$SnMg_2$ + Eutectic B [Mg + $SnMg_2$]
DCd	$SnMg_2$	*Dkid*	$SnMg_2$ + Eutectic D [Sn + $SnMg_2$]
DEf	Sn	*Dflk*	Sn + Eutectic D [Sn + $SnMg_2$]

The branch *AB* of the fusion curve appears much more developed in the diagram than does the branch *ED*. This is, however, due to the use of weight per cents in graduating the concentration axis. If concentrations are expressed in atomic per cent, the point *B* becomes located at 11.60 atomic per cent tin, and the point *D* at 11.13 atomic per cent magnesium, values which merely chance to virtually coincide.

Kurnakow and Stepanow[1] have also investigated this alloy series. Their results agree with those of Grube in all essential points, and their fusion diagram need not be reviewed here. Nevertheless, we propose to devote some attention to their microphotographs because, in the first place, they have been prepared with great care and, owing to marked differences between the properties of compound and components, show the structure unusually well, and then again, because comparison of the evidence from the fusion diagram, which is particularly clear in this instance, with the conclusions to be drawn from structural relations of the sections, which are in turn unusually pictorial in this case, is well adapted to show how far both methods of investigation support and ultimately elaborate one another.

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[1] Kurnakow and Stepanow, Z. anorg. Chem., 46, 177 (1905).

We may say, relative to the properties of the three crystalline varieties, that the compound Mg_2Sn shows octahedral cleavage, and that its hardness (=3.5) is considerably greater than that of either pure component. (Tin =1.8, magnesium =2.) Furthermore, the solidified alloys oxidize in damp air at a rate which increases with their magnesium content.

The sections shown in Figs. 19, 20 and 21 represent alloys containing from 10 to 30 per cent tin, and therefore fall within the field with two crystalline varieties *aBhg* (Fig. 18). Primary separation of magnesium has followed the curve branch *AB*.

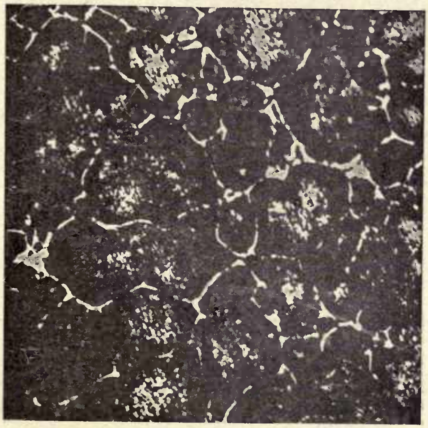

FIG. 19. 10% Sn, magnified 70 times.

The reguli were first ground and then polished by means of very finely ground emery, placed wet upon a metal plate covered with chamois. The dampness of the leather pad brought about complete surface oxidation of the sections. After being etched in this manner, the sections were rubbed down on dry chamois, covered with finely ground "saflor" (cobalt glance). As a result of this process, the harder constituent, namely, the compound, $SnMg_2$, which was least worn away by rubbing, and therefore remained somewhat in relief, lost its coating of oxide and became brilliant, while the metallic magnesium remained dark. Fig. 19 represents a section containing 10 per cent tin, magnified 70 times. It consists, for the most part, of grains of magnesium. Enclosed

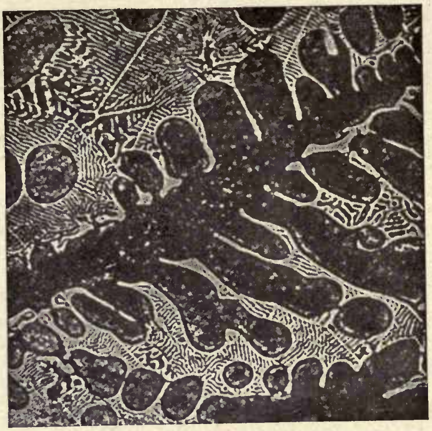

FIG. 20. 24% Sn, magnified 100 times.

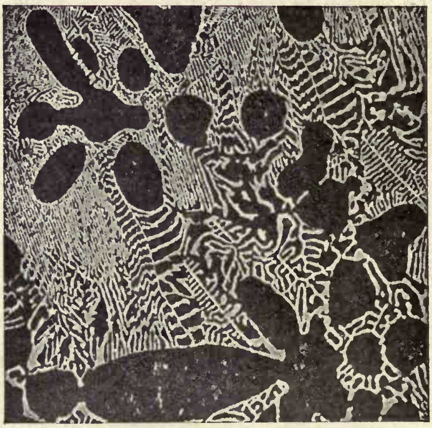

FIG. 21. 30% Sn, magnified 100 times.

within the mass of these grains, we find appreciable quantities of light eutectic, which permeates the predominant material in the form of thin veins. In Fig. 20, which represents a section containing 24 per cent tin, magnified 100 times, dark dendrites of primarily separated magnesium are visible. The interstices are filled with beautifully developed eutectic, composed of alternate layers of darkly etched magnesium and light compound $SnMg_2$. We may roughly estimate the relative quantity of eutectic at one-half by volume. Fig. 21, corresponding to 30 per cent tin, presents essentially the same picture; there is merely a decrease in the relative quantity of primarily separated magnesium, and, conversely, an increase in the relative quantity of eutectic, as required by the diagram.

FIG. 22. 39% Sn, magnified 170 times.

Fig. 22 corresponds to 39 per cent tin (concentration *B* in the diagram). It must, therefore, show nothing but eutectic. This section was prepared in the same manner as were sections 19, 20 and 21. The typical lamellar eutectic structure — called typical on account of its general occurrence — appears here, under the chosen magnification of 170 times, with a sharpness and distinctness which is seldom attained in practice.

Figs. 23–27 correspond to concentrations from 42 to 62 per cent tin, and accordingly belong in the field of two crystalline varieties

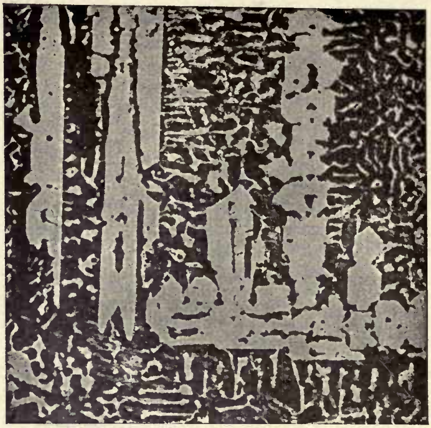

FIG. 23. 42% Sn, magnified 70 times.

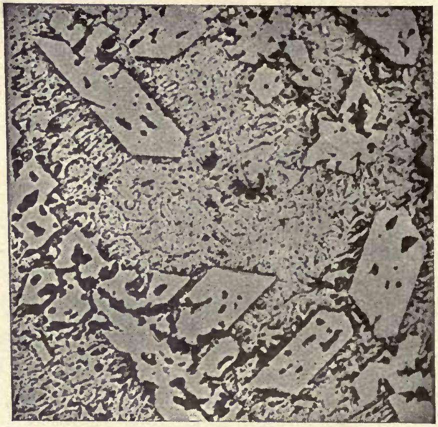

FIG. 24. 46% Sn, magnified 70 times.

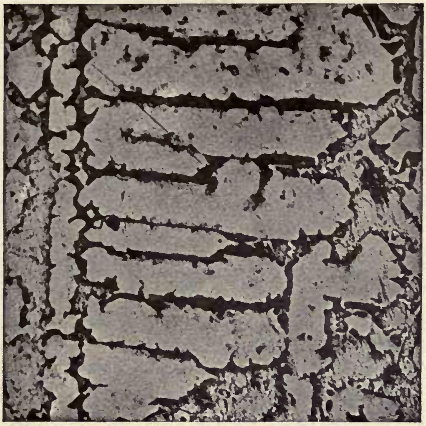

FIG. 25. 50% Sn, magnified 70 times.

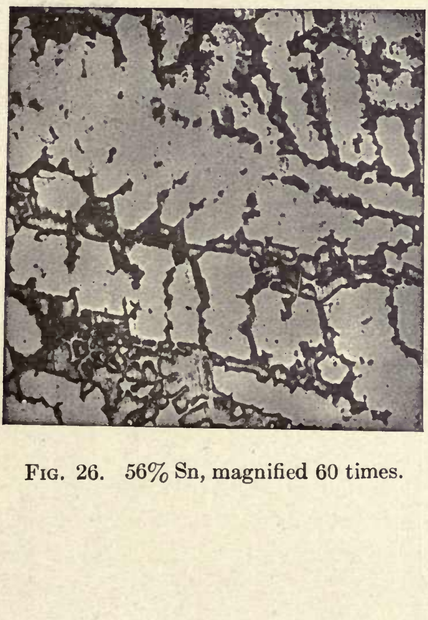

FIG. 26. 56% Sn, magnified 60 times.

Bcih. A glance at the diagram informs us that, in these concentrations, a new crystalline variety, namely, the compound $SnMg_2$, separates along the curve branch CB, but that the eutectic, crystallizing last, must be the same as in the former sections. No change was made in the preparation of the sections. We at once recognize the difference between the primary structure element of these sections, and that of the sections previously considered. The light sharp-edged crystals of the compound $SnMg_2$, often elongated in one direction, cannot be confused with the rounded grains, or dentrites, of magnesium, coated with a dark layer of oxide. We also recognize conformity with the diagrammatic evidence, in the sense that the quantity of primarily separated crystals increases with the tin-content of the alloys, while the quantity of eutectic simultaneously decreases. The structure of the eutectic, however, is not as clear in these photographs as it was in Figs. 20–22. We could scarcely affirm, on the basis of the microscopic examination alone, that this eutectic is identical with the one observed in the former sections. In reaching this conclusion, we must make use of the unambiguous diagrammatic evidence which, although unsupported in this special case by the appearance of the eutectic, is not contradicted by the same.

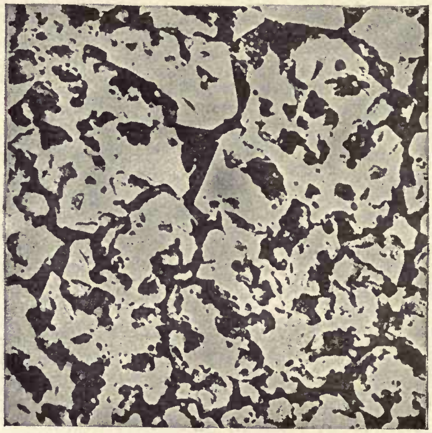

FIG. 27. 62% Sn, magnified 70 times.

Figs. 28 and 29 represent sections containing 83 and 91 per cent tin, respectively, and therefore belong to the field with two crystalline varieties *Dkid.* Primary separation of the compound has here occurred along the branch *CD.* Hence, we must observe the same primary crystalline variety, namely the compound $SnMg_2$, as in sections 23–27. However, in these sections the second eutectic appears. This is composed of the compound $SnMg_2$ and pure tin (in the place of magnesium). Moreover, a simple calculation based upon the composition of this eutectic, as given in the diagram, and use of the lever relation shows us that it contains more than 90 per cent tin.

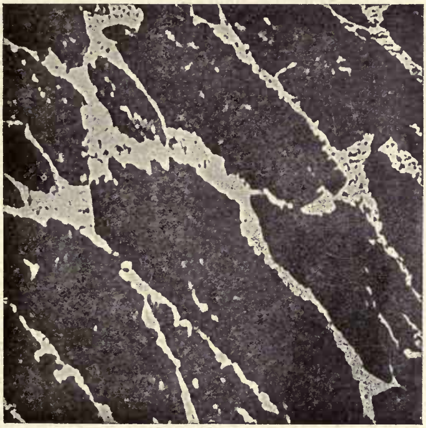

Fig. 28. 83% Sn, magnified 40 times.

The preparation of these sections was somewhat different from that of the former sections. It was limited to simple grinding, followed by polishing on the leather-covered metal plate, with use of fine emery. This process causes oxidation of the compound $SnMg_2$ only; the tin remaining unchanged. Subsequent rubbing down was omitted. The dark appearance of the primarily separated compound $SnMg_2$ find its explanation in this altered method of preparation. As is well represented in Fig. 29, the contour of these primary crystals is apparently the same as that shown in the preceding pictures. The eutectic has remained almost completely bright and, in accordance with its composition

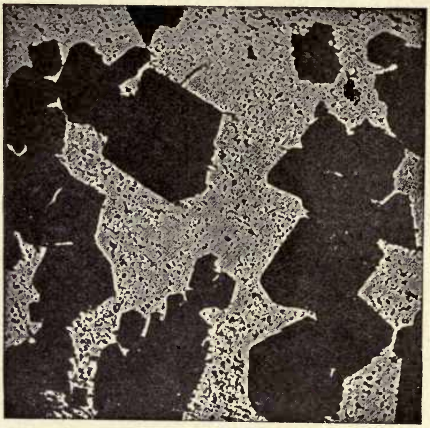

FIG. 29. 91% Sn, magnified 45 times.

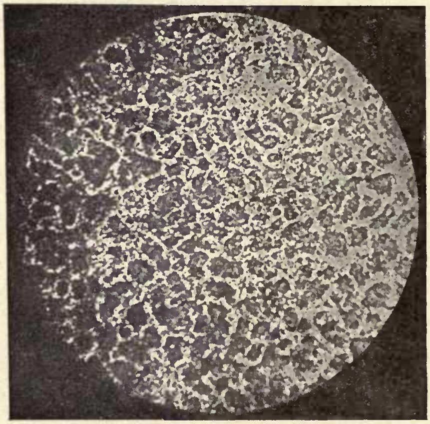

FIG. 30. 99% Sn, magnified 50 times.

as noted above, shows only small quantities of the compound $SnMg_2$ in the form of small dark evenly distributed crystals. As the tin-content increases, the quantity of eutectic increases and that of primary crystals decreases, in line with the requirements of the diagram. It is also plainly evident that this bright eutectic is different from the eutectic of the first sections (composed of approximately equal parts of magnesium and compound). Indeed, wet polishing of sections 19–27 caused simultaneous oxidation of both structure elements, so that subsequent dry polishing on rouge was necessary in order to give the compound a bright appearance. Since the latter step was not observed in the treatment of sections 28 and 29, the eutectic which they contain would of necessity have presented a dark appearance if it had been identical with that of the first sections.

Fig. 30 shows a section containing 99 per cent tin, viz., one falling within the field *Dflk*, magnified 50 times. The diagram informs us that a new crystalline variety, namely pure tin, has separated primarily along the curve branch *ED*. The eutectic does not differ from that shown in the two preceding pictures. This photograph is taken from Grube's paper; his use of a different etching agent precludes comparison of this section with preceding ones. However, we note the presence of a liberal quantity of a bright eutectic, forming a matrix in which dark crystals of tin are imbedded.

We have seen above that the diagrammatic evidence is corroborated by the appearance of the sections, as far as they present characteristic structure, and that no contradiction is to be noted. As a result, the general conclusions must be accredited with a high degree of certainty.

3. MAGNESIUM-BISMUTH ALLOYS. — The fusion diagram of the System Magnesium-Bismuth has also been studied by GRUBE.[1] His experimental results are summarized in Table 4, and his diagram is reproduced in Fig. 31. Observed points are denoted by crosses. We note the occurrence of complete miscibility in the liquid state, the entire absence of miscibility in the crystalline state, the absence of polymorphous transformation, and that the two metals unite to form one compound — of formula Bi_2Mg_3.

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[1] GRUBE, Z. anorg. Chem., 49, 83 (1906)

This diagram serves to illustrate the earlier mentioned possibility (Fig. 14, p. 71; p. 88) that a branch of the fusion curve be so dwarfed as to practically disappear. This is observed on the side of pure bismuth, the melting point of which is immediately elevated along the curve branch *DC* by addition of magnesium. The temperature of the eutectic horizontal *Dc* (268 degrees) practically coincides with the melting temperature of pure bismuth (268 degrees). Again, the compound Bi_2Mg_3 invariably separates primarily from bismuth-rich melts, never pure bismuth. Accordingly, the eutectic must be composed of a single crystalline variety, namely, pure bismuth.

TABLE 4.

Bismuth-content of the alloys.		Temp. of breaks.	Temp. of eutectic halting points.	Duration of eutectic crystallization in seconds.	Supercooling during eutectic crystallization.
Wt. per cent.	At. per cent.				
0	0	M.P. of pure Mg 650.9°. Time of crystallization 125			
10.00	1.28	640	552	5	....
20.00	2.84	626	553	20	....
30.00	4.77	623	552	40	....
40.00	7.39	604	554	60	....
50.00	10.46	583	551	80	....
60.00	14.46	564	553	95	....
70.00	21.42	610	551	75	....
80.00	31.85	677	552	30	....
82.50	35.51	698	550	15	....
83.50	37.16	710	....	....	....
85.09	40.00	M.P. of the pure c'p'd Bi_2Mg_3 715°. Time of crystallization 72			
87.50	44.98	699	269	55	2
90.00	51.26	612	268	120	4
95.00	68.92	527	268	150	8
97.50	81.97	432	268	230	7
100.00	100.00	M.P. of pure Bi 268°. Time of crystallization 250			

The maximum *C* of the fusion curve at the concentration of the compound appears to be unusually sharp; in fact, there is practically no distinction between this maximum and a sharp peak. On this basis, we might be led to conclude that the compound Bi_2Mg_3 is practically undissociated in the molten condition at its melting temperature (*cf.* p. 79). When, however, we graduate the concentration axis in atomic per cent, instead of

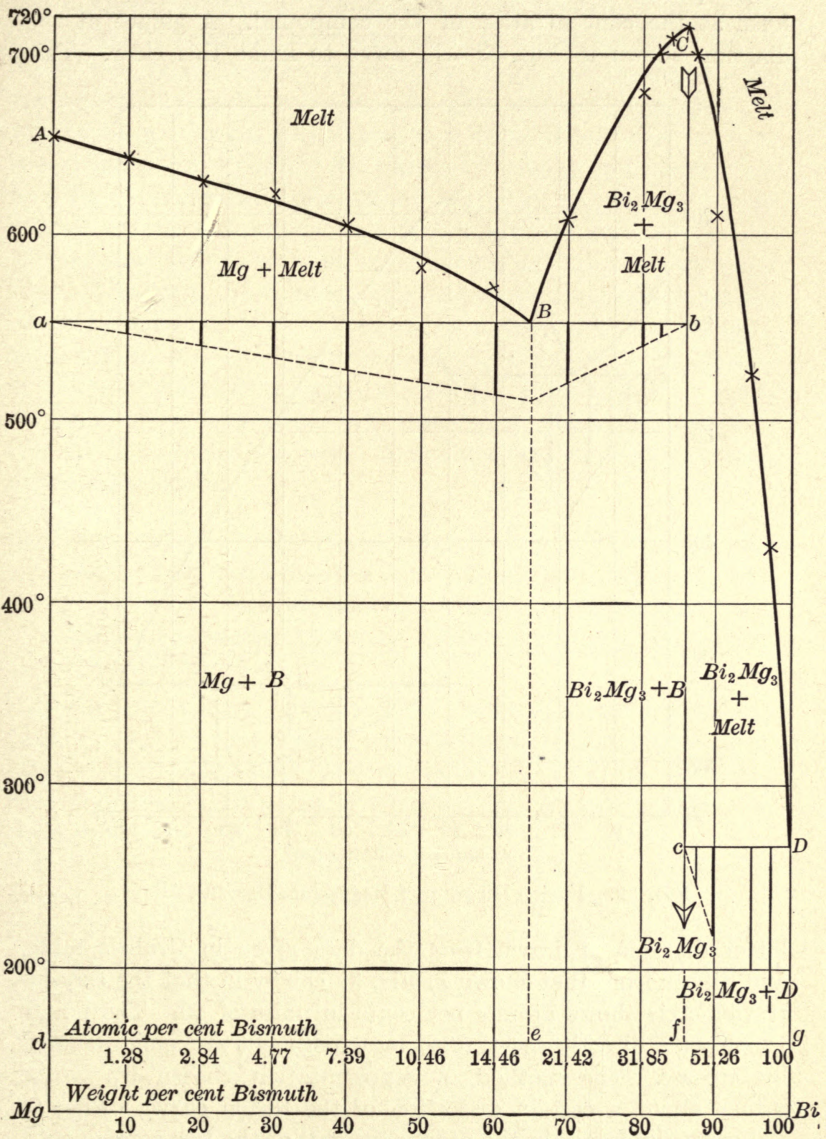

FIG. 31. Fusion Diagram of Magnesium-Bismuth Alloys according to Grube.

weight per cent, the fusion curve shows a maximum of the usual form at the concentration of the compound. A glance at the diagram shown in Fig. 32 will serve to make this clear. This latter diagram is drawn from the data given in Grube's table, and differs from that shown in Fig. 31 chiefly in that the concentration axis shows atomic per cents in units of 10. The points which were directly ascertained by experiment are again denoted by crosses. The method of representation chosen by Grube brings about a certain distortion of the fusion curve, owing to the great difference in the atomic weights of the two components.

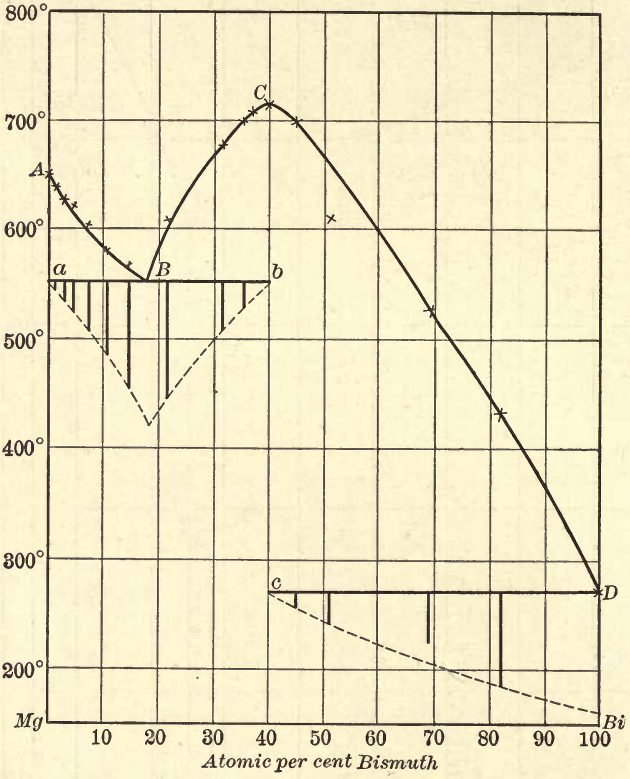

FIG. 32. Fusion Diagram of Magnesium-Bismuth Alloys.

We should note, in conclusion, that division of the concentration axis according to atomic per cent requires an additional change. We are aware that the relative quantity of eutectic, *i.e.*, quantity referred to a unit weight total substance, is a linear function of the concentration expressed in *weight per cent.* Obviously this relation loses its validity when concentrations are expressed in atomic per cent. In this case, the quantity by weight of eutectic per gram-atom is a linear function of the concentration. The quantity by weight of eutectic per gram-atom may be experimentally ascertained by noting the crystallization periods at the eutectic halting points, when equal numbers of gram-atoms are taken in all experiments. If the relative quantities of eutectic have been experimentally ascertained on the basis of equal quantities of material by weight in all experiments, these values may obviously be made to yield the quantities of eutectic on the basis of equal numbers of gram-atoms, by recalculation. This was done in constructing the fusion diagram (Fig. 32) from Grube's figures. A separate recalculation was made for each horizontal.

C. *Polymorphous Transformations do not Occur. The Components when Fused in Conjunction Unite to Form a Chemical Compound which does not Melt Unchanged, but Decomposes to a Melt and a Second Crystalline Variety on Heating* (*Case of the Concealed Maximum*).

Under the general discussion of heterogeneous equilibrium (from p. 31), we encountered an example of a compound which failed to melt unchanged, and we learned at the same time that such a process must occur at constant temperature (under constant pressure).

1. FUSION OF GLAUBER'S SALT, $Na_2SO_4 \cdot 10\,H_2O$. — A generally known and thoroughly investigated example of this type of fusion is offered by Glauber's salt. This substance melts under atmospheric pressure at 32.4 degrees, yielding, instead of a clear liquid, a pasty mixture, the crystalline constituent of which is anhydrous sodium sulphate. The fused portion is composed of sodium sulphate and water, and must obviously represent a saturated solution of Glauber's salt as well as of anhydrous sodium sulphate. For, when partial fusion is effected, and the system then protected from loss or gain of heat, both crystalline varieties are capable of remaining indefinitely in contact with the melt

without any change in the system whatever. The system is therefore in equilibrium; a condition requiring saturation of the solution with both substances.

We describe the above process in the familiar manner by using the equation: $Na_2SO_4 \cdot 10\,H_2O \rightleftarrows Na_2SO_4$ + Saturated Solution (49.6 parts water per 100 parts Na_2SO_4), in which the arrows indicate reversibility. When heat is added, the reaction proceeds from left to right; when heat is abstracted, it proceeds from right to left.

We have here a condition of complete heterogeneous equilibrium between melt, anhydrous sodium sulphate and Glauber's salt. When the reaction proceeds from left to right, the quantities of anhydrous sodium sulphate and of melt increase, the composition of both phases remaining unchanged. We are already aware that, in a case of this sort, the temperature remains constant during addition or abstraction of heat until the reaction has proceeded to completion. The temperature 32.4 degrees therefore constitutes a limiting temperature, and the substance under consideration possesses this at least in common with a substance which melts without decomposition, viz., whose melting point represents a limiting temperature above which (under atmospheric pressure) the liquid state alone is stable and below which the crystalline state alone is stable. In the present case, Glauber's salt is stable below 32.4 degrees, while a mixture of anhydrous sodium sulphate and its saturated solution is stable above this limiting temperature. Both crystalline varieties are in equilibrium with one another and with a solution saturated with respect to both at this temperature only.

It follows from the above, that at 32.4 degrees, Glauber's salt and sodium sulphate must possess the same solubility in water (figured on the basis of the common constituent, anhydrous sodium sulphate). For, if this were not the case, — if, for example, the Glauber's salt possessed a greater solubility than the anhydrous sodium sulphate — the two substances could not remain in equilibrium. The saturated solution of Glauber's salt would then be supersaturated with respect to anhydrous sodium sulphate, and would of necessity proceed to deposit the latter until this condition had become relieved. At this point, however, the solution would no longer be saturated with Glauber's salt and would, in consequence, dissolve the salt anew, whereupon the dissolved material would again separate in the form of anhydrous sodium sulphate, etc. This process would continue until all of the Glauber's salt had become transformed into anhydrous sodium sulphate, that is to say, under these conditions, Glauber's salt and anhydrous sodium sulphate would not be in equilibrium; on the contrary, the latter alone would be stable. Now, this is actually the case at temperatures above 32.4 degrees only, and we conclude that, at these temperatures, the unstable Glauber's salt is more soluble in water than anhydrous sodium sulphate. Conversely, at temperatures below 32.4 degrees, the stable Glauber's salt must be less soluble than anhydrous sodium sulphate. In other words, the stable crystalline variety invariably possesses the lesser solubility. The two varieties possess the same solubility at the equilibrium temperature alone — where both are stable. At this temperature, the saturated solution contains 49.6 parts Na_2SO_4 and 100 parts water. These figures are from Lowel,[1] and hold equally well whether water is saturated with Glauber's salt or with anhydrous sodium sulphate. Löwel was also able to prove that anhydrous sodium sulphate is actually much more soluble than Glauber's salt at temperatures below 32.4 degrees. A saturated Glauber's salt solution prepared at 20 degrees by agitating a mixture of the salt and water until no more of the salt dissolves, or by allowing a solution which has previously been saturated at a temperature above 20 degrees to remain in contact with Glauber's salt at this temperature until the salt no longer separates is found to contain 19.4 parts anhydrous sodium sulphate for every 100 parts water. But, if Glauber's salt is fused in a glass vessel, the liquid heated so high that the solution above the separated anhydrous sodium sulphate begins to boil, the vessel then closed and allowed to cool down to 20 degrees, this solution is found to contain 52.76 parts anhydrous sodium sulphate for every 100 parts water, viz., nearly three times as much as the previous solution at the same temperature. However, the crystalline variety in contact with the liquid in the latter case is not Glauber's salt; it is anhydrous sodium sulphate, which has separated during fusion of the former. Hence, the figures obtained from this experiment refer to the

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[1] Löwel, Ann. chim. et de phys. (3) 49, 50 (1857).

solubility of anhydrous sodium sulphate in water. The solution was boiled merely to dissolve away such minute crystals of Glauber's salt as may have adhered to the cooler walls of the vessel. This was essential, since our solution was supersaturated with respect to Glauber's salt, and merely a minute crystal of the salt, on reaching the solution, would suffice to bring about immediate formation (with rise in temperature) of a pasty mixture of Glauber's salt and dilute solution. We have here an excellent example of the saturation of a solution with respect to one crystalline form, and its supersaturation with respect to another form. It is also seen at once, from this example, that the form which is stable under certain conditions is also the least soluble under these very conditions. Above 32.4 degrees, the saturated Glauber's salt solution would obviously be supersaturated with respect to anhydrous sodium sulphate. Nevertheless, it is extremely difficult to prepare such a solution.[1]

It is clear from the above considerations what method must be adopted in practice to actually realize reversibility of the reaction represented by the equation:

$$Na_2SO_4 . 10\ H_2O \rightleftarrows Na_2SO_4 + \text{Sat'd Sol'n.}$$

The reaction proceeds from left to right, in measure determined by the quantity of heat added, and regardless of any special precautionary measures. If it be required that the reaction proceed in the opposite direction, *i.e.*, if formation of Glauber's salt from anhydrous sodium sulphate and saturated solution be prescribed, such reaction must be started by inoculation of the solution with a crystal of Glauber's salt.

We may predict the following, relative to cooling processes which will take place in mixtures of water and sodium sulphate under the customary assumption that equilibrium invariably ensues without delay. (This signifies a resort to inoculation in order to avoid supersaturation.)

(*a*) If the mixture corresponds to the formula $Na_2SO_4 . 10\ H_2O$, *i.e.*, if it contains 78.9 parts of anhydrous sodium sulphate for every 100 parts water (the former, partly crystallized and partly dissolved), then the total quantity of anhydrous sodium sulphate

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[1] Telden and Shenstone, Phil. Trans., 175, 28 (1884).

will react with the solution when the temperature has fallen to 32.4 degrees, with formation of Glauber's salt. The temperature will remain constant until this transformation has become complete, when all the material will have crystallized. Further cooling is unattended by heat effect. We shall have a single halting point upon the cooling curve, and this will be located at 32.4 degrees (the possible appearance of breaks is neglected in this discussion).

(*b*) If the mixture contains more than 78.9 parts anhydrous sodium sulphate for every 100 parts water, a halting point will occur at 32.4 degrees, as in the above case. However, there will not be sufficient water in the mixture to permit transformation of the entire quantity of anhydrous sulphate into Glauber's salt, and, consequently, when the reaction has proceeded to completion, a certain quantity of the former will still remain. But, withal, after the equilibrium temperature 32.4 degrees has been passed, the whole material will have become crystalline, so that further cooling will be unattended by heat effect. As in the above case, we shall observe a single halting point upon the cooling curve, and this will likewise be located at 32.4 degrees.

(*c*) If, on the other hand, the mixture contains less than 78.9 parts anhydrous sodium sulphate (corresponding to $Na_2SO_4 . 10\,H_2O$), but more than 49.6 parts (corresponding to the saturated solution at the equilibrium temperature, 32.4 degrees), then, as before, anhydrous sodium sulphate will be present with saturated solution when the temperature has fallen to 32.4 degrees. This anhydrous sodium sulphate must then react with the solution to form Glauber's salt. We shall, therefore, again observe a period of constant temperature at the above point. When the reaction has proceeded to completion, however, not all of the material will have crystallized. That is, there will be more water in the mixture than corresponds to the formula $Na_2SO_4 . 10\,H_2O$, and, consequently, when the total quantity of anhydrous sodium sulphate has become changed to Glauber's salt, a certain quantity of saturated solution (at 32.4 degrees) must remain. On further cooling, the crystalline variety stable below 32.4 degrees (Glauber's salt) will separate from the solution. This process is accompanied by fall in temperature and will continue until the temperature of eutectic crystallization of Glauber's salt and water, namely, −1.2 degrees, has been attained. The solution which solidifies without change in composition at this temperature to a mixture of Glauber's salt and ice crystals contains four parts Na_2SO_4 for every 100 parts water.

Cooling curves of these concentrations will thus show two halting points; the first, at 32.4 degrees, corresponds to transformation of anhydrous sodium sulphate into Glauber's salt, and the second, at −1.2 degrees, to eutectic crystallization of Glauber's salt-ice.

(*d*) If the mixture contains not more than 49.6 parts sodium sulphate (corresponding to saturation at the equilibrium temperature, 32.4 degrees), and not less than four parts (corresponding to the composition of the eutectic), for every 100 parts water, then no anhydrous sodium sulphate will separate at 32.4 degrees, since the solution is, at most, saturated at this temperature. For the same reason, there will be no transformation at 32.4 degrees, and no halting point upon the cooling curve. The first separation of crystals must occur below 32.4 degrees, and these will be crystals of Glauber's salt, the variety stable below this temperature, and therefore the less soluble variety. The temperature will fall continuously, as crystallization of Glauber's salt proceeds, until the eutectic point −1.2 degrees is reached. At this point, the remainder of the solution will solidify to a mixture of Glauber's salt and ice crystals. We shall, therefore, observe a single halting point upon each of the cooling curves of these concentrations, as was the case with concentrations *a* and *b*. But the halting point in this case will be otherwise located, namely, at −1.2 degrees, the temperature of eutectic crystallization, Glauber's salt-ice.

(*e*) Finally, if the mixture contains less than four parts anhydrous sodium sulphate (corresponding to composition of the eutectic, Glauber's salt-ice) for every 100 parts water, ice will separate first, as we have learned previously, and will continue to separate until the solution has become enriched in sodium sulphate up to the eutectic concentration. Then complete crystallization will ensue, as above, at the temperature −1.2 degrees. The cooling curves will each show a single halting point at −1.2 degrees.

We have seen that the melting point of Glauber's salt is to be observed in all sodium sulphate-water mixtures containing more than 49.6 parts sodium sulphate for every 100 parts water. Hence, this temperature is admirably adapted to use as a thermometric fixed point. The salt is easily prepared and purified, and moreover, it is not essential in this connection that the material correspond very closely to the formula $Na_2SO_4 . 10\,H_2O$. Glauber's salt is superior for this purpose to any salt fusing without decomposition, since the melting point of such a salt must represent a maximum upon the fusion curve, as we know, and will be lowered by an excess of either component. Richards and Wells[1] have determined this point with great accuracy. The value which they give is 32.383 degrees. Glauber's salt is recommended by them as a most simple means for the production of constant temperature. In this connection, it is obviously superior to any thermostat. Its melting point is less dependent upon external pressure than the melting points of most other substances, for reasons which we shall not discuss here.

2. General Case. — Let the components of the system — again assumed to be elements — and their melting points as well be denoted by A and B. Let A_mB_n represent the formula of the compound, and $t_1°$ the temperature at which it melts, whereby a liquid and a second crystalline variety are produced. If we assume on account of simplicity that this is the only compound existing between the two elements, then the crystalline variety which separates during fusion must be either pure A or pure B (pure, in accordance with our leading assumption of complete immiscibility in the crystalline state). Suppose that it be the latter. Then the equation descriptive of this reversible process will read:

$$\underset{\textbf{crystals}}{A_mB_n} \rightleftarrows \underset{\textbf{crystals}}{aB} + \underset{\textbf{melt}}{[mA + (n - a)\,B]}.$$

Fusion, *i.e.*, progress of the reaction from left to right, is effected by heat addition. The opposite effect is secured by heat abstraction. During reaction, the quantities of the several phases change, but their individual composition remains constant: throughout the change we have complete equilibrium, and therefore constant

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[1] **Richards and Wells, Z. phys. Chem., 43, 471 (1903).**

temperature. The conditions which prevail here have been treated in detail in the preceding discussion (relative to Glauber's salt). We shall now proceed to apply the information therein presented to the general case in terms of the following brief outline:

(1) The crystalline variety A_mB_n is stable below $t_1°$, the crystalline variety B above $t_1°$ and both crystalline varieties at $t_1°$.

(2) Both crystalline varieties B and A_mB_n must be equally soluble in A at the equilibrium temperature $t°$. (Equal solubility signifies the same content of B, the common constituent of both crystalline varieties, in the melt.) For, if the B-saturated A solution were still capable of dissolving A_mB_n, it would thereby become supersaturated with respect to B, and continuous solution of A_mB_n, attended by continuous separation of corresponding amounts of B, would, of necessity, occur. That is to say, there would be no equilibrium. Under these conditions, then, the crystalline variety B is most soluble in A at temperatures above $t°_1$, where it is the stable variety, while the crystalline variety A_mB_n is most soluble in A at temperatures below $t_1°$, where *it* is the most stable variety (we obviously imply comparison at the same temperature).

(3) Accordingly, the composition of the melt is unequivocally defined at the equilibrium temperature. This melt is nothing other than a saturated solution of B (and, therefore, of A_mB_n) in A at the corresponding temperature t_1.

(4) All concentrations which are B-richer than the melt $[mA + (n - a) B]$, saturated at $t_1°$, must show halting points upon their cooling curves at the temperature t_1, since all of them, with exception of pure B, are composed of crystalline B and this melt at the temperature in question, and become either completely or partially transformed into A_mB_n, according to the proportion in which they are present.

(5) All mixtures which are A-richer than the compound A_mB_n must show halting points at the temperature of eutectic crystallization of $A_mB_n - A$. We shall call this temperature t_2. Concentrations which are richer in B than A_mB_n fail to show this halting point. It is clear that those concentrations which are intermediate between A_mB_n and the saturated melt $[mA + (n - a) B]$ will show halting points at $t_1°$, as well as at $t_2°$.

The diagram shown in Fig. 33 represents such mutual relations between two substances as we have just discussed: its essential properties are ordered according to the above stipulations. It is apparent at the start that no maximum can appear upon the fusion curve at the concentration which corresponds to the composition of the compound, since such a maximum melting point is the especial characteristic of a compound which fuses without decomposition. But, instead, a horizontal *Dc* must meet the fusion curve at the concentration *D*, corresponding to the composition of the melt $[mA + (n - a)B]$. This horizontal extends to pure *B*, according to (4) above, and corresponds to the halting points at t_1° upon the cooling curves.

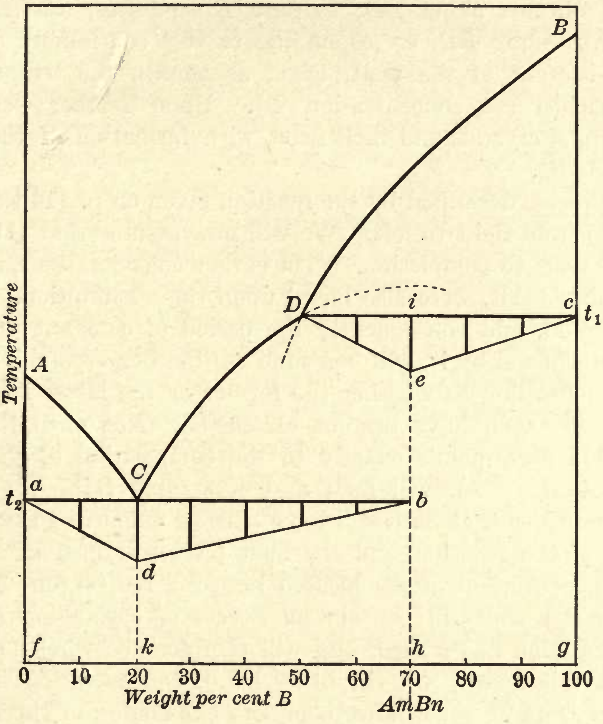

FIG. 33.

Upon adding a certain quantity of A to molten B, the melting point of the latter is lowered. This is indicated by the branch BD. The crystalline variety B crystallizes first upon cooling melts which are intermediate in concentration between B and D. Crystallization begins at that point upon the curve branch BD which corresponds to the concentration of the melt. Incomplete equilibrium obtains along BD; as pure B separates, the temperature sinks along BD, corresponding to the continually increasing A-content of the melt, until, at length, the temperature t_1 is reached (at concentration D). Upon further heat abstraction, B crystals and melt react with formation of the compound A_mB_n.

The process described by the reaction given on p. 114 therefore proceeds from right to left. We will now assume that this reaction proceeds to completion. (The earlier considerations, relative to Glauber's salt, were also based upon this assumption.) Then the reaction, and consequently the period of constant temperature determined by it, will continue until either crystalline B or melt — according to whether the former or the latter is present in excess — shall have become exhausted. Not until the concentration corresponds exactly to the composition of the compound A_mB_n $(= h)$, will melt and crystalline B be present in such quantities that both will have become exhausted after completion of the reaction, and the melt have solidified as a whole to A_mB_n. Concentrations located between 100 (= pure B) and h $(= A_mB_n)$ will still contain an excess of crystalline B after transformation has ceased, and will therefore be wholly crystallized at this point. On the other hand, concentrations located between D and h must, after complete exhaustion of the B crystals, still contain an excess of melt, which will continue to crystallize along the curve branch DC. It is the compound A_mB_n, however, which separates primarily along this branch, since we are now within its temperature range of stability, namely, below $t_1°$. The end point C of the branch DC is determined by intersection of this branch with the branch AC. We reflect here that the melting point of A is lowered by addition of B (or, what amounts to the same thing, of A_mB_n). This lowering is shown by the branch AC, representing primary separation of A and enrichment of the melt in A_mB_n. Thus, the point of intersection C of

AC and *DC* corresponds to the eutectic point — where the melt is saturated with both crystalline varieties. Accordingly, these two varieties separate simultaneously at the temperature of *C*, in the proportions indicated by its concentration. Eutectic crystallization at the point *C* (temperature t_2) will obviously occur in all concentrations containing a lesser quantity of *B* than corresponds to A_mB_n. Consequently, the eutectic horizontal *aCb* extends from concentration 0 (=pure *A*) to concentration *h* (= A_mB_n).

According to the above, the following cooling curves correspond to the various concentrations of our diagram:

(1) A melt of concentration 0, corresponding to pure *A*, crystallizes as a whole at the constant temperature *A*. Its cooling curve accordingly shows a single halting point, located at *A*.

(2) Melts which are intermediate in concentration between 0 and *C* separate *A* primarily. Crystallization follows the branch *AC*, having begun at that point upon this branch which corresponds to the concentration in question. When the melt has become enriched in A_mB_n up to the concentration of the eutectic *C*, its temperature will have fallen to $t_2°$, and eutectic crystallization, characterized by simultaneous separation of *A* and A_mB_n crystals at constant temperature, thereupon ensues. A break, as well as a halting point, the latter at $t_2°$, will be found upon these cooling curves.

(3) Melts which are intermediate in concentration between *C* and *D* separate A_mB_n primarily. Crystallization of A_mB_n follows the branch *DC*. When the melt has become enriched in *A* up to concentration *C*, eutectic crystallization ensues at $t_2°$, as in the previous case. We shall again have a break and a halting point upon each cooling curve, the latter at $t_2°$.

(4) Melts which are intermediate in concentration between *D* and *h* (=A_mB_n) separate *B* primarily. Crystallization follows the branch *BD*. The melt becomes continually *A*-richer and its temperature constantly falls, as *B* separates. When the concentration *D* has been attained, the temperature will have fallen to $t_1°$, and the melt will have become saturated with both *B* and A_mB_n. At this point transformation of *B* + melt into the new crystalline variety occurs. The temperature remains constant at $t_1°$ until the end of transformation. A certain quantity of

melt will then remain, as we have seen above. This will separate A_mB_n crystals along the branch DC with continuous fall in temperature, until it has become enriched in A up to the eutectic concentration C. By this time, the temperature will have fallen to $t_2°$, and a second period of constant temperature will now be observed, namely, that corresponding to eutectic crystallization at C. At its conclusion, the whole alloy will be crystallized. According to the above, cooling curves of these concentrations will be characterized by a break and two halting points, the latter located at $t_1°$ and $t_2°$ respectively.

(5) A melt of concentration h, corresponding to the pure compound A_mB_n, also separates B primarily along the branch BD. The initial temperature of crystallization is given by the intersection of the (projected) dotted line hi with DB. When the melt has reached the concentration and temperature of the point D, owing to continuous separation of B, transformation of B + melt into the crystalline variety A_mB_n takes place. At the conclusion of this transformation, the whole alloy will have become crystalline, and A_mB_n will alone be present. The cooling curve of this concentration, which represents the pure compound A_mB_n, will, therefore, show a break, and a halting point at $t_1°$. Such a break, situated above the halting point, serves to differentiate the cooling curve of a compound which melts under decomposition from that of a compound which melts unchanged.

(6) Melts which are intermediate in concentration between h ($= A_mB_n$) and 100 ($= B$) also separate B at the start. When the concentration and temperature of such a melt have fallen to the values defined by the point D, transformation of B + melt into A_mB_n takes place. In this case, however, more B is now present than can react with the melt, whence, B crystals are found with A_mB_n crystals in the solid alloy after transformation. At all events, the cooling curves which correspond to these concentrations also show breaks, and halting points at $t°_{,1}$ and are obviously comparable to the cooling curve of the pure compound in this respect.

(7) A melt of concentration 100 (corresponding to pure B) solidifies completely at the constant temperature B. A single halting point, at B, is found upon its cooling curve.

The diagram is characterized first of all by the three branches which compose the fusion curve, namely, AC, CD and DB; none of them possessing a maximum. Each branch corresponds to primary separation of an individual crystalline variety. Here, the three varieties are A, A_mB_n and B.

As a second characteristic, we have the appearance of two horizontals (of constant temperature) both of which cover the same concentration range for a certain distance. The horizontal aCb passes through the eutectic point C, and is, therefore an eutectic horizontal. It extends from concentration 0 (corresponding to pure A) to the concentration of the compound A_mB_n. The relative quantity of eutectic has a maximum value 1 at the point C, and decreases lineally toward the zero value of both end points. Upon erecting verticals above the eutectic horizontal as base line, at lengths which are proportional to the relative quantities of eutectic throughout the different concentrations (and to the eutectic periods of constant temperature), and joining their end points, two straight lines da and db are obtained. The first of these intersects the horizontal at the point a, corresponding to pure A, and the second, at the point b, corresponding to the compound A_mB_n.

The second horizontal extends from the break D upon the fusion curve to concentration 100 (corresponding to pure B). This is also commonly called an eutectic horizontal. In common with the actual eutectic horizontal, this horizontal of constant temperature represents equilibrium between two crystalline varieties and melt. But, along the actual eutectic horizontal, we have the concentration of melt situated between the concentrations of the two crystalline varieties with which it is in equilibrium; on this account, the melt is invariably exhausted when crystallization is brought about by abstraction of heat. In the other case, the melt is richer in one constituent (A, in the present instance) than the two crystalline varieties with which it is in equilibrium, and, when crystallization of the melt is effected by heat abstraction, the crystalline variety which differs most in composition from this melt (here B) is utilized, as we have seen, in forming the crystalline variety of intermediate composition (here A_mB_n). Thus, when a melt solidifies eutectically, two crystalline varieties are formed, but in a case of this sort a new crystalline variety is formed from melt and a variety already present, and it must depend upon the quantitative relations between melt and the crystalline variety first separated, whether or not a balance of melt will remain after completion of the reaction.

Now, the relative quantity of the variety A_mB_n, formed by reaction between B and melt, is obviously at its maximum 1 in the concentration which corresponds exactly to the formula A_mB_n. In all other concentrations, an excess of either A or B will be present after reaction. If B is present after reaction, *i.e.*, if the concentration of the original alloy is situated between h $(=A_mB_n)$ and 100 $(=B)$, then the relative quantity of A_mB_n which can be formed will be directly proportional to the percentage content of A in the alloy. Consequently, this quantity decreases lineally between concentrations h and 100 from a maximum 1 to 0. If, on the other hand, the total quantity of crystalline B is exhausted during reaction, and an excess of liquid remains, *i.e.*, if the concentration of the original alloy is situated between h $(=A_mB_n)$ and D (concentration of the break), then the relative quantity of A_mB_n produced will be proportional to the relative quantity of B which has separated primarily by the time the temperature has fallen to $t_1°$ and the composition of the residual melt has been brought to concentration D. But this latter quantity is proportional to the difference in B-content between the alloy under consideration and melt of composition D. Therefore, the relative quantity of A_mB_n produced will decrease lineally between concentration A_mB_n and D from a maximum 1 to 0. If the concentration of the original alloy is equal to, or A-richer than, D, it is clear, as a matter of course, that no A_mB_n will be formed by reaction between B and melt, since no B can have separated. Separation of A_mB_n from such melts occurs directly. The relative quantity of A_mB_n produced by reaction between crystalline B and melt in the different concentrations is shown in the usual manner along the horizontal Dc. The periods of constant temperature at $t_1°$ upon the cooling curves are (under the customary assumptions) proportional to these relative quantities.

The entire concentration-temperature diagram is divided into seven fields of condition by the curves and straight lines. Of these fields, one represents melt, a second, third and fourth are fields with one crystalline variety, and a fifth, sixth and seventh, fields with two crystalline varieties.

The fields of condition are characterized by the following properties:

(1) Above the fusion curve $ACDB$ all is liquid.

(2) In the triangle ACa, the crystalline variety A, having separated primarily along the curve branch AC, is in equilibrium with melt.

(3) In the field $DCbi$, the crystalline variety A_mB_n is in equilibrium with melt. Separation of A_mB_n from concentrations which are A-richer than D takes place exclusively along DC, viz., directly. Separation of A_mB_n from concentrations which are B-richer than D occurs as a result of reaction between primarily separated B and melt.

(4) In the triangle BDc, the crystalline variety B, having separated primarily along BD, is in equilibrium with melt.

(5) The rectangle $aCkf$ is the field of primarily separated A and eutectic C — composed of A and A_mB_n.

(6) The rectangle $Cbhk$ is the field of A_mB_n crystals, either separated directly or produced as a result of reaction between B and melt, and eutectic C.

(7) The rectangle $cihg$ is the field of primarily separated B crystals and A_mB_n crystals — separated directly or produced as a result of reaction between B and melt.

The structure of sections from the reguli must of course correspond with the thermal results. Accordingly, in concentrations located between 0 (= pure A) and k (= C), we shall observe primarily separated A, surrounded by eutectic C. The quantity of eutectic increases with the B-content. Solidified alloys of concentration k consist entirely of eutectic C. In concentrations located between k (= C) and h (= A_mB_n), the same eutectic must occur as in preceding concentrations. It decreases in quantity with increasing B-content. We have here a different crystalline variety imbedded in the eutectic, namely, A_mB_n. A section of composition h, corresponding to the pure compound A_mB_n, must be entirely composed of the crystalline variety A_mB_n. In sections which contain more B than corresponds to the compound A_mB_n, *i.e.*, which are intermediate in composition between h and 100, the primarily separated B will have been incompletely transformed into A_mB_n, and, consequently, this unaltered B material is surrounded by the more recently formed compound A_mB_n. The structure of these sections differs from that of the preceding ones in that the primarily separated crystalline variety B is not imbedded in an eutectic, but, rather, in a structure element, which, even under the highest powers, proves to be homogeneous — cannot be resolved into two constituents. Concentrations 0 (pure A) and 100 (pure B) must obviously present the homogeneous appearance of a pure substance.

The following may be said relative to the geometrical form of the fusion curve:

It follows from the stability relations (see p. 114) that, at temperatures above t_1°, the crystalline variety B, and, at temperatures below t_1°, the crystalline variety A_mB_n, must possess the lesser solubility in A, or, what amounts to the same thing, that above t_1°, a melt in equilibrium with B, and below t_1°, a melt in equilibrium with A_mB_n, must show the lesser B-content.

Thus, when we prolong the curve branches BD and CD beyond D, as is done in Fig. 33, both prolongations must correspond to B-richer concentrations than does the (full) curve branch of stable equilibrium, which relation is plainly shown in the figure. That is to say, prolongation of a curve branch beyond its end point signifies continuation of the equilibrium between the crystalline variety separating along the respective curve and melt into a field where this crystalline variety is no longer stable. We have seen in the Glauber's salt example that unstable conditions of this sort may actually be realized. Hence, the above construction is justified by experimental results. It follows, however, from the fact that these dotted prolongations correspond to unstable conditions, that the points of these dotted lines must lie at higher B concentrations than the points of the (full) curve branches of stable equilibrium for corresponding temperatures — for the very reason that, on theoretical grounds, the greater solubility must be conceded to the unstable crystalline variety A. Similarly, the unstable character of the dotted curve branches is evidenced by the fact that the points of these curves lie at lower temperatures than the points of the full branches for corresponding concentrations (corresponding to supercooled conditions).

Thus we see that *BD* and *CD* cannot pass continuously into one another, but must intersect at *D*. Moreover, an apex directed toward the solid field must occur at this point, *i.e.*, *DB* must run steeper than *CD* at *D*. Culmination of these branches (*CD* and *DB*) in an apex directed toward the liquid field, as shown in Fig. 34 at *D*, is impossible from the present considerations, for we perceive at once that, in such case, the dotted prolongations of the two curve branches would necessarily represent stable conditions of equilibrium. If the experimental investigation points to such disposition of the curve branches, the reason must be sought in inaccurate measurements. At length, the difference in solubility between the two crystalline varieties may be very inconsiderable. In such event, the branches *CD* and *BD* will obviously differ so slightly in direction that the angular intersection at *D*, required by theory, will fail to show on the experimentally determined fusion curve (Fig. 35). Incidence of the horizontal *Dc* at

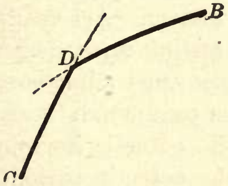

FIG. 34.

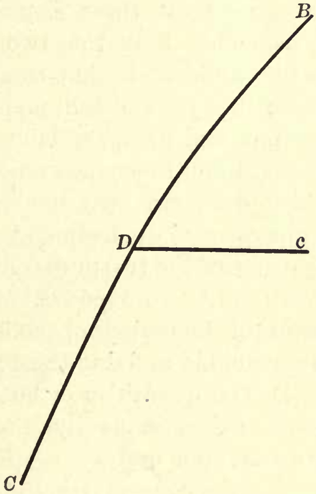

FIG. 35.

D will then constitute the only indication of a break at this point.

In Fig. 33, the curve branch *CD* is continued beyond *D*, according to the relations which would obtain if the compound were fusible without decomposition. We are aware that a maximum would be expected at the concentration of the compound A_mB_n in such case. This maximum fails of appearance, since it is covered, or concealed, by the curve branch *BD*, corresponding to the crystalline variety *B* which is stable within this temperature interval. For this reason, the present case, representing fusion of a compound with separation of a new crystalline variety, is also called the case of the "concealed maximum."

Our fusion diagram is characterized, on the one hand, by a fusion curve consisting of three branches without maximum, and, on the other hand, by two constant temperature horizontals partially covering one another. Conversely, if on constructing the fusion diagram of a two component system from experimental data, we meet these characteristic properties, it is permissible to conclude that the two substances are completely miscible in the liquid state and completely immiscible in the crystalline state; that they sustain no polymorphous transformation which is accompanied by appreciable heat effect; and that, under the customary limitations, they unite to form a single chemical compound, which does not melt unchanged, but decomposes at a definite temperature into melt and another crystalline variety — in this case, one of the two pure components of the system. According to TAMMANN,[1] two expedients, both of them resting upon determination of the periods of the halting points upon the cooling curves are available in fixing the composition of the compound:

(1) The quantities of eutectic *C* along the eutectic horizontal *aCb*, and, consequently, the duration of the eutectic periods of constant temperature, reach the zero value at the point *b*, representing the concentration of the pure compound A_mB_n.

(2) The maximum of the periods of constant temperature along the horizontal *Dc* occurs at the point *i*, representing the concentration of the compound A_mB_n, since, at this point, the whole alloy solidifies uniformly to A_mB_n.

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[1] TAMMANN, Z. anorg. Chem., 37, 303 (1903).

The fusion curve can play no part in the determination of the composition of the compound, as it possesses no maximum. It should be particularly noted that, in general, the break *D* upon the fusion curve does not correspond to the composition of the compound.

The first check upon the composition of the compound, as ascertained by use of these two criteria, consists in obtaining satisfactory agreement between the results. Then again, microscopic investigation of a section corresponding in composition to the pure compound should reveal the presence of a single structure element. Conformity of the composition of the compound to the law of multiple proportions, *i.e.*, its representation by a comparatively simple formula, is not of especial significance as a check upon the results, as was shown on p. 87, but may serve in certain cases by way of lending additional support to the mature conclusions.

The rule given on p. 88, namely, that the number of compounds is equal to the number of branches of the fusion curve diminished by two, is also valid here, but is of no practical service when the break *D* upon the fusion curve is not well marked, and may therefore escape observation, as is frequently the case. The other rule introduced at the same time, namely, that the number of compounds is equal to the number of eutectic horizontals diminished by one, is valid only when we regard *Dc* as an eutectic horizontal, and extend our conception of the term eutectic horizontal to cover any horizontal along which two crystalline varieties are in equilibrium with melt.

3. SODIUM-BISMUTH ALLOYS. — The Sodium-Bismuth System, studied by MATHEWSON,[1] may serve as an example of the general case developed in the preceding section. It is true that sodium and bismuth form a compound which melts unchanged, in addition to the one which melts under decomposition. This is seen at once in the diagram (Fig. 36). However, complete analogy to the above conditions is found in that part of the diagram which lies to the right of the dotted vertical *Bax*.

Concentrations are expressed in atomic per cent. Small crosses are used in entering observed temperatures.

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[1] MATHEWSON, Z. anorg. Chem., 50, 187 (1906).

Certain details may be noted as follows: The fusion curve is composed of three branches, namely, *ABC*, *CD* and *DE*. The first branch possesses a maximum at *B*. Since two compounds, and therefore four different crystalline varieties, including pure sodium and pure bismuth, appear in this system, a fusion curve of four branches is to be expected. Here again, one branch of the fusion curve is dwarfed into insignificance (see pp. 72 and 89). In the present instance, this is the branch corresponding to primary separation of sodium. The melting point of sodium, which was found to be 97.5 degrees according to the table given by Mathewson (*l. c.*), is raised by the first appreciable additions of bismuth. The temperature of eutectic crystallization along the horizontal *Aa* is practically identical with the melting point of pure sodium, whence, the eutectic consists of practically pure sodium.

The formula Na_3Bi of the compound which melts unchanged at 775 degrees is deduced as follows: At the concentration 25 atomic per cent Bi are located:

(1) the maximum *B* of the curve branch *ABC*,

(2) the end point *a* of the eutectic horizontal *Aa*, and

(3) the end point *c′* of the horizontal *Ccc′* (445 degrees). (The lengths of the halting point periods are shown in the customary manner by construction of verticals upon the corresponding horizontal.)

The formula of the compound which melts under decomposition at 445 degrees is determined from the following data:

(1) The maximum of the periods along the horizontal *Ccc′* (445 degrees) is located at the concentration $c = 49.7$ atomic per cent sodium.

(2) The end point *D* of the eutectic horizontal *dDd′* (218 degrees) is located at 50.6 atomic per cent sodium.

The mean of these determinations is 50.15 atomic per cent sodium, a value which corresponds, within a rational error limit, to the formula NaBi.

According to the diagrammatic evidence, this compound melts at the temperature of the horizontal $Ccc' = 445$ degrees to a liquid of concentration *C*, with separation of the crystalline variety Na_3Bi. This process is described quantitatively by the equation: $1\ NaBi \rightleftarrows 0.06\ Na_3Bi + \text{Melt}\ (0.82\ Na + 0.94\ Bi = 53\ \text{at. per cent Bi})$.

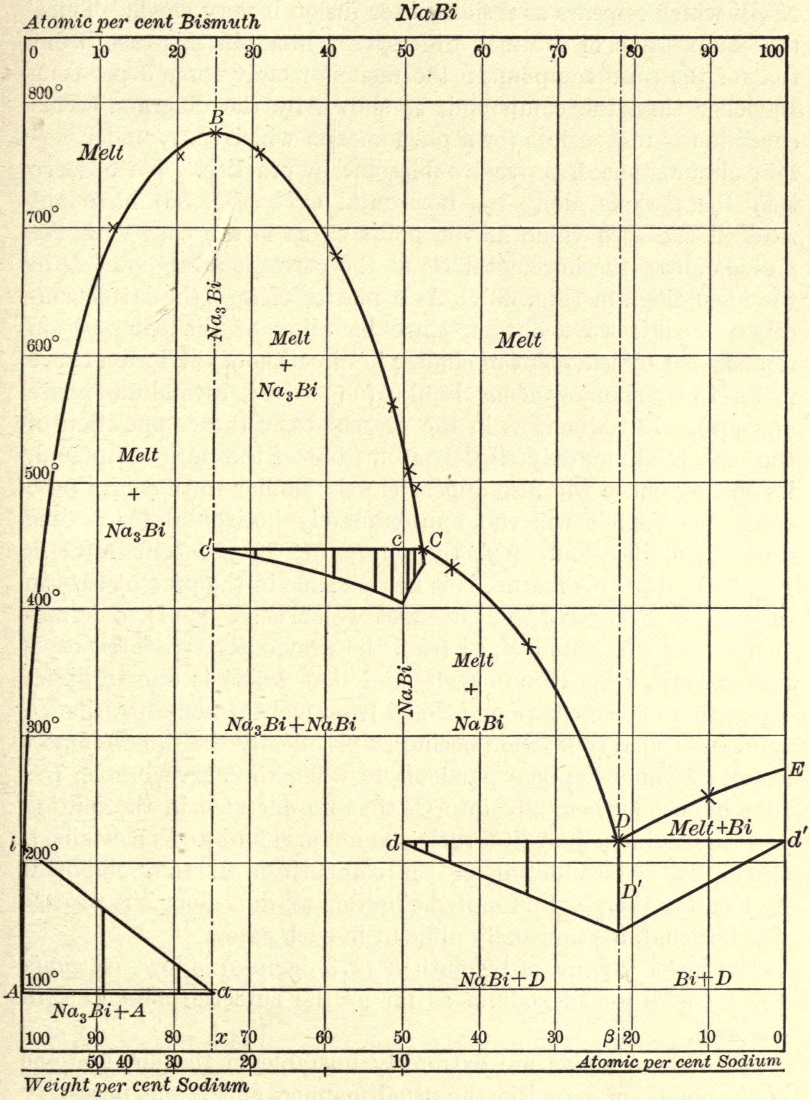

FIG. 36. Fusion Diagram of Sodium-Bismuth Alloys according to Mathewson.

As is apparent from this equation, the quantity of compound Na_3Bi which appears as residue after fusion is very small. Thus, the composition of the melt differs very little, in this case, from that of the pure compound: the melt is merely some 3 per cent Bi-richer than the compound, as shown by the diagram. This condition is responsible for a phenomenon which may, under certain circumstances, prove troublesome in practice. We observe that the periods along the horizontal *Ccc′* (Fig. 36) have not reached the zero value at the point *C*, as is the case with the periods along the horizontal *Dc* at the corresponding point *D* in the ideal diagram (Fig. 33). As a matter of fact, the latter condition must always obtain, since an alloy of the composition represented by the point of change in direction of the fusion curve melts to an homogeneous liquid (no second crystalline phase appears). But when, as in the present case, the composition of the melt *C* differs only slightly from that of the pure compound, its cooling curve will also appear closely similar to that of a pure substance, *i.e.*, it will run approximately horizontal for a time during solidification. (*Cf.* the curve for 2½ per cent NaCl in Fig. 9a.) For this reason, it is not possible in the present case to distinguish between the heat effect which corresponds to formation of the compound NaBi from the previously separated crystalline variety Na_3Bi and melt, and that which is due to direct separation of the compound NaBi from melt of concentration *C*, as long as such separation occurs at practically the same temperature. It may happen, particularly when the curve branch *CD* runs almost horizontally into *C*, that no decrease in the halting periods is evident just after their maximum value has been attained. Obviously, determination of the composition of the compound by locating the maximum of the halting periods along the respective horizontal is unusually difficult in such cases.

The melting point of bismuth *E* (273 degrees) is lowered along *ED* by addition of sodium as far as the eutectic point *D* (218 degrees).

Since these alloys are extremely unstable in the air, sections could not be prepared in the usual manner, and it was necessary to use freshly prepared cleavage surfaces for the direct examination. The appearance of these samples substantiated the results of thermal analysis.

4. Gold-Antimony Alloys. — The fusion diagram of the Gold-Antimony System, as contributed by Vogel,[1] is given in Fig. 37.

Concentrations are expressed in weight per cent.

The fusion curve is composed of the three branches *AB*, *BC* and *CD*, which correspond to primary separation of the three respective crystalline varieties, pure gold, pure compound and pure antimony. Since no maximum is to be observed upon any one of the three branches, we are forced to conclude, according to previous considerations, that the compound does not fuse unchanged, but decomposes into melt and another crystalline variety — in this case, antimony — at the temperature of the horizontal *Cd*. This fails, however, to represent the actual conditions, as is seen on considering the halting periods along the two horizontals. We have here the remarkable case in which the composition of the compound practically corresponds with the concentration of the break *C* upon the fusion curve. This case may be regarded as a limiting case of either of the two previously considered general cases. Thus, reasoning from the case of the concealed maximum (Fig. 33, p. 115), we assume that the point *i*, corresponding to the concentration of the pure compound A_mB_n, advances along the horizontal *Dc* up to a position of coincidence with *D*. Reasoning from the case of the open maximum (Fig. 16c, p. 78), we assume that one arm *CE* of the curve branch *DCE* becomes continually smaller and finally disappears when the maximum *C* and the eutectic point *E* coincide.

The formula of the compound $AuSb_2$ (54.93 per cent Sb) is fixed as follows:

(1) The periods of crystallization at the temperature of the horizontal *Cd* (460 degrees) increase as gold is added to antimony, reaching a maximum at 55 per cent Sb.

(2) The halting periods along the eutectic horizontal *aDc* (360 degrees) decrease from *B* toward *c*, reaching the zero value at 55 per cent Sb.

(3) The cooling curve of an alloy containing 55 per cent Sb possesses one halting point only — located at 460 degrees. Such an alloy crystallizes after the manner of a pure substance.

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[1] Vogel, Z. anorg. Chem., 50, 151 (1906).

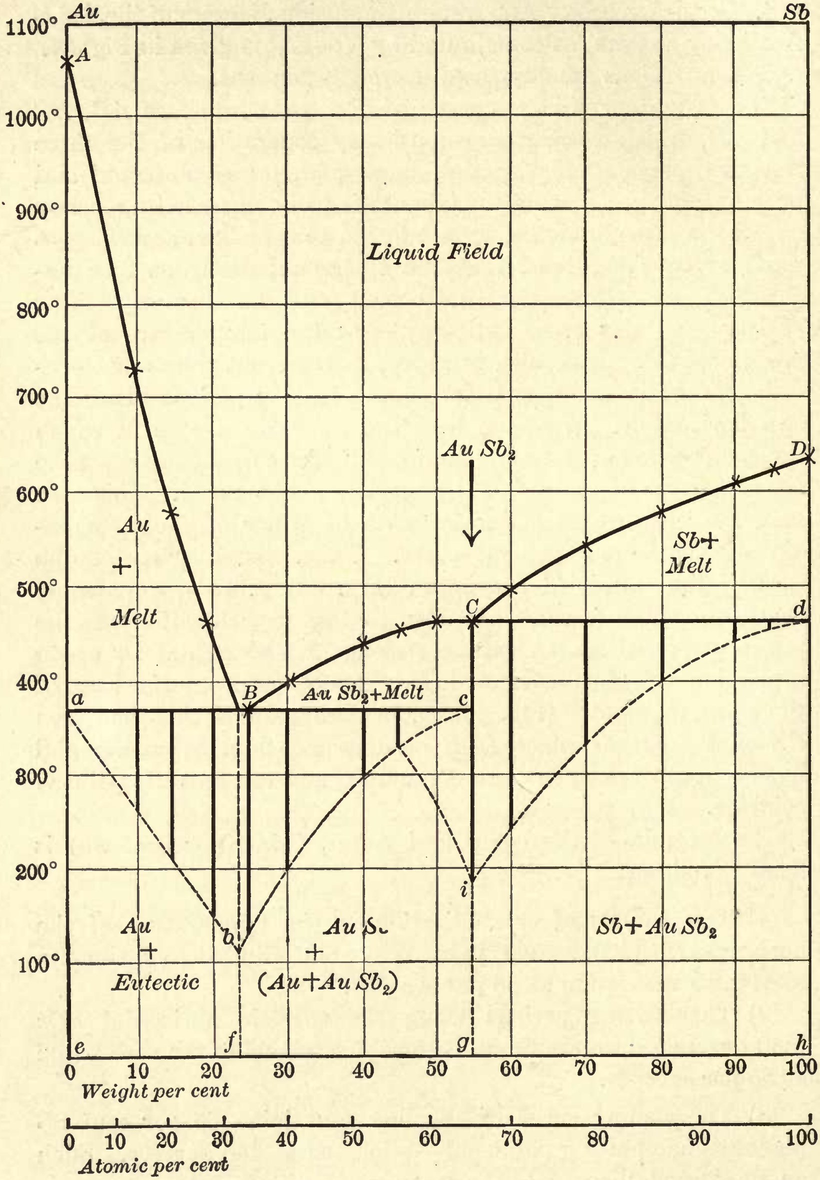

FIG. 37. Fusion Diagram of Gold-Antimony Alloys according to Vogel.

(4) A section containing 55 per cent Sb presents a completely homogeneous appearance.

We note here that the curve branch *BC* enters at *C* horizontally. Although, strictly considered, the horizontal *Cd* ends at *C* (see p. 128), its horizontal course in this vicinity leads to the observation of halting points upon the cooling curves of alloys containing less antimony than corresponds to the point *C* (one containing 50 per cent Sb, for example) at temperatures which are practically identical with that of the horizontal *Cd* (460 degrees). This is shown in the diagram by a dotted line beginning at *i*, concentration *C*, and falling away toward the left.

A description of the crystallization processes which occur upon cooling the melts of various concentrations follows:

(1) A melt of concentration (0 = pure gold) solidifies uniformly at the point *A* (= 1064 degrees).

(2) Pure gold separates primarily along the curve branch *AB*, from concentrations which are located between 0 and *f* (= *B*). This separation commences at that point of the branch which corresponds to the respective concentration. The melt becomes enriched in antimony, as the temperature of solidification continues to fall, until the concentration *B* is reached. Then the temperature will have fallen to 360 degrees, and eutectic crystallization will ensue. The eutectic consists of pure gold and the compound $AuSb_2$.

(3) A melt of concentration *f* = *B* solidifies eutectically at 360 degrees.

(4) The compound $AuSb_2$ separates primarily along the curve branch *CB*, from concentrations which are located between *f* (= *B*) and *g* (= *C*). During this process, the gold content of the melt increases, and the temperature of solidification falls until the point *B* is reached. Here, the remainder of the melt crystallizes eutectically.

(5) A melt of concentration *g*, corresponding to the pure compound $AuSb_2$, solidifies uniformly at the temperature *C* = 460 degrees.

(6) Concentrations which are intermediate between *g* (= *C*) and 100 separate pure antimony along the curve branch *DC*. The gold-content increases as the temperature of solidification falls, until the point *C*, corresponding to the pure compound

$AuSb_2$, is reached. The remainder of the melt then solidifies uniformly at constant temperature (460 degrees) to crystals of the pure compound $AuSb_2$. Thus, we have a single crystalline variety instead of eutectic — a practically pure substance at any rate — as secondary element throughout this concentration interval.

(7) A melt of concentration 100 (= pure Sb) solidifies uniformly at the temperature *D* (= 631 degrees).

FIG. 38. 80% Au + 20% Sb, etched with NaOH. Magnified 27 times.

The concentration-temperature plane embraces seven fields of condition, which are summarized in Table 5.

TABLE 5.

Fields of Condition.

I. Liquid Field: bounded below by the Fusion Curve *ABCD*

II. Fields with one crystalline variety + melt:

ABa	Au
BCc	$AuSb_2$
CDd	Sb

III. Fields with two crystalline varieties:

aBfe	Au + Eutectic (Au + $AuSb_2$)
Bcgf	$AuSb_2$ + Eutectic (Au + $AuSb_2$)
Cdhg	Sb + $AuSb_2$

The thermal evidence is generally substantiated by the structure of the sections. Fig. 38 represents a section containing 20 per cent Sb, magnified 27 times. This section was etched by long-continued action of caustic soda. The primarily separated gold crystals have remained bright during etching: they are situated side by side in rectilinear chains which form crosses with one another. Light gold particles, and dark etched particles pertaining to the compound $AuSb_2$ — in reality colored red — are to be plainly seen in the eutectic which surrounds the primary gold crystals. The structure of the eutectic appears to much

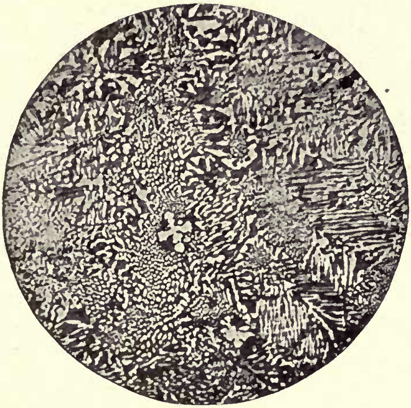

FIG. 39. 75% Au + 25% Sb, etched with NaOH. Magnified 70 times.

better advantage in Fig. 39, which represents a section containing 25 per cent Sb, *i.e.*, very close to the eutectic concentration (24 per cent Sb). This section is magnified 70 times. Caustic soda was also used in this case. The lamellar structure of the eutectic is apparent, particularly in the right-hand portion of the figure.

Fig. 40 shows another section, also etched with caustic soda. This contains 40 per cent Sb and is magnified 70 times. According to the evidence of the diagram, primarily separated crystals of the compound $AuSb_2$ must show in this picture. These appear as reddish (black in the photograph) crystalline polygons, quadratic in shape, and show enclosures of eutectic in many instances. The secondary structure element must be the same eutectic *B* here, as in the previous sections. This, however, cannot be decided from the figure. It appears equally bright all over the surface, and gives no evidence of dual composition. The etching may have been less energetic in this case than before, resulting in little or no action upon the compound $AuSb_2$ contained in the eutectic. We may, of course, assume that the compound which is associated with gold eutectically is protected from the action of the etching agent by the surrounding gold, and is therefore less attacked than the primarily separated crystals of the same composition.

FIG. 40. 60% Au + 40% Sb, etched with NaOH. Magnified 70 times.

Fig. 41 represents a section containing 60 per cent Sb, magnified 22 times. According to the diagrammatic evidence, a small quantity of antimony must have separated primarily in this concentration. Accordingly, we note dark-colored antimony crystals of dendritic form with rounded edges, imbedded in a homogeneous mass of bright compound. Aqua regia was used in etching. This reagent fails to attack the compound, when used with care.

5. INCOMPLETE PROGRESS OF THE DECOMPOSITION. — Thus far, we have dealt exclusively with reactions which proceed to completion, *i.e.*, we have considered that equilibrium between the separate phases in all parts of the system can be consummated with all necessary rapidity. This requirement will, from

the very nature of things, be realized during decomposition of the compound on heating. Here, the progress of the reaction is such that the compound decomposes into melt and a new crystalline variety. Quite different are the relations when the compound is formed. In this case, the crystalline variety stable at the higher temperature reacts with melt, on cooling, to produce the compound in question, and, where the reaction must proceed completely within a short period of time, it is obviously necessary that the first crystalline variety come in contact with the melt. Such contact may be hindered in various ways.

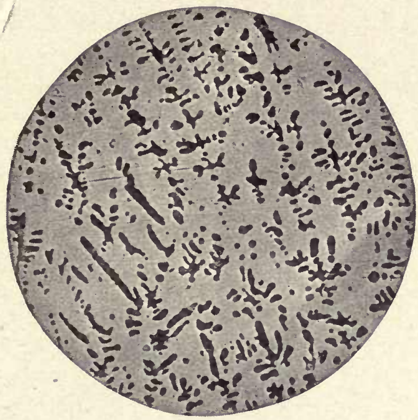

FIG. 41. 40% Au + 60% Sb, etched with aqua regia. Magnified 22 times.

We may imagine, for example, that the resulting compound be deposited as a layer upon the surface of the first crystalline variety, and in this manner practically prevent the melt from coming in contact with the latter and reacting completely with it. A very slight quantity of compound — practically negligible — might possibly suffice to produce this effect. Since, however, such "total envelopment" has not as yet been observed, we need not attempt to discuss it.

On the other hand, envelopment may be incomplete. Subjoining our reasoning to the general case presented on p. 113, suppose we assume that the protection afforded the primarily separated *B* crystals by envelopment with the compound $A\ B_n$, is so effective that, with sufficient quantities of melt, in maximo, only half of the B crystals can sustain transformation into A_mB_n crystals. Then the equation,

$$aB + [\underset{\text{melt } D}{mA + (n - a)} B] = A_mB_n$$

(see p. 113), does not correctly describe the reaction between B and melt. In reality, according to our assumption that only half of B can become transformed, the process conforms to the equation,

$$2\,aB + [\underset{\text{melt } D}{mA + (n - a)} B] = A_mB_n + aB.$$

Thus it follows that thermal investigation cannot lead to the correct formula of the compound, A_mB_n, but yields, rather, the formula A_mB_{n+a}: for the maximum quantity of compound is formed when the concentration corresponds to the stochiometrical relations given by our equation. Change in quantity of either B or melt effects decrease of A_mB_n. We shall, therefore, find the maximum of crystallization periods along the horizontal Dc (Fig. 33) displaced from its normal position at the concentration A_mB_n, to the concentration $A_mB_n + aB$, which equals A_mB_{n+a}. The eutectic horizontal aCb also ends at this concentration, since, at this point, as well as in all B-richer concentrations, complete exhaustion of melt occurs.

These considerations appear to show that, in case of a concealed maximum, deduction of the same formula for the compound by ascertaining the maximum of crystallization periods along the horizontal Dc as by ascertaining the end point b of the eutectic horizontal aCb in itself fails to guarantee that this formula will actually correspond to the composition of the compound. We can merely affirm, on the basis of the experimental results, that the composition of the compound lies between D and the maximum of halting periods along Dc.

At this point, however, microscopical investigation is of assistance. Thus, if the reaction has proceeded to completion, an alloy of concentration i, the location of the maximum of halting periods along Dc (Fig. 33), must appear completely homogeneous, as we have seen (since it is composed exclusively of pure compound A_mB_n). Alloys of all concentrations between i and D may contain two, and only two, structure elements, namely, the compound A_mB_n and the eutectic C. If, on the other hand, envelopment has occurred, the maximum i of crystallization periods along Dc does not coincide with the composition of the compound A_mB_n, but lies further toward the B side, and, consequently, an alloy of the composition of this maximum cannot be homogeneous; it must contain two structure elements, primarily separated B crystals as nucleii, surrounded by A_mB_n crystals. Alloys of concentrations between i and D must show three structure elements, — embracing eutectic C, in addition to the two previously enumerated.

The presence of three structure elements in one section has not been encountered up to the present. We have become familiar with those cases alone in which the solidified alloy shows two structure elements. The contingency that three structure elements appear in one section depends upon a more or less constrained protection of one structure element from contact with the melt. *Normally, viz., when equilibrium has become perfectly established, not more than two structure elements appear in any section of an alloy composed of two metals.* We therefore characterize a structure corresponding to the above as abnormal. The upper portion of Fig. 42, which shows a section composed of 42 per cent palladium and 58 per cent lead, etched with dilute hydrochloric acid, reveals abnormal structure of this sort. A

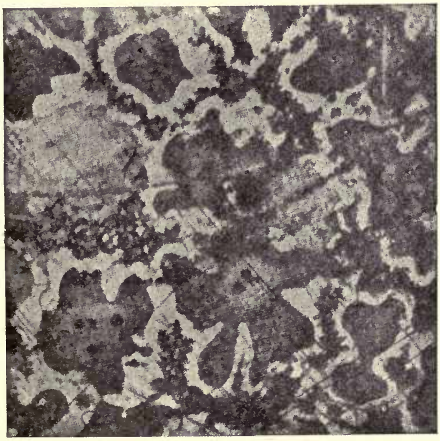

FIG. 42. 42% Pd + 58% Pb, etched with dilute nitric acid. Magnified 70 times.

dark nucleus of the primarily separated crystalline variety (corresponding to B) is to be seen [1] surrounded by a zone of the new crystalline variety (corresponding to A_mB_n), itself, in turn, surrounded by eutectic of coarsely granular structure.

According to the above, the formula of a compound melting under decomposition, as determined thermally, can be regarded as conclusive only when microscopical investigation supplies proof of normal structure. Now, all systems thus far investigated in which a concealed maximum occurs and the maximum i of crystallization periods along the horizontal Dc (Fig. 33) corresponds in concentration with the end point b of the eutectic horizontal aCb reveal perfectly normal structure under the microscope, whence it is clear that reaction has been complete. Where reaction has been incomplete, however, the eutectic horizontal aCb invariably fails to end at the concentration of the maximum i of crystallization periods along Dc, but extends beyond this point. Hence, we conclude that incompleteness of reaction is not due exclusively to envelopment.

A further cause of incomplete reaction may consist in unequal distribution of the primarily separated crystalline variety in the melt, just at the point of reaction. The crystals may have settled more or less to the bottom of the reaction vessel (segregation). In such event, reaction will be incomplete in certain portions of the mixture — above, in the present case — owing to early exhaustion by the melt of the inadequate quantity of B crystals which are available. Other portions of the mixture — below, in this particular instance — react incompletely, on account of insufficient melt and excess of B crystals. Thus, the consequence of such derangement is incomplete exhaustion of B crystals, as well as of melt, within certain intervals of concentration. Considering, first of all, the rather simple case wherein the same proportion — one-half — of the theoretically possible quantity of crystals and melt is transformed in all concentrations (between D and c), we must alter the equation,

$$aB + [mA + \underset{\text{melt } D}{(n-a)} B] = A_mB_n,$$

to,

$$aB + [mA + \underset{\text{melt } D}{(n-a)} B] = \tfrac{1}{2} A_mB_n + \tfrac{1}{2} aB + \tfrac{1}{2} [mA + \underset{\text{melt } D}{(n-a)} B].$$

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[1] Ruer, Z. anorg. Chem., 52, 345 (1907).

Since the proportion by weight between *B* and melt remains the same in the latter equation, no displacement of the maximum of crystallization periods along *Dc* follows. The verticals in Fig. 33, which are proportional to these crystallization periods, must, however, be shortened one-half, corresponding to formation of only half of the theoretical quantity of compound in all cases. Thus, the increase in period of crystallization along *Dc* from *D* to *i*, and from *c* to *i*, remains linear, and we shall accordingly expect a sharp maximum at concentration *i*, corresponding to composition of the compound A_mB_n. On the other hand, according to our assumption, half of the melt remains unexhausted in all concentrations, and, therefore, gives rise to eutectic crystallization at *C*. Hence, the eutectic horizontal *aCb* must extend throughout the whole diagram — up to 100 per cent *B*. It thus appears that, of the two criteria used for determination of the composition of a compound A_mB_n, the first, which consists in location of the maximum along *Dc*, retains its application under the present conditions, while the second, which consists in location of the end point *d* of the eutectic horizontal *aCb*, fails.

Relative to an extension of these results to actual conditions, it is at once clear that the irregularities caused by uneven distribution of *B* in the melt will be confined to the central portion of the horizontal *Dc*. As long as melt is present to considerable excess, namely, in concentrations from *D* to *i* (Fig. 43), segregation of *B* crystals in the lower portion of the containing vessel will not prevent their complete exhaustion by the melt. On account of the excess quantity of melt, each *B* crystal will, even under these conditions, articulate with enough melt to effect its normal transformation. The point *l* approaches closer to *D*, in proportion as the irregular distribution of *B* crystals in the melt becomes emphasized. On the other side of *i*, the point *m* represents the limit of abnormality. In all concentrations located between *c* and *m*, the separated crystalline variety *B* is present in such excess that the melt is invariably exhausted, notwithstanding uneven distribution. Thus, the diagram suffers no alteration between *D* and *l* on the one hand, and between *m* and *c* on the other hand.

Formation of A_mB_n falls somewhat below the theoretical amount between *l* and *m*. The influence of irregular distribution of

B crystals in melt must become more noticeable in proportion as the excess of the predominating component diminishes; that is to say, in proportion as we approach the concentration of pure A_mB_n from either side. Consequently, a more and more gradual increase in the period of crystallization along *Dc* will result as we pass from *l* to the maximum *i*, as well as from *m* to *i*. On this account, the curve *Dec*, joining the corresponding verticals, will fail to show a sharp point, as in Fig. 33, but will culminate in a flat summit, as represented in Fig. 43. The position of this maximum must, however, remain unaltered. It coincides with the concentration of the pure compound A_mB_n. The eutectic horizontal *aCb* (Fig. 43) reaches on beyond the maximum as far as that concentration in which the first trace of melt fails to react

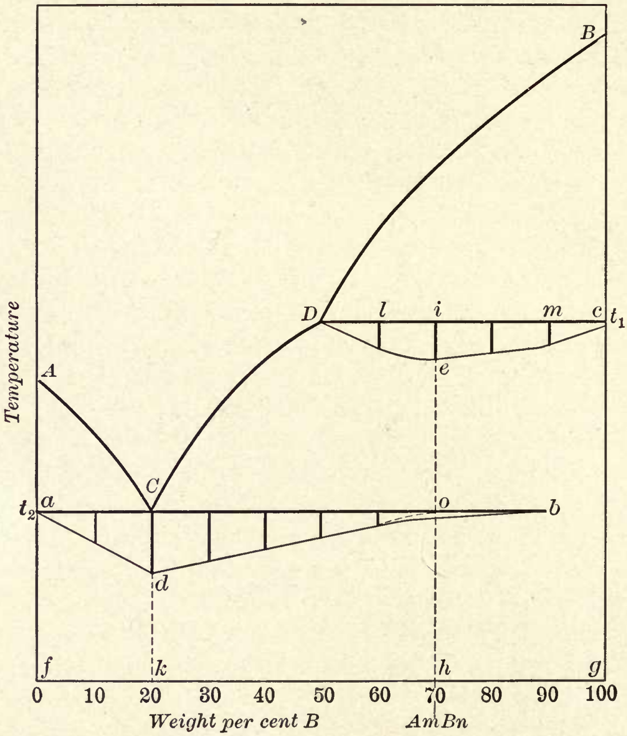

FIG. 43.

with the B crystals: as far as concentration m, in terms of our special assumption.

These deductions are in complete harmony with the experimental facts. Incomplete progress of the transformation, for the most part, effects no alteration in the position of the maximum of crystallization periods along Dc. Such position agrees with the concentration of the compound A_mB_n. However, on account of the imperfectly marked character of the maximum, its position is, in general, difficult of determination. There are cases in which the periods along Dc between l and m remain equal within the experimental error limit. In certain cases, the maximum may still be determined with a tolerable degree of accuracy. Such determination then constitutes a valuable indication of the composition of the compound. On the other hand, the eutectic horizontal in these cases invariably reaches beyond the concentration of the compound, whereby this means of check upon the composition of the compound is lost. The structure of the sections will be abnormal, in the sense that, in certain portions, we shall observe primarily separated B crystals, surrounded by crystals of the compound A_mB_n, while, in other portions, we shall see crystals of the compound, surrounded by eutectic.

Obviously, it is also possible for segregation and envelopment to appear in close association. The resulting complications may be appreciated from the above without difficulty.

We take note here of the obvious fact that a fusion diagram corresponding to incomplete reaction, as above, is in complete agreement with Fig. 33 from concentration 0 (= pure A) as far as concentration D, since the abnormalties due to envelopment, segregation, etc., can only appear between D and 100 per cent B. This is made evident by the relative quantities of eutectic shown along the horizontal aCb (Fig. 43). These quantities decrease lineally toward A_mB_n from concentration C to concentration D (or to the respective concentration at which abnormality begins), and, in principle at least, the dotted prolongation from dn to the point of intersection o with the eutectic horizontal aCb always serves for determination of the composition of the compound A_mB_n. We have seen, however, in earlier examples that the eutectic halting periods are not invariably proportional to the eutectic quantities from an experimental standpoint, whence it appears that too much reliance should not be placed upon such determination, unless verified by independent means.

We see from the above that incomplete progress of reaction, whatever its cause, operates effectively against accurate determination of the composition of a compound. The maximum of crystallization periods is often imperfectly developed, and therefore difficult to determine. Again, we have no guarantee that its concentration coincides with the composition of the compound, as in normal cases, where homogeneous structure of the alloy in question testifies to this effect. Verification of the result on the basis of the second criterion, which calls for location of the eutectic end point b (horizontal aCb) at the concentration of the compound, is also excluded, for, as we have seen, the eutectic line extends beyond this concentration. It is, therefore, particularly fortunate that complete progress of the reaction may be superinduced in certain cases, as pointed out by Tammann.[1] To this effect, the cooled alloy is first pulverized, whereby it is brought into a state of comparative uniformity, previously enclosed crystals being opened up. This material is thereupon heated almost to the transformation temperature, and maintained there for some time. In this way, B crystals and melt are frequently led to react further, with formation of A_mB_n. If this process is effectual, the mixture on cooling will no longer show eutectic crystallization, except in such concentrations as are A-richer than A_mB_n, *i.e.*, in those concentrations which must still contain melt after complete disappearance of B. Thus, the eutectic horizontal aCb now ends at the concentration of the compound, and may serve in the determination of its composition. The structure of the section must be normal, and a section of the concentration of the compound A_mB_n must appear homogeneous under the microscope. Finally, the maximum of halting periods along Dc may also be accurately ascertained by taking heating curves. All criteria and checking methods pertaining to the normal case are thus available. When the above-mentioned expedient fails of results, the problem of accurately fixing the composition of the compound must be left unsolved, as far as our present methods are concerned. (Compare, for example, R. Sahmen, Kupfer-Kadmiumlegierungen, Z. anorg. Chem., 49, 301 (1906).)

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[1] Tammann, Z. anorg. Chem., 47, 296 (1905).

D. *Changes in the Crystalline State.*

Up to the present, our attention has been confined to such two component systems as sustain no further change after solidification. That alloys may undergo change after solidification has occurred is, however, clearly proven by thermal investigation. This condition is by no means infrequent, and such changes are often accompanied by very considerable heat effects. Two reasons may be given for these changes. In the first place, a single crystalline variety may become transformed into another variety which is stable at some lower temperature. We are already familiar with a process of this sort under the title polymorphous transformation. On the other hand, cases are known wherein two crystalline varieties react upon each other with formation of a third variety: a chemical compound. This phenomenon is at variance with common experience, as well as with the old rule: "*Corpora non agunt nisi fluida.*" The rate at which a substance diffuses when dissolved in a solid body is in general so slow that, even though the possibility of reaction between two crystalline substances be directly conceded, such reaction can hardly be expected to make much progress in a short time. The sum total of our experience in these matters leads to the belief that an extremely intimate contact, or molecular interpenetration, of the substances in question is pre-essential to chemical reaction, and such a condition can be realized in the case of solid bodies only as a result of reciprocal diffusion. As a matter of fact, certain examples may be adduced to show that the capability of solid bodies to diffuse may be rather considerable at high temperatures. In general, reactions in the solid state appear to become possible only when the reacting substances are noticeably soluble in one another. We shall, however, refrain from all critical discussion of these phenomena, the mechanism of which have not as yet been adequately investigated, be content to consider the possibility of reaction between two crystalline varieties with formation of a third as settled, even though it constitute an unexpected experimental development.

Now, it is easily possible, as TAMMANN has pointed out,[1] to

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[1] TAMMANN, Z. anorg. Chem., 47, 296 (1905).

distinguish between polymorphous transformation and chemical reaction whereby two crystalline varieties combine to form a third on cooling.

Polymorphous transformation is characterized by the alteration of a given crystalline variety in such manner that another variety is formed without change in composition. Transformation of this sort occurs at constant temperature in the case of a pure substance, as explained on p. 11, and as follows at once from the text on p. 32. Since we have excluded solubility in the crystalline state from present considerations, the crystalline variety sustaining polymorphous transformation is to be regarded as pure. Its transformation will, therefore, invariably occur at the same temperature, and in all concentrations where it is present, whether as primary structure element, or as constituent of an eutectic. The heat effect is of course proportional to the quantity of material which undergoes transformation. Thus, cooling curves made under the usual conditions will show halting points at the temperature of transformation. Moreover, the halting periods will show a maximum at the concentration of the changing variety, and a linear decrease from this value, on both sides, toward those concentrations wherein the quantity of this crystalline variety becomes zero. The diagram given in Fig. 44 represents a case according to which two substances A and B form no compound with one another, but the substance A sustains polymorphous transformation from the β form into the α form (see p. 11) at a temperature t_2, located below the eutectic temperature t_1. The heat of transformation liberated in the several concentrations is represented by verticals located upon the horizontal cd, and decreases, as we see, from concentration 0 (pure A), where the maximum value obtains, lineally toward concentration 100 (pure B), where the zero value is reached.

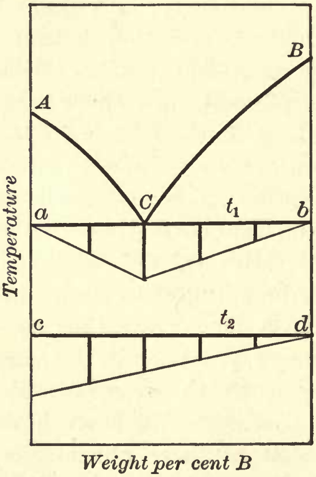

FIG. 44.

Let us now turn to the case given in Fig. 45, according to which two substances form no compound on being fused in conjunction, but separate, on cooling, in the pure state, along the respective curve branches AC and BC. At the temperature t_2, located below the eutectic temperature t_1, however, they are assumed to enter into the chemical combination A_mB_n, the corresponding reaction being accompanied by a considerable heat effect. The equation describing this complete (per assumption) reaction, reads:

$$mA + nB \rightleftarrows A_mB_n.$$

According to p. 32, the reaction takes place at constant temperature. On abstracting heat, the quantity of A and B crystals decreases, while the quantity of A_mB_n crystals increases, without change in the composition of any phase; in other words, complete equilibrium obtains, and the temperature remains constant until reaction ceases. On supplying heat, reaction proceeds in the reverse direction; the compound A_mB_n decomposes into the two crystalline varieties A and B at constant temperature (t_2°). Above t_2°, the crystalline varieties A and B are stable in the presence of one another; below t_2°, either A and A_mB_n, or B and A_mB_n, according to concentration, are mutually stable.

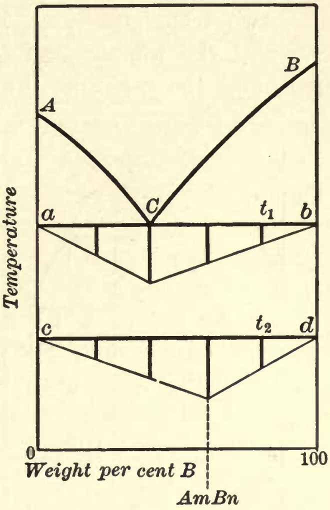

FIG. 45.

The maximum heat effect along the horizontal cd occurs at the concentration of the compound A_mB_n, and we have a linear decrease from this concentration toward pure A and pure B, as shown in Fig. 45. The distinction between the case of polymorphous transformation (shown in Fig. 44) and the case of chemical combination between two crystalline varieties with formation of a third (shown in Fig. 45) may now be drawn. Briefly, it lies in the characteristic location of the maximum heat effect, in the first case, at a concentration wherein the system is composed of a single crystalline variety, and, in the second case, at a concentration wherein two varieties are present (in the proportions given by the equation of the reaction).

If a compound A_mB_n sustains polymorphous transformation, as many additional criteria (supplementing those given previously) are thereupon available in the determination of its composition as the number of its transformations. The case according to which a compound A_mB_n, melting unchanged at C, sustains two transformations, is shown in Fig. 46. One of these occurs at the temperature t_1, above the two eutectic temperatures, and the other at the temperature t_4, below the eutectic

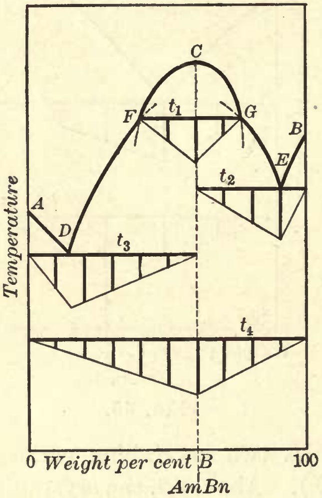

FIG. 46.

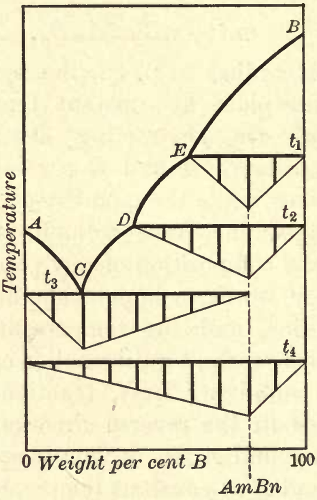

FIG. 47.

temperatures. We note that the positions of the maxima of halting periods along the two horizontals t_1 and t_4 serve as independent expedients relative to determination of the composition of the compound, since these maxima must occur at the concentration of the pure compound, as previously pointed out. The fusion curve must show breaks at the respective points F and G, and the dotted continuations of the curve branches into the unstable region must possess the positions, relative to the full curve of stable equilibrium, shown in the figure, owing to the lesser solubility of the stable crystalline variety at the corresponding temperatures (see p. 110). Pure A is to be regarded as solvent at F, and pure B at G. It is true, however, that such breaks frequently escape observation, in line with the general difficulty of obtaining an exact experimental determination of the fusion curve.

Completely analogous relations obtain when a compound which melts under decomposition sustains polymorphous transformation. In Fig. 47, the compound A_mB_n decomposes into B crystals and melt of concentration E, at the temperature t_1. The maxima of reaction periods along the horizontals t_2 and t_4, corresponding to polymorphous transformations, coincide with the concentration of the compound A_mB_n. When the reaction between crystalline variety B and melt E is incomplete, the complications treated on p. 134 *et seq.* ensue.

Under normal conditions, obviously that crystalline variety alone which is stable at the lowest temperature will appear in sections of the reguli. It is, nevertheless, possible, in many instances, to hinder the processes which occur in the crystallized alloys by very rapid cooling (so-called quenching), and to transfer the crystalline varieties which are stable at higher temperatures into a region of lower temperature without change, notwithstanding their instability under the latter condition. Such practice is quite analogous to that of obtaining a liquid in the amorphous-glassy form (p. 9) as a result of sudden cooling, regardless of the actual stability of the crystalline form at the lower temperature. Its feasibility rests upon the invariable decrease in reaction velocity, and of crystallization velocity, with falling temperature.

If it is desired to examine an alloy, the components A and B of which exhibit the relations depicted in Fig. 45 (viz., unite chemically to form A_mB_n at the temperature t_2) at ordinary temperature, in the condition which it normally assumes between the temperatures t_1 and t_2 — a condition of mixture embracing A, B and eutectic — it will be necessary to rapidly conduct it through the temperature range wherein the rate of formation of A_mB_n is at all rapid, and bring it into a temperature region where this rate is practically zero. With this in view, the alloy is quenched by plunging in cold water as soon as it has become completely solidified, *i.e.*, when the temperature has fallen below t_1, but not as far as t_2. Under these conditions, the reaction of formation of A_mB_n frequently fails to materialize to any considerable extent, owing to the rapidity of cooling at the temperature t_2, while, immediately thereafter, the temperature will have fallen so far below t_2 that the rate of reaction will have become practically zero. Then again, the once cooled alloy may be subsequently heated above $t_2°$, in order to decompose the quantity of compound which was originally formed on slow cooling, and thereupon quenched. Obviously, the same process applies where a single crystalline variety sustains polymorphous transformation, as represented in Fig. 44. Whether or not the quenching process will yield satisfactory results, of course depends upon the relation between rate of cooling and rate of reaction for the respective change. If the rate of reaction at t_2 is unusually rapid, it will scarcely be possible to secure sufficiently rapid cooling to restrain the process. In practice, cases in which quenching is quite futile, on account of excessive rate of reaction, are encountered, as well as those in which the result is entirely satisfactory, viz., in which the reaction is practically eliminated by proper quenching. Between these two extremes, we find instances in which a greater or lesser portion of the crystalline varieties stable at higher temperatures may be safely transferred into the region of ordinary temperature.

Finally, attention may be drawn to the fact that the rule placing the number of compounds equal to the number of branches of the fusion curve diminished by two, fails to hold when changes occur in the crystalline state. In Fig. 45, the fusion curve is composed of two branches only, and yet a compound A_mB_n exists. In Fig. 46, there are four points D, F, G and E of the fusion curve which correspond to abrupt change in its direction. Thus, there are five branches, although no more than one compound (A_mB_n) exists.

In consideration of the many horizontals of constant temperature which traverse the diagram where polymorphous transformation occurs, it appears that the rule placing the number of compounds equal to the number of eutectic horizontals diminished by one, is robbed of all practical significance. It may be retained, to be sure, if the horizontals arising from polymorphous transformation be excluded from the enumeration. Differentiation between the individual horizontals, however, cannot be attempted unless knowledge of the whole diagram is at hand.

§ 2. The Liquid State is Characterized by Incomplete Miscibility; the Crystalline State by Complete Immiscibility.

We have observed on p. 37 that the case of complete immiscibility of two pure substances is to be regarded theoretically as a limiting case of extremely slight miscibility. When we bring two liquid substances *A* and *B* into close association at a temperature t_1 where they fail to mix completely with one another, and take care that they reach equilibrium, by means of stirring or shaking, each will become saturated with the other. If, now, the system be left to itself, the two solutions will separate after standing a sufficient length of time, by reason of their varying specific weight, and two layers will result. One of these consists of *A*, saturated with *B*; the other of *B*, saturated with *A*. We characterize the *A*-richer layer as solution of *B* in *A*, and the *B*-richer layer as solution of *A* in *B*. The respective concentrations of the two saturated solutions at the given temperature may be ascertained by quantitative analysis. Now, in general, the solubility of substances in one another increases with the temperature. We will therefore assume this to be the case relative to molten metals when dissolved in one another. If, then, the composition of two layers which have reached equilibrium at some higher temperature t_2 be investigated, we shall find that the solution of *B* in *A* has become *B*-richer, and the solution of *A* in *B*, *A*-richer.

A concentration-temperature diagram is again used to bring out these relations (Fig. 48). The point a_1 corresponds to a saturated solution of *B* in *A* at the temperature t_1, and the point b_1 to a saturated solution of *A* in *B* at the same temperature. The corresponding points for a temperature t_2 are a_2 and b_2; they must be nearer together than the first points, as explained above. On proceeding with the determination of composition of the saturated solutions for higher temperatures, we continually obtain closer values until, at length, coincidence results (at the point *c*) — unless the mixture commences to boil at some lower temperature.

The saturated solution of *B* in *A* then possesses the same composition as the saturated solution of *A* in *B*, *i.e.*, both solutions are identical at this and all higher temperatures. Thus, the mixture can no longer separate into two layers; we have reached the region of complete miscibility. By passing a continuous curve through the experimentally determined points, we obtain the *solubility curve*, which supplies exhaustive information relative to all questions concerning this particular phenomenon.

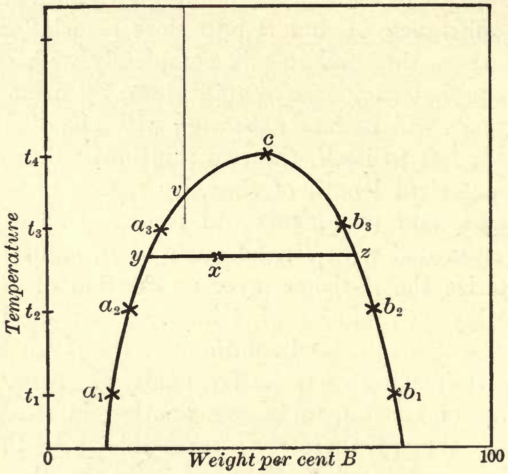

FIG. 48.

In the region situated without the solubility curve, the system is homogeneous, while within the solubility curve the system is composed of two layers. Assuming that a given system is defined as to concentration and temperature by the point x, the points of intersection y and z of the solubility curve with a horizontal passing through x define the composition of the two layers which are in equilibrium at the temperature corresponding to x. Thus, the system x must have separated into layers of the respective concentrations y and z, and the relative quantities of y and z may be determined in the usual manner, according to the lever relation.

$$(\text{Quantity } y) \cdot xy = (\text{Quantity } z) \cdot xz.$$

In spite of the fact that limited miscibility in the molten state is by no means rare among the metals, solubility curves are available in case of two pairs only, namely, lead-zinc and bismuth-zinc. The first of these pairs is of some interest in the arts (see p. 37). Previous investigation has been for the most part confined to the behavior of transparent liquids at rather low temperatures. In such cases, the method of Alexejew[1] constitutes a very simple procedure for determining the points of the solubility curve. Mixtures of known concentration are prepared by weighing, and the temperature at which the cooling liquid begins to separate is observed. The resulting turbidity may be sharply recognized. We note that by this method no determination of the points of intersection y and z of the constant temperature horizontal with the solubility curve is effected (this would require separation and analysis of the two layers); it is the point of intersection v of a definite concentration vertical with the solubility curve which is hereby located (requiring only one temperature observation, since a weighed quantity of material is used at the start). A process of this sort is obviously inapplicable to opaque substances (metals). The substitution of an analogous method, prescribing thermal determination of the initial temperature of separation, might seem well advised in connection with metallic mixtures. Unfortunately, however, the heat effect attending separation is too small for this purpose.

On separation of the homogeneous liquid into two layers, a certain quantity of heat must be liberated, if our assumption that the miscibility increases with rising temperature is correct. Otherwise, our system could not be stable in the form of two layers. This will be understood from the following considerations: If the separation which occurs on cooling were attended by heat absorption, the reverse process of mixture on heating would of necessity be attended by liberation of heat. Thus, if the system composed of two layers in equilibrium were existent at a certain temperature t_1, the slightest elevation of temperature would increase the miscibility. Since heat would be liberated during the ensuing mixture, further elevation of temperature, and, therefore, further increase in miscibility, would be inevitable. The same process would thereupon repeat itself, and become progressive, whereby a homogeneous mixture would be ultimately produced. Thus, the original system of two layers would have been unstable. Hence, for stability when miscibility increases with rising temperature or, what amounts to the same, when separation occurs with falling temperature, this latter process must be accompanied by liberation of heat. The above reasoning is of general

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[1] Alexejew, Wied. Ann., 28, 305 (1886).

application. An assumption of equilibrium in a system is equivalent to a concession that heat addition can effect such changes only as are attended by heat absorption. If, for example, we add heat to a crystal which is in equilibrium with its melt, it is justifiable to conclude from the ensuing fusion that this process must be attended by heat consumption. For, if the fusion were attended by evolution of heat, the slightest addition of heat would suffice to effect complete fusion, with spontaneous rise in temperature, — progressive fusion, even though inappreciable in its individual stages, would represent an ever-increasing source of further heat evolution. The same statements hold in the case of transformation from an α form into the corresponding β form (see p. 11). We are at liberty to conclude with equal right that the reaction,

$$A_mB_n \rightleftarrows mA + nB \text{ (p. 145)},$$

which proceeds from left to right on addition of heat, is attended by heat absorption, and that, in proceeding in the reverse direction on cooling, is attended by heat evolution. As long as we are dealing with equilibrium conditions, any process which occurs on cooling is accordingly attended by heat evolution.

Van't Hoff's Principle as above, which, in association with an analogous principle relating to the effect of pressure upon displacement of equilibrium, is commonly designated as LeChatelier's Principle, places no limit upon the magnitude of the heat effect. It may be indefinitely small. As a matter of fact, the heat quantity liberated during separation of a homogeneous liquid into two layers is so slight that it causes no noticeable break upon the cooling curves (see above).

Separation of the two layers at the temperatures for which points of the solubility curve are to be determined therefore constitutes the sole remaining expedient relative to determination of the solubility curve of two fused metals. The experimental difficulty associated with work of this sort is responsible for our insufficient knowledge of the prevailing conditions in such cases. Spring and Romanoff,[1] to whom we are indebted for investigation of the metal pairs, lead-zinc and bismuth-zinc, used crucibles of clay mixed with graphite, the side walls of which contained at a certain elevation, an aperture which was closed by a plug of the same material. They were filled in such a manner that the dividing line of the two layers was situated at the opening, after occurrence of equilibrium. The mixture was heated to

[1] Spring and Romanoff, Z. anorg. Chem., 13, 29 (1896).

the temperature of investigation, stirred, and then left to stand. A sample from the upper layer was at length obtained by means of a spoon. Ultimately, the plug was removed from the opening with the aid of an iron rod, and the upper layer allowed to flow off, whereby its separation from the lower layer was effected. The results of these authors certify to increasing solubility of the two substances in one another with rising temperature, and also show agreement with the conditions represented in Fig. 48 in all other respects.

We may now proceed to study the fusion diagram as it appears in several special cases under the above heading.

A. *The Components do not Unite to Form a Chemical Compound.*

Two elements *A* and *B* possessing the melting points *A* and *B* (Fig. 49) are now to be considered. Let *DFE* represent the solubility curve of the two melts. This is given by a dotted line, since the very inconsiderable heat of separation of the two liquid layers precludes its determination thermally. Then, in the region outside of the curve *DFE*, we have liquid alloy consisting

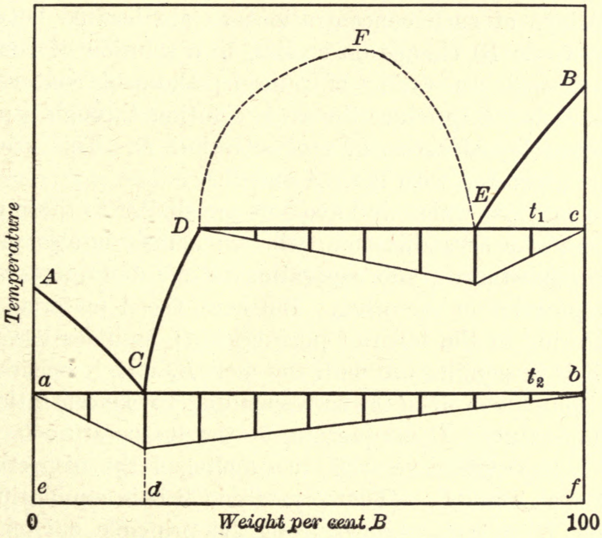

FIG. 49.

of a single layer: complete miscibility in the liquid state, and in the crystalline state as well according to previous assumption, obtains here. The law of freezing-point depression must therefore hold in this case, whence the melting point of *A* is lowered along the curve branch *AC* by addition of *B*, and the melting point of *B* along the curve branch *BE* by addition of *A* (*cf.* p. 38).

Now, one of these curve branches will intersect the solubility curve *DFE* at the higher temperature, namely, the branch *BE* at *E*, corresponding to the temperature t_1. It may thereupon be shown that the solubility curve no longer represents stable conditions below the temperature t_1, since a solution of concentration *E* is the solution of *A* in *B* which is stable at the lowest temperature. (Those solutions situated upon the *B*-rich side are called solutions of *A* in *B*, and those upon the *A*-rich side, solutions of *B* in *A*.) This follows from the fact that *E* represents a point of the solubility curve *DFE* and of the fusion curve *BE* as well. Alloys of such concentrations as are located between *E* and 100 (pure *B*) change on cooling to a solution of concentration *E* through separation of pure *B*; those of concentrations between *D* and *E* produce the same solution through separation of a second liquid layer, of concentration *D*. This solution is therefore saturated with both *A* and *B*.

The conditions which we have here are similar to those pertaining to eutectic crystallization, wherein a melt is also saturated with two substances, and separation of one determines simultaneous separation of the other. But here, the *A* material, instead of separating in the form of pure crystals, assumes the form in which it is in equilibrium with the melt *E*, viz., it occurs as saturated solution of *B* in *A*, corresponding to concentration *D* at this temperature. Consequently, at the temperature t_1, crystalline *B* is in equilibrium with two melts, of the respective concentrations *D* and *E*. (That crystalline *B* is in equilibrium with the melt *D* as well, follows from the principle enunciated on p. 27, according to which a given equilibrium is independent of the arrangement of the several phases.) If the melt *E* separates an additional quantity of crystalline *B*, a definite amount of melt *D*, determined by its *A*-content, must simultaneously appear. Thus, the equation of the reaction reads:

$$\text{Melt } E \rightleftarrows \text{Crystalline variety } B + \text{Melt } D.$$

On cooling, melt of composition E disappears, while the quantity of B crystals, and of melt of composition D, increases, without change in the composition of any phase, *i.e.*, we are dealing with a condition of complete equilibrium, and the temperature must remain constant until one phase becomes exhausted — on cooling, this is the melt E. No fall of temperature can ensue, on continued cooling, until all E is exhausted and only melt D and crystalline B remain. When the temperature has finally fallen below t_1, however, further separation of B must occur in the form of B crystals, not as solution of A in B, since such a solution is no longer stable below this temperature: indeed, the only B-rich solution which could exist at the temperature t_1 would have become completely exhausted by the time this temperature had been reached. A single type of solutions, namely, the A-rich solutions, of concentrations from D to O (= pure A), are capable of existence below $t_1°$. We have designated these as solutions of B in A. Thus it is clear that the stable portion of the solubility curve DFE ends at the points D and E of temperature t_1. Since we have again reached the region of complete miscibility in the liquid state in concentrations from D to O (= pure A), it is at once seen that further separation of B is attended by falling temperature and enrichment of the melt in A along the curve branch DC. Eutectic crystallization occurs at the point C, representing intersection of the curve branches DC and AC (temperature t_2). Crystallization of the various melts proceeds as follows:

(1) Separation of crystalline B follows the branch BE in all concentrations which are located between 100 (= pure B) and E, having commenced at that point of this branch which corresponds to the concentration in question. The melt increases its A-content, through separation of B, until the temperature t_1 is reached at concentration E. Continued crystallization of B occurs at this constant temperature, accompanied by separation of a second liquid layer of composition D, containing the excess of A. The period of constant temperature lasts until no melt E remains in presence of B crystals and melt. Further separation of B then ensues along the branch DC, whereby the temperature falls, and the melt becomes richer in A up to the concentration C. The remainder of melt (of concentration C) then crystallizes

at constant temperature to an eutectic composed of B and A. Cooling curves therefore show breaks at the time of passing the curve branch BE, halting points at $t_1°$, and halting points at $t_2°$.

(2) The cooling curve of a melt of concentration E shows no break to correspond with the curve branch BE, but merely the two halting points at $t_1°$ and $t_2°$, respectively.

(3) The same is true of the cooling curves which correspond to concentrations from D to E, since the heat effect due to separation of the melt into two layers on traversing the solubility curve DFE is so slight as to escape observation.

(4) The cooling curves of concentrations located between D and C no longer show halting points at $t_1°$. On the contrary, primary crystallization of B sets in at that point of the curve branch DC which corresponds to the respective concentration, without previous separation of the melt into two liquid layers. Such crystallization continues along DC up to the point D, when the remainder of the melt solidifies eutectically. Thus, the cooling curves show breaks below $t_1°$, and halting points at $t_2°$.

(5) A melt of concentration C solidifies eutectically. Its cooling curve therefore shows a single halting point at $t_2°$.

(6) Alloys of concentrations from 0 (= pure A) to C separate crystalline A primarily along the curve branch AC and also complete their solidification eutectically at C. Hence their cooling curves show breaks, followed by halting points at $t_2°$. As we have seen, the following process takes place at the constant temperature t_1:

$$\text{Melt } E \rightleftarrows \text{Crystalline variety } B + \text{Melt } D.$$

Thus, the heat quantity liberated during the change, and, under the customary assumptions, the length of the halting point at $t_1°$ as well, is given by the relative quantity of melt E present at this temperature. The maximum value 1 of these halting periods at $t_1°$ is reached at concentration E. From E, this value decreases lineally toward concentrations D and 100 (= pure B), where the zero value obtains.

Similarly, the relative quantity of eutectic attains its maximum at concentration C and decreases lineally toward concentrations 0 (= pure A) and 100 (= pure B), where zero is reached.

This is depicted in Fig. 49, according to the usual practice, by erection of verticals along the horizontals DEc and aCb.

It is characteristic of this diagram that two constant temperature horizontals are present, notwithstanding the entire absence of compounds and polymorphous transformations. The non-existence of a compound is determined by the fact that the eutectic horizontal *aCb* extends throughout the whole diagram, and that the relative quantity of eutectic decreases lineally from the eutectic concentration toward both sides.

As to the fields of condition, we note that the region of melt above *ACDEB* is divided into two portions:

(1) The field of homogeneous melt above *ACDFEB*, and

(2) The field of two liquid layers, bounded by the solubility curve *DFE* and the horizontal *DE*.

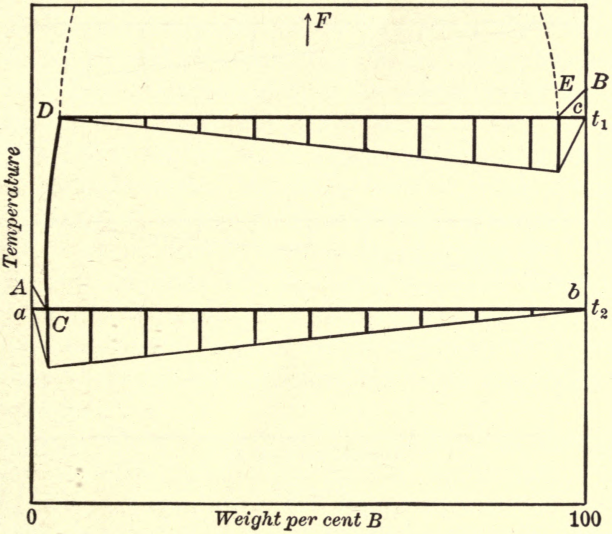

FIG. 50.

Furthermore, we have two fields with one crystalline variety, namely:

(1) The field *BEDCb* of *B* crystals and melt, the latter generally consisting of two layers along the horizontal *DEc*, and

(2) The field *ACa* of *A* crystals and melt.

The two fields with two crystalline varieties are:

(1) *bCdf*, corresponding to primarily separated *B* crystals and eutectic *C*, and

(2) *aCde,* corresponding to primarily separated *A* crystals and eutectic *C*.

The partial miscibility of *A* and *B* in the vicinity of the melting point of the least fusible component may differ considerably in extent. It is assumed to be inconsiderable in Fig. 50, *i.e.*, the compositions of the two layers differ only slightly from those of the respective pure substances at the melting point of *B*. On this account, the point *E* falls only a trifle below *B*, in that the curve branch of primary *B* separation meets the solubility curve soon after leaving *B*. Thus, the temperature t_1 of the horizontal *cED* is very little lower than the melting point of *B*. The same holds relative to the temperature t_2 of the eutectic horizontal *aCb* — this temperature lies very little below the melting point of pure *A*. The limiting case in which both substances fail entirely to dissolve in one another in the liquid state at the melting point of *B*, viz., in which both layers represent pure substances, is shown in Fig. 51. Here, the point *E* coincides with *B*, and the point *C* with *A*. All concentrations, with exception of the pure substances, give cooling curves with two halting points, t_1 and t_2, corresponding to the melting points of the pure metals.

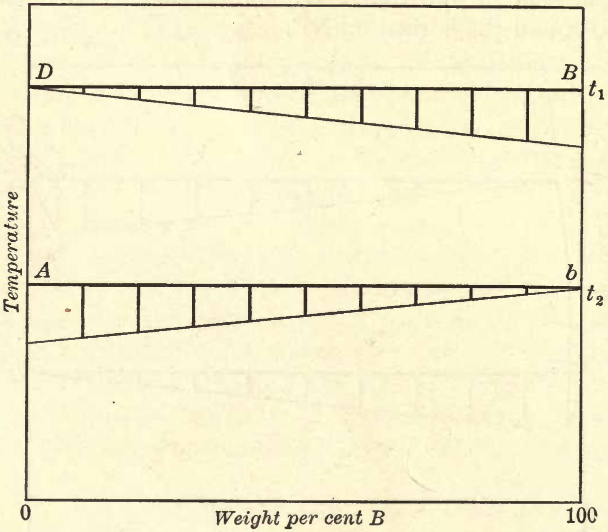

FIG. 51.

It is then evident that, although thermal analysis yields no information concerning the course of the solubility curve of the two melts, it does fix the two lowest points *D* and *E* of this curve.

Concerning the structure of the sections, we infer that, provided the two substances are rather soluble in one another, as was assumed in the construction of Fig. 49, the present conditions practically duplicate those presented by the case of complete miscibility in the liquid state, unaccompanied by chemical combination (Fig. 11a). For, we have in this case as well, primarily separated *A* or *B*, according to concentration, surrounded by eutectic. However, primary separation of the crystalline variety *B* from concentrations between 100 per cent *B* and *D* will have occurred in the *B*-rich layer alone, during the first stage. Not until this layer has disappeared, does the *D* layer begin to crystallize — yielding *B*, and subsequently eutectic. It is often possible to determine from the appearance of the section under the microscope that crystallization has taken place in two layers. In general, the layers become more distinct as mutual solubility in the liquid state decreases. At times, however, when the specific weights of *A* and *B* are not widely different, separation into two layers fails to show, even in cases of slight miscibility. In such cases, the two solutions will not have separated sharply, but will have formed an emulsion — one layer impregnating the other in the form of minute drops — at the beginning of crystallization. These characteristic enclosures are easily recognized under the microscope.

The systems Na-Al[1] and Tl-Al[2] may be cited as examples of practically complete immiscibility in the liquid state. Mutual solubility of the components at the temperature of initial crystallization is quite appreciable in the systems Na-Mg,[3] Al-Bi[4] and Zn-Tl.[5] In the system Tl-Cu,[6] molten copper is capable of dissolving some 35 per cent of thallium at the temperature of its melting point (1084 degrees), while molten thallium will dissolve some 2 per cent of copper only at this temperature. Further

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[1] Mathewson, Z. anorg. Chem., 48, 191 (1906).

[2] Doerinckel, Z. anorg. Chem., 48, 185 (1906).

[3] Mathewson, *l. c.*

[4] Gwyer, Z. anorg. Chem., 49, 311 (1906).

[5] v. Vegesack, Z. anorg. Chem., 52, 32 (1907).

[6] Doerinckel, *l. c.*

discussion of these examples appears unnecessary: bare mention of the fact that examples of the cases represented in Figs. 49, 50 and 51 are actually known, as above, may, indeed, be deemed sufficient.

B. *The Components Unite to Form a Chemical Compound.*

Obviously, nothing new would be introduced by assuming, relative to Fig. 49, that one of the components of the system, *B*, for example, were a compound A_mB_n instead of an element. As a matter of fact, we observed on p. 77, where the first consideration of changes in the fusion diagram due to presence of a compound was entered, how a fusion diagram may be divided at the concentration of a compound which melts unchanged, and the separate parts regarded as individual diagrams. In view of these considerations, the diagram presented in Fig. 52 requires no especial explanation. The dotted vertical at the concentration of the compound A_mB_n divides the diagram into two separate diagrams. Incomplete miscibility in the liquid state prevails at the left of this line; complete miscibility at the right. The compound A_mB_n fuses unchanged, although no difficulty would be

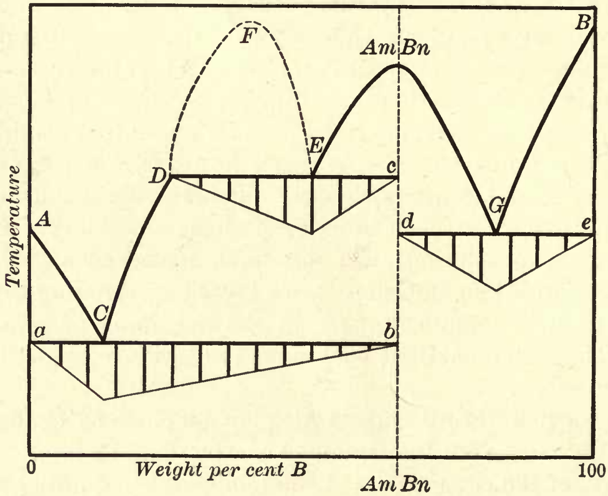

FIG. 52.

encountered if it were replaced by a compound melting under decomposition ("concealed maximum").

The diagrammatic relations which obtain when the composition of the compound lies between concentrations *D* and *E* are not apparent without some further consideration. The compound will not melt to a homogeneous liquid, but must separate into a mixture (emulsion) of two liquids. Fig. 53 represents the fusion diagram for this case.

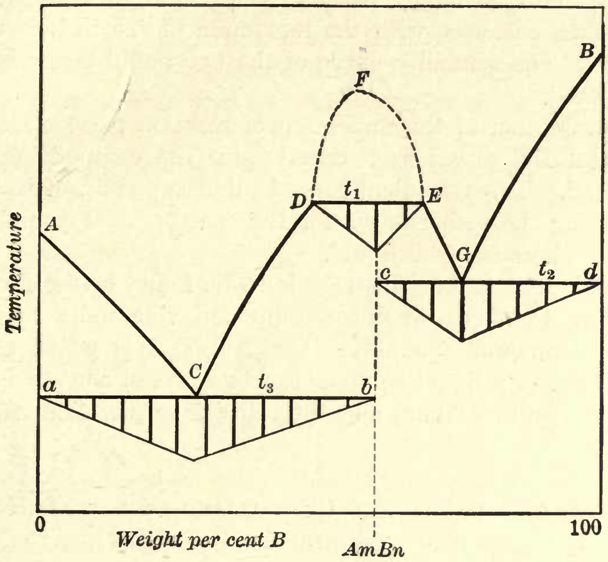

Fig. 53.

The equation of the reaction reads:

$$A_mB_n \rightleftarrows \text{Melt } D + \text{Melt } E,$$

and it indicates that complete equilibrium is at hand, whence the process must take place at constant temperature (t_1). When the compound decomposes on heating, the quantity of both melts increases, and the quantity of A_mB_n crystals decreases. The reverse effect ensues on re-formation of the compound as heat is abstracted. No phase changes its composition.

The relative quantity of A_mB_n which melts at the temperature. t_1, with formation of two liquid layers, is largest at the concentration of the compound, and is zero at concentrations *D* and *E*.

This is shown as usual in the diagram. In other respects, the present diagram is not fundamentally different from that shown in Fig. 16c, p. 78, representing the ordinary case of a compound which melts without decomposition. The earlier case may be derived from the present case by shortening the horizontal *DE* (Fig. 53) until it finally becomes contracted to a single point, which then coincides with the maximum of the fusion curve of Fig. 16c. The solubility curve of the two liquid layers has now disappeared.

Determination of the maximum of reaction periods along the horizontal *DE* serves as a criterion for the composition of the compound. This expedient replaces determination of the maximum along the fusion curve for the case of a compound which melts to a homogeneous liquid.

A single example of this case is to be found in the literature. According to MATHEWSON,[1] sodium and zinc unite to form a Zn-rich compound (possibly $NaZn_{11}$ or $NaZn_{12}$) which melts at 557 degrees to a liquid composed of two layers, one consisting of practically pure sodium, and the other Zn-richer than the compound.[2]

§ 3. BOTH THE LIQUID AND CRYSTALLINE STATES ARE CHARACTERIZED BY COMPLETE MISCIBILITY.

We have already noted (p. 37) that it is by no means a rare occurrence for substances to dissolve in one another in the crystalline state. Indeed, the formation of mixed crystals is very often observed in the case of metals. On this account, investigation of the nature of metallic alloys is subject to increased difficulty. Now, it is precisely the alloys of predominant importance in the industries — Iron-Carbon alloys, the Bronzes, Brasses, etc., — whose components show miscibility in the crystalline state, and it is largely owing to this condition that, in spite of the many exact investigations which have been devoted to these systems, various problems still await solution.

We will make the assumption in this paragraph that the two

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[1] MATHEWSON, Z. anorg. Chem., 48, 191 (1906).

[2] SMITH, Z. anorg. Chem., 56, 119 (1907), has recently observed similar conditions in the K-Zn System. The compound, in this case, is also Zn-rich, corresponding to some formula approximating $K\text{-}Zn_{12}$.

metals A and B are miscible in the crystalline, as well as the liquid, state in all proportions. In such a case, considerable analogy is to be noted relative to the respective behavior of the crystalline and liquid phases. The assumption of complete miscibility in the liquid state denotes that homogeneous melts of all concentrations between 0 per cent B and 100 per cent B (pure A to pure B) may be prepared, and that the properties of these melts will vary continuously with the concentration. The same is true relative to the case of complete miscibility in the crystalline condition — frequently designated as the case of complete, or unbroken, isomorphism. VAN'T HOFF has given expression to the analogy between mixed crystals and liquid mixtures, which appears to be very close in many instances, by introduction of the term "solid solution."[1]

Complete miscibility in the liquid and crystalline states requires that the crystals which are in equilibrium with the melt be alike in composition *among themselves*. It is quite as contrary to our original assumption for the crystals which are in equilibrium with the melt to be of different varieties (*e.g.*, as is the case relative to crystallization of an eutectic), as it is for the melt to separate into two layers. If the crystals were of different varieties, equilibrium corresponding to complete miscibility in the crystalline state could no longer be in evidence. Let us imagine, for example, that two liquids which are miscible in all proportions, such as water and alcohol, be arranged in layers. Then the system cannot come to rest, viz., equilibrium cannot result, until the two liquid layers have attained the same concentration as a result of diffusion. Precisely the same conditions obtain when two crystals which are miscible in all proportions are brought in contact. According to the principle that equilibrium is independent of the arrangement of the separate phases (see p. 27), direct contact of both crystalline varieties is not essential, for equalization of concentration may be attained through the medium of melt, which is itself in contact with both varieties. We thus conclude that, if the miscibility is complete in both the liquid and crystalline phases, the system, in order to be in equilibrium, must comprise only a single liquid phase and a single crystalline phase.

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[1] VAN'T HOFF, Z. phys. Chem., 5, 322 (1890).

The simplest and most suggestive supposition regarding the crystallization process would be that the crystals which are in equilibrium with the melt possess not only the same composition among themselves, but also the same composition as the melt. There is, as a matter of course, no reason for supposing that a separation of the constituents should occur on crystallization, if they are completely miscible in both the liquid and crystalline states. This supposition may easily be tested according to p. 32. We need only take cooling curves of mixtures of various concentrations between *A* and *B*. If crystallization occurs in the manner suggested above (such that the separating crystals are of the same composition as the remaining mother liquor), we have a condition of complete heterogeneous equilibrium during the whole process. The amount of crystalline material increases and the amount of melt decreases, but neither of the phases changes its composition. Crystallization must proceed at con-

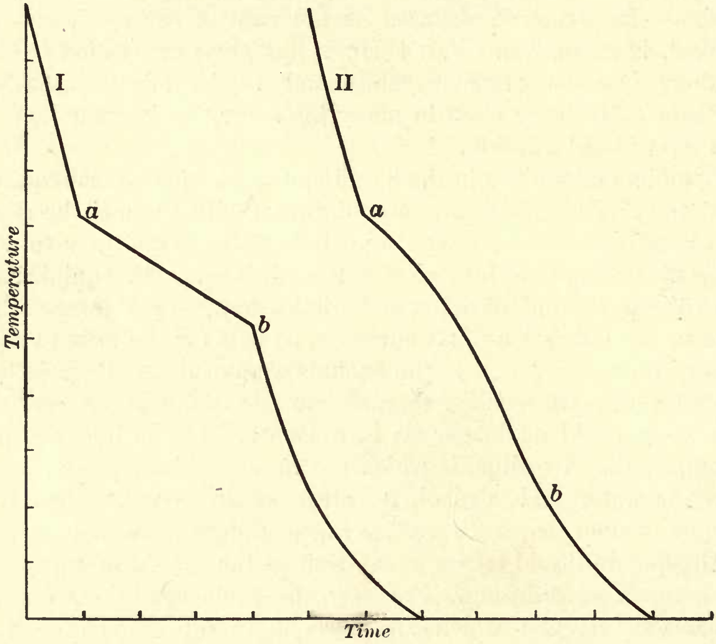

FIG. 54.

stant temperature, just as would the case for a pure substance, and the cooling curves must show constant temperature halts.

Experience teaches us, however, that our supposition is not justified by the facts in hand. In by far the greater number of cases, the cooling curves show no halts, even in cases of complete miscibility in the crystalline condition, but, rather, so-called crystallization intervals. The temperature at which the separation of crystals begins is different from the temperature at which crystallization ends. This is made evident on the cooling curves (Fig. 54), in that, after the beginning of crystallization at the point *a*, no period of constant temperature ensues, but a period of decreased rate of cooling instead.

More accurate theoretical investigation of crystallization processes relating to miscibility in the crystalline condition, for which we are indebted to BRUNI[1] and to ROOZEBOOM,[2] has shown that the above assumption fails of a theoretical basis as well. Before proceeding to a discussion of these questions, we will introduce a general principle which was deduced by WILLARD GIBBS[3] from theoretical considerations, and which, among other things, furnishes information as to when a melt solidifies without change in composition in a two component system especially characterized by complete miscibility in the liquid and solid states.

GIBBS' PRINCIPLE.

The portion of this principle which is of particular interest at present reads: *If, in a two component system consisting of two phases in equilibrium under constant pressure, the composition of both phases is the same, then the temperature, in general, possesses a minimum or maximum value.*

We will proceed to construe this principle rather more definitely with respect to its bearing upon solidification processes in a two component system[4]:

In a two component system consisting of a single liquid and a single crystalline phase, the composition of both phases is the same

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[1] BRUNI, Rend. Acad. Lincei, 1898, II, 138, 347 (Sept. 4 and Dec. 18).

[2] ROOZEBOOM, Acad. Wiss. Amsterdam, Sept. 24, 1898; Z. phys. Chem., 30, 385 (1899).

[3] GIBBS, Thermodynamische Studien (Ostwald's translation), Leipzig, 1892, p. 118; Trans. Conn. Acad., iii, 1875–8.

[4] RUER, Z. phys. Chem., 59, 1 (1907).

at those concentrations and at only those concentrations where the fusion curve of the concentration-temperature diagram (pressure-constant) possesses a horizontal tangent, viz., a tangent parallel to the concentration axis.

Thus, we are now dealing with conclusions which are to be drawn from the geometrical form of the fusion curve. The following three cases represent, in broad generality, the possibilities of occurrence of curves with horizontal tangent:

(1) The curve possesses a more or less flat summit, as shown in Fig. 55a. We have already become familiar with this case, as that of a maximum. The tangent is indicated by a dotted line.

(2) Analogous to the first type, but represented by a minimum, instead of a maximum. (Shown in Fig. 55b.)

(3) The curve possesses a horizontal inflexional tangent, as in Fig. 55c. Such a curve is convex above and concave below. The point of change in direction *a* separates these two portions of the curve. We may regard this curve as derived from the curve shown in Fig. 55d, which possesses both a maximum *a* and a minimum *b*. On bringing the points *a* and *b* closer together until they coincide, we obtain Fig. 55c. Thus, a point of change in direction *a*, when it constitutes a point on a horizontal tangent to the curve, is also called a maximum-minimum.

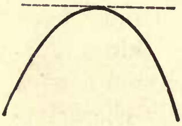

FIG. 55a.

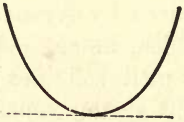

FIG. 55b.

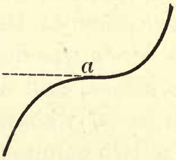

FIG. 55c.

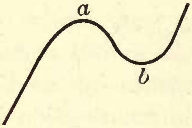

FIG. 55d.

We will first apply Gibbs' principle to several previously discussed cases. It is clear that the assertion made on p. 78 that never a sharp point, but invariably a maximum, is present on the fusion curve at the concentration of a compound which melts without decomposition constitutes a special case under this general principle. For, when two branches of a curve meet in a sharp point directed upwards, the tangent at this point is not horizontal (rather, indeterminate). Again, we must grant, on the basis of our principle, that, *e.g.*, in the fusion diagram of the gold-antimony alloys according to Vogel (see p. 130, Fig. 37), the curve branch *BC* runs horizontally into the point *C*. At this latter point, corresponding to the concentration of the pure compound, solidification without change in composition takes place, and, hence, the branch of the fusion curve corresponding to this crystalline variety must possess a horizontal tangent at this point. Since the form of the fusion curve is, as we are well aware, very difficult to determine with great accuracy (see p. 86), it will of course be impossible to draw an accurate conclusion, on this basis, relative to the composition of the compound.

Our principle holds only for a two component system composed of two phases. The melt must therefore solidify to a crystalline variety *of uniform composition.* Thus, we are not able to apply it when the melt crystallizes eutectically, *i.e.*, yields two crystalline varieties on solidification. The fusion curve possesses no horizontal tangent at the eutectic point, but a sharp point directed downwards, as is well known.

Since, as we have seen, only a single liquid and a single crystalline phase can occur if miscibility is complete in the liquid and crystalline phases, Gibbs' principle must apply to the crystallization processes in all such cases. It teaches us at once that, in general, the composition of the crystals will differ from that of the melt; that agreement in composition will result only at concentrations where the fusion curve possesses a horizontal tangent. By systematic consideration of the existing possibilities, we shall be able to separate the cases wherein such concentrations are found in the system from the simplest cases, wherein no such concentrations occur, and to begin with a discussion of the latter.

A. *Throughout all Concentrations the Separated Crystals Differ in Composition from the Melt with which they are in Equilibrium. Type I, according to Roozeboom.*

The melting points of the two metals *A* and *B* are denoted in the usual manner by *A* and *B*. The metal *B* melts at the higher temperature. On determining the temperatures at which crystallization begins in the various concentrations (the points *a* on the cooling curves (Fig. 54), entering these temperatures (points) in a co-ordinate system and joining them, according to previous practice, we obtain the curve which has been consistently called the fusion curve. The fusion curve of course ends at the melting points of the pure substances *A* and *B*. Concerning its course, we may say, first of all, that it cannot exhibit any abrupt change in direction. Breaks, angles and sharp points appear on fusion curves (and on equilibrium curves in general) only where two branches of the curve, each relating to different equilibrium conditions, intersect. Such discontinuity on the equilibrium curve corresponds to discontinuous change in the system, *e.g.*, consisting in the appearance of a new crystalline variety. In such cases, we have recognized the necessity of a sudden change in the direction of the fusion curve, owing to the possibility of realizing certain conditions which are outside of the stability jurisdiction of the curve. But when complete miscibility in both the liquid and crystalline phases is prescribed, the composition, and, therefore, the properties of the crystalline variety which is found in equilibrium with the melt, must vary continuously with the composition of the alloy. Hence, the curve which represents this equilibrium must consist of a single branch. Furthermore, we are able, in terms of Gibbs' principle, to say, relative to the form of the fusion curve, that it must continually sink to lower temperatures from *B* toward *A*, as the *A* concentration increases. For, pursuant to our original assumption that the separated crystals shall be different in composition from the mother liquor throughout all concentrations, maxima, minima and horizontal inflexional tangents may not appear on the curve. (Since, according to the above, the melting point of the lowest melting component *A* must be raised by addition of *B*, we see that the law of lowering of the melting point, given on p. 38, which rests on the assumption of non-miscibility in the crystalline condition, actually fails of application when this special assumption is not realized.)

We are also in a position to make an assertion concerning the composition of the crystals which are in equilibrium with the melt of certain definite concentration. Use has already been made (p. 39) of the self-evident proposition that, as long as crystallization does not occur at constant temperature, the freezing point of a mixture falls as freezing progresses. Now, since the fusion curve constantly falls to lower temperatures as the *A*-

content of the mixture increases (the freezing point of a mixture lies deeper in proportion as the *A*-content becomes greater), the above proposition means, in the present case, that the melt must become richer in the lowest melting component (A) as freezing progresses. This can obtain only in the event that the separating crystals contain more *B* than the melt with which they are in equilibrium.

We will now take up the further task of determining not only the initial temperatures of crystallization, but also the compositions of the first crystals to separate in successive concentrations — every 10 per cent. If we permit only a very small amount of the melt to crystallize, the composition of the remaining mother liquor will agree within the experimental error limit with that of the original melt. Thus, only the crystals need be analyzed. Let the results be entered in a co-ordinate system, and the separate points be joined to form continuous curves (Fig. 56). Two curves are obtained. On the first, or *l*-curve (liquidus), we have the temperatures at which melts of the respective concen-

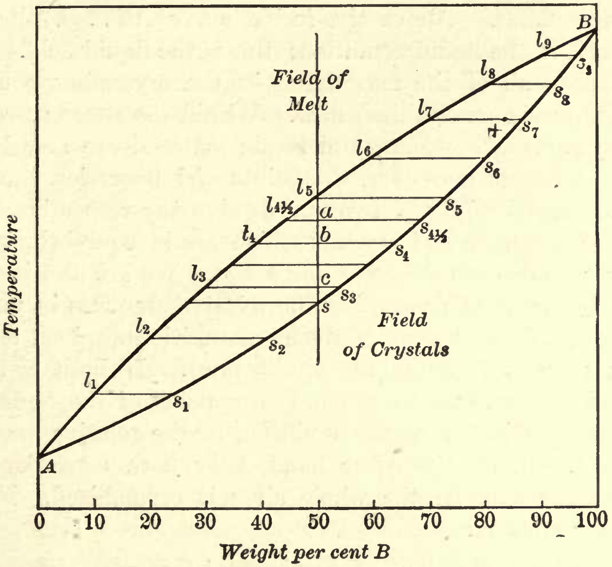

FIG. 56.

trations show the first evidence of crystallization. This is, then, the ordinary fusion curve. On the second, or *s*-curve (solidus), we have the concentrations of the crystals which correspond to each respective *l*-point. Both curves coincide at their highest and lowest points (viz., at the concentrations 0 and 100). In all other concentrations, the crystals are invariably richer in *B* than the melt from which they have separated.

When complete miscibility in the crystalline condition is in evidence, the same relations (pp. 165–7) hold for the *s*-curve as for the *l*-curve.[1]

The two curves divide the Concentration-Temperature Diagram into three fields. Above the fusion curve *All . . B*, all of the material is in the liquid condition: this is the liquid field. Below the *s*-curve, all of the material is in the crystalline condition: this is the solid (crystalline) field. Within the space surrounded by both curves, crystalline and liquid material are associated in equilibrium, and, moreover, the points of intersection *l* and *s* of each horizontal with the two curves give the respective compositions of the melt and crystals which are in equilibrium at the temperature of the respective horizontal. We are also in possession of information concerning the relative amounts of melt and crystals of which an alloy of given composition at given temperature is composed (assuming equilibrium). If both concentration and temperature correspond to a point of the *l*-curve, the whole alloy is in the liquid condition, or the relative amount of melt is 1. If, on the other hand, they both correspond to a point of the *s*-curve, the whole alloy is crystallized. For any point, the relation:

$$(\text{Amount Melt}) \cdot xl = (\text{Amount Crystals}) \cdot xs,$$

or

$$\frac{(\text{Amount Melt})}{(\text{Amount Crystals})} = \frac{xs}{xl},$$

holds.

If we assume, according to Roozeboom (l.c.) that equilibrium constantly obtains during the crystallization, the diagram fur-

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[1] For limited miscibility in the crystalline condition, the *s*-curve is made up of separate, unconnected branches. For complete immiscibility in the crystalline condition, it would be made up of as many verticals, all situated at the concentrations of pure substances and compounds, as there were crystalline varieties of different composition present.

nishes us with information on all questions concerning the course of the crystallization. Suppose we consider the process of crystallization of any chosen melt, of concentration 50 per cent, for example, under this assumption. On cooling, the first separation of crystals occurs at the temperature l_5. These crystals possess the composition s_5. Owing to separation of *B*-rich crystals, the melt gradually becomes poorer in *B*; at the end of a finite time its concentration may have become 45 per cent *B*. The crystallization temperature will then have fallen to $l_{4\frac{1}{2}}$, and the separating crystals will then be of the concentration $s_{4\frac{1}{2}}$ according to the evidence of the diagram. But the crystals which have separated thus far and which are richer in *B* than $s_{4\frac{1}{2}}$ are not in equilibrium with a melt of this concentration. We will now assume that cooling proceeds slowly enough to allow the separated crystals the necessary time for reaching equilibrium with the melt by diffusion. On this basis, we must credit the components of the crystals with a very considerable capacity for diffusion, which assumption is indeed justified to a certain extent by practical experience (see p. 143). It is true that extremely slow cooling is essential to the fulfillment of this requirement. Assuming that such is effected, the separated crystals will all possess the composition $s_{4\frac{1}{2}}$ when the temperature and concentration of the melt are given by the point $l_{4\frac{1}{2}}$. We may now apply the relation:

$$\frac{\text{(Amount Melt)}}{\text{(Amount Crystals)}} = \frac{s_{4\frac{1}{2}}a,}{l_{4\frac{1}{2}}a}{}'$$

whereby we conclude that the alloy consists of $s_{4\frac{1}{2}}$ crystals and melt $l_{4\frac{1}{2}}$, in the respective proportions — (somewhat less than) 1 part: (somewhat more than) 3 parts. The concentration and temperature of the alloy are represented by the point *a*. When, after further crystallization, the concentration of the melt has fallen to 40 per cent *B*, by reason of the continued separation of *B*-rich crystals, its temperature corresponds to the point l_4, and the concentration of the crystals which are in equilibrium with this melt corresponds to the point s_4. Crystals of the concentration $s_{4\frac{1}{2}}$ would, therefore, be no longer in equilibrium with the melt. But such crystals are no longer present, having found time, in accordance with our assumption, to reach equilibrium with the melt, in that they have become so rich in A_1, owing to reaction with the melt by the time the crystallization temperature has fallen to l_4, that their composition corresponds to the point s_4. Since we have now reached the point b in the diagram, the alloy consists of some 45 per cent crystals and 55 per cent melt. The process continues in the above manner. When the temperature has fallen to c, the alloy is composed of crystals s_3 (85 per cent) and melt l_3 (only 15 per cent). Finally, at the point s the s-curve is attained, and *the whole alloy is now solidified to a conglomerate of mixed crystals which one and all possess the composition s* — 50 *per cent B, in the present case.*

If crystallization has progressed in this ideal manner, the cooling curve (Fig. 54, I) must show two breaks. Crystallization has begun at the point a, whereby the rate of cooling has diminished, and has ended at the point b, whereby the rate of cooling has regained its normal value, proceeding to completion in accordance with Newton's Law. It is clear that by taking cooling curves of various concentrations we are in possession of a means of determining not only the course of the l-curve, but that of the s-curve as well, without the least necessity for separating the initial crystals from the melt — a process which is always difficult and in many cases impossible — and analyzing them. For, just as the point a of the cooling curve gives us a point on the l-curve (corresponding temperature and concentration), the point b gives us a point on the s-curve. As a matter of fact, this procedure, or one resting upon the same basis, is always used in the study of metallic alloys. The temperature difference between a and b is called a crystallization interval.

Aside from the question of supercooling, the determination of points on the l-curve (given by the a points on the cooling curves) is independent of our original assumption relative to the course of the crystallization (that it be sufficiently slow) and is, therefore, free from objection. This, however, is not true relative to the determination of the s-curve. The points on the s-curve will correspond to the b points of the cooling curves only when it is certain that equilibrium between crystals and melt has actually reached adjustment, and consequently that, after all crystallization has ceased, every part of the crystalline conglomerate possesses the same composition, which must be that of the original liquid mixture. It may be urged, at the outset, that this necessary concentration adjustment between crystals and melt is never completely realized. Thus, a certain error will always be associated with data concerning the course of the *s*-curve.

In order to become familiar with the effect of incomplete concentration adjustment between crystals and melt, we will follow the crystallization of an alloy of the same concentration as before — 50 per cent *B* — under the assumption that this concentration adjustment fails entirely of realization. Obviously, the initial temperature of crystallization *a* (Fig. 54, II), corresponding to l_5 (Fig. 56), will not be influenced under this new assumption (in line with the previous statement that the determination of the *l*-curve is independent of any special assumption pertaining to the course of crystallization). But, when a certain amount of crystalline material has separated without attendant concentration adjustment (such adjustment requiring appropriation of *A* by the crystals from the melt), the melt is left *A*-richer than it would be if adjustment had occurred, and the temperature at which it will begin to crystallize is lower (according to the diagram, Fig. 40) than it would be under normal conditions. The curve branch *ab* must, therefore, show a more rapid temperature fall in Fig. 54, II than in Fig. 54, I (representing ideal conditions). Moreover, the concentration of the melt must pass through all values from the initial concentration, 50 per cent *B*, up to 0 per cent *B* (= pure *A*), whereby the amount of melt is continually reduced. The last quantity of melt, even though inappreciably small, must consist of practically pure *A*. The crystals which have separated during the process must likewise exhibit all concentrations from s_5 down to pure *A*, and must also fall off consistently in amount as the *A*-content increases. The heat quantity which is liberated during crystallization thus becomes smaller and smaller, until finally the zero value is reached at the melting point of *A*. Thus we see that the cooling curve, Fig. 54, II, must agree with the ideal curve, Fig. 54, I, as far as the point *a*, where crystallization first sets in, but must show a more rapid temperature fall, directly this point is reached, than the latter. The end point of crystallization *b* will coincide with the melting point of pure *B*, although the quantity of heat liberated toward the end of crystallization will have become so trifling, owing to the small remaining quantity of melt, as to escape observation. The curve reaches its last stage at *b* *without* *discontinuity* (no break), thereafter representing normal cooling of the completely solidified alloy according to Newton's Law.

Such crystallization processes as are actually realized in practice will lie between the extreme cases represented in Figures 54, I and 54, II. Concentration adjustment between crystals and melt will develop to a certain extent, but never completely. Therefore, crystallization will practically cease at a temperature which is *lower* than that of the point on the *s*-curve which corresponds to the concentration in question, but higher than the melting point of the lowest melting component. In any event, the cooling curves must show more extended crystallization intervals (owing to incomplete concentration adjustment) than are theoretically given by the distances between the points on the *l*- and *s*-curves for the respective concentrations. Practical determination of the position of the *s*-curve by means of cooling curves will therefore result in a consistently abnormal (too low) placement of the same. Such a result will approach the true equilibrium condition (*ceteris paribus*) in proportion as the time allowed the crystals for reaching concentration adjustment with the melt is extended, *i.e.*, in proportion as cooling is retarded. The point *b* will become less marked on the cooling curve in proportion as concentration adjustment becomes less perfect. Thus, under certain conditions, it will escape observation. As a matter of fact, in by far the greater number of cases wherein mixed crystals are encountered, the point *b* on the cooling curve is only faintly perceptible. This renders the determination of the *s*-curve still more uncertain.

The form of the *l*-curve and of the *s*-curve may be very different for different pairs of components. Figures 57, 58 and 59 represent fusion diagrams, according to Ruer,[1] of alloys of palladium with the metals, copper, silver and gold, which constitute a natural group of the periodic system.

According to the evidence of these diagrams, palladium forms an unbroken series of mixed crystals with each of the three metals.

The experimentally determined points of the *l*-curves are made apparent by crosses, and the curve itself is drawn with a heavy line. The course of the *s*-curves, as derived from the cooling curves by determination of crystallization intervals, is likewise entered in the diagrams, although these curves are drawn in dotted lines on

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[1] Ruer, Z. anorg. Chem., 51, 223, 315, 391 (1906).

account of the uncertainty which attaches itself to the method of their determination. The form of the fusion curve is very different in the three diagrams. We see in the Palladium-Copper System (Fig. 57) a very gradual initial rise in the fusion curve (from copper to palladium), followed by a very rapid rise; hence, convex curvature with respect to the concentration axis. In the Palladium-Gold System (Fig. 59), just the opposite is noted: at first a rapid rise in the fusion curve, and finally a gradual rise from gold to palladium, whereby the curve is concave with respect to the concentration axis. The fusion curve of the Palladium-Silver System (Fig. 58) occupies an approximately mean position between these two extreme cases. It shows some curvature, to be sure (concave to the concentration axis), and yet its form more nearly approaches that of a straight line. The following summary may serve for

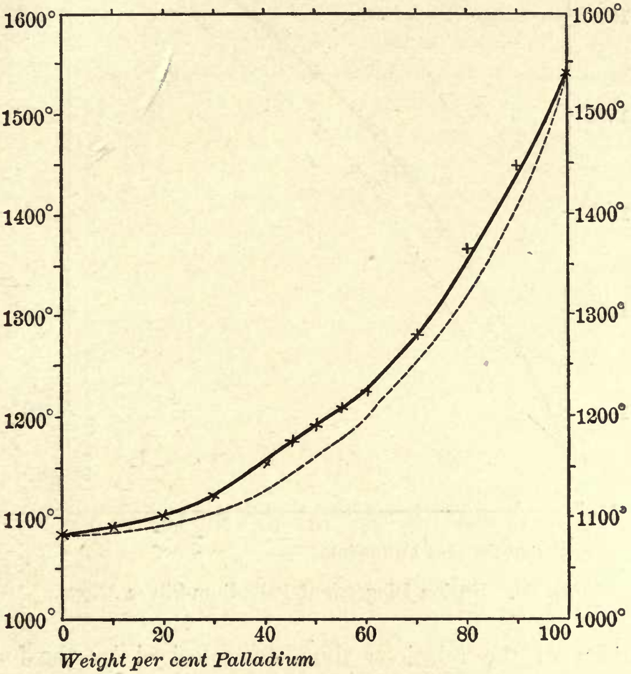

Fig. 57. Fusion Diagram of Palladium-Copper Alloys.

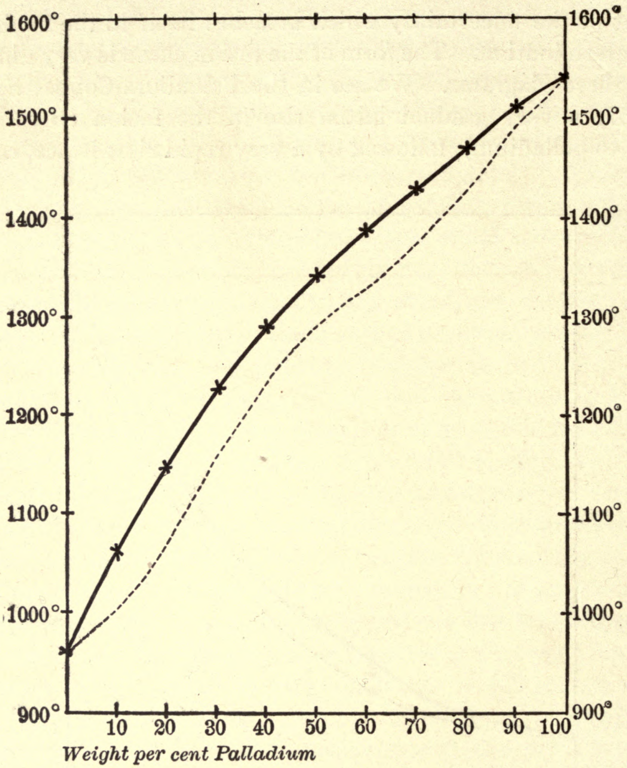

Fig. 58. Fusion Diagram of Palladium-Silver Alloys.

comparison of the relations thus characterised by the form of fusion curve:

The melting point of palladium is lowered:

94°	by addition of	10 per cent Cu,
26°		10 per cent Ag,
7°		10 per cent Au.

The addition of 10 per cent palladium raises the melting point of

Cu..... 7°,
Ag.....98.5°,
Au....207°.

It is observed that the crystallization intervals (given by the distances between the *l*- and *s*-curves) are uniformly largest in the Palladium-Silver series, and smallest in the Palladium-Gold series. They, of course, become smaller as the pure metals are approached, at which points they reach the zero value. In the Palladium-Gold series it is, moreover, apparent that the intervals on the gold-rich side are larger than those on the palladium-rich side.

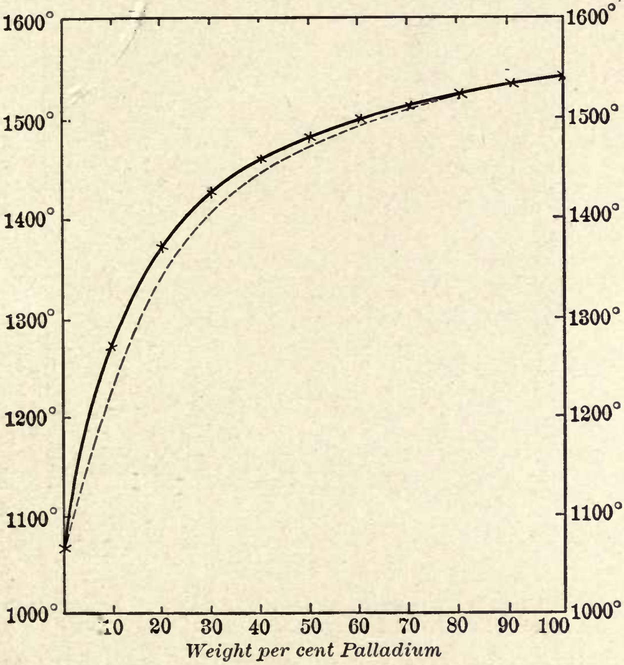

FIG. 59. Fusion Diagram of Palladium-Gold Alloys.

If crystallization had progressed in an ideal manner, whereby all the resulting crystals would have attained the original composition of the mixture, the structure of the reguli would necessarily have been homogeneous, as is true in case of pure substances (*cf.* Fig. 12a and 12f). In actual practice, homogeneous structure may be expected in those alloys alone which have crystallized within a very small interval of temperature (small crystallization interval), *i.e.*, in which the separating crystals come very close in composition to the melt with which they are in equilibrium. Such an interval is to be noted on the palladium side of the Palladium-Gold System — from approximately 50 per cent palladium to 100 per cent palladium. A section of the 60 per cent Pd + 40 per cent Au alloy, etched with dilute aqua regia, is shown, magnified 70 times in Fig. 60. The individual crystalline polygons are very uniformly etched from the center of the section to the sides, showing highly homogeneous composition. The circumstance that a few of the polygons have offered considerable resistance to the action of the etching liquid, and have thus remained brilliant, while others have been considerably attacked by the etching liquid, and thus appear darker in the photograph, is directly traceable to the fact that the surface plane of the section cuts the different crystals in different directions (relative to the crystalline axes). Phenomena of this sort are associated with the pure metals as well; particularly with pure palladium, as is evident on consideration of Fig. 61, representing a section of this metal, etched with concentrated nitric acid and magnified 70 times. Here we have polygons which have remained brilliant as before, and are very readily distinguishable from the darker, etched surroundings.

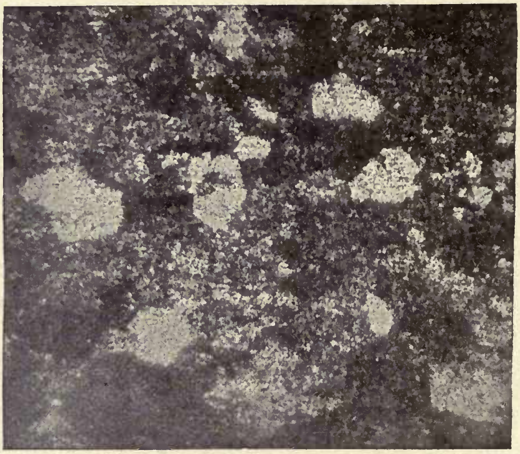

FIG. 60. 40% Au+60% Pd. Etched with dilute aqua regia. Magnified 70 times.

FIG. 61. Pure Palladium. Magnified 70 times.

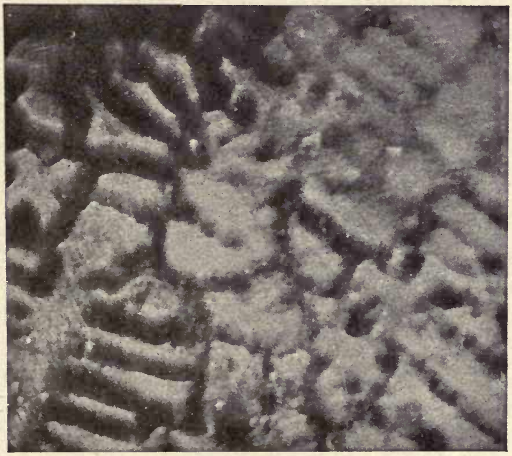

FIG. 62. 30% Cu + 70% Pd. Etched with dilute nitric acid and then re-polished. Magnified 70 times.

If the crystallization interval is large, *i.e.*, if the crystals which first separate differ considerably in composition from the melt, the appearance of the section will be less uniform. This is well illustrated by Fig. 62, which represents a section composed of 30 per cent Cu + 70 per cent Pd, etched with dilute nitric acid, and then lightly re-polished. According to the diagram, Fig. 57, the crystals separating first are richest in palladium, since palladium is the higher melting component of the system. These crystals have served as nuclei for subsequent crystallization, and are, accordingly, enveloped by the material which separates — and becomes progressively richer in copper — later. Now, copper is more readily attacked by nitric acid than is palladium, whence we observe that the polygons of this section appear lighter in the interior, *i.e.*, are less attacked here than at the sides. Microscopical examination of the section in this case shows conclusively that complete concentration adjustment has not taken place.

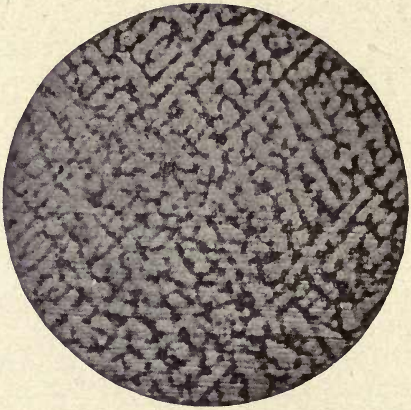

FIG. 63. 70% Iron + 30% Manganese. Magnified 40 times.

Inhomogeneity of the section may be even more marked. Fig. 63 shows a section consisting of 70 per cent Fe + 30 per cent Mn, magnified 40 times; Fig. 64, another section in this series, containing 50 per cent Fe + 50 per cent Mn, magnified 100 times. The photographs are from LEVIN and TAMMANN'S[1] work on this series. Two structure elements are plainly in evidence, namely, primarily separated crystals, which have remained brilliant throughout the etching process, and a surrounding mass, which is etched to a darker color. (A saturated solution of picric acid, or an alcoholic solution of hydrochloric acid, served as etching agent.)

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[1] LEVIN and TAMMANN, Z. anorg. Chem., 47, 136 (1905).

On studying these figures, one will scarcely be inclined to admit that the results of thermal analysis in this case (l. c.), indicating complete miscibility in both liquid and crystalline states, are correct. Indeed, a plausible explanation for the appearance of these two structure elements can hardly be advanced. Even if it be assumed that the tendency toward nucleii formation is so marked that envelopment of the crystals which first separate by those which follow, after the manner of

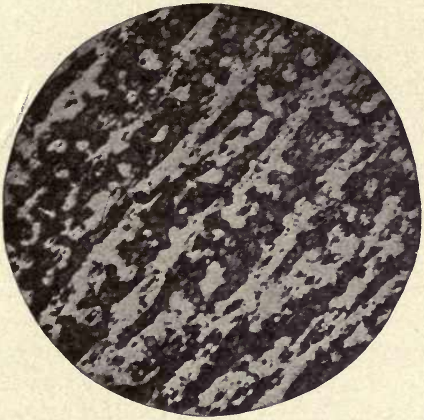

FIG. 64. 50% Iron + 50% Manganese (rapidly cooled). Magnified 100 times.

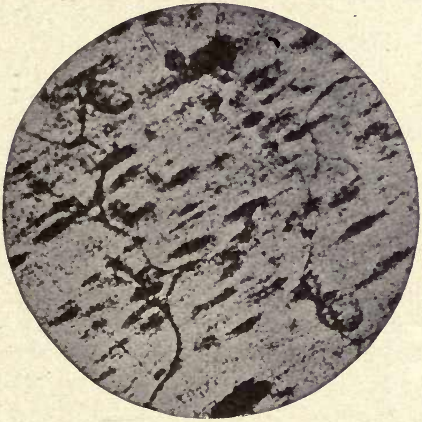

FIG. 65. 50% Iron + 50% Manganese (slowly cooled). Magnified 100 times.

layers, occurs to a very limited extent only, it is, nevertheless, difficult to see how such sharply defined structure elements can result. That complete miscibility in the crystalline condition is actually to be conceded, is apparent from Fig. 65, which likewise represents a section consisting of 50 per cent Fe + 50 per cent Mn (same concentration as that shown in Fig. 64; also magnified 100 times. But, while crystallization in the first case progressed rapidly, occupying some 30 seconds from beginning to end, cooling was conducted so slowly in the latter case that approximately an hour elapsed between the initial and final crystallization. We see that this very slow cooling has resulted in an almost completely homogeneous structure. The section shows large crystals separated from one another by fine lines. Etching was very uniform over the whole surface of the crystals. (The black, drawn-out oval spots correspond to air holes.)

For the purpose of rendering the alloy homogeneous, we may, instead of retarding crystallization, frequently obtain good results by maintaining the crystallized conglomerate for some time at a temperature as close as possible to that of the point on the *s*-curve which corresponds to the concentration of the alloy, or, perhaps, a few degrees above this. The crystals may then (at a temperature close to their melting point) be expected to reach a certain concentration adjustment, owing to diffusion, particularly when such diffusion is facilitated by the presence of an amount (even though it be small) of melt. Nevertheless, more positive success is assured by resorting to slow crystallization from the melt.

B. *At Given Concentrations the Separated Crystals Possess the Same Composition as the Melt with which they are in Equilibrium.*

According to page 166, the fusion curve must possess either a maximum or a minimum or a horizontal inflexional tangent in such cases. By combination of these three simple cases, more complicated types are attained. No abrupt changes in direction (breaks, angles and peaks) on the *l*- and *s*-curves are possible (see p. 168).

1. THE FUSION CURVE POSSESSES A SINGLE MAXIMUM. TYPE II, ACCORDING TO ROOZEBOOM. — In this case, the melting point

of the highest melting component B must be raised at the start by addition of A, as well as the melting point of the lowest melting component A, by addition of B. The l-curve is of the general form shown in Fig. 66, ACB (drawn in full). The maximum is at C. For the purpose of acquiring a preliminary conception relative to the position of the s-curve, we will again make use of the principle that, in case a mixture fails to freeze at constant temperature, its freezing point is lowered as material freezes out. Thus, according to the l-curve of Fig. 66, if we allow a melt of some concentration between B and C to crystallize, its melting point can be lowered only in that the melt becomes B-richer as freezing progresses. The separated crystals must, then, contain more A than the melt with which they are in equilibrium, *i.e.*, the s-curve must run to the left of the l-curve in this concentration area. From analogous considerations, it follows that, in the concentration area between A and C, the separated crystals must contain more B than the melt with which they are in equilibrium, a demand which is met in the figure by placement of the s-curve

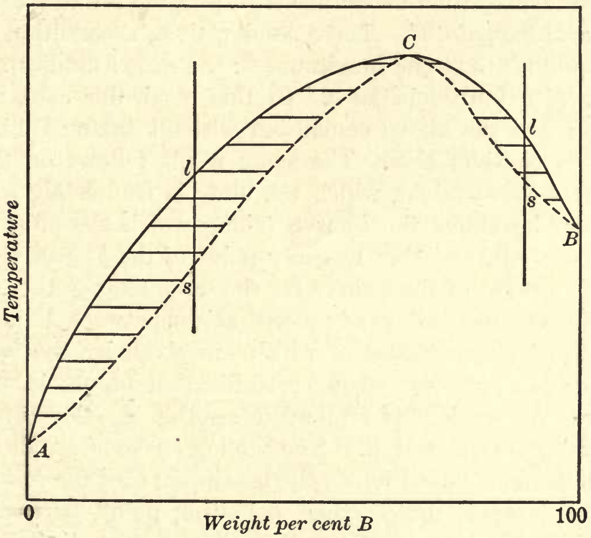

FIG. 66.

to the right of the *l*-curve. The following considerations relating to the maximum *C* may be offered. On approaching this point from the *A*-rich side of the fusion curve, the separated crystals are *B*-richer than the melt, but, on approaching from the *B*-rich side, the separated crystals are *A*-richer than the melt. Since the presence of complete isomorphism requires that the composition of the crystals, which are in equilibrium with a melt, change continuously with continuous change in composition of the melt, it follows that at the maximum *C* these crystals can neither be richer in *A* nor in *B* than the melt; they must possess the same composition as the melt. *Thus, the l- and s-curves will coincide at the point C.* There results, then, a condition of complete equilibrium at the maximum *C*: the melt solidifies after the manner of a pure substance. In this particular case, we were able to reach the above conclusion without taking Gibbs' Principle into consideration. The same result follows on the basis that the *s*-curve (along which the alloy is completely solidified) can never lie above the *l*-curve (along which the alloy is completely melted), and that to every point of the *l*-curve there corresponds a point of the *s*-curve for the same temperature.

Cooling curves of alloys of concentrations between *A* and *C* show intervals, the magnitudes of which are given by the respective distances *ls* (Fig. 66), when crystallization occurs in the ideal manner. An analogous statement applies to alloys of concentrations between *C* and *B*. The cooling curve of an alloy which corresponds in composition to the maximum *C* of the fusion curve shows no interval, but, rather, a halting point, as does a pure substance. The structure of the alloys must be completely homogeneous in all concentrations.

If concentration adjustment between crystals and melt is imperfectly attained in concentrations between *A* and *C*, the central portions of the crystals will be *B*-richer than the outside portions; in concentrations between *B* and *C* the central portions will be *A*-richer than the outside portions. The structure of an alloy of concentration *C* will invariably be completely homogeneous.

No example of this case (a simple maximum on the fusion curve for miscibility in both liquid and crystalline states) is known as far as metallic alloys are concerned. According to ADRIANI,[1] *d*- and *l*-carvoxim show these relations.

2. THE FUSION CURVE POSSESSES A SINGLE MINIMUM. TYPE III, ACCORDING TO ROOZEBOOM. — In this case, the *l*-curve appears as shown in Fig. 67, *ACB* (drawn in full). We note in particular that the melting point of *A* is lowered by addition of *B*, as well as the melting point of *B* by addition of *A*. The minimum is situated at *C*. In a manner analogous to that given under Case 1, we decide that the first crystals which separate in concentrations between *A* and *C* are *A*-richer than the melt; that the first which separate in concentrations between *B* and *C* are *B*-richer than the melt; and that, at the point *C*, crystals and melt possess the same composition. These requirements are met in the construction of the diagram (*s*-curve dotted; *l*-curve drawn in full).

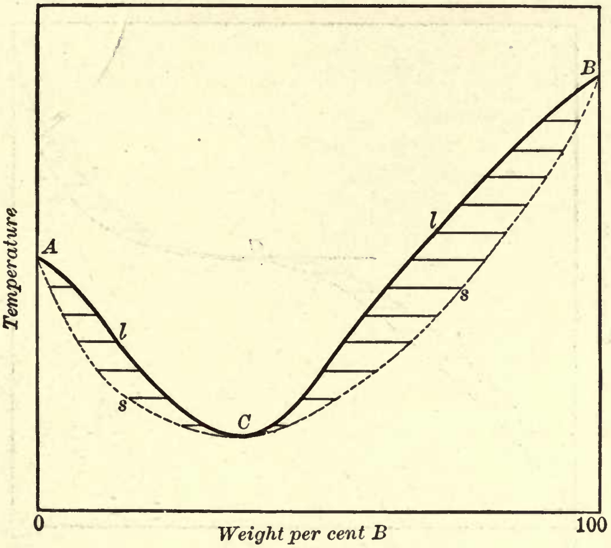

FIG. 67.

The cooling curves of all melts of concentrations between *A* and *C* and *B* and *C* show crystallization intervals. At the minimum *C*, the alloy crystallizes at constant temperature, as does a pure sub-

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[1] ADRIANI, Z. phys. Chem., 33, 453 (1900).

stance: the cooling curve of this alloy shows a halting point. For incomplete concentration adjustment between crystals and melt in concentrations between *A* and *C*, the central portions of the crystals are *A*-richer than the outside portions; while, in concentrations between *B* and *C*, the central portions of the crystals are *B*-richer than the outside portions. At the minimum *C*, the alloy must be homogeneous under all conditions.

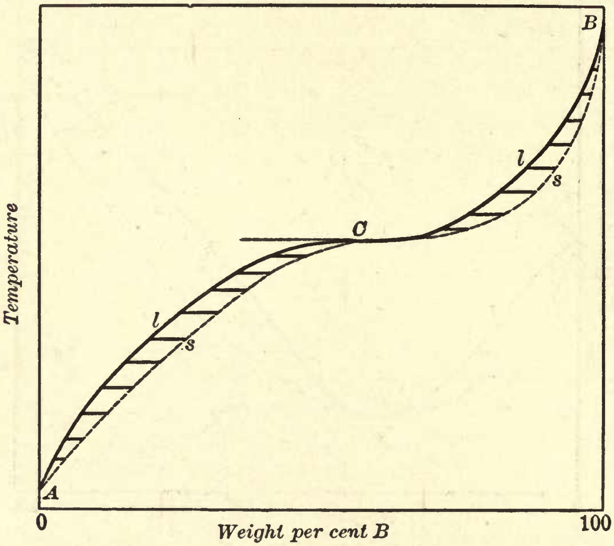

FIG. 68.

Two metal pairs, each giving a fusion curve with simple minimum, have recently been discovered, namely, Mn-Cu[1] and Mn-Ni.[1], [2]

3. THE FUSION CURVE POSSESSES A SINGLE HORIZONTAL INFLEXIONAL TANGENT. — This case is represented by Fig. 68. The *l*-curve is drawn in full; the *s*-curve dotted. The course of the fusion curve is here quite similar to that under Type I, according to Roozeboom (Fig. 56). The melting point of *B* is also lowered by addition of *A*, and the melting point of *A* raised by addition of *B*. The horizontal direction of the fusion curve at the point of inflection

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[1] ŻEMCŻUŻNYJ, URASOW and RYKOWSKOW, J. Russ. phys. Chem. Soc. 7, Sept. 20 (1906).

[2] DURDIN. The Gœttingen Laboratory (Tammann).

C is easily overlooked in the experimental determination of the curve. At *C*, the melt solidifies like a pure substance (see p. 165). The cooling curve corresponding to this concentration, therefore, shows a halting point, as do the curves for the pure substance *A* and *B*, while the cooling curves corresponding to all other concentrations show crystallization intervals. Conversely, this condition, which will not in general be overlooked on working out the fusion diagram, demands a horizontal tangent at *C*. Two systems of element pairs are known which, in all probability, belong to this type. These are Br-I and Mg-Cd. Discussion of these systems is reserved for subsequent pages. This type is not cited by Roozeboom. On account of the general resemblance of this type of fusion curve to Type I, we will denote it as Type Ia.

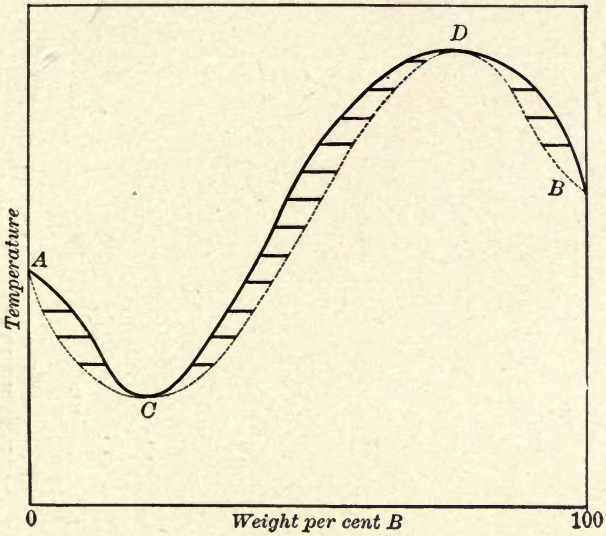

FIG. 69.

4. MORE COMPLICATED FORMS OF THE FUSION CURVE.—In the cases previously treated, either the melting point of the lowest melting component *A* is raised by the first additions of *B*, and that of the highest melting component *B* lowered by the first additions of *A* (Types I, Ia), or both melting points are raised (Type II) or

lowered (Type III) by first additions of the other (respective) component. We may imagine a further possibility, namely, that the melting point of the lowest melting component *A* be lowered by the first additions of *B*, and that of the highest melting component *B* raised by the first additions of *A*. The fusion curve would then show a maximum as well as a minimum (Fig. 69). The possibility of such a type, first advanced by NERNST[1] relative to vapor pressure curves, must not be summarily rejected in the present connection (fusion curves) as long as no definite assumptions bearing upon the molecular condition of the participating substances are made. The fusion curve given in Fig. 70 also shows a maximum and a minimum. Type Ia may be regarded as a limiting case under this type. Finally, two maxima and one minimum, two minima and one maximum, etc., might appear as further complications. No examples of these cases are known.

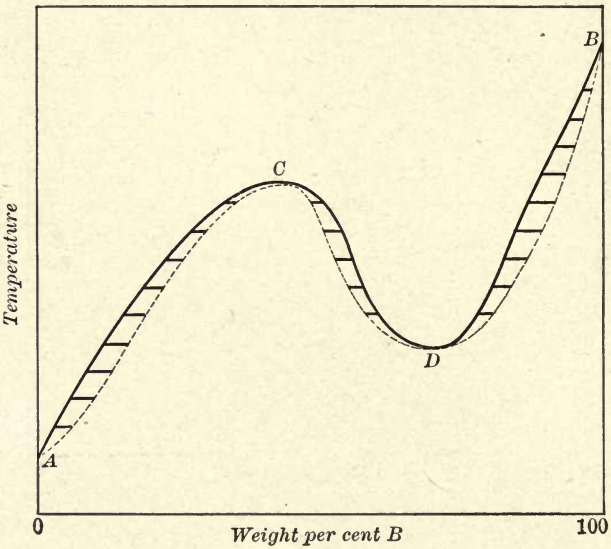

FIG. 70.

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[1] NERNST, Theoretische Chemie, 4th ed., p. 113.

C. *Horizontal Course of the Fusion Curve through a Finite Concentration Interval.*

If the fusion curve runs horizontally through a finite concentration interval, alloys of all concentrations which fall within this interval must, according to pp. 165–6, solidify after the manner of pure substances. Such an interval might reach as well throughout the whole diagram as through a portion of it. The former condition is shown in Fig. 71. All mixtures, as well as the components themselves, solidify at the same temperature, after the manner of pure substances. The *l*- and *s*-curves coincide completely. The only known example of this case is the system *d*- and *l*- camphoroxime.[1] Owing to the necessary theoretical condition that the melting points of the two components be identical, we may well consider this case restricted to optically someric substances; however, it does not constitute a necessary eventuality even here. In the case of metals, it is excluded for the above reason.

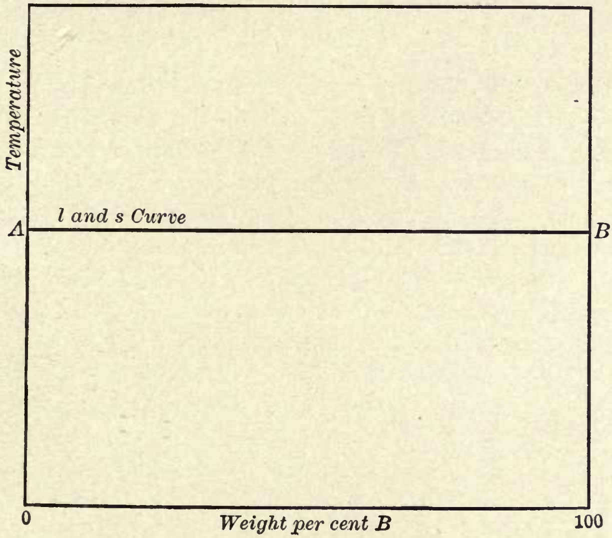

FIG. 71.

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[1] ADRIANI, Z. phys. Chem., 33, 453 (1900).

From theoretical considerations, occurrence of the second possibility, viz., a partly horizontal fusion curve, appears improbable. On the other hand, an experimental realization of this case — within an error limit, on temperature observations, of ±5 degrees — seems to have been secured by GUERTLER and TAMMANN[1] in their investigation of the system Co-Fe. The melting points of the cobalt steels between the concentration limits 100 to 5 per cent Co lie at the melting temperature of cobalt.

D. *Polymorphous Transformations.*

The thoroughly different character of the fusion diagrams which we have lately described from that of the diagrams previously considered is due solely to the circumstance that, in all the later diagrams, complete miscibility of the two components in both phases constituted an essential condition, while, in the earlier diagrams, miscibility in one of the phases was excluded. We may, therefore, apply the general deductions given on these last pages to all equilibria which refer to complete miscibility of the two components in both of the participating phases. Let us now assume that each of the substances is capable of existence in two modifications: the α modifications, A_α and B_α, stable at lower temperatures, and the β modifications, A_β and B_β, stable at higher temperatures. Let the transitions be reversible, and, moreover, let the two α modifications, as well as the two β modifications, be miscible in all proportions with one another. Then, in completely describing the transition phenomena which will result under the above assumption, we have only to use Figs. 56, 66, 67 and 68 — denoting the *l*-curve, which referred to liquid phase (stable at higher temperatures), as β-curve, *i.e.*, the curve referring to the crystalline variety stable at higher temperatures, and, analogously, the *s*-curve as α-curve. Thus, we shall require to differentiate between the same types of transformation curves as of fusion curves. The α crystals which separate on cooling from the β crystals will, then, in general, differ from the latter in composition, and transformation will accordingly take place throughout an interval. If transformation occurs in an ideal manner (according to the

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[1] GUERTLER and TAMMANN, Z. anorg. Chem., 45, 205 (1905).

description on p. 171), the α crystals present after complete transformation will all possess the same composition, and this is given by the concentration of the transforming β crystals. Transformation will occur at constant temperature only in those concentrations which correspond to pure substances, or to certain characteristic points on the diagram.

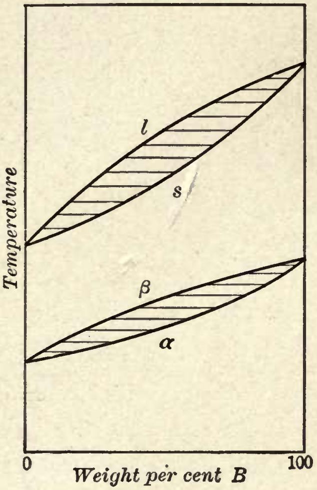

FIG. 72.

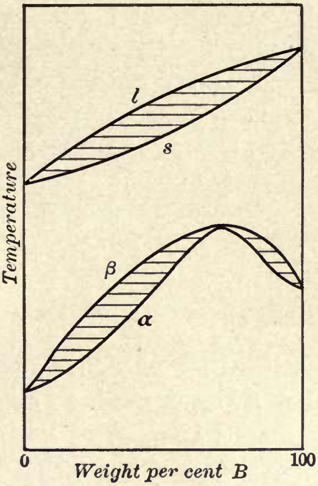

FIG. 73.

Fig. 72 represents the combination of a fusion diagram in which neither maximum nor minimum occurs with a transformation diagram of which the same is true. Fig. 73 represents the combination of a fusion diagram like the above with a transformation diagram in which a maximum occurs. Obviously, the whole category of combination among the various equilibrium types may be made. When only one of the components, B, for example, possesses a trans-

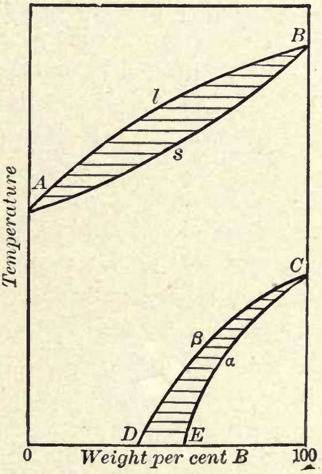

FIG. 74.

ition point, the condition of affairs shown in Fig. 74 will result, according to Roozeboom.[1] The β- and α-curves proceed from the transition point of the pure substance to lower temperatures and decreasing B concentrations, without ever reaching the concentration, 100 per cent A. The B-content of mixed crystals which are A-richer than corresponds to the concentration D is not great enough to cause transformation to take place. The system Cu-Ni[2] may be mentioned as an example of this case. Nickel changes to a magnetic modification at a low temperature. However, reguli containing less than 40 per cent nickel show no action on the compass needle.

E. *The Components Unite to Form a Chemical Compound.*

The earlier view that a compound may not form mixed crystals with its components may be regarded as effectually disproven by the investigations of Hollman.[3] It is nevertheless true that indisputable proof of the existence of a compound between two isomorphous substances will be obtainable only in rare cases. We have no right to assume such proof to be at hand, as we have seen above, when a mixture of a given concentration solidifies after the manner of a pure substance. Since the law of freezing point lowering does not hold here, the presence of a maximum or of a minimum does not prove the existence of a compound. On the other hand, it cannot be gainsaid that the presence of a maximum, etc., *may* be due to the existence of a compound. Proof that the components unite chemically in such cases will, then, be forthcoming only when criteria of other nature (polymorphous transformations, for example — see below) are brought into play.

It is, indeed, true that a method adapted in principle to the solution of this problem may be proposed. This is completely analogous to the method by means of which Roscoe demonstrated that constant boiling mixtures of water and formic acid, water and hydrochloric acid, etc., are not chemical compounds. The composition of a chemical compound must be independent of the method of preparation of the compound, and Roscoe was able to

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[1] Roozeboom, Z. phys. Chem., 30, 413 (1899).

[2] Guertler and Tammann, Z. anorg. Chem., 52, 27 (1906).

[3] Hollman, Z. phys. Chem., 37, 193 (1901).

show that this condition fails to obtain in the above cases; that the composition of these constant boiling mixtures is dependent on the pressure under which distillation is effected. In precisely the same manner, it may be determined that the maximum, etc., of the fusion curve is due to chemical combination when, and only when, its concentration is independent of the pressure under which fusion occurs. Unfortunately, considerable difficulty is associated with the practical application of this method in the present connection, since the effect of external pressure on the processes which take place in the crystalline and liquid phases is very slight in comparison to its effect on those which relate to the gas phase.

Perhaps we are most inclined to decide in favor of, or against, the acceptation of a compound, according as the maximum, etc., does, or does not, correspond to a simple formula.

Of the two systems, I-Br and Mg-Cd, each of which shows a point of inflection with horizontal tangent upon its fusion curve, in the first, the concentration of this point very probably corresponds, and in the second most certainly corresponds, to a compound. It is to be expected that this will always be the case, for, from theoretical considerations,[1] the, to a certain extent, chance occurrence of such a point is very improbable; in any event, less probable than that of a maximum or minimum, which is itself represented by very few known examples.

1. THE SYSTEM: BROMINE-IODINE. — Fig. 75 gives the fusion diagram of the system Br-I, according to MEERUM TERWOGT.[2] The concentration axis is graduated in atomic per cent iodine. We see that the *l*-curve apparently sinks continuously from the melting point of pure iodine (+ 110.6 degrees) to that of pure bromine (− 7.3 degrees). It is met by the *s*-curve close to the concentration, 50 per cent iodine, for concentrations between 50 and 53 atomic per cent I solidify completely within a temperature interval of 1 degree, *i.e.*, nearly after the manner of pure substances. The close agreement of this particular concentration with that corresponding to the formula IBr renders the existence of a compound of such formula extremely probable. If the compound possesses a sharp melting point, then the tangent to the *l*-curve at this con-

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[1] RUER, Z. phys. Chem., 59, 6 (1907).

[2] MEERUM TERWOGT, Z. anorg. Chem., 47, 203 (1905).

centration will, according to p. 166, be horizontal, and, for complete isomorphism, coincidence of the *l*- and *s*-curves must correspond with that shown in the vicinity of the point *C* in Fig. 68 (p. 186). The *s*-curve in the Br-I System actually possesses a point of inflection at about 50 per cent I, and the inherent uncertainty of the determination at once permits of the assumption that the tangent is, in reality, horizontal at this point. Admitting that an error of from 1 to 2 degrees may apply to the temperature determination of the *l*-curve, the existence of a point of inflection with horizontal tangent within the concentration limits, 50 to 53 per cent I may be assumed.

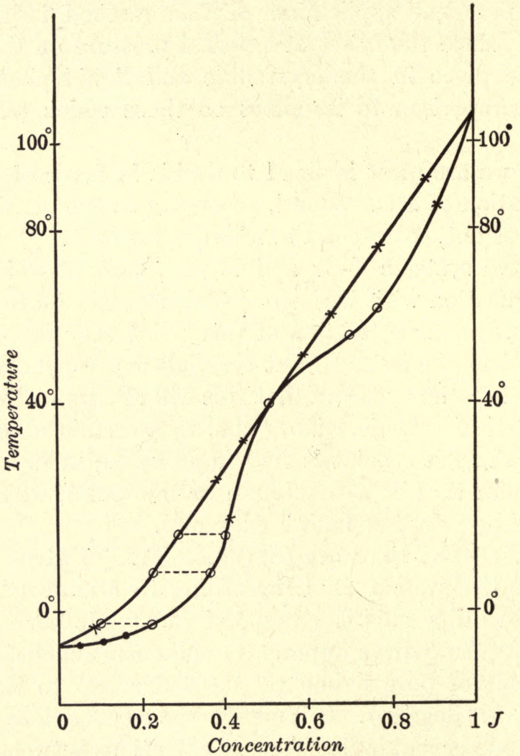

FIG. 75. Fusion Diagram of the System Bromine-Iodine according to Meerum Terwogt.

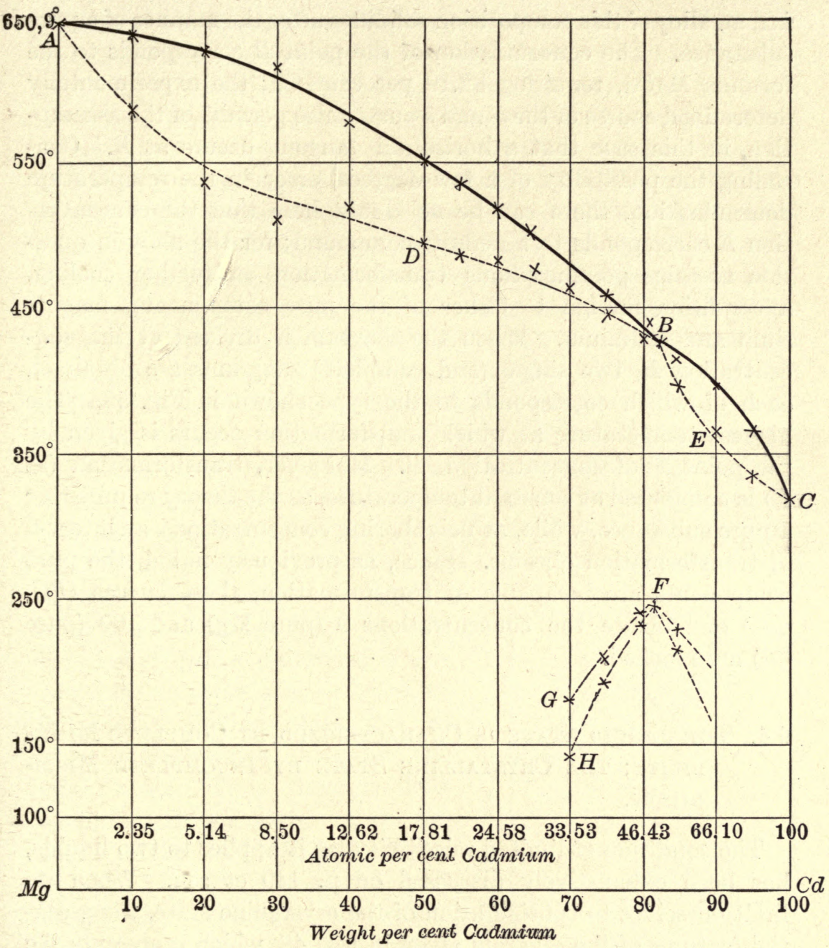

FIG. 76. Fusion Diagram of Magnesium-Cadmium Alloys according to Grube.

2. MAGNESIUM-CADMIUM ALLOYS. — Fig. 76 gives the fusion diagram for the Mg-Cd System, as constructed by GRUBE[1] on the basis of experimental cooling curves. The *l*-curve, *ABC*, is drawn in full and the *s*-curve, *ADBEC*, dotted. Both curves coincide at the point *B* where the crystallization interval becomes zero,

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[1] GRUBE, Z. anorg. Chem., 49, 72 (1906).

i.e., an alloy of this composition solidifies after the manner of a pure substance. The concentration of the point B corresponds to the formula MgCd, requiring 82.19 per cent Cd; the experimentally determined course of the l- and s-curves also permits of the assumption in this case that a horizontal tangent occurs at B. Conceding the possibility of a few degrees' error in the temperature determination, there can be no doubt here that the concentration B corresponds to a definite compound; for the alloy in question sustains polymorphous transformation on further cooling, a condition foreign to either of the pure components, magnesium and cadmium. When the diagram is divided at the concentration B, two single (and complete) diagrams are obtained, each of which corresponds to the type shown in Fig. 52. The highest temperature at which transformation occurs is given by the point F of concentration B. Moreover, transformation (at F) is completed at constant temperature, as the theory requires for a pure substance, while, at neighboring concentrations, an interval of transformation obtains. Since, as previously noted, the pure components are incapable of transformation, these curves (FG, etc.) end before the concentrations 0 (pure Mg) and 100 (pure Cd) are reached.

§ 4. THE LIQUID STATE IS CHARACTERIZED BY COMPLETE MISCIBILITY; THE CRYSTALLINE STATE BY INCOMPLETE MISCIBILITY.

The condition of limited miscibility, as it applies to two liquids, has been exhaustively discussed on p. 149 et seq. When we limit ourselves to consideration of the crystalline state, the essential features of the diagram given in Fig. 48, which represents the corresponding relations for the liquid state, may be brought into play. For every temperature, there exist concentrations, a and b, which are in equilibrium with one another, and which we designate as saturated mixed crystals. Using the previously chosen method of characterization, we designate the mixed crystals of A, saturated with B at the corresponding temperature t_1, as a_1 mixed crystals, and, likewise, the mixed crystals of B, saturated with A at the temperature t_1, as b_1 mixed crystals. If the concentration of an alloy corresponds to a point without the solubility curve, only one crystalline variety is present; if it corresponds to a point within the area surrounded by the solubility curve, then the crystalline phase has separated into two crystalline varieties, namely, *A* mixed crystals and *B* mixed crystals, each saturated at the corresponding temperature, just as a liquid phase separates into two layers under similar conditions. The concentrations of these two varieties of saturated mixed crystals will be given by the intersections of the solubility curve with a horizontal corresponding to this temperature. The lever relation also supplies information concerning the relative amounts of the two varieties in the present case. The condition represented in Fig. 48, viz., that miscibility increases with the temperature, and that the two saturation concentrations *a* and *b* approach closer to one another as the temperature increases, will be considered generally descriptive of the crystalline state as well. On this point, we are well in accord with practical experience.

In two respects, however, direct application of the diagrammatic relations deduced for the liquid state to the crystalline state requires amplification or modification, as the case may be. In the first place, a difference is evident, in that the area of stability for the crystalline state lies at lower temperatures than for the liquid state. Thus, there is little possibility of encountering an example of the fusion diagram shown in Fig. 77. It is assumed here that, after homogeneous solidification has occurred, separation ensues; represented in the usual manner by the *m*-curve. That we have thus far failed to find an actual example of this type, in which the upper portion of the solubility curve for the crystalline state is realized, is presumably due to the circumstance (apart from any consideration of the difficulty which is associated with determination of the solubility curve (see p. 202))

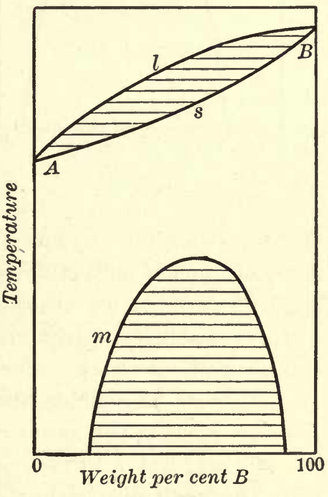

FIG. 77.

that this curve has invariably met the *s*-curve for the equilibrium, liquid crystalline, at some inferior position, whereby this upper portion has been eliminated. The same condition which sets a limit to the realization of the solubility curve for liquids below certain temperatures (see p. 154) hinders the realization of this curve for the crystalline state above certain temperatures. Thus, the solubility curve for the two crystalline varieties reaches its natural end at the temperature t_1, at which fusion begins, and

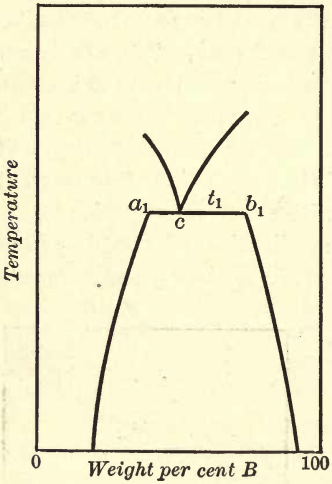

FIG. 78.

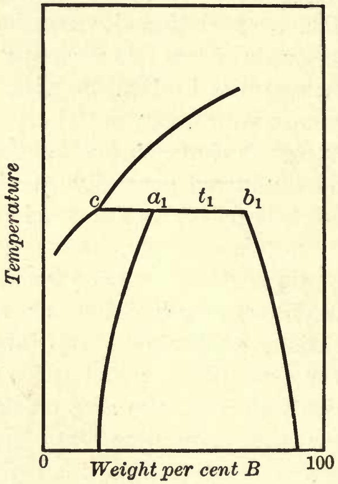

FIG. 79.

therefore consists of two separate branches. Now, in general, the compositions of melt and crystals, in equilibrium with one another, are different, as we are well aware. Hence we grant that the melt appearing at any given temperature will be of different composition from the crystals with which it is in equilibrium, and reserve the consideration of special cases in which melt and crystals possess the same composition for subsequent pages (see pp. 207 and 211). Two cases are, then, possible: The composition *c* of the melt lies either at a concentration which is situated between the two saturated mixed crystals a_1 and b_1 (Fig. 56), or at a concentration which is richer in one of the two components of the system; in *A*, for example (Fig. 79). In the first case (Fig. 78), reaction between both crystalline varieties a_1 and b_1

is necessary for production of melt, and we write the descriptive equation:

Sat. Mixed Crystals a_1 + Sat. Mixed Crystals $b_1 \rightleftarrows$ Melt c.

On heating, this reaction proceeds from left to right. We have here complete equilibrium, whence the temperature t_1 will remain constant until one of the phases becomes exhausted. If the total concentration of the system corresponds to the point c, then neither crystalline variety will be present after completion of the reaction, but all of the material will exist in the liquid condition. If the total concentration lies between a_1 and c, however, crystals of the concentration a_1 will remain in contact with melt after reaction; if it lies between b_1 and c, crystals of the concentration b_1 will remain. Thus, in the two latter cases, further elevation of temperature is necessary for complete fusion, and we readily see that the straight line a_1cb_1 must be covered by two branches of the l-curve, both of which intersect at the point c, and one of which corresponds to equilibrium between A-rich crystals and melt; the other, to equilibrium between B-rich crystals and melt (Fig. 78).

In the second case (Fig. 79), when the melt is A-richer than either of the two crystalline varieties a_1 and b_1 with which it is in equilibrium, it is obviously impossible to obtain melt c from any mixture of a_1 and b_1. This melt can be formed only in the following manner. The A-richer of the two varieties of crystals, namely, the saturated a_1 mixed crystals, yield melt of composition c, while their excess of B is not liquefied, but plays its constituent part in a crystalline residue of B-saturated A mixed crystals, corresponding in composition to the point b_1, as previously noted. At the temperature t_1, then, the saturated mixed crystals a_1 disappear, in that they fall to melt c and saturated mixed crystals b_1. The equation of the reaction reads:

Sat. Mixed Crystals $a_1 \rightleftarrows$ Melt c + Sat. Mixed Crystals b_1.

We have here, as before, complete equilibrium, whence the temperature t_1 will remain constant until one of the phases becomes exhausted.

On continued heat addition at the temperature t_1, the A-rich crystals a_1 disappear completely. After the temperature has been increased just beyond this point, B-rich crystals only will remain unfused, some higher temperature being required for their fusion. Thus, only a single branch of the *l*-curve — corresponding to equilibrium between melt and *B*-rich crystals — can exist above the straight line ca_1b_1.

On considering the course of the above reaction from right to left (on cooling), we see that all concentrations between b_1 and *c* must be concerned in the change. If the mixed crystals b_1 and melt *c* are present in such proportions that their average concentration (the total concentration of the system) corresponds to the point a_1 (saturated *A*-rich mixed crystals), all of the material will have become solidified to a_1 mixed crystals after the reaction has proceeded to completion. If the b_1 crystals are present in excess, *i.e.*, if the average concentration lies between a_1 and b_1, we shall have complete solidification at the temperature t_1, as in the above case, but the conglomerate will now consist of a_1 and b_1 mixed crystals. Finally, if melt *c* is present in excess, *i.e.*, if the average concentration lies between a_1 and *c*, melt *c* will still remain after completion of the reaction, and its concentration cannot change until the temperature falls again. As long as the total concentration of the alloy lies between *c* and b_1, melt *c* and mixed crystals b_1 must exist in the presence of one another when the temperature has fallen to t_1. Not until the point *c* is reached, does the quantity of these mixed crystals become zero. It follows from the above discussion that:

(1) The branch of the *l*-curve corresponding to equilibrium between *B* crystals — stable at higher temperatures — and melt must meet the line a_1b_1 at *c*, and that,

(2) A branch of the *l*-curve running to lower temperatures, and corresponding to equilibrium between *A*-rich mixed crystals, stable at lower temperatures, and melt, must join the other curves at *c* (Fig. 79).

To summarize, then, we note that, for incomplete miscibility in the crystalline state, two different forms of fusion diagram may develop, according to the particular composition of the melt *c*. Roozeboom arranges the cases represented in Figs. 79 and 78 in sequence with the three cases of complete isomorphism (according to his classification), whereby they constitute Types IV and V, respectively. Both types will be discussed at greater length shortly.

A second difference between incomplete miscibility in the liquid and crystalline states is determined by the fact that, on the part of crystalline bodies, there remains the factor of specific crystalline form, in addition to that of composition, to be duly considered. On general principles, we would have here two cases to differentiate, according to whether both saturated mixed crystals of the components A and B crystallized in the same or in different forms. We should, then, distinguish the first case, that of "limited isomorphism," from the second, that of "isodimorphism." Obviously, a classification of this sort does not apply to liquid solutions. However, we shall disregard any differences of this sort in the present connection, since the fusion diagrams for both cases agree in those particulars to which we limit our observations; and let it remain undecided whether the mixed crystals a and b do or do not differ in form.

Finally, we should allude to the fact that the recovery of equilibrium during temperature changes which are accompanied by changes in composition of all the crystals, in such alloys as possess concentrations within the limits of the solubility curve, calls for a very considerable power of diffusion on the part of the substances A and B which are dissolved in the crystals.

A. *Type IV, according to Roozeboom.*

The complete fusion diagram representing this case, the essential characteristics of which we have already noted, is shown in Fig. 80. The l-curve ACB is susceptible to very close determination, limited only by the accuracy of the temperature measurements; provided, of course, that supercooling is absent. This curve is, therefore, drawn in full, as is the horizontal CDE, along which the previously considered reaction:

$$\text{Sat. Mixed Crystals } E + \text{Melt} \rightleftarrows \text{Sat. Mixed Crystals } D$$

takes place at constant temperature (t_1) from left to right on abstraction of heat.

According to the above, then, a change in stability takes place along this horizontal. At temperatures above CDE ($= t_1$), the B-rich crystals are stable, while, at temperatures below CDE, the A-rich crystals are stable. Hence, the l-curve ACB shows a break at the temperature t_1, falling more gradually from C than it rises from the same point (see p. 123).

The s-curve, consisting of the two separated portions BE and DA which give the compositions of crystals corresponding to different melts at different temperatures, is drawn in dotted lines for the purpose of indicating that exact determination of these concentrations is subject to the same difficulty as was noted under Type I (complete isomorphism). This difficulty becomes manifest to a still greater extent in the determination of the two branches of the solubility curve which are capable of realization up to the temperature limit t_1, since the heat of mixture for the crystalline phase is probably extremely slight, as is the case relative to the liquid phase. For this reason the process of separation is not indicated by the cooling curve. (A second reason for the circumstance that no actual observation of the theoretically required break on the cooling curve at the initial

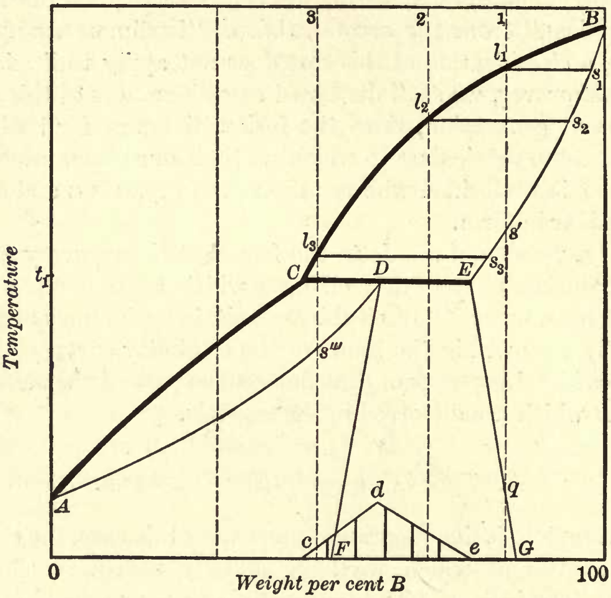

FIG. 80.

temperature of separation ever materializes could lie in an insufficient rapidity of the process.)

Suppose we consider the crystallization process in molten alloys of various composition, under the assumption that it is ideal, whereby cooling proceeds so slowly that equilibrium continually obtains.

Let an alloy numbered 1 have some concentration intermediate between *E* and 100 per cent *B* (Fig. 80). When the temperature has fallen to the point l_1, the *l*-curve is reached and crystallization begins. The composition of the separating crystals will then be given by the point s_1 of the *s*-curve, which corresponds to the temperature of l_1. Since the separating crystals are bound to constantly maintain a condition of equilibrium with the melt, in the manner described on p. 171, this melt will have solidified to a conglomerate of mixed crystals, all possessing the composition s' of the original mixture, by the time the temperature has fallen to s'. In consequence, the cooling curve of this alloy can show but one interval, namely, one reaching from l_1 to s'.

The structure of sections taken from the solidified alloy will, nevertheless, be completely homogeneous only when the vertical numbered 1 utterly fails to cut the solubility curve of the two crystalline varieties, or fails to cut it except at some temperature below that at which the section is subjected to examination. Let us make the assumption that the structure of all sections is investigated at the temperature zero of our co-ordinate system; the same considered to be room temperature. Then the intersection *q* of this vertical with the branch *EG* of the solubility curve lies above the temperature of examination, and we shall observe a mixture of two different crystalline varieties, namely, *A*-saturated *B* mixed crystals and *B*-saturated *A* mixed crystals, into which the originally homogeneous crystals have subsequently separated (unaccompanied by noticeable heat effect). The concentrations of these crystals correspond to the points *F* and *G*, while their relative amounts are given by the lever relation.

Let an alloy numbered 2 have some concentration intermediate between *D* and *E*. The vertical numbered 2 cuts the *l*-curve at the point l_2. Initial separation of crystals occurs at this temperature, and these crystals have the composition s_2. When the temperature has fallen to that of the horizontal *CDE*, the alloy consists of melt of composition *C* and crystals, which, on account of the previously assumed idealistic concentration balance, are uniformly of concentration *E*. If heat is further removed from the system, an increased lowering of temperature does not at once result; the first thing that occurs is transformation of *B*-rich saturated mixed crystals *E* + melt into *A*-rich saturated mixed crystals *D*, after the manner previously noted. This reaction persists until the melt is entirely exhausted. The alloy has then become completely solidified, and consists of the two crystalline varieties *D* and *E*. At this point, further abstraction of heat causes temperature fall, accompanied by alteration in composition of these crystals along the curve branches *DF* and *EG*, until the temperature of the surroundings is reached. In line with our general assumptions, the *B*-rich crystals will possess the composition *G*, and the *A*-rich crystals, the composition *F*. Since this last change along *DF* and *EG* has proceeded without noticeable heat effect, the cooling curve will show no added peculiarity over and above its break at l_2 and its halting point at the temperature of the horizontal *CDE*.

Let an alloy numbered 3 have some concentration intermediate between *C* and *D*. Initial separation of crystals occurs at the temperature l_3. These crystals have the composition s_3. When the temperature has fallen to that of the horizontal *CDE*, the whole alloy consists of melt *C* and *B*-rich crystals of concentration *E*, as did alloy 2 at this temperature. On further abstraction of heat, transformation of these *B*-rich crystals + melt into the crystalline variety *D* occurs. When this reaction has proceeded to completion, no *B*-rich crystals are left, and the alloy consists of *A*-rich crystals of composition *D* and melt *C*. (Only when the composition of the alloy corresponds exactly to the point *D* are melt and crystalline variety *E* present in such proportions that both are exhausted when reaction has ceased.) Further solidification of the melt *C* follows the branch *CA* of the *l*-curve, whereby the composition of the crystals with which it is in equilibrium is given by the branch *DA*. In accordance with our assumption of complete concentration balance between crystals and melt, the latter will have become completely solidified by the time the temperature s''' is reached, and will now be replaced by a conglomerate of homogeneous crystals of this composition. Relative to subsequent separation in the event of intersection of vertical number 3 with the branch *DF* of the solubility curve, the remarks offered under alloy 1 are pertinent. In line with the above description, the cooling curve of such an alloy (Fig. 81) shows a break at l_3, an interval between the temperature l_3 and that of the horizontal *CDE*, a halting point at the latter temperature, and finally another interval reaching from this temperature to the temperature s'''.

The last series of cooling curves, those furnished by alloys intermediate between *C* and *A* in concentration, are similar to the first series (*B*—*E*); they show a single interval.

The length of the periods of constant temperature which correspond to reaction at the horizontal *CDE* reaches its maximum, as is apparent from the equation of the reaction given earlier, at the concentration *D*, and decreases linearly toward *C* and *E*, where the zero value obtains. This is indicated in the figure by the thin line *cde* which joins the end points of verticals erected upon the concentration axis as base, at lengths proportional to these periods in the corresponding concentrations. Observation of these periods thus constitutes a method of determining the position of the points *C*, *D* and *E*.

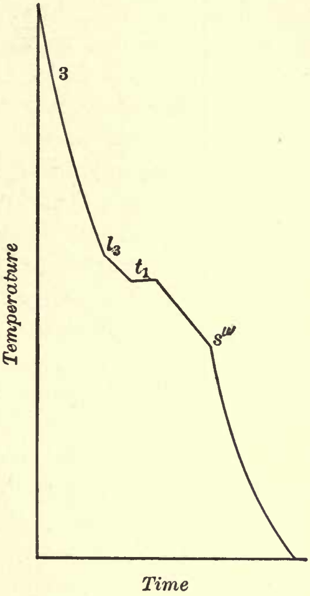

FIG. 81.

The structure of sections is homogeneous between 0 (= pure *A*) and *F*, and again between *G* and 100 (= pure *B*). Between *F* and *G*, two varieties of crystals appear in the sections; for the included range *D*–*E*, these consist of primarily separated saturated *B*-rich mixed crystals surrounded by saturated *A*-rich mixed crystals, which have been formed secondarily by reaction at the temperature of the horizontal, while for the rest of these concentrations, namely, the ranges *F–D* and *E–G*, the alloys consist entirely of *A*-rich or *B*-rich mixed crystals, respectively, just after solidification, and become inhomogeneous only after the curve branches *DF* and *EG* have been cut on further cooling. It is clear that abnormalities due to incomplete concentration balance (to be generally expected) will be productive of results similar to those described under the case of complete isomorphism (see p. 177). Other abnormalities, due to incomplete reaction between crystalline variety *E* and melt, may obtain here. We have become acquainted with the same general condition in the case of the concealed maximum (see p. 134 et seq.).

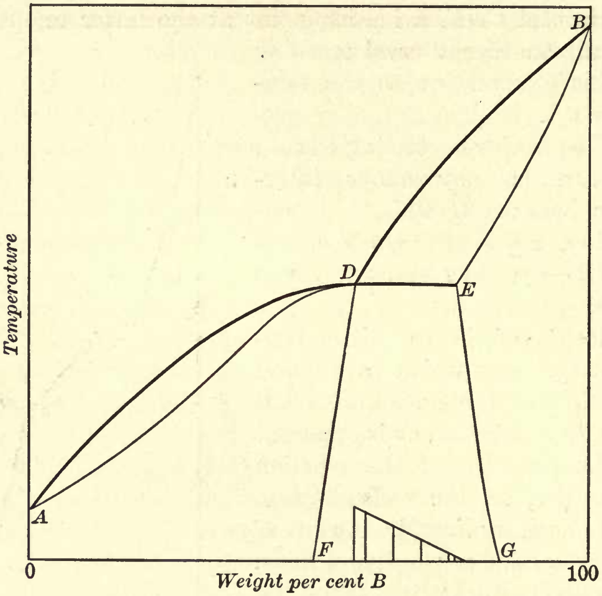

FIG. 80a.

The system Hg-Cd[1] serves as an example of this type. Here, the gap in miscibility at the temperature of complete equilibrium is comparatively small. A very considerable gap in miscibility was observed by ISAAC and TAMMANN,[2] relative to the system

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[1] BIJL, Z. phys. Chem., 41, 641 (1902).

[2] ISAAC and TAMMANN, Z. anorg. Chem., 53, 281 (1907).

Fe-Au. We should note, along with the above citation of examples, that this type is of comparatively infrequent occurrence.

The following limiting cases under Type IV may be obtained:

(1) We suppose here that the concentration difference between melt *C* and the crystalline variety *D* continues to decrease until *C* and *D* coincide. Fig. 80a represents the conditions corresponding to such coincidence. Since solidification occurs after the manner of a pure substance at *D*, both the *l*- and *s*-curves *DA* must enter *D* horizontally, *i.e.*, they must possess a horizontal tangent in this vicinity (see p. 165). The systems Au-Cd,[1] Ag-Zn[2] and Cu-Zn (brass)[3] are, in all probability, examples of this case.

(2) We grant that the gap in miscibility *DE* (Fig. 80) continually becomes smaller (*i.e.*, that the points *D* and *E* continually approach one another), until it disappears completely.[4] Thus we develop the case of complete isomorphism — Type I, according to Roozeboom (Fig. 56). The break *C* on the *l*-curve must obviously disappear also, since only one variety of mixed crystals can now be existent at all temperatures. In consequence, no halting points (brought about by disappearance of one crystalline variety) may appear on the cooling curves.

(3) We grant that all three points *C*, *D* and *E* coincide. Then Type Ia (Fig. 68), in which the fusion curve possesses a point of inflection with horizontal tangent, results.

(4) We grant that the gap in miscibility for the crystalline state continually becomes larger until the concentrations *D* and *E* correspond to the pure substances, viz., lie at 0 and 100 respectively. Then the point *C*, which corresponds to the composition of the melt, must obviously become coincident with *D*, and, therefore, with *A* also, *i.e.*, the lower branch *CA* must disappear. In this way, we are led to the diagram shown in Fig. 14 (p. 71), which type was previously shown to be a limiting case for complete immiscibility in the crystalline state — deduced by imagining one branch of the fusion curve to continually become shorter and finally disappear. In terms of the above, we see that this same type appears as limiting case for the conditions which we have been considering on these latter pages.

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[1] Vogel, Z. anorg. Chem., 48, 333, (1906).

[2] Petrenko, Z. anorg. Chem., 48, 347, (1906).

[3] Shepherd, Journ. Phys. Chem., 8, 421, (1904).

[4] The curve of separation is not considered in this connection.

B. *Type V, according to Roozeboom.*

The essential features of this type have already been anticipated. The complete melting-point diagram is to be found in Fig. 82. The *l*-curve *ACB*, as well as the horizontal *DCE*, are drawn in heavy lines because they may be readily determined thermally, while both portions of the *s*-curve *AD* and *BE*, as well as both portions of the solubility curve *DF* and *EG*, are drawn in thin lines because they are not susceptible to accurate determination thermally, or, indeed, to any such determination at all in some instances. At the horizontal *DCE*, the following reaction takes place toward the right at the constant temperature t_1 when heat is abstracted:

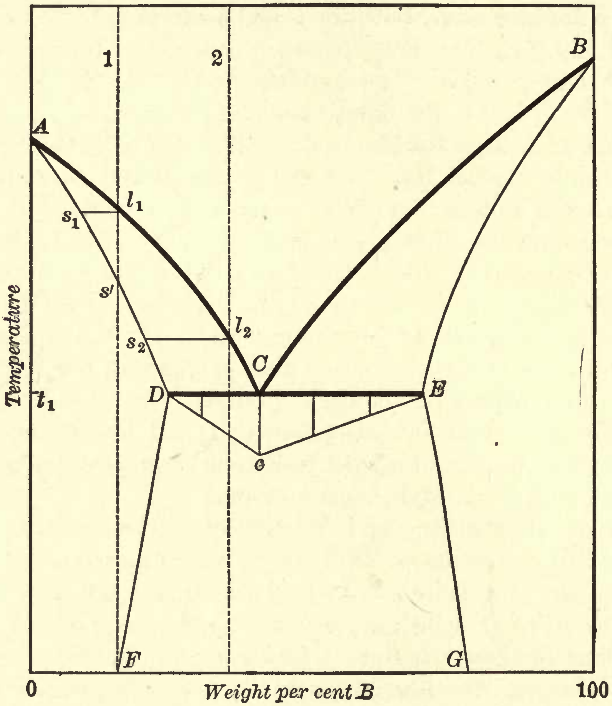

FIG. 82.

Melt $C \leftrightarrows$ Sat. Mixed Crystals D + Sat. Mixed Crystals E.

The duration of the halting points which appear upon the cooling curves, owing to solidification during this reaction, has its maximum, according to the above equation, at the concentration *C*, and decreases lineally toward the concentrations *D* and *E*, where it becomes zero. This is indicated in the figure, according to usual custom, by a line *DcE*, which joins the end points of verticals erected upon the base (horizontal) line *DCE* at lengths which are proportional to the halting periods. The determination of these halting periods thus constitutes a means of locating the three points *C*, *D* and *E*.

A melt 1, of concentration between 0 (= pure *A*) and *D*, first separates crystals of composition s_1 at the temperature l_1. Assuming that complete concentration balance obtains, the alloy will have completely solidified to a conglomerate of crystals, all possessing the same concentration as the original mixture, by the time its temperature has fallen to s'. Whether a subsequent separation of these homogeneous crystals into two saturated mixed crystals will occur on further cooling to the temperature of the surroundings (taken as 0 degrees in our coördinate system), depends upon whether the corresponding vertical cuts the portion *DF* of the solubility curve or not. Since a process of this sort is not accompanied by a very considerable heat effect, merely one interval, of the magnitude $l_1 s'$, will be observed upon the cooling curve in each and every case.

Alloy 2, of concentration between *D* and *C*, first separates crystals of the composition s_2 at the temperature l_2. When the temperature has fallen to that of the horizontal *DCE*, the melt will possess the concentration *C*, and the entire body of crystals, the concentration *D*. Complete solidification at constant temperature will now ensue, whereby saturated mixed crystals of the two varieties *D* and *E* are formed. The cooling curve consequently shows an interval beginning at the temperature l_2 and ending at the temperature t_1 (that of the horizontal *DCE*), followed by a halting point at the latter temperature. The change in composition of the saturated mixed crystals *D* and *E* along the curves *DF* and *EG* on further decrease in temperature is not revealed by the cooling curve.

An alloy of composition *C* solidifies like a pure substance. A single halting point is present upon the cooling curve.

What was said relative to alloy 2 applies to concentrations between *C* and *E*, except that we now have crystals of the composition *E* in equilibrium with the (same) melt *C* when the temperature has fallen to that of the horizontal *DCE*.

Remarks relative to alloy 1 apply to concentrations between *E* and 100 (= pure *B*).

The structure of sections of the different reguli (investigated at ordinary temperature) between 0 and *F* and between *G* and 100 must be homogeneous. Sections of concentrations between *F* and *G* show mixed crystals of *B* in *A* and of *A* in *B*, corresponding to concentrations *F* and *G* respectively (*i.e.*, saturated at ordinary temperature), side by side. Primarily separated *A*-rich mixed crystals of concentration *D* at the temperature of the horizontal *DCE*, must appear in concentrations between *D* and *C*. These are surrounded by a mixture of *D* and *E* crystals, which, owing to its manner of formation, must reveal an eutectic structure. Since the concentration differences between *D* and *F* and between *E* and *G* are, in general, only trifling, changes which take place at temperatures below that of the horizontal *DCE* will cause no marked changes in the structure of the sections. In sections of concentrations between *C* and *E*, the primarily separated crystals will all possess the composition *E* at the temperature of the horizontal *DCE*. The secondary mixture of *D* and *E* crystals which has been formed on crystallization of the residue of melt at this temperature is the same as that present in concentrations between *D* and *C*. The originally homogeneous structure of alloys between *D* and *F* and *E* and *G* becomes inhomogeneous, owing to subsequent separation.

Incomplete concentration balance between the crystals which first separate in concentrations 0 to *F*, or *G* to 100, and melt will primarily result in an inhomogeneous (for the most part zonal) structure. Moreover, in the case of concentrations which are *A*-richer than *D*, and *B*-richer than *E*, an appreciable amount of melt of concentration *C* will finally be left, whereby the point *D* will be displaced toward the *A*-rich side, and the point *E* toward the *B*-rich side. Thus, determination of the interval *DE* is rendered uncertain. This is the same condition which effects an extension of the melting interval, *i.e.*, a displacement of the portions *AD* and *BE* of the *s*-curve toward lower temperatures (see p. 174). For remarks concerning the reduction of this defect by means of slow cooling, etc., see p. 182.

The following cases can be realized as limiting cases of Type V:

(1) We assume here that the concentration difference between melt *C* and the crystalline variety *D* (Fig. 82) continually decreases, so that *C* and *D* finally coincide. Fig. 82a represents this case for coincidence of the points *C* and *D* (at *C*). At the point *C*, uniform solidification occurs, whereby, according to p. 166, the *CA* portion of both the *l*- and *s*-curves must possess a horizontal tangent at *C*. It is clear that there are two different possible types of curve for the case wherein the melt with which both saturated mixed crystals are in equilibrium possesses the same composition as one of the crystalline varieties (Figs. 80a and 82a), according to whether we regard it as the limiting case of Type IV or of Type V. Obviously,

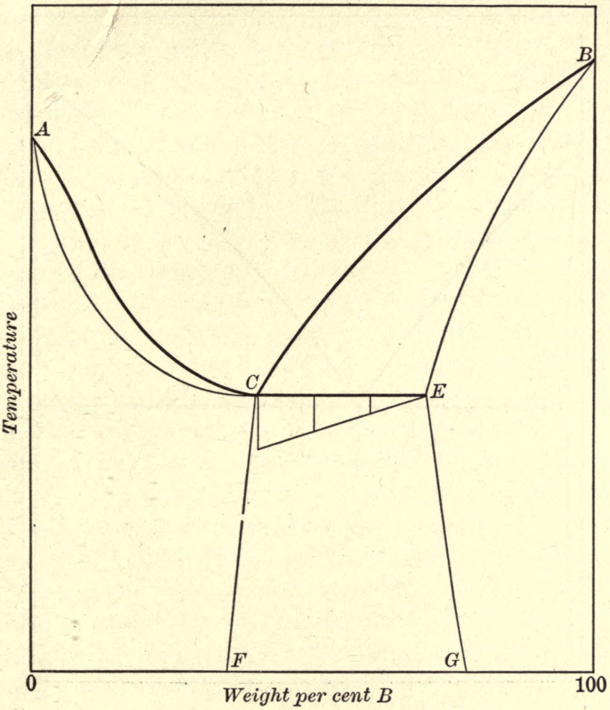

FIG. 82a.

it will be found very difficult in practice to determine whether *D* and *C* coincide perfectly or not. Cases which, in any event, closely approximate the conditions represented in Fig. 80a are frequently observed (compare, for example, R. RUER, Z. anorg. Chem., 52, 355 (1907)).

(2) In this case, we imagine the gap in miscibility *DE* (Fig. 82) to become continuously smaller, until finally the two points *D* and *E* and the intermediate point *C* become coincident. Thus we obtain the case of unlimited miscibility, wherein the melting-point curve possesses a maximum, shown in Fig. 45. We may, therefore, obtain Type III as a limiting case of Type V.

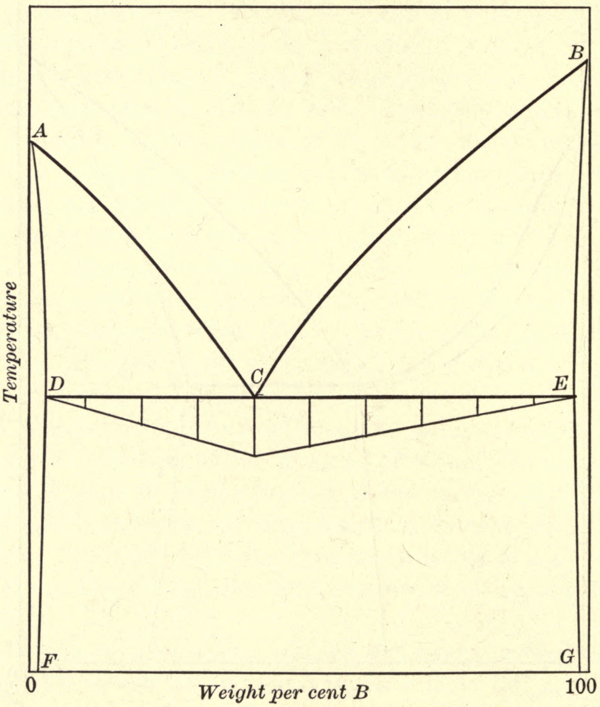

FIG. 82b.

(3) On the other hand, we may imagine the gap in miscibility to become continuously larger, *i.e.*, the points *D* and *E* to con-

stantly retreat from one another (Fig. 82b). In this case, the saturated *A* mixed crystals become continuously *B*-poorer and the saturated *B* mixed crystals continuously *A*-poorer. If *D* and *E* finally meet the temperature axis, the substances *A* and *B*, respectively, separate from all melts in the pure condition, *i.e.*, we have the case first considered (p. 56), and represented by Fig. 11a ("Complete miscibility in the liquid state, complete immiscibility in the crystalline state, no compounds and no polymorphous transformation") as a limiting case under Type V. In fact, the specification of complete immiscibility in the crystalline state when no compounds are existent merely signifies that the composition of the crystals which are in equilibrium with melts of all concentrations must correspond to the concentrations 0 or 100, viz., to pure *A* or pure *B*. We should note, in this connection, that it is impossible in practice to determine with certainty whether or not the limiting case of complete immiscibility is at hand. We simply find ourselves in a position to designate an outside limit beyond which there can be no miscibility in the crystalline state, and this limit will become more rigorous in proportion as the adopted methods of investigation improve in accuracy (see p. 69). Theoretical considerations even demand that a condition of absolute immiscibility be fundamentally excluded. Nevertheless, experience has shown that this condition may be so closely approximated that we are justified in using the term complete immiscibility in a practical sense, and in neglecting the extremely limited miscibility which always obtains in such cases, but which is not revealed experimentally. Part of the modern theory of solution is based upon this disregard of inappreciable solubilities, and the brilliant agreement of theoretical conclusions with the results of general experience further supports the rectitude of such idealization. In principle, Fig. 82b represents the mutual behavior of two substances more correctly than the limiting case, Fig. 11a.

The mutual solubility of the two substances (invariably present, according to theory) will vary with the temperature; in general becoming less as the temperature falls. This is indicated by the portions *DF* and *EG* (Fig. 82b) of the curves of incomplete equilibrium, which give the equilibrium concentrations of both crystalline varieties in their relation to the temperature, and which, in accordance with the above statements, may practically coincide with the temperature axes.

The main difference between the two melting-point diagrams given in Figs. 82 and 82b, as opposed to that given in Fig. 11a, may be thus defined: in the first case, the horizontal *DCE* ends before the concentrations of the pure substances are reached, while, in the second case, it reaches throughout the whole diagram (p. 69). The horizontal *DCE* is known in all cases as the eutectic horizontal.

Cooling curves of alloys whose concentrations lie between *D* and *E* (Fig. 82) and which, in consequence, show eutectic halting points are not different in form from those of alloys whose components do not appreciably mix in the crystalline state. For example, on the cooling curve of alloy 2, a period of eutectic crystallization follows the crystallization interval beginning at l_2 and ending at the temperature of the eutectic horizontal. The process of crystallization during this interval is, indeed, different from the analogous process pertaining to complete immiscibility in the crystalline state. In the first case, the composition of the crystals changes as they continue to be formed, and, provided normal concentration balance is maintained, that of the previously separated crystals also changes continuously as the temperature falls, while, in the second case, the same crystals are deposited from the beginning to the end of the process. On the cooling curve this difference is not evident. A break is observed on the cooling curve of alloy 2 at the initial temperature of crystallization l_2, from which point a retarded fall in temperature ensues, owing to heat evolution attending the separation of crystalline material. At the temperature of the eutectic horizontal, this retarded temperature fall is succeeded by a period of constant temperature. Thus we have just the sort of curve which would have resulted in the entire absence of miscibility in the crystalline state. In place of a conglomerate composed of the pure substances *A* and *B* (corresponding to complete immiscibility), the cold alloys of concentrations between *D* and *E* (neglecting the possibility of any subsequent separation) consist of the saturated mixed crystals *D* and *E*, of which one variety occurs as primary crystals and as a constituent of the eutectic, and the other variety purely as a constituent of the eutectic.

Very many examples of this type might be cited. It is the most frequently observed type of melting-point diagram of two components which mix completely in the liquid state and form no chemical compounds with one another. By a strict interpretation, the system Antimony-Lead (p. 72) would properly belong here, since, according to the above, we are not justified in attributing complete absence of mutual miscibility to these components. In the systems Au-Cu[1] and Ag-Cu,[2,3] mutual solubility of the components in the crystalline state is well marked. Still greater miscibility is to be observed in the system Au-Ni.[4] Considerable miscibility appears on the aluminium side in the system Al-Zn[5, 6]; trifling miscibility on the zinc side.

C. *Polymorphous Transformations.*

If polymorphous transformations occur after completion of crystallization, the mutual miscibility of the α crystals, stable at the lower temperature, may be greater or lesser than that of the β crystals, first separating. In case the β crystals (which have separated from the melt) are miscible in all proportions, while the α crystals show a gap in their miscibility, earlier explanations serve as well in this connection by way of presenting an adequate exposition of the prevailing conditions. We have here, as before, equilibrium between one phase in which complete miscibility occurs and another characterized by incomplete miscibility. Moreover, since the transition from complete to incomplete miscibility is affected by lowering the temperature, it follows that Types IV and V, with which we have become familiar for the case of liquid-crystalline equilibrium, when combined with the types which represent complete isomorphism, must adequately describe the mutual relations of the two substances in question. Thus, Fig. 83 shows the melting-point diagram of two substances *A* and *B* which first solidify to a complete series of β-mixed crystals, according to Roozeboom's Type I. On further abstraction of

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[1] Roberts Austin and Kirke Rose, Proc. Roy. Soc., 67, 105 (1900).

[2] Heycock and Neville, Phil. Trans., 189a, 25 (1897).

[3] Osmond, Bull. soc. Encouragement, 5th series, 2, 837 (1897).

[4] Levin, Z. anorg. Chem., 45, 238 (1905).

[5] Heycock and Neville, Jour. Chem. Soc., 71, 383 (1897).

[6] Shepherd, Jour. Phys. Chem., 9, 504 (1905).

heat, transformation into crystals stable at lower temperatures will occur in all concentrations. These α crystals are not capable of as extended mutual solubility as the β crystals, whereby transformation must follow either Type IV or Type V, which latter condition is represented in the figure. The case shown in Fig. 84 is somewhat different. Here, the β crystals exhibit a gap in miscibility, according to Type IV, while the α crystals are completely miscible with one another. This diagram cannot be obtained by simple combination of the types which have already been studied, since it includes limited miscibility of the modifications stable at higher temperatures. The fact that the central concentrations are not composed of crystals of a single variety

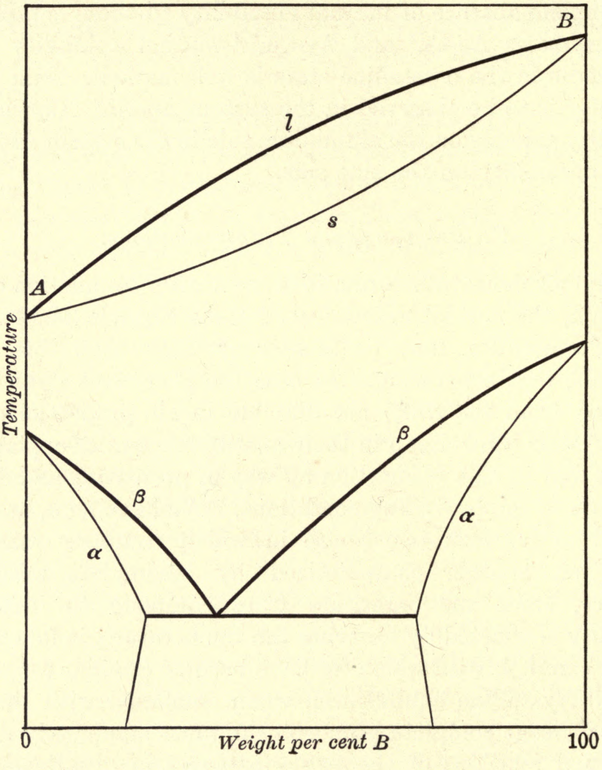

Fig. 83.

is responsible for the association of discontinuity with the transformation of β crystals into the continuous series of α crystals. At the temperature a, where the transformation curve cuts the solubility curve of the β crystals, there are present not only

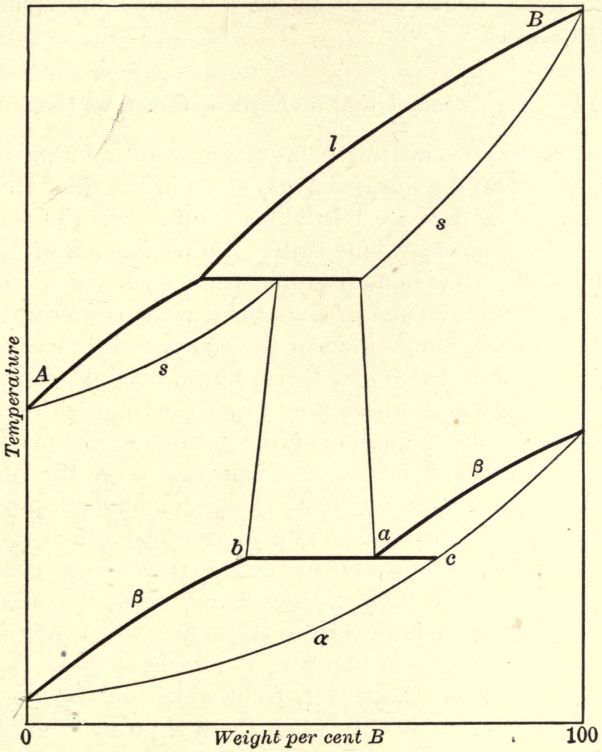

FIG. 84.

saturated mixed crystals a of the β modification, but also the saturated mixed crystals b, likewise of this modification, and crystals of the α modification of concentration c (stable at all lower temperatures), all in equilibrium (compare the similar case — p. 153). On abstraction of heat, the temperature remains constant until the reaction:

$$a \leftrightarrows b + c$$

has proceeded to completion, *i.e.*, until the *a* crystals have been used up.

Finally, if we make the assumption that the β crystals, as well as the α crystals, are incompletely miscible, the relations become very complicated. Detailed information on this point may be obtained from Roozeboom's paper, "Umwandlungspunkte bei Mischkristallen." [1]

D. *The Components Unite to Form a Chemical Compound.*

On combining two melting-point diagrams of the form shown in Fig. 82, we obtain the single diagram given in Fig. 85. Here, both components A and B are partially miscible with the compound $C = A_mB_n$ in the crystalline state. Determination of the composition of the compound is difficult in such cases, since the eutectic horizontals *ab* and *cd* do not end at the concentration corresponding to the composition of the compound, but at the concentrations of the A-rich and B-rich mixed crystals, respectively. There remains a single criterion by which the composition must be judged, namely, determination of the position of the maximum C on the melting-point curve, in connection with the fact that solidification must occur without change of temperature at this concentration, *i.e.*, the melting interval must be zero at this point. The uncertainty reaches so far in this case that we are, conversely, unable to draw a positive conclusion regarding the question of chemical combination between two substances when they show the mutual relations given in Fig. 85. For we know that the law of depression of the melting point, from which our inferences (see p. 76) are drawn, holds only when there is no miscibility in the crystalline condition, viz., when the composition of the crystalline variety which separates from the melt within certain concentration intervals is practically independent of the composition of the melt. If this condition is not realized, as is true in the present case relative to those concentrations which lie between *b* and *c*, our deductions in the above connection fail to be conclusive. Thus, we would not be justified in concluding from the presence of a maximum C that a chemical compound of this composition is existent, as long as we are not certain that the position of C is inde-

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[1] Roozeboom, Z. phys. Chem., 30, 413 (1899).

pendent of the pressure on the system, and experimental evidence relating to the latter point is not readily obtainable.

On the other hand, it is to be emphasized that the mutual relations of the two substances A and B are described in the most natural and unconstrained manner under the assumption that a compound A_mB_n exists. Otherwise, the existence of two gaps in miscibility would have to be conceded. In the case of liquids, no such condition occurs — more than one gap in miscibility is never observed, *i.e.*, at a given temperature only two liquids of different composition (namely a saturated solution of B in A and a saturated solution of A in B) are capable of existing in equilibrium with one another. In the crystalline state, the possibility of existence of several gaps in miscibility cannot be contradicted *a priori*, since we must here regard the question of crystalline form in addition to that of solubility as a second factor of importance. Such a double gap in miscibility might find an explanation in limited isomorphism of the two components, associated with isodimorphism (see p. 201).[1] An example of the case just discussed is furnished by the system Mg-Ag, according to the investigation of ŻEMCZUŻNYJ[2]. Here a compound (of the formula MgAg) undoubtedly corresponds to the maximum C (Fig. 85). In addition, the existence of a compound of the formula Mg_3Ag, which does not melt unchanged, was proven. Further illustration of this case is offered by the systems Au-Zn[3] and Ni-Si.[4]

Fig. 86 may be regarded as a combination of Types IV and V, and is, therefore, traceable to a double gap in miscibility. An interpretation recognizing the existence of a concealed maximum in this type will appear simpler and more natural. The case is then analogous to that shown in Fig. 33 (p. 115), except that limited miscibility in the crystalline state characterizes the mutual relations of the compound melting under decomposition with each component. The compound melts at the temperature of the horizontal Dc, in that it decomposes to melt of concentration D and

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[1] If it could be proven that the three crystalline varieties show limited isomorphism, the existence of the compound would be established without question.

[2] ŻEMCZUŻNYJ, Z. anorg. Chem., 49, 400 (1906).

[3] VOGEL, Z. anorg. Chem., 48, 319 (1906).

[4] GUERTLER and TAMMANN, Z. anorg. Chem., 49, 93 (1906).

mixed crystals of concentration *c* (*B* crystals saturated with the compound A_mB_n, instead of pure *B* crystals). Determination of the maximum of crystallization periods along the horizontal *Dc*, namely *i*, is our only means of ascertaining the composition of the compound, since the eutectic horizontal *ab* fails to reach as far as the concentration of the compound (see below). The uncertainty associated with an interpretation of experimental results in case of miscibility in the crystalline state should not, however, be overestimated. Trifling miscibility in the crystalline condition is, indeed, always present (see p. 213), and is quite unimportant. In general, on consideration of the cases shown in Figs. 85 and 86, we are inclined to assume that a compound A_mB_n exists — largely by reason of the enhanced simplicity and rationality of characterization along these lines — and to consider this assumption better grounded in proportion as the observed miscibility is smaller, *i.e.*, as the gaps in miscibility are larger. Furthermore, in the event that the composition of the questionable compound in the given case

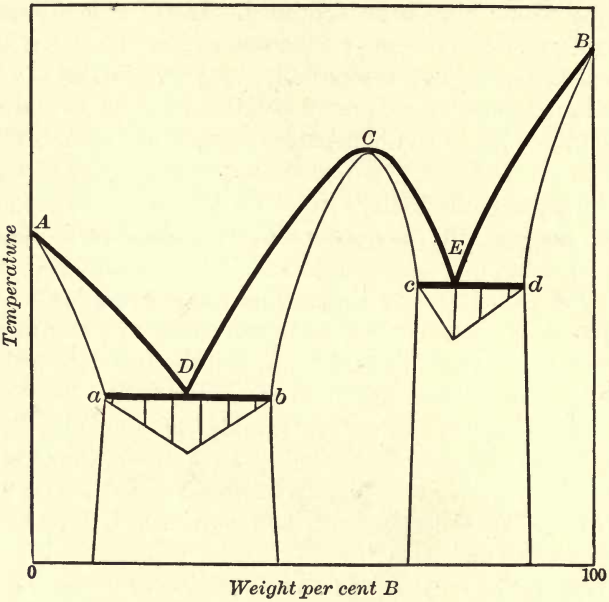

FIG. 85.

can be represented by a simple formula, we are possessed of substantial evidence supporting this view. Similar reasoning applies to the relations shown in Figs. 80 and 82. One would be inclined to conclude that compounds exist at the points *D* and *C*, respectively, in case these concentrations should correspond to simple formulas.

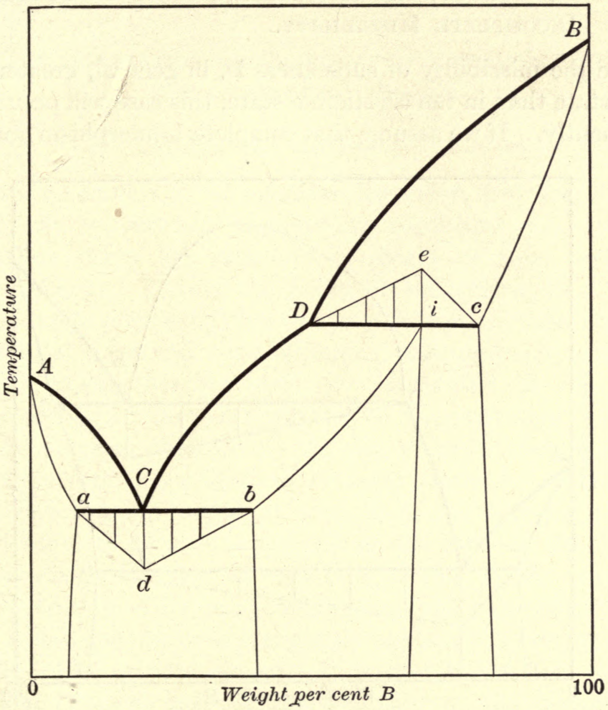

FIG. 86.

Determination of the composition of those compounds which are indicated in the diagrams given in Figs. 80, 82 and 86 is based upon the hypothesis that the respective compound is capable of dissolving only one component appreciably in the crystalline state (the component *A* in the present instances), whereby the composition of mixed crystals composed of A_mB_n saturated with *B* practically corresponds to the formula A_mB_n. The portion of the solubility curve of the two crystalline varieties A_mB_n and *B* which is adjacent to the concentration of the compound must, therefore, run vertically, provided no increase in solubility takes place as the temperature falls. Experimental evidence in this direction is not readily obtained, for reasons given on p. 202.

§5. THE LIQUID STATE IS CHARACTERIZED BY INCOMPLETE MISCIBILITY; THE CRYSTALLINE STATE BY COMPLETE OR INCOMPLETE MISCIBILITY.

Since the miscibility of substances is, in general, greater in the liquid state than in the crystalline state, this case will occur rather infrequently. If we assume that complete isomorphism obtains as regards the crystalline state, we may use the lower portion of Fig. 84 in representing this case since here, as in the other instance, limited miscibility occurs in the state which is stable at the higher temperature. We must, then, make a further assumption that the two curves which enter at a and b, respectively, from above are branches of the solubility curve of the melt. At the temperature of the horizontal bac, the B-rich layer of concentration a is resolved into mixed crystals of composition c and A-rich melt of concentration b.

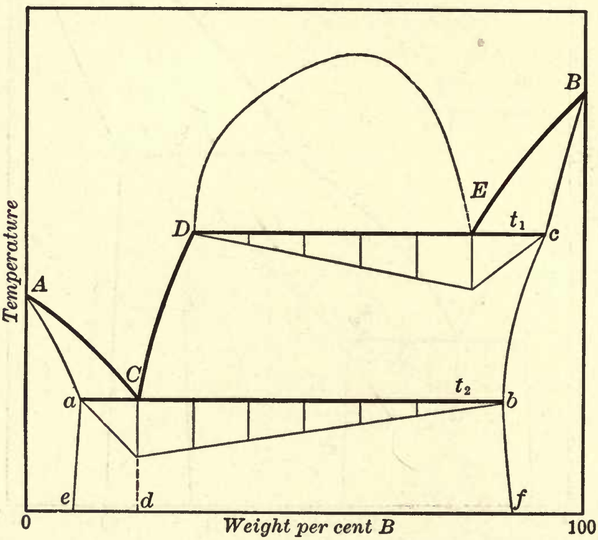

FIG. 87.

A case in which limited miscibility characterizes both crystalline and liquid states is represented in Fig. 87. This is completely analogous to the case given in Fig. 49, but here saturated mixed crystals of *B* in *A* and of *A* in *B* separate, instead of the pure substances *A* and *B*, respectively. Finally, the reader is referred to the discussion of an additional case by TAMMANN.[1]

§ 6. THE SEPARATION OF CRYSTALLINE VARIETIES WHICH ARE NOT COMPLETELY STABLE.

A. *The System: Antimony-Cadmium.*

We have assumed in all previous discussion that every system treated has represented equilibrium conditions, *i.e.*, that the systems on being left alone for a length of time would not undergo change. During the study of the system Sb-Cd, phenomena due to non-realization of this assumption were observed. TREITSCHKE[2] obtained two different melting-point diagrams, according to whether the melt was inoculated at the proper time on cooling, or allowed to crystallize spontaneously. Fig. 88a gives the diagram obtained by the aid of inoculation, and consequently refers to equilibrium between perfectly stable crystalline varieties. We read at once from the diagram that Sb and Cd unite to form a compound of the formula SbCd which melts at about 460 degrees and fails to mix in the crystalline state with either of its components (concerning an accessory condition, which has not been completely explained, reference should be made to the original paper). In particular, we note that this compound forms an eutectic with antimony at 455 degrees (*B* — containing 60 per cent Sb). This compound appears in the sections of the reguli in the form of long needles.

If inoculation is omitted, the branch *AB*, along which primary separation of antimony occurs, is realized at lower temperatures and higher cadmium concentrations, namely, as far as the point *B'* (Fig. 88b) corresponding to 408 degrees and 54 per cent Sb. A

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[1] TAMMANN, Ann. der Phys. (4) 19, 421 (1906).

[2] TREITSCHKE, Z. anorg. Chem., 50, 217 (1906). The results given in a preliminary communication to the Jour. Russ. Phys. Chem. Soc., 37, 580, (1905), by Kurnakow and Konstantinow appear to generally agree with those of Treitschke.

compound C′, which melts at 424 degrees, separates primarily in concentrations between 54 and 30 per cent Sb. This compound is miscible with antimony in the crystalline state in all proportions up to the concentration B′. Its probable formula is Sb_2Cd_3. It must be an unstable compound, for it is clear that a melt which

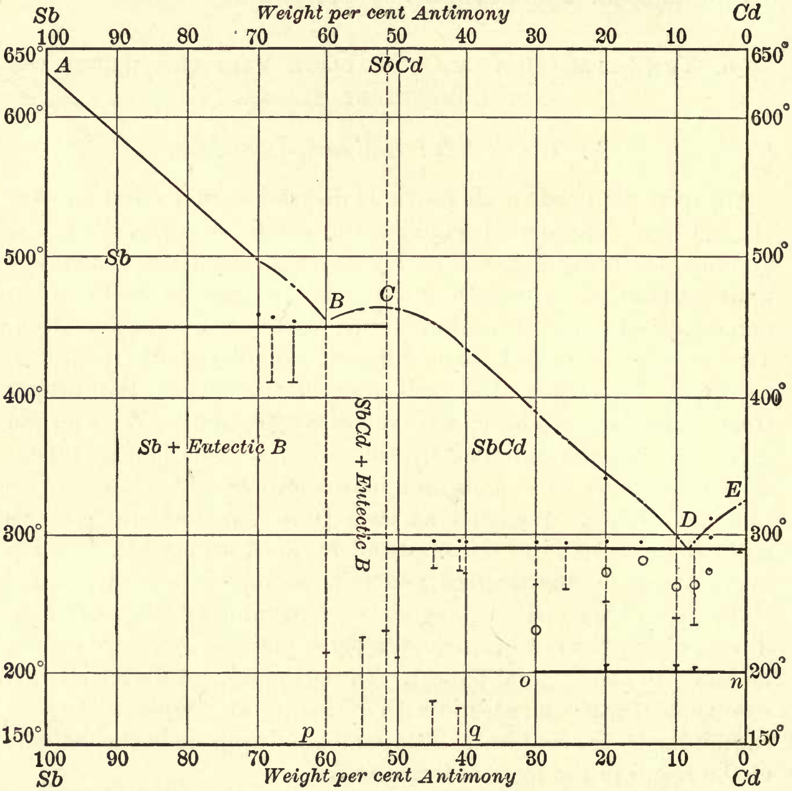

Fig. 88a. Fusion Diagram of the stable System Antimony-Cadmium according to Treitschke.

has been cooled as far as the branch *B′C′*, for example, must be super-cooled with respect to the compound SbCd — separating at a higher temperature. On this account, the spontaneous evolution of considerable heat is noted on further cooling — due to decomposition of the compound Sb_2Cd_3 (or its mixed crystals), with formation of the stable compound SbCd (whereby the temperature may rise momentarily by as much as 50 degrees). There was no regularity in the temperature at which this sudden temperature elevation began — noted in the diagram by crosses.

It was found possible to bring the unstable compound within a sphere of low reaction velocity by quenching the reguli at 400 degrees in water. In this way, the above reaction was practically prevented (see p. 147). Reguli containing 42, 48, and 52 per cent Sb, which were treated as above, revealed large homogeneous polygons of the compound Sb_2Cd_3, or of the mixed crystals Sb_2Cd_3 + Sb, when viewed under the microscope.

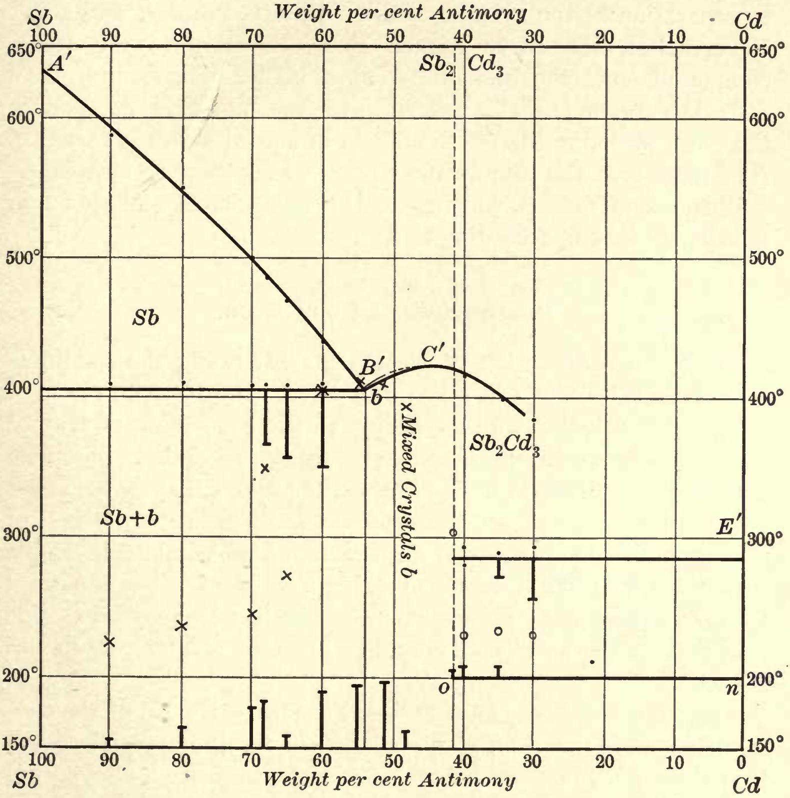

FIG. 88b. Fusion Diagram of the unstable System Antimony-Cadmium according to Treitschke.

The equilibrium curves shown in Figs. 88a and 88b may be entered in a single coördinate system, whereby one melting-point diagram, giving both the stable and unstable conditions, is obtained. The points A and A', corresponding to the melting point of antimony, will then coincide, as will the branch AB with its length along the branch $A'B'$, since both correspond to separation of the same crystalline variety, namely, antimony. Nevertheless, the curve branch BCD, referring to the stable compound, cuts the branch AB at a higher temperature than does the branch $B'C'$, referring to the unstable compound, thereby concealing the latter branch, in accord with the fact that $B'C'$ represents the equilibrium curve of a supercooled system.

Phenomena quite analogous to the above are encountered in the system Zn-Sb, according to ŻEMCŻUŻNYJ[1].

B. *The System: Iron-Carbon.*

The above description of phenomena attending the solidification of Sb-Cd alloys will serve as a key to the interpretation of the iron-carbon system. According to the conception of HEYN,[2] we have here conditions of varying stability, so that the complete melting-point diagram of the iron-carbon alloys may be regarded in a composite sense, *i.e.*, as resulting from the superposition of two separate diagrams, one corresponding to completely stable conditions, and the other to unstable conditions. The tendency towards supercooling is, nevertheless, much more marked in this case than in the previously considered case of antimony-cadmium alloys.

Great interest has always followed the investigation of the constitution of iron-carbon alloys, obviously for the especial reason that these alloys are by far the most important of all alloys from a technical standpoint, but in some degree due to the fact that the interpretation of certain observed processes has proven unusually difficult. The development of Metallography has been most vitally associated with the progressive investigation of the iron-carbon system. SORBY and MARTENS brought the microscope into the service of Metallography in this way. A

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[1] ŻEMCŻUŻNYJ, Z. anorg. Chem., 49, 384 (1906)

[2] HEYN, Z. Electrochemie, 10, 491 (1904).

few steps in advance, the names of OSMOND and ROBERTS-AUSTIN are especially prominent in connection with the systematic experimental realization of the melting-point diagram. The extension of our theoretical conceptions of observed phenomena, largely due to LECHATELIER, OSMOND, and ROBERTS-AUSTIN, has kept pace with the progressive accumulation of knowledge relating to actual facts. It meant further progress in the former connection, when ROOZEBOOM, intent upon fathoming the mutual relationship of iron and carbon, studied the processes of formation of mixed crystals from their melts, both theoretically and experimentally, and applied his conclusions to the crystallization processes of iron-carbon alloys. The melting-point diagram which he evolved[1] on the basis of Roberts-Austin's experimental data appears, however, somewhat at variance with the facts relative to general stability relations, an issue first pointed out by Heyn (l. c.). Recently WÜST,[2] CHARPY,[3] and BENEDICKS[4] have testified to results of the same description. The main points according to Heyn are presented in the following discussion. We take occasion to remark, in common with Heyn, that these relations are in no wise to be considered as completely substantiated. Consideration of certain phenomena is omitted in the interest of simplicity.

1. THE INCOMPLETELY STABLE SYSTEM: IRON-CARBON. — The melting-point diagram given in Fig. 89a represents the crystallization processes which occur under normal rate of cooling in such iron-carbon alloys as do not exceed 4.2 per cent in carbon content — corresponding to the point *B'*. If we assume with Heyn that, in spite of normal cooling, this diagram in part represents conditions which are not completely stable, but more or less supercooled, then we must concede to the iron-carbon alloys a marked tendency towards solidification and subsequent persistence in the form of unstable crystalline varieties. Characteristic of the melting-point diagram shown in Fig. 89a is the (incompletely stable)

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[1] ROOZEBOOM, Z. phys. Chem., 34, 437 (1900).

[2] WÜST, WÜLLNER-Festschrift, Leipzig, 1905, 240; Metallurgie, 31 (1906).

[3] CHARPY, Compt. rend., 141, 948 (1905).

[4] BENEDICKS, Metallurgie, 3, 393 (1906). This has also appeared in pamphlet form, Halle a. S. 1907)

iron-carbon compound of formula Fe_3C (corresponding to 6.7 % C). This iron carbide, called cementite by metallurgists, possesses no capacity for dissolving iron in the crystalline state. It exhibits very considerable hardness and resistance to the action of etching agents, whereby it may be readily separated from any slightly resistant associated material by treatment with dilute acids. It dissolves in concentrated acids with evolution of hydrogen and hydrocarbons. There has been no doubt of its existence since the investigations of MYLIUS, FOERSTER and SCHOENE.[1]

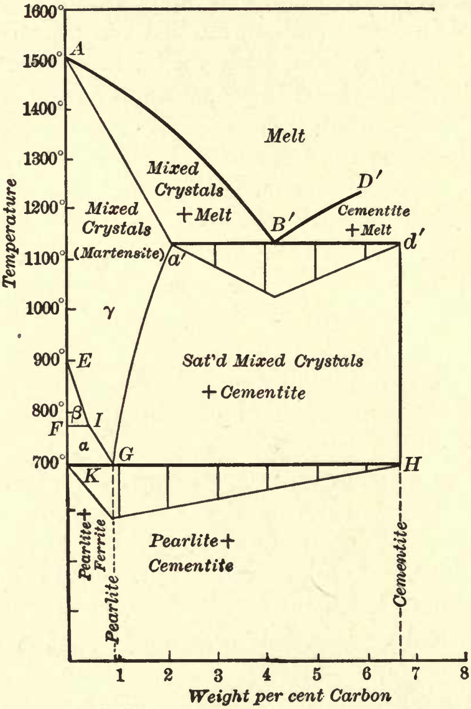

FIG. 89a. Fusion Diagram of Iron-Carbon Alloys. The incompletely stable system.

The following details may be recognized in Fig. 89a. The melting point of pure iron, *A*, is 1510 degrees. Iron undergoes

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[1] MYLIUS, FOERSTER and SCHOENE, Z. anorg. Chem., 13, 38 (1896).

two polymorphous transformations on cooling. The non-magnetic γ form, which is stable at the highest temperatures, changes at 890 degrees (at the point E) into the β form, which is also non-magnetic. At 770 degrees (at the point F) heat is again liberated, owing to transformation of the β form into the magnetic α form, which is stable at lower temperatures. Pure α iron, in its rôle of structure element in solid alloys, bears the name ferrite. All polymorphous modifications of iron crystallize in the isometric system. Primary separation of iron in the form of mixed crystals takes place along the curve AB'. Their composition is indicated by the curve Aa'. Primary separation of cementite is represented by the branch $D'B'$ and is characterized by the absence of mixed crystal formation, as previously noted. Since the tendency toward formation of incompletely stable crystalline varieties becomes very prominent in the case of alloys of appreciably higher carbon content than corresponds to B', the course of this branch of the curve is uncertain, and has never been determined for concentrations near that of pure cementite (corresponding to d'). The concentration of the point B' is approximately 4.2 per cent; its temperature, approximately 1130 degrees.[1] Mixed crystals of concentration between 0 and a' (= approximately 2.1% C) are known as martensite (in honor of A. Martens) in their rôle of structure element in solid alloys.

When crystallization along the horizontal $a'B'd'$ has ended, the alloy is entirely solid and consists of a mixture of saturated carbon-rich martensite crystals of the composition a', on the one hand, and pure cementite crystals of the composition d', on the other hand. The diagram shows which of these constituents separates primarily in the different cases. The relative amounts of eutectic B' are given by verticals upon the horizontal $a'B'd'$. The capability of iron to dissolve cementite in the crystalline state decreases with the temperature. Consequently, a separation of cementite takes place along the branch $a'G$. Cementite which has separated primarily in the pure condition suffers no subsequent change in composition, as shown by the vertical $d'H$. We have already noted the polymorphous transformations of iron which take place at E = 890 degrees, and at F = 770 degrees. The diagram shows that γ iron is capable of forming

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[1] Compare Wüst, Charpy, and Benedicks, l. c.

solid solutions[1] (even though they are not completely stable with certain amounts of cementite. This occurs at temperatures below *E*, the transformation point, as well as in the region of higher temperature, where pure γ iron is stable. We will now assume, on account of simplicity, that β and α iron possess no appreciable capability for dissolving carbon.[2] Under this assumption, viz., if β crystals separate in a pure state from solid solutions of cementite and iron, the temperature of separation of these β crystals in other words, the transformation temperature of γ iron to β iron, must decrease along *EI* as the carbon content increases — as far as the temperature $I = 770$ degrees, at which the pure β crystals become transformed into α crystals. Thus, a change in stability occurs in concentrations between *F* and *I*, in that the β crystals, which have separated thus far become transformed at the constant temperature of the horizontal *FI* into α crystals, which now constitute the stable modification. The condition that, from now on, α iron must separate from the solid solution, "γ iron-cementite," is made evident by an abrupt change in the direction of the transformation curve at *I*. We encounter conditions which are closely analogous to those of eutectic crystallization at the point *G* where the two curves *EIG* and *a'G* meet. The solid "solution of cementite and iron" (= martensite) is at this temperature saturated with cementite as well as with α iron. Consequently, on further abstraction of heat, there occurs simultaneous separation of both crystalline varieties in such proportions that the concentration of the solid solution is not altered. The temperature remains constant until the martensite of concentration *G* has been completely transformed into an eutectic mixture of α iron and cementite. This eutectic, which shows a beautiful lamellar structure, is called pearlite. The point *G* corresponds to 0.85 % C and 690 degrees. The eutectic horizontal reaches from *K* to *H*, while the relative amounts of eutectic have their maximum at *G*, and decrease lineally on both sides to zero. In case crystal-

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[1] See p. 163.

[2] Compare, however, the investigation of Benedicks in this connection (Recherches phys. et phys.-chim. sur l'acier au carbone, Upsala, 1904), according to which β iron may dissolve 0.27 per cent hardening carbon. No distinction between temper carbon and carbide-carbon is made above. The form in which carbon is to be found by preference in solution in iron cannot be given with certainty. Compare v. Jüptner, Ber., 39, 2385 (1906).

lization has proceeded as described above, cold alloys of concentrations between 0 and 0.85 % C consist of ferrite (α iron) and pearlite (eutectic G); the alloy of concentration 0.85 % C consists of pearlite; and those between 0.85 and 6.7 % C consist of cementite (Fe_3C) and pearlite.

Now, it is possible by means of sufficiently rapid cooling to retard the processes which take place along $EIGa'$. We are therefore in possession of a method for realizing conditions which are even more unstable than those given in our diagram.

2. The Completely Stable System: Iron-Carbon. — According to Heyn (l. c.), the following experimental facts testify in favor of an assumption that the diagram which we have discussed above, in part represents incompletely stable conditions:

(1) Alloys appreciably greater in carbon content than corresponds to the point $B' = 4.2\ \%$, contain, on solidification, not only cementite, but primarily separated graphite as well. The amount of graphite increases as the rate of cooling decreases.

(2) If iron-carbon alloys are exposed for a sufficiently long period (some days) to a high temperature (about that of red heat), there results on cooling (at least in part) a mixture of practically pure iron and carbon. Carbon separated in this manner is called "hardening carbon" by metallurgists. It closely resembles graphite in its properties, and is possibly identical with the latter. (Graphite and hardening carbon constitute the residue of uncombined carbon obtained on treating the alloys with acids.)

We conclude from these observations that the iron-carbon system which is stable at red heat consists of pure iron and pure carbon. Now, on crystallization of iron-carbon alloys, iron never separates in the pure state, but always in the form of mixed crystals. One might be inclined to attribute this phenomenon to unstable conditions; nevertheless, such appears improbable, so long as we assume that the liquid solution of carbon in iron exists in only one condition (and there is no reason for believing otherwise). For, the melting-point lowering which a pure substance sustains on addition of a second substance is greatest when it (the solvent) crystallizes out in the pure state (see p. 70). Thus, a curve which corresponds to the equilibrium between A crystals and A + B melt will run at a lower temperature in all concentrations than a curve which corresponds to the equilibrium between A + B mixed crystals and A + B melt. Hence, as long as separation of a given crystalline variety both in the pure state and in the form of mixed crystals is possible, and as long as melt and the crystals separating from it are in equilibrium, the pure form will be unstable. On this account, we prefer to regard primarily separated iron in the form of mixed crystals as stable. Fig. 89b is drawn to this effect with due regard for Heyn's views. In this completely stable system, iron separates primarily in the form of mixed crystals in concentrations from *O* to *B* along the curve branch *AB*. The composition of these mixed crystals is indicated by the branch *Aa*. The courses of these two branches are identical with those of the respective branches *AB′* and *Aa′* of the incompletely stable system (Fig. 89a). On the other hand, primary separation of

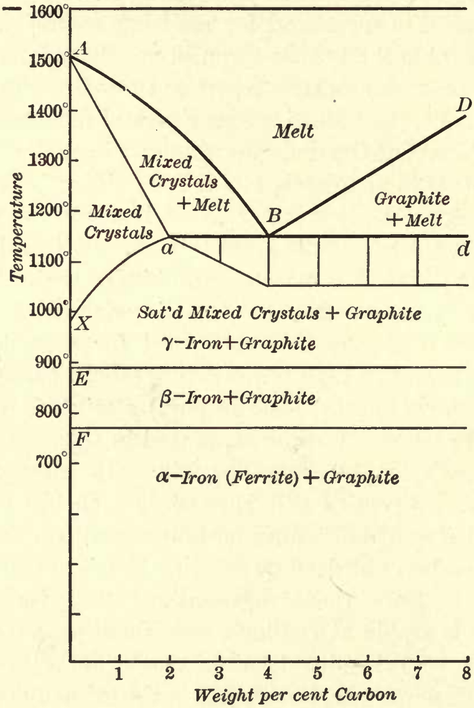

FIG. 89b. Fusion Diagram of Iron-Carbon Alloys. The completely stable system.

carbon in the completely stable system does not occur in the form of cementite, but in the form of graphite. This is represented by the branch *DB* (Fig. 89b), which must run at a higher temperature than the curve *D'B'* (Fig. 89a) for all concentrations. According to this conception, a completely stable iron-carbon compound is not existent within the concentration range under consideration. If this holds true for higher carbon concentrations as well, and if complete miscibility between iron and carbon in the liquid state continues, *DB* must ultimately reach to the melting point of pure graphite. However, nothing definite is known relative to concentrations containing more than 8% C.

According to the investigation of Charpy (l.c.), the eutectic point *B* of the completely stable system (Fig. 89b) lies about 10 to 15 degrees higher than the eutectic point *B'* of the incompletely stable system (Fig. 89a). Hence, we place the temperature of the point *B* at 1150 degrees in round numbers, and its concentration at 4% C. The concentration of the stable saturated mixed crystals *a* (iron, saturated with graphite) is about 2% C. When the temperature has fallen to that of the horizontal *aBd* (= 1150 degrees), all of the material crystallizes, and after crystallization the alloys of concentrations between *O* and *a* consist entirely of mixed crystals, all of which, if crystallization has proceeded in ideal manner, possess the composition of the original alloy. At higher concentrations, the alloys contain two structure elements, namely, saturated mixed crystals *a*, on the one hand, and graphite, on the other hand. According to the concentration in question, either one or the other of these constituents appears primarily as well as in the eutectic. The relative amounts of eutectic (Mixed crystals *a* + Graphite) are indicated in the usual manner by verticals erected upon the horizontal *aBd*. Now, as we are well aware, the mutual solubility of substances decreases in general with the temperature. Therefore, the saturated mixed crystals *a* will separate carbon (not in the form of cementite, as in the incompletely stable system, but in the pure form) on further cooling. We now conform to Heyn's conception by assuming a very rapid decrease in the solubility of carbon as the temperature falls, such that it becomes practically zero at about 1000 degrees (the point *X*). This may be represented by the curve *aX*. This essentially hypothetical curve stands in recognition of the assumption that the iron-carbon alloys existing below X (= 1000 degrees) are stable only in the form of pure iron and pure carbon (graphite or hardening carbon).[1] Under normal cooling conditions, the curve aX is invariably overstepped. If, however, an alloy is held several days at as high a temperature as is possible without exceeding X (this is done in tempering), at least a partial realization of the separation required by our diagram is effected.

Since, according to the diagram, all alloys existing below the temperature of X (= approximately 1000 degrees) must have become resolved into pure iron and pure carbon, the transformation temperatures of γ iron and β iron, respectively, cannot be altered by the presence of carbon in the original alloy. Hence, we draw horizontals through the points $E = 890$ degrees and $F = 770$ degrees (see p. 214) in order to indicate constant transformation temperature of iron throughout the whole concentration range. Thus, we see that the completely stable iron-carbon alloys must consist exclusively of pure iron and pure carbon at temperatures below 1000 degrees, provided our melting-point diagram is accurate. Complete realization of the stable condition is, nevertheless, invariably precluded, as previously mentioned, by the inherent tendency of these alloys towards supercooling.

3. THE COMPLETE SYSTEM: IRON-CARBON. — The fact that very varied properties may be imparted to an iron-carbon alloy of a given percentage composition finds its explanation in the variable stability of the system. This diversity is clearly revealed on combining both diagrams. Fig. 89c shows such combination (omitting several complications, such as verticals upon the eutectic, and the horizontal through E and F). The equilibrium curves which correspond to stable conditions are drawn in dotted lines,

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[1] BENEDICKS (l. c.) assumes a less rapid decrease in the solubility of carbon in iron with the temperature on the basis of experiments by MANNESMANN and CHARPY and GRENET. The temperature field within which the alloys are capable of resolution into pure iron and carbon is then placed below 800 degrees (at about 750 degrees). An experiment by WÜST (Metallurgie, 3, 11 (1906)), appears to contradict this, in that a partial resolution of iron, containing 3.8 per cent C., into pure iron and hardening carbon was effected at the high temperature of 980 degrees. We shall be unable to affirm more positively on this point until it has been decided by experiment whether or not complete resolution of the iron-carbon alloys into iron and carbon may actually occur and, if so, at what temperature.

since they have not been realized thermally, and are, consequently, to a certain extent hypothetical. In contradistinction, the equilibrium curves which are drawn in full lines represent the "realizable," incompletely stable conditions. Both diagrams agree only with respect to the points *A*, *E*, and *F* and the equilibrium curves *Aa* and *AB*, which latter are, for this reason, drawn in alternating full and dotted lines. Where the two fail of agreement, curves drawn in full lines must represent supercooled conditions and therefore lie below the dotted lines. In accordance with the above exposition, the following constituents may be found in solid iron-carbon alloys at ordinary temperature.

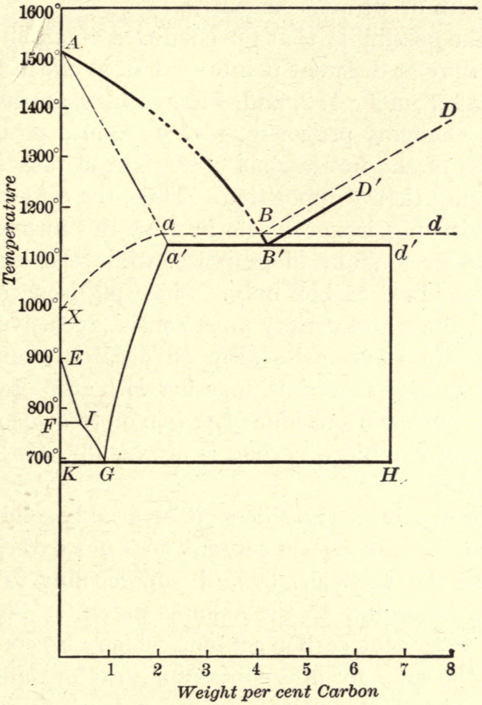

FIG. 89c. Fusion Diagram of Iron-Carbon Alloys.
The complete system.

(1) Under absolutely stable conditions (Fig. 89b): pure α iron (= ferrite) and graphite (or "hardening carbon").

(2) Under incompletely stable conditions (Fig. 89a):

(a) ferrite and pearlite (eutectic of ferrite and cementite),
(b) pearlite alone,
(c) pearlite and cementite.

(3) Under the least stable condition, *i.e.*, when the curve *EJGa'* has been overstepped: martensite (mixed crystals of γ iron and cementite), with or without cementite.

Owing to the possibility that the condition of stability may vary in the same alloy at different points — that, in effect, the constituents enumerated under 1, 2, and 3 above may appear simultaneously and in changing proportions — we are in a position to alter the properties of the iron-carbon alloys within rather wide limits without altering their composition. Thus, the difference between gray and white pig iron consists in that the former contains a greater or lesser amount of graphite, while the latter contains chemically combined carbon only. Since pig iron contains more than 1.8% C, the white variety must consist exclusively of cementite and pearlite (martensite also, on occasion), and the white variety of these same materials, together with graphite. The latter, variety alone will leave a residue of carbon on treatment with acids, since chemically combined carbon is always liberated in the form of hydrocarbons.

If the pig iron contains no silicon, it invariably solidifies as white cast iron, provided its carbon content does not exceed 4 per cent. Silicon lessens the tendency toward supercooling to a greater or lesser extent, according to the amount present. Pig iron of approximately 4 per cent carbon content, which also contains silicon, solidifies to the gray form — containing graphite and, of course, varying amounts of cementite. In the case of pig irons containing a greater amount of carbon, *i.e.*, exceeding 4 per cent, it is also possible, even in the absence of an appreciable quantity of silicon, to bring about primary separation of graphite by slow cooling.[1] Manganese, on the other hand, is effectual in inducing supercooling. Hence, varieties of pig iron which contain manganese solidify, in general, in the white form, even when their carbon content exceeds 5 per cent. Separation of carbon from samples of iron containing

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[1] This, however, appears somewhat doubtful, according to recent experiments by WÜST.

cementite on lengthy exposure to a temperature of bright redness has already been discussed (p. 231).

Iron-carbon alloys of 1.8 per cent carbon content and less are known as steel, wrought iron, etc. The diagram shows us that the possibility of varying conditions in this region is particularly extended, owing to the presence of the curve *EIGa'*. In setting out to prepare an iron of certain prescribed properties, familiarity with the diagram, in connection with knowledge of the properties of the individual structure elements (see the following table), is of great service.

TABLE 6.

	Hardness.	Coloring with tincture of iodine.	Behavior towards 10 per cent sulphuric acid — cold.
Ferrite, Fe	Softest structure element.	Very faint or none at all.	Dissolves readily with evolution of hydrogen.
Cementite, Fe_3C.	Hardest structure element.	None.	Fails to dissolve.
Pearlite, $Fe+Fe_3C$.	Medium.	Inappreciable.	Dissolves partially.
Martensite, mixed crystals of cementite $+\gamma$ iron.	Varying hardness according to C-content. Invariably softer than cementite.	Yellow to brown.	Dissolves with evolution of hydrogen and hydro-carbons.

For example, if it is desired to impart the greatest possible hardness to an iron of definite carbon content, say approximately, 1 per cent, the formation of pearlite, which is moderately soft, should be hindered. That is to say, the alloy should be conducted with all possible rapidity from the martensite field into the field of trifling reaction velocity, where the (hard) martensite no longer undergoes transformation into pearlite and cementite. This process of quenching is called hardening. The temperature at which rapid cooling should begin lies above *EIGa'*, and may be read directly from the diagram when the carbon content is known. If the hardened steel is subjected to a temperature of more than 200 degrees, it is then in a condition to favor the resolution of martensite into ferrite and cementite with appreciable rapidity (compare Heyn, loc. cit., p. 226). In this manner, a steel of greater hardness than is desired may be tempered to a lesser degree of hardness (tempering of steel).

§ 7. SUPPLEMENTARY.

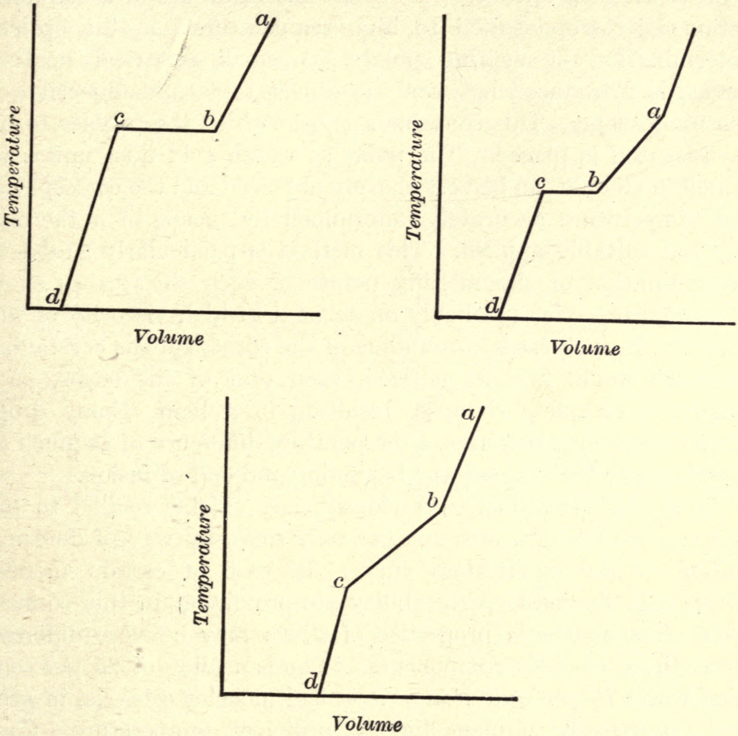
For progress in our perception of the nature of metallic alloys we are primarily indebted to thermal methods. In that they teach us concerning not only transient conditions encountered, but also concerning the whole history of alloy formation, these methods furnish a key to the understanding of the ofttimes complicated inter-relations of the components. Nevertheless, these methods fail of results in two cases: in the first place, when the reaction is accompanied by a very slight heat effect, and, in the second place, when the rate of reaction under the given experimental conditions is so trifling that the reaction no longer becomes regulated by flow of heat (p. 10). For this reason, several other methods which have found application in the investigation of binary systems will now be briefly treated. These methods come under two categories: those which are applicable to the determination of equilibrium curves, and those which are merely adapted to investigation of the solidified mixture. Among the latter is included one which has been discussed at length, namely, the microscopical investigation of prepared sections.

A. *Methods of Determination of Equilibrium Curves.*

1. METHOD OF SOLUBILITY DETERMINATION. — This method is identical in principle with the thermal method. While the concentration of the liquid mixture is known in the case of the thermal method, and we determine the temperature at which it begins to solidify, *i.e.*, the temperature at which it is in equilibrium with a crystalline phase, in the present case the composition of the liquid mixture which is in equilibrium with this crystalline phase at a given temperature is determined. This method has proven of service chiefly in the study of equilibria between salts and water. It is characterized by great accuracy and does not fail of application where the heat effects are small. The equilibrium may be accurately followed in the practice of this method

by allowing it to reach adjustment from both sides. Application of the method to metallographical investigation is materially hindered by the difficulty associated with the necessary separation of crystals from mother liquor (see *Introd.*).

2. DILATOMETRICAL METHODS. — Most substances contract on solidification. If the specific volume of a pure substance is determined at different temperatures, a curve similar to that



FIGS. 90, 91 and 92.

given in Fig. 90 is obtained. From this curve, it is seen that the substance has solidified as a unit, in that a marked decrease in volume at the constant temperature of the horizontal *bc* has resulted during passage from the liquid into the crystalline state. Fig. 91 gives the temperature-volume curve of a mixture. Here, solidification has commenced at the temperature *a* and has become complete eutectically at the temperature *bc*. Fig. 92 gives the temperature-volume curve characterizing solidification to mixed crystals. The crystallization interval is at *bc*. Obviously, this method may be used in connection with all such transformations as are accompanied by change in volume. Its use is independent of the magnitude of the heat effect, but is subject to considerable experimental difficulty at high temperatures.

3. OPTICAL METHODS. — DÖLTER[1] has made use of a crystallization microscope suited to high temperatures[2] in the optical determination of melting points. A small electrical heating device is introduced between the object table and objective of the microscope. This contains a cup in which the powder to be investigated is placed. The point at which gold dust unites to a molten globule can be very sharply observed and the corresponding temperature accurately determined by means of a thermoelement suitably applied. This method is particularly suited to determination of the melting points of such silicates as show abnormal behavior (probably on account of high viscosity of the melt).[3] In such cases, a rounding of the corners of the crystalline particles would first be noticed, then that of the edges, and, finally, a complete collapse, resulting in a light, glassy drop. Under some circumstances, a temperature difference of as much as 100 degrees characterizes the beginning and end of fusion.

4. OTHER METHODS. — Obviously, any change related to the passage of one form into another may serve by way of determination of the equilibrium curve. In case of certain metals, changes in magnetic permeability are prominent in this connection. The magnetic properties of alloys may be very different from those of their components. Thus an alloy of 25 per cent nickel and 75 per cent iron — so-called nickel steel — is, in general, practically unmagnetic at ordinary temperature. Conversely, metals which are themselves non-magnetic may form magnetic alloys. As an example of this, an alloy of Cu, Mn and Al[4] may be mentioned. According to WEDEKIND,[5] certain

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[1] DÖLTER, Z. Elektrochemie, 12, 617 (1906).

[2] DÖLTER, Phys.-chem. Mineralogie, Leipzig, 1905, p. 130.

[3] See p. 8.

[4] HEUSLER, Über die Synthese ferromagnetischer Manganlegierungen, Marburg, 1904.

[5] WEDEKIND, Ber., 40, 1259 (1907).

definite compounds of manganese are carriers of ferro-magnetism (compare, in this connection, a paper by WILLIAMS, Z. anorg. Chem , 55, 1 (1907)).

B. *Methods of Investigation of the Solidified Mixtures.*

1. DETERMINATION OF THE SPECIFIC VOLUME OF THE COMPLETELY SOLIDIFIED ALLOY. — The specific volumina of mixtures may be calculated according to the rule of mixture. If two substances form no compound with one another, the relation of specific volume to concentration in the mixtures will be given by a straight line, provided no miscibility in the crystalline state occurs (Fig. 93a). If, on the contrary, a compound of concentration indicated by the formula A_mB_n is formed, this relation will be given by two straight lines which coincide at the concentration of the compound[1] (Fig. 93b). The use of this method, which appears, at first sight, free from all objection in the absence of miscibility in the crystalline state, has led to many errors. The method is based upon the hypothesis that only two structure elements are present in the respective mixture, namely, the compound, and either of the components, *A* or *B*. We have seen, relative to the discussion of the concealed maximum, that this condition is not realized in case of incomplete progress of the reaction (see pp. 137, 141). In all such cases, this method must

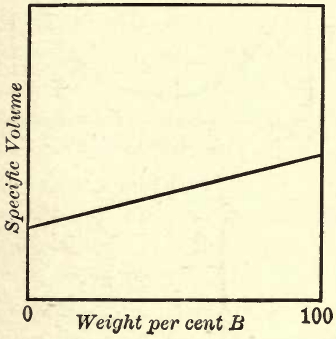

FIG. 93a.

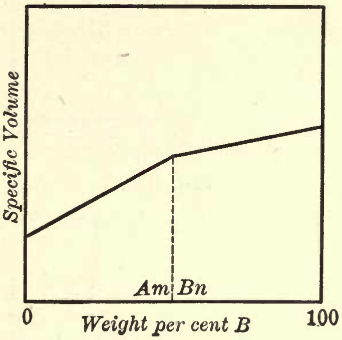

FIG. 93b.

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[1] MAEY, Z. phys. Chem., 29, 119, 1899; 38, 292 (1901).

lead to false conclusions.[1] Again, the observation of KAHLBAUM and STURM[2] that the specific weights of pure metals may vary somewhat according to their previous treatment may be cited, although of relatively lesser practical importance in this connection.

2. DETERMINATION OF ELECTRICAL CONDUCTIVITY. — Owing to the far-reaching and exact investigations of MATTHIESSEN,[3] we have learned to discriminate between two groups of alloys, namely, those whose specific conductivity may be approximately calculated from that of their components according to the rule of mixture, and those in which small additions of one metal to the other

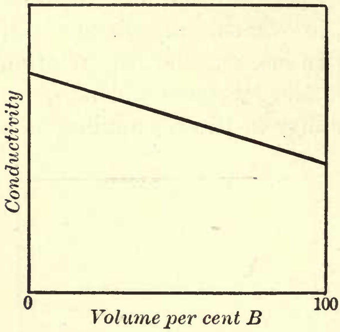

FIG. 94a.

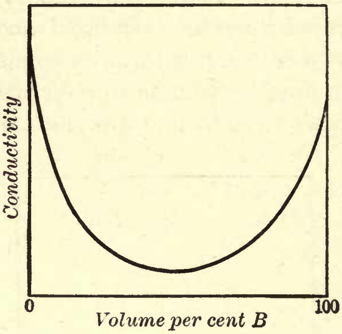

FIG. 94b.

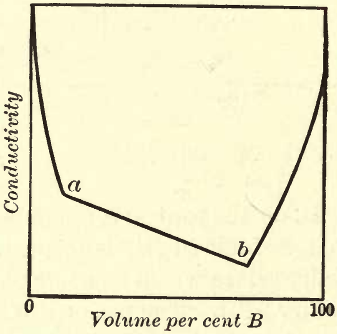

FIG. 94c.

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[1] VOGEL, Z. anorg. Chem., 45, 20 (1905).

[2] KAHLBAUM and STURM, Z. anorg. Chem , 46, 217 (1905).

[3] MATTHIESSEN, Pogg. Ann., 110, 190 (1860).

bring about great decrease in conductivity. On entering the conductivity in its relation to volume-concentration in a coördinate system, we obtain a straight line for the first group (Fig. 94a), and, when both metals behave similarly, a curve of the form shown in Fig. 94b for the second group. Five examples of the first type are known, namely, Sn-Zn, Sn-Pb, Sn-Cd, Pb-Cd and Zn-Cd. Examples of the second type are Au-Ag, Au-Cu and Cu-Ni. LeChatelier[1] was the first to recognize the correct relationship between constitution and conductivity, notwithstanding the very limited perception of the general constitution of metallic alloys then prevalent. He held the opinion that linear variation of specific conductivity with volume concentration (Fig. 94a) ensued when the components were disposed side by side in the crystalline condition, and that the frequently observed condition of greatly diminished conductivity in an alloy with respect to that of its components (Fig. 72b) was due to mixed crystal formation. This latter conclusion appeared to him, "seriously controvertible in the case of alloys of iron with nickel and manganese, and of silver with gold." The occurrence of an angular maximum in the conductivity curve indicated the existence of a compound, according to LeChatelier.

Roozeboom[2] made the following observations relative to LeChatelier's inferences. In the first place, he pointed out that even in case an alloy crystallizes to a conglomerate of the pure metals, it is not essential that a linear relation between conductivity and volume-concentration obtain. Consider two different bars of an alloy which is composed of equal volume percentages of two components which are immiscible in the liquid state and possess the respective specific conductivities λ_1 and λ_2. In the first bar, let the components lie side by side in the direction of the current, as shown in Fig. 95a. Then the average conductivity Λ is $\frac{1}{2}(\lambda_1 + \lambda_2)$, according to the rule of mixture. Now, let the components lie at right angles to the direction of the current in the second bar, as shown in Fig. 95b. Then the average resistivity $\frac{1}{\Lambda}$, as calculated from the rule of mixture, is $\frac{1}{2}\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2}\right)$.

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[1] LeChatelier, Revue générale des sciences, 6, 531, 1895: Contribution à l'étude des alliages, Paris, 1901, p. 446.

[2] Roozeboom, Die heterogenen Gleichgewichte, II Teil, 1904, p. 186.

Whence, $\Lambda = \frac{2 \cdot \lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$, in this case, a value consistently smaller than before, the difference being proportional to $(\lambda_1 - \lambda_2)^2$. Roozeboom concludes that neither the conductivity nor its reciprocal value can be a linear function of the volume concentration, on account of the inherently irregular arrangement of particles.

Although the above conclusion seems well founded in principle, we must in general expect an approximately linear relationship between specific conductivity and volume concentration in metallic conglomerates. Suppose we assume, for example, the arrangement given in Fig. 95c, which must more closely approximate the actual conditions than either of the arrangements previously given. Calculation of the conductivity in such a case, even under the simplifying assumption that we are dealing with a surface (thin plate), is a task which cannot be solved in an elementary manner. Imagining the figure to be divided into two sections at *ab*, and considering mean conductivity, we conclude that specific resistivity is calculated according to the rule of mixture, thus:

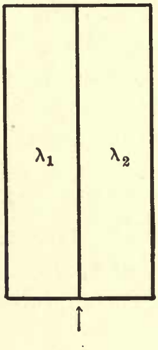

FIG. 95a.

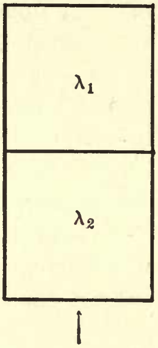

FIG. 95b.

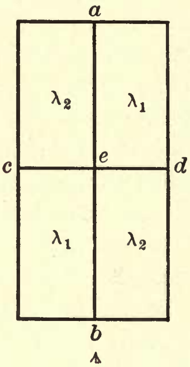

FIG. 95c.

$$\frac{1}{\Lambda} = \frac{1}{2}\left(\frac{1}{\lambda_1} + \frac{1}{\lambda_2}\right).$$

If, however, division is made at *cd*, the same applies to specific conductivity, and we obtain:

$$\Lambda = \frac{\lambda_1 + \lambda_2}{2}.$$

In the first case, we have presumed a division according to Fig. 95d; in the second case, a division according to Fig. 95e. Neither of the solutions can be considered rigid, since the assumption made in the second case that *cd* is a line of potential follows from the assumption made in the first case that *ab* is a line of current. Still, the assumption made in the second case, that the potential is the same at the points *c* and *d*, will be approximately realized for a conductor having the form of a wire, and it thus appears probable that a very closely linear relationship between conductivity and concentration exists. In this connection, no allowance has been made for possible thermo-electric effects.

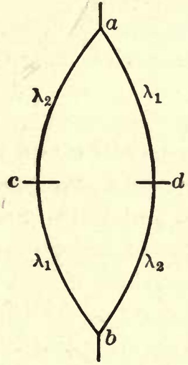

Fig. 95d.

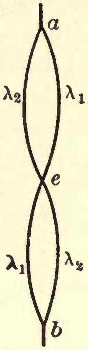

Fig. 95e.

A second of Roozeboom's objections rests upon the fact that, even in the case of pure metals, conductivity results depend upon previous treatment of the material, such as compression, torsion, annealing, etc. The specific volume also varies along these lines, as we have seen on p. 242, although to a much lesser extent than the conductivity.

While the fundamental qualifications of the above exceptions cannot be gainsaid, LeChatelier appears, nevertheless, to have hit upon the truth of the matter in its essentials. In particular, modifications of the conductivity-concentration relations in metallic conglomerates, due to the causes represented by Roozeboom, are not sufficiently prominent to impair in any way the typical distinction between "approximate lineality" (Fig. 72a) and "marked lowering by small additions" (Fig. 72b). LeChatelier's views have recently been vigorously supported by GUERTLER,[1] who compared conductivity diagrams, drawn principally from Matthiessen's results, with corresponding melting-point diagrams, as did LeChatelier. Guertler had more accurate melting-point diagrams and a larger number of them at his disposal than did LeChatelier, owing to immense progress in this sort of work during the intervening time. He differentiates three types: the two extreme cases, Fig. 94a, wherein no miscibility in the crystalline state occurs, and Fig. 94b, corresponding to complete miscibility in the crystalline state, with an intermediate case of limited miscibility, shown in Fig. 94c, which is beautifully illustrated by the system Cu-Co. In this system, miscibility marks the two concentration ranges, 0 to *a* and *b* to 100, whence we note a sharp decrease in specific conductivity from concentrations 0 and 100 respectively (the pure metals). The specific conductivity is a linear function of the volume-concentration between concentrations *a* and *b*, in which interval the alloy represents a conglomerate of the two saturated mixed crystal varieties *a* and *b*. Cases covering the appearance of compounds are represented by combination of the three simple types in the well-known manner.

Relative to the practical value of conductivity determinations in studying the constitution of alloys, we note that it is frequently impossible, on account of brittleness, to obtain alloys in the form most suited to accurate conductivity determinations, namely, that of wire. Thus, a method for the exact determination of specific conductivity in a metallic regulus just as it leaves the furnace would be of great value. In using the conductivity method for determination of the composition of compounds, we must be assured that only two structure elements are present in the mixture, as was the case relative to use of the specific volume method in the same connection (see p. 241).

It appears questionable to conclude that a compound exists on the basis of a faint break in the conductivity curve. By way of example, we may cite Guertler's first combination of the conductivity and fusion diagrams for the system Au-Sn,[2] and his sub-

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[1] GUERTLER, Z. anorg. Chem., 51, 414 (1906).

[2] GUERTLER, Z. anorg. Chem., 51, 414 (1906). Fig. 13.

sequent correction of the same.[2] The break *a* in the conductivity curve,[1] which, owing to use of (no longer current) equivalent weights by Matthiessen, would at first sight appear to correspond to the compound AuSn, has lost all claim to existence by subsequent correction.[2] (It "may be discarded, being only faintly perceptible, without thereby working any constraint upon Matthiessen's experimental figures.") The conclusions from both sources (conductivity and melting-point diagrams) still fail of complete agreement, however, and an explanation of the difference is to be sought in incomplete progress of reaction (see p. 134). The only Au-Sn compound which finds sharp and unaffected expression on the conductivity curve is the compound AuSn, which had already been described by VOGEL[3] on the basis of thermal and microscopical investigation.

Another example which aids to show that uncertainties are at present connected with this method is furnished by the system Cu-Sb. BAIKOW[4] has concluded on the basis of his melting-point diagram that two compounds of the respective formulas, $SbCu_2$ and $SbCu_3$, exist. GUERTLER[5] found abrupt changes in direction on the conductivity curve which he constructed from the experimental measurements of KAMENSKY[6] at just these concentrations: at the concentration $SbCu_2$, a sharp break directed upwards, and, at the concentration $SbCu_3$, a break directed downwards. KAMENSKY[6] himself constructed a curve (on the basis of his own experiments, carried out with the induction balance) which exhibited the upward peak at the concentration $SbCu_2$ (as above), but located the other break at the concentration $SbCu_4$, and he, of course unaware of the melting-point relations in this system, drew the conclusion that two alloys of "well-defined" compositions, possessing the respective formulas, $SbCu_2$ and $SbCu_4$, are existent.

Regarding the system Cu-Ag as well, it appears that the manner in which GUERTLER[7] has endeavored to reconcile the evidence of

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[1] GUERTLER, Z. anorg. Chem., 51, 414 (1906). Fig. 13.

[2] GUERTLER, Z. anorg. Chem., 54, 88 (1907). Fig. 13.

[3] VOGEL, Z. anorg. Chem., 46, 73 (1905).

[4] Publications of the Czar Alexander I Road Building Institute, St. Petersburg (1902): Landolt-Börnstein, Phys.-chem. Tables, III ed. (1905), p. 300.

[5] GUERTLER, Z. anorg. Chem., 51, 418 (1906).

[6] KAMENSKY, Phil. Mag. (5), 17, 270 (1884).

[7] GUERTLER, Z. anorg. Chem., 51, 406 (1906).

the conductivity diagram with that of the melting point diagram is not entirely beyond criticism. The melting point diagram indicates existence of mixed crystals with a gap in miscibility. We would thus expect a conductivity curve of the type, Fig. 94c. The curve for the case of complete miscibility, which is uniformly convex with respect to the concentration axis, is not completely realized when a gap in miscibility occurs, being relieved by a linear section between the concentrations of the saturated mixed crystals. Now, in this system, it is not possible to join the two portions of the conductivity curve which are interrupted by a linear portion into a single continuous convex curve. Isodimorphism between the components might be responsible for this condition. If such were the case, we should be dealing with an additional, viz., a fourth, type, and we would then possess a means, *i.e.*, by conductivity measurements, of distinguishing between the cases of isomorphism and isodimorphism. However, there is not sufficient experimental material available to warrant such general conclusions: in particular, the gap in miscibility may be much wider than assumed by Guertler.[1]

Decrease in specific conductivity appears to constitute a most sensitive test of miscibility in the crystalline state.[2] In many cases, *e.g.*, in the system Cu-Co, which has been mentioned, this method will be found suited to accurate determination of the extent of the gap in miscibility of the components. In other cases, *e.g.*, in the systems Au-Cu and Cu-Ag (see above), it appears much inferior to the thermal and microscopic methods in this respect.

When, in case of complete isomorphism between the two components, a melt solidifies after the manner of a pure compound, we are not at liberty to conclude, aside from all other considerations, that a compound is existent (p. 193). Guertler assumes that if a compound exists, the conductivity-concentration curve will be composed of two branches, as shown in Fig. 94b, and must, there-

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[1] Osmond, Bull. soc. encouragement (V) 2, 1, 837 (1897).

[2] Recently published results by Stoffel (Z. anorg. Chem., 53, 137 (1907)) appear in a light contradictory to the above statement. According to Stoffel, tin forms mixed crystals with lead, and also with cadmium, to a limited extent. Since an approximately linear relation between conductivity and volume-concentration has been determined in these cases (see p. 243), further test of the former results is to be desired. Compare also Sackur, Z. Elektrochemie, 10, 522 (1904).

fore, show a sharp peak at the concentration of the compound. *A priori,* this assumption does not, of necessity, need to hold true, even if absolute accuracy be conceded to the purely empirical rules relating to conductivity, since we know nothing concerning the degree of dissociation of a crystallized compound which forms mixed crystals with its components. Thus, the absence of such a peak fails to justify a negative conclusion regarding the possibility of existence of a compound, even in case of isomorphous mixtures.

3. DETERMINATION OF THE TEMPERATURE COEFFICIENT OF ELECTRICAL CONDUCTIVITY. — According to CLAUSIUS, the specific conductivity of metals is approximately proportional to the absolute temperature. Denoting the specific resistivity of a metal at 0° C. by A_0, and at t° C. by A_t, according to the above,

$$A_t = A_0 (1 + \alpha t),$$

where α is the same for all metals, and is equal to the expansion coefficient of a gas. The value $\alpha = 0.004$ is sufficiently close in this connection, on account of the solely approximate validity of the law. Polymorphous transformations, so far as they are attended by appreciable alteration in the electrical behavior of the material, are excluded from the following discussion.

We are primarily indebted to MATTHIESSEN and VOGT[1] for experimental material relating to the temperature coefficient of electrical conductivity. The following regularity discovered by them is of value for our present purpose. We will indicate the measured specific resistivity of an alloy by C. If the specific conductivity should show a linear relationship to the volume-concentration (see p. 243), we might calculate the former, according to the rule of mixture, from the conductivities of the components. We will indicate the specific resistivity, calculated in this manner, by A. Now, Matthiessen and Vogt found the following rule to hold well in many cases:

"The difference between measured and calculated resistivity is independent of the temperature."

That is, $C - A = \textit{constant}$ for each single mixture.

LIEBENOW[2] brought forward the following equation (called by

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[1] MATTHIESSEN and VOGT, Pogg. Ann., 122, 19 (1864).

[2] LIEBENOW, Z. Elektrochemie, 4, 201, 217 (1897). Compare also the account of "Liebenow's Theory and Its Consequences," by NERNST, Theoret. Chem., IV Ed. (1907), p. 406.

him the leading equation) for the relation between specific resistivity and temperature of alloys:

$$C_0\,(1 + \gamma t) = A_0\,(1 + \alpha t) + B_0\,(1 + \beta t). \tag{1}$$

In this equation, C_0 and A_0 signify measured and calculated conductivities, respectively, at 0° C., t signifies the temperature in degrees centigrade, γ, the actually observed temperature coefficient of specific resistivity, α, the temperature coefficient of the pure metals, B_0, the "*addition resistivity*" which results from alloying the two metals at 0°, and β, the temperature coefficient of the latter.

Thus, Liebenow divides the total resistivity of an alloy into two parts, A and B, of which A is attributed to the metals in a purely individual connection, while B is due to simultaneous presence of the two metals. It is obviously of no consequence, as regards the deductions which we shall draw from the above equation, whether the "addition resistivity" be ascribed to presence of thermoelectric forces, pursuant to Liebenow's procedure, or be regarded as incidental to the structure of the alloy (appearance of mixed crystals, etc.). Liebenow accounts for the regularity discovered by Matthiessen and Vogt by placing

$$\beta = 0,$$

in closest approximation, for these cases. He then obtains

$$C_0\,(1 + \gamma t) = A_0\,(1 + \alpha t) + B_0. \tag{2}$$

As long as this equation holds, any term including t has the same value as when t-free. Thus, we obtain

$$C_0 = A_0 + B_0 \tag{3}$$

and

$$C_0\gamma = A_0\alpha, \text{ or } \frac{C_0}{A_0} = \frac{\alpha}{\gamma}. \tag{4}$$

Equation 4 corresponds to a rule also given by Matthiessen and Vogt, from which they derived the first by transformation.

We may draw the following (Liebenow's) conclusions from the above equations:

(*a*) If $B_0 = 0$, then $C_0 = A_0$ and $\gamma = \alpha$. The measured resistivity is equal to the calculated resistivity at all temperatures, and its temperature coefficient is equal to that of the resistivity of the pure metals. We have become familiar with five metal pairs which behave approximately in this manner (p. 243).

(*b*) If B_0 is large in comparison with A_0, then, $\frac{C_0}{A_0} = \frac{A_0 + B_0}{A_0} = \frac{\alpha}{\gamma}$ (large).

Alloys of highly reduced specific conductivity thus possess a small temperature coefficient of conductivity.

The curve which represents the temperature coefficient of specific resistivity, and, likewise, the temperature coefficient of specific conductivity, at a given temperature in its relation to concentration, must, according to the above, show a course analogous to that of the curve which represents the specific conductivity itself in its relation to concentration.

Thus, on entering in a coördinate system, the values for temperature coefficient of specific conductivity at a given temperature in their relation to concentration, we obtain a straight line for case (*a*), *i.e.*, a diagram analogous to the conductivity-concentration diagram corresponding to this case (Fig. 94a) with the mere reservation that this line must run in a nearly horizontal direction on account of the approximate equality between the temperature coefficients of conductivity for both metals. In all other cases as well, the character of the curve remains the same, in that its form preserves an analogy to that of the corresponding conductivity-concentration curve (Fig. 94b, 94c, or a more complicated curve obtained by various combinations — compare p. 246 — between a, b and c, Fig. 94).

The above deductions from equation (2) — under *a* and *b* — led GUERTLER[1] to propose determination of the temperature coefficient at different concentrations as a means of establishing the constitution of metallic alloys. He would obviate, in this way, the difficult task of directly determining conductivity in brittle alloys. The "addition resistivity" *B* is attributed to mixed crystal formation, according to LeChatelier. Guertler also assigns a specific "compound resistivity" to chemical compounds.

Relative to the reliability of this method, it may be noted that both of Matthiessen and Vogt's rules, and the equivalent equation

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[1] GUERTLER, Z. anorg. Chem., 54, 58 (1907). Compare also LIEBENOW, Z. Elektrochemie, 4, 219, (1897).

2, possess none other than conditional validity. For example, although it follows from equation 4 that γ is always positive, since C_0, A_0 and α are always positive, there are alloys which possess negative temperature coefficients of resistivity below certain temperatures, *e.g.*, Cu-Ni and Cu-Mn alloys.[1] If the above division of total resistivity into two parts is to be retained in such cases, only the general equation (1), in which β assumes a negative value throughout the respective temperature range, remains valid, according to Liebenow.

In consideration of the conditional accuracy of Matthiessen and Vogt's rules, of errors which may be introduced owing to occurrence of polymorphic transformation and of the scarcity of experimental material, we are not inclined to attach great importance to determination of the temperature coefficient of conductivity as an independent method of establishing the constitution of alloys in general. Obviously, it is capable of supplying evidence of a confirmatory nature in certain cases. An example of this is to be found in Liebenow's location of the compound Cu-Zn by the aid of this method.[2] In many cases, determination of the relation between conductivity and temperature may be advantageously applied in the demonstration of polymorphous transformation.[3]

4. DETERMINATION OF THE VAPOR PRESSURE OF A COMPONENT. — A salt containing water of crystallization may hold its several water molecules with varying tenacity. By way of example, we may cite blue vitriol, $CuSO_4 + 5\,H_2O$, which slowly effloresces at ordinary temperature, gives off four molecules of water in the drying oven at 100 degrees, and loses its last molecule of water at temperatures above 200 degrees. Thus, such a salt forms a number of compounds with water, called hydrates. An accurate insight into the conditions which prevail here is to be obtained by determining the aqueous tensions at constant temperature of samples of salt which contain varying amounts of water.

We will first consider a rather simple case in which the respective salt forms no hydrate under the chosen experimental conditions.

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[1] FEUSSNER and LINDECK, Abh. d. Phys.-Techn. Reichsanstalt, 2, 501 (1895).

[2] LIEBENOW, Z. Elektrochemie, 4, 234 (1897).

[3] LECHATELIER, Revue générale des sciences, 6, 533 (1895): Contribution à l'étude des alliages, p. 448.

Ordinary salt — sodium chloride — is well suited to this purpose, and our task is, in effect, to study the aqueous tension in the system, NaCl-H_2O, at all possible concentrations; but with restriction as to temperature, which we will recognize by choosing the temperature 50° C. We will effect the determination in the following manner: An aqueous solution of sodium chloride of definite concentration is enclosed in an evacuated cylinder *A* (Fig. 96), fitted with an airtight piston *B*. Since sodium chloride does not evaporate to a measurable extent, water vapor alone can be present in the closed space above the solution. We will assume that determination of the pressure of the water vapor, which serves as a measure of its concentration in the gas chamber, may be effected at any time by means of the manometer *C*.

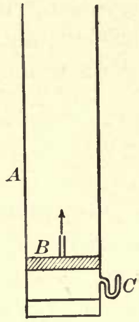

FIG. 96.

According to the law of vapor-pressure lowering, which is quite analogous to the law of melting-point lowering, the vapor pressure of pure water will be lowered by solution of another substance to an extent which is proportional to the concentration of the solution. The vapor pressure over a solution is unequivocally fixed at any given temperature, since the pressure over the solution is unequivocally fixed at any given temperature. Since the pressure of vapor over pure water at 50 degrees is about 92 mm. of mercury, the pressure of vapor over the solution will be less than 92 mm. We will assume that it approximates 91 mm. Now, on gradually raising the piston in our cylinder, further vaporization of water from the sodium chloride solution results. On this account, the solution becomes more concentrated, and a lowering of the vapor tension takes place. This lowering will continue until the solution becomes saturated with sodium chloride. The vapor tension of a saturated solution of sodium chloride at 50 degrees amounts to approximately 70 mm. If, now, further increase in the volume of the gas chamber and further evaporation of water are effected by continual elevation of the piston, no change in vapor pressure can result, since the saturated solution can suffer no change in *concentration* at constant temperature. By further evaporation of water, merely the *amount* of saturated solution changes, in that a definite amount of sodium chloride crystallizes out for every gram of water which leaves the solution. The vapor tension of the solution, *i.e.*, the concentration of water vapor in the gas chamber, is, nevertheless, independent of the amount of solution present. Thus, from the moment when the first crystal of sodium chloride separates, we have equilibrium between the three phases of invariable composition: "saturated solution, crystallized sodium chloride and water vapor at 70 mm. pressure." The equation of the reaction may be written in the form:

$$\underset{\text{Satd. Soln.}}{(NaCl + nH_2O)} \leftrightarrows \underset{\text{Cryst.}}{NaCl} + \underset{\substack{\text{Water vapor}\\ \text{at 70 mm. pressure.}}}{nH_2O}, \quad (t = 50°).$$

Elevation of the piston causes reaction to take place from left to right; it effects a decrease in the amount of saturated solution and an increase in the amount of sodium chloride crystals and water vapor — no one of the phases changes its composition until the last drop of saturated solution has disappeared. Depression of the piston causes reaction to proceed in the opposite direction, whereby the pressure of the water vapor remains constant as long as the last salt crystal remains undissolved. On account of the invariability of composition of each phase which takes part in the equilibrium, the term, *complete*[1] (heterogeneous) equilibrium is used in this connection.

When, on continued elevation of the piston, the last trace of water has passed from the liquid phase into the gas chamber, there is a momentary condition of equilibrium between crystallized salt and water vapor at 70 mm. pressure. Further elevation of the piston can simply result in an increase in the volume of water vapor, and a corresponding decrease in vapor pres-

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[1] The complete equilibrium which here obtains is perfectly analogous to that hitherto considered. Up to the present, we have regarded the pressure exerted upon the system as unchangeable (= 1 atm.); the temperature, however, subject to alteration. Equilibrium was complete as long as change in the heat content of the system was unaccompanied by change in temperature (see p. 33, and, concerning the idealization generally underlying this interpretation, pp. 281 and 282). In the present instance, we maintain the temperature of the system constant, and equilibrium is complete as long as a change of volume is unaccompanied by a change of pressure. In both cases, the composition of every phase remains unchanged during progress of the reaction in either direction, until one of the phases is exhausted.

sure, which may be calculated with ease under the assumption that the gas laws hold in this case. It is clear that, by using a cylinder of sufficient length, we may cause the pressure of water vapor above the salt crystals to fall below any chosen value, *i.e.*, to finally approximate zero.

We may combine our experimental results in a volume-pressure diagram, as shown in Fig. 97a. The volume of the gaseous phase,

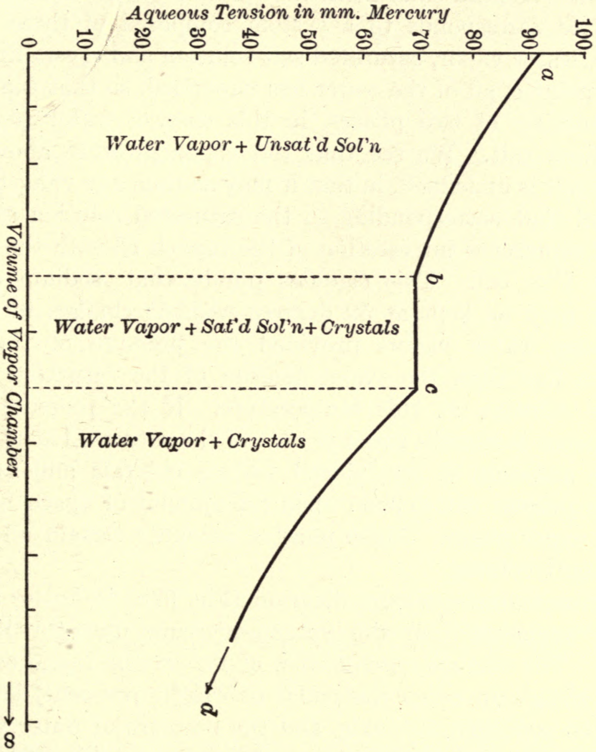

FIG. 97a.

measured by the length to which the piston has been drawn out, is entered upon the horizontal axis, and the corresponding pressure of the water vapor in the gas chamber, shown by our manometer, is entered upon the vertical axis. We see that the volume-pressure curve consists of three distinct branches which correspond to the three different conditions of the system. In the case of a sufficiently dilute solution, *a* (the highest point on the branch *ab*) practically coincides with a point representing the vapor tension of pure water at this temperature. Between *a* and *b* we have a system composed of two phases — vapor and solution of salt in water; the latter increasing in concentration as the pressure falls. The solution has reached its maximum concentration at the point *b*, and, beginning with this point, we note the added presence of crystallized sodium chloride in the system. Thus, the horizontal portion *bc* corresponds to a system composed of three phases, namely, water vapor, saturated salt solution and crystallized salt. At the point *c*, all of the water has vaporized, so that the system again consists of two phases, in this case, of water vapor and crystallized salt. We see that the vapor pressure above crystallized salt is undefined, in that it may assume any value between zero and that corresponding to the saturated solution at *c* (the point *d* represents intersection of the branch *cd* with the volume axis at $V = \infty$). This signifies purely that sodium chloride crystals may be kept at 50 degrees without change, in a space containing water vapor, provided the pressure of the water vapor is less than the vapor tension of the saturated sodium chloride solution at this temperature. If the pressure of the water vapor is exactly equal to that of the saturated solution, the relative amounts of crystallized sodium chloride and saturated solution present will depend upon the amount of space available for the vapor phase. These relative amounts remain unchanged at constant volume.

A concentration-pressure diagram (Fig. 97b) is better adapted to our purposes than the volume-pressure diagram just discussed. The *average concentration of the existent liquid and crystalline phases* (in either molecular or weight per cent) is entered along the concentration axis, and the pressure of water vapor in equilibrium with the other phases at this temperature (50 degrees) is entered along the pressure axis. Here, as in the previous case, the portion *ab* corresponds to equilibrium between solution (pure $NaCl + H_2O$) and vapor, and the horizontal portion *bc* corresponds to equilibrium between solution (pure $NaCl + H_2O$), crystallized sodium chloride (pure) and vapor. The portion *cd* here coincides with the pressure axis, in accordance with the capability of vapor at different pressures to remain in equilibrium with pure sodium chloride. Conversely, if a system shows the relations represented in the two preceding figures, we are at liberty to draw the conclusion that we are dealing with a pure salt, *i.e.*, that the salt forms no compound, or hydrate, with water.

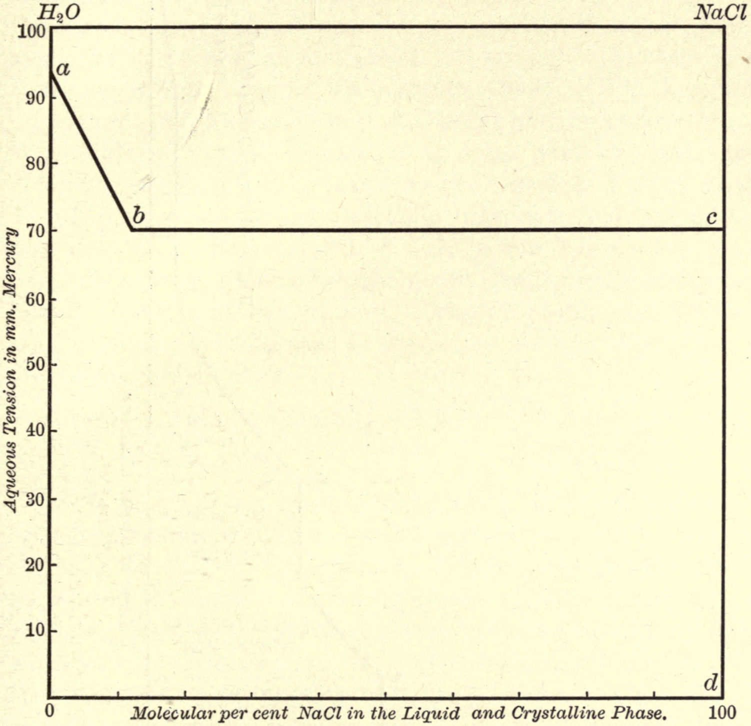

FIG. 97b.

We will now proceed to consider the vapor-tension values for all possible concentrations in the system copper sulphate-water at constant temperature. Fig. 98a gives the approximate course of the volume-pressure curve for this system. On continually increasing the volume of the gas phase, we obtain here, as in the case previously considered, an increasing depression of vapor pressure corresponding to the branch *ab* of the curve (Fig. 98a), until the saturation concentration of the solution is reached, and crystallization of blue vitriol ($CuSO_4 + 5\,H_2O$) first sets in. The

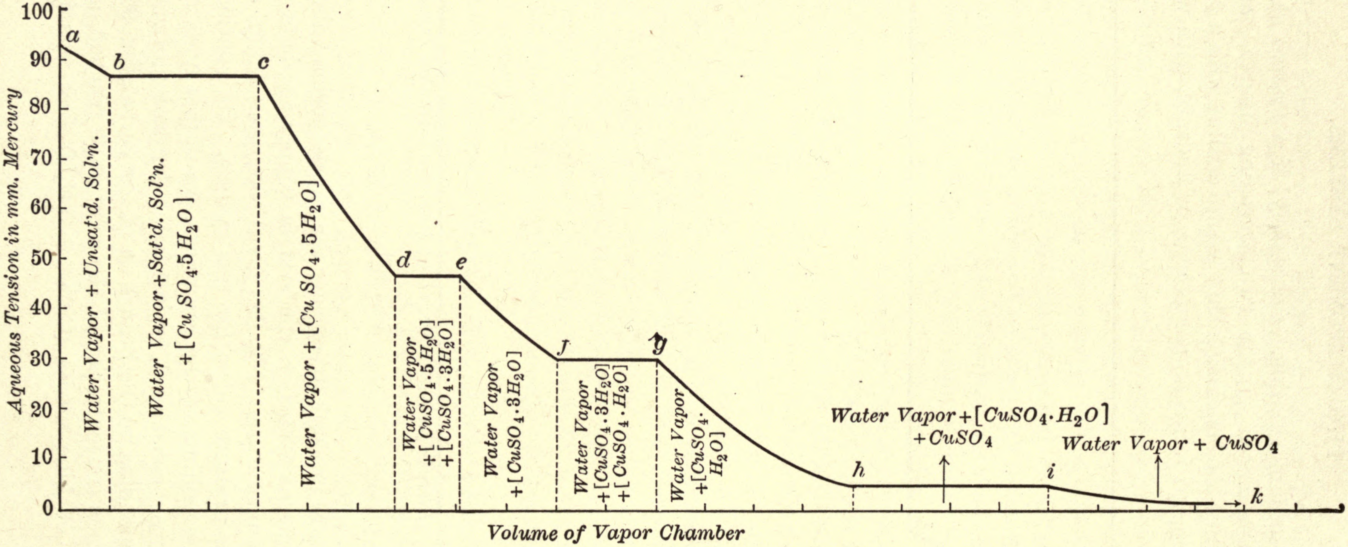
Aqueous Tension in mm. Mercury
100
90
80
70
60
50
40
30
20
10
0
a
b
c
d
e
f
g
h
i
k
Water Vapor + Unsat'd. Sol'n.
Water Vapor + Sat'd. Sol'n. + [$Cu\,SO_4 \cdot 5\,H_2O$]
Water Vapor + [$Cu\,SO_4 \cdot 5\,H_2O$]
Water Vapor + [$CuSO_4 \cdot 5H_2O$] + [$CuSO_4 \cdot 3H_2O$]
Water Vapor + [$CuSO_4 \cdot 3H_2O$]
Water Vapor + [$CuSO_4 \cdot 3H_2O$] + [$CuSO_4 \cdot H_2O$]
Water Vapor + [$CuSO_4 \cdot H_2O$]
Water Vapor + [$CuSO_4 \cdot H_2O$] + $CuSO_4$
Water Vapor + $CuSO_4$
Volume of Vapor Chamber

FIG. 98a.

pressure of water vapor above the saturated solution amounts to 87 mm. at this point, and, corresponding to the horizontal portion *bc*, remains constant, in spite of continued elevation of the piston, until the last drop of solution has disappeared. All of the copper sulphate is now in the form of solid hydrate, $CuSO_4 + 5\,H_2O$. On further enlarging the gas chamber, a lowering of vapor pressure along the curve *cd* is at first noted. However, this lowering will continue only as long as the hydrate, $CuSO_4 + 5\,H_2O$, remains unchanged. Such a condition is realized at pressures above 47 mm. When this pressure is reached, it is noted that the manometer indicates no change in pressure as the piston is further raised. This is represented by the horizontal branch *de*, and is due to the fact that blue vitriol ($CuSO_4 + 5\,H_2O$) now loses water, either partially or completely (the subsequent description supplies positive information in this respect). Assuming that the former is true, in that two molecules of water are lost at this point, we may write the equation:

$$\underset{\textbf{Cryst.}}{(CuSO_4 + 5\,H_2O)} \rightleftarrows \underset{\textbf{Cryst.}}{(CuSO_4 + 3\,H_2O)} + \underset{\substack{\textbf{Water vapor at}\\ \textbf{47 mm. pressure.}}}{2\,H_2O}, \quad (t = 50°),$$

to cover this new condition of complete equilibrium. Elevation of the piston causes reaction to take place from left to right; it effects a decrease in the amount of water-rich hydrate, and an increase in the amount of lower hydrate and water vapor, without changing the composition of any phase; for, as long as a crystal of water-rich hydrate remains, the vapor pressure cannot fall below the value at which this hydrate loses water. When the last crystal of water-rich hydrate has disappeared, however, further elevation of the piston causes dilution of the water vapor, and, therefore, lowering of its pressure (along *ef*), until the hydrate, $CuSO_4 + 3\,H_2O$, begins to lose water. This decomposition occurs at 30 mm., and a third period of constant vapor pressure ensues, according to the equation:

$$\underset{\textbf{Cryst.}}{(CuSO_4 + 3\,H_2O)} \rightleftarrows \underset{\textbf{Cryst.}}{(CuSO_4 + 1\,H_2O)} + \underset{\substack{\textbf{Water vapor}\\ \textbf{at 30 mm. pressure.}}}{2\,H_2O}, \quad (t = 50°).$$

The above period continues until the last crystal of hydrate, $CuSO_4 + 3\,H_2O$, has become transformed into the lowest hydrate, $CuSO_4 + 1\,H_2O$. Not until then, can further increase in volume cause renewed lowering of vapor pressure. The course of this fourth lowering is indicated by the curve *gh*. Thus, it continues until a pressure of 4.4 mm. is reached, when the last molecule of water is lost, and a fourth period of constant pressure is shown by the manometer. This is indicated by the horizontal *hi*, and ceases when the very last trace of water has entered the gas phase. The equation of the reaction is as follows:

$$\underset{\text{Cryst.}}{[CuSO_4 + 1\,H_2O]} \rightleftarrows \underset{\text{Cryst.}}{CuSO_4} + \underset{\substack{\text{Water vapor at}\\ \text{4.4 mm. pressure.}}}{1\,H_2O}, \qquad (t = 50°).$$

Continuous decrease of vapor pressure toward the zero limit accompanies further (continuous) increase in volume. This is

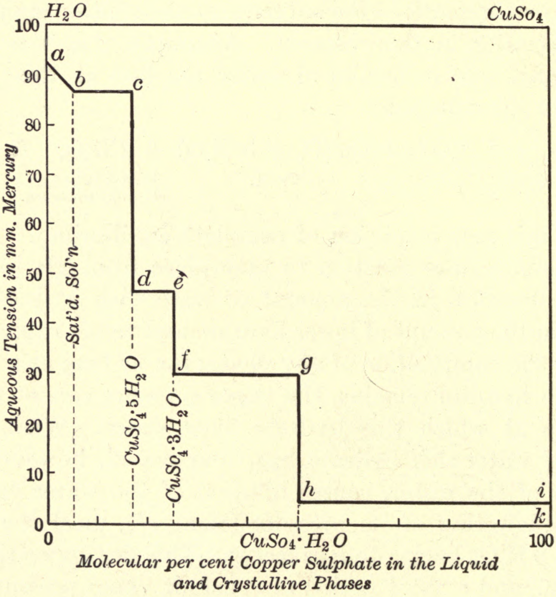

FIG. 98b.

indicated by the branch *ik* which approaches the volume axis asymptotically.

Fig. 98b shows the arrangement of these results in a concentration-pressure diagram. As in the analogous diagram, Fig. 97b, the average concentration of existent liquid and crystalline phase, expressed in molecular per cent, is entered along the axis of abscissas. Corresponding breaks in both curves, 98a and b, are lettered in the same manner. We again recognize the fact observed relative to the system $NaCl-H_2O$ that a single crystalline variety may be in equilibrium with water vapor at varying pressures.

Thus, the hydrate, $CuSO_4 + 5\,H_2O$, is in equilibrium (at 50 degrees) with water vapor of any pressure between *d* and *c*, *i.e.*, it may remain infinitely long in contact with water vapor at any of these pressures, without efflorescence or deliquescence. If a vapor pressure *c* exists in the gas chamber, it then depends upon the relation of the size of the latter to the quantity of water present in the system whether the copper sulphate will occur as saturated solution, as crystallized hydrate, $CuSO_4 + 5\,H_2O$, or as a mixture of both. If a vapor pressure *d* exists in the gas chamber, the same is true with respect to the two phases, $CuSO_4 + 5\,H_2O$ and $CuSO_4 + 3\,H_2O$. Thus, the vapor pressure is definitely fixed for any given concentration value only when an amount (even though trifling) of the second phase (saturated solution or another hydrate) is present. Consequently, it is incorrect, at least in principle, to speak of an aqueous tension of the hydrate, $CuSO_4 + 5\,H_2O$, for example, without adducing further information as to whether this is the tension at which the crystals may absorb water (*deliquesce*) or that at which they may lose water (*effloresce*). We shall, nevertheless, simply designate the aqueous tension of a hydrate as that tension at which it may lose water, *i.e.*, that which corresponds to equilibrium with the lower hydrate. In this sense, the tension of the horizontal *bc* is that of the saturated solution; *de*, that of the hydrate, $CuSO_4 + 5\,H_2O$; *fg*, that of the hydrate, $CuSO_4 + 3\,H_2O$; and *hi*, that of the hydrate, $CuSO_4 + 1\,H_2O$.

We accordingly perceive that there are as many different hydrates, if the saturated solution be included in the total, as horizontal portions in our step-formed vapor-pressure curve, and it follows that, in the determination of the relation between vapor pressure and concentration, we possess a means of ascertaining the number of compounds which a given salt forms with water.

Possible complications will not be considered. The experimental determination may be carried out by simply placing hydrates which have been deprived of successively increasing amounts of water in the vacuum of a barometer tube and measuring the decrease in height of the mercury column after pressure has reached self-adjustment. The determination may be made in many other ways, however.[1]

An investigation by ANDREA[2] has served to dispel any possible doubt relative to the occurrence of discontinuous change in vapor tension, as above. Such change is wedded to the condition that one phase disappear completely at a given temperature, and that another take its place, as may be seen at once from the diagram (Fig. 98b). Thus, in concentrations to the left of *cd*, the saturated solution is stable in the presence of hydrate, $CuSO_4 + 5\ H_2O$, and in those to the right of this line the hydrate, $CuSO_4 + 3\ H_2O$, is stable in the presence of penta-hydrate. Consequently, a condition of practical immiscibility must characterize the mutual relations of the phases. If such is not the case, we are confronted by relations such as those occurring between *a* and *b*, according to which the composition of the liquid phase and the vapor pressure vary continuously from pure water *a* to saturated solution *b*. This class of relationship between two hydrates will accordingly find expression in the general diagram.

If our system is composed, in a general sense, of a volatile and a practically non-volatile substance, in place of water and a salt, we may obviously make use of the practical information outlined above in determining whether chemical combination occurs between these components or not. Any appearance of the non-volatile component in the gas phase (either in the pure state or as a compound) is precluded, however, if the method is to be adjudged reliable. The relations in other systems may be much more complicated. This method has been of little service in metallographical investigation, since the vapor pressure of most metals is extremely small, except at such high temperatures that very considerable experimental difficulty is connected with its determination. The above detailed description of this method has been introduced chiefly in consideration of the method to be described under 6.

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[1] Compare, for example, MÜLLER-ERZBACH, Z. phys. Chem., 19, 135 (1896).

[2] ANDREA, Z. phys. Chem., 7, 241 (1891).

5. DETERMINATION OF THE SOLUBILITY OF A COMPONENT. — The comprehensive analogy which characterizes the behavior of gases and of solutions has been brought prominently into view with the development of physical chemistry. A particularly sharp expression may be given to this analogy by defining the vapor condition as solution of a substance in space, or in vacuum. If, in dealing with a system composed of two components, one of which is alone soluble in a third indifferent substance called solvent, we prepare a solubility-concentration diagram at constant temperature, relations of the same general nature as those characterizing the vapor pressure-concentration diagram (discussed under 4) will be encountered. ABEGG and HAMBURGER[1] investigated the polyiodides of the alkali metals in this way, using benzine as solvent. This method has also found no application in the study of metallic alloys.

6. DETERMINATION OF ELECTROLYTIC SOLUTION TENSION. — Chemical change is invariably associated with the solution of a metal in any other substance which is not a metal, for example, in water, so that it is impossible to recover the metal from its solution by crystallization. NERNST has shown that the experience gained from investigation of ordinary solution processes, *e.g.*, the solution of sugar in water, may, nevertheless, be used to explain the process of solution of metals in water, by ascribing a so-called electrolytic solution tension to the metal in place of the ordinary solution tension associated with other substances. The electrolytic solution tension of a metal represents the tendency of the latter to pass into solution, not as molecules, but as positive ions, and plays fundamentally the same rôle as vapor tension and ordinary solution tension (discussed under 4 and 5, respectively). Thus, if we have a system of two metals, one of them possessing a strong tendency to pass into the ionic condition, and the other possessing practically no such tendency, we are in a position to obtain complete information regarding the mutual relations of the two metals at the corresponding temperature by working out an "electrolytic solution tension-concentration diagram." The metal of considerable solution tension is called a base metal, while that of inappreciable solution tension is called a noble metal. Viewing Fig. 97b in the above light, *i.e.*, as electrolytic

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[1] ABEGG and HAMBURGER, Z. anorg. Chem., 50, 403 (1906).

solution tension-concentration diagram, in which the concentration axis is graduated in atomic per cents of the noble metal B, we must recognize solubility of the two metals within the concentration range a–b. Within the concentration range b–c, we consider the alloy to consist of a mixture of two varieties of saturated mixed crystals, one possessing the concentration a, and the other practically identical with the (pure) noble metal. Fig. 98b, viewed in this connection, subscribes, moreover, to the existence of three compounds between these metals, of the respective formulas, A_5B, A_3B and AB.

The solution tension value defines, within range of an additive constant,[1] the potential difference between the alloy in a solution of the base metal of definite ionic concentration, and any normal electrode. Thus, a continuous or an abrupt change in solution tension corresponds to a continuous or an abrupt change in such potential difference, and the prosecution of this method lies, for the most part, in the direction of potential measurement. According to SACKUR,[2] the relation between the solution tension of a pure metal A and that of an alloy of this metal with a second metal B may be established by experimental determination of the equilibrium concentrations up to which the metal A, on the one hand in pure condition and on the other hand alloyed with B, is capable of displacing the metal B from its salt solution.

The method of determination of electromotive force for investigating the constitution of alloys was first applied by LAURIE,[3] and later by HERSCHKOWITSCH,[4] who was able to eliminate one of the possible sources of error[5] connected with Laurie's experiments. Nevertheless, it is scarcely possible to reconcile Herschkowitsch's results with those obtained by thermal methods. On the other hand, BIJL[6] (see p. 206), in an investigation of cadmium amalgams, obtained complete agreement between results based upon the determination of electromotive force and those furnished by the melting-point diagram. Moreover, he was able, by means of the former method, to follow the course of the curve of separation, relative to limited miscibility of the com-

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[1] Compare, however, NERNST, Z. phys. Chem., 22, 539 (1897).

[2] SACKUR, Z. Elektrochem., 10, 522 (1904); Ber., 38, 2186 (1905).

[3] LAURIE, Jour. Chem. Soc., 65, 1031 (1894).

[4] HERSCHKOWITSCH, Z. phys. Chem., 27, 123 (1898).

[5] OSTWALD, Z. phys. Chem., 16, 750 (1895).

[6] BIJL, Z. phys. Chem., 41, 641 (1902).

ponents in the crystalline condition, down to a point corresponding to ordinary temperature. Absolute agreement between the results of both methods cannot be expected, for, obviously, reactions of low velocity, or of very inconsiderable heat tone, may be overlooked in thermal investigation. Evidently, a parallel method for determining the constitution of metallic alloys, which shall apply to completely solidified mixtures (supplementing the microscopic method), is greatly to be desired for purposes of comparison, since, in the event of general agreement between the different classes of results, our final conclusions would acquire a greater degree of credibility, bordering upon certainty, and then, again, eventual differences in this connection would point to the occurrence of reactions which had escaped observation thermally.

Relative to the value along these lines of the method now under discussion, we may state that it possesses an advantage over the methods which are based on conductivity determination in that its theoretical foundation has been accurately established. The preliminary condition that all reactions shall have proceeded to completion is also essential here. Determinations may be rendered more difficult by the occurrence of passivity phenomena, according to which the metal in question exhibits a more noble behavior than it should, in consequence of conditions which are not well understood. This defect could invariably be overcome, however, by a suitable choice of electrolyte, or by operating at an elevated temperature. Care should always be taken that the measured value of electromotive force actually represents the end value. Bijl observed that in some cases this was true only after several days had elapsed. The circumstance that a relatively small change in electromotive force corresponds to a considerable change in electrolytic solution tension (an increase of $\frac{0.058}{n}$ volts in the electromotive force of an n-valent metal corresponds to a ten-fold increase in its solution tension at room temperature) cannot, in view of the great accuracy which characterizes the experimental determination of potential differences,[1] be generally regarded as prejudicial to the application of this method.

[1] Compare in this connection, Richards and Forbes, Z. phys. Chem., 58, 683 (1907).

7. Determination of Heat of Formation. — If chemical combination between two substances is accompanied by considerable heat evolution, different heat effects will be observed when the compound, on the one hand, and the components in uncombined condition in corresponding proportions by weight, on the other hand, are dissolved. This difference, neglecting heat of mixture, is equal to the heat of combination of the substances. Of course, we assume primarily that the final nature of the solution is the same in both cases. Thus, the observation that temperature elevation accompanies solution of many anhydrous salts in water frequently finds explanation in the formation of hydrates. This method has not yet been successfully used for investigating the structure of metallic alloys (concerning experimentation, compare Herschkowitsch, l. c.).

8. The Method of Analysis of Residues. — When the components of a compound offer varying resistance to the action of a certain chemical reagent, the compound is generally more resistant than the least resistant component. It is, therefore, possible, if the alloy contains the less resistant component in excess, to dissolve out the same, leaving pure compound, which latter may then be analyzed. This process is called the method of analysis of residues. Much use has been made of it in the past; frequently to good effect. Thus, Mylius, Förster and Schoene[1] isolated the iron carbide which is known as cementite, Fe_3C (see p. 228), in this way. Use of the method has, however, led to erroneous conclusions in numerous other cases.

Determination of the relative susceptibility of alloys of various concentrations to chemical action by acids[2] rests upon the same basis. When two metals do not unite chemically, such susceptibility is a continuous function of the composition of the alloys, while, if a compound occurs, it undergoes discontinuous change at the concentration corresponding to the composition of the compound.

Finally, we note that the development of structure on polished sections also rests upon the same basis.

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[1] Mylius, Förster and Schoene, Z. anorg. Chem., 13, 38 (1896).

[2] Sackur, Z. Elektrochem., 10, 526 (1904): Ber. 38, 2186 (1905).

CHAPTER IV.

THREE COMPONENT SYSTEMS.

GRAPHICAL representation of the composition of a three component system is best effected, according to Gibbs, by using an equilateral triangle[1] (Fig. 99). Familiarity with the following geometrical properties is essential in this connection.

(1) In an equilateral triangle, the sum of three lines drawn from a point P in the interior of the triangle perpendicularly to the three sides, respectively, is equal to the altitude h.

$$PD + PE + PF = h \text{ (Fig. 99).}$$

Proof: Divide the triangle into three small triangles PBC, PAC and PAB by the dotted lines PA, PB and PC. Denoting the length of a side of the large triangle by s, the areas of the three small triangles are given by the expressions:

$$s \cdot \frac{PD}{2},\ s \cdot \frac{PE}{2} \text{ and } s \cdot \frac{PF}{2},$$

respectively. The sum of these areas is equal to the total area of the large triangle:

$$s\left(\frac{PD}{2} + \frac{PE}{2} + \frac{PF}{2}\right) = s \cdot \frac{h}{2},$$

whence follows the truth of the above assertion.

(2) If lines are drawn through P, parallel to the three sides respectively, viz., PG, PH and PI, the relationship

$$PD : PE : PF = PG : PH : PI$$

holds, and further:

$$PG + PH + PI = s.$$

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[1] Triangular coördinate paper has recently been offered for sale by SCHLEICHER & SCHÜLL, Düren. (The filter paper manufactured by this firm is familiar to the American trade. — Trans.)

The proof is based upon similarity of the triangles *PDG*, *PEH*, *PFI* and *AKB*.

With the aid of these theorems, we are able to express the composition of a three component system according to weight, or atomic per cent by means of a point in the interior of the triangle.

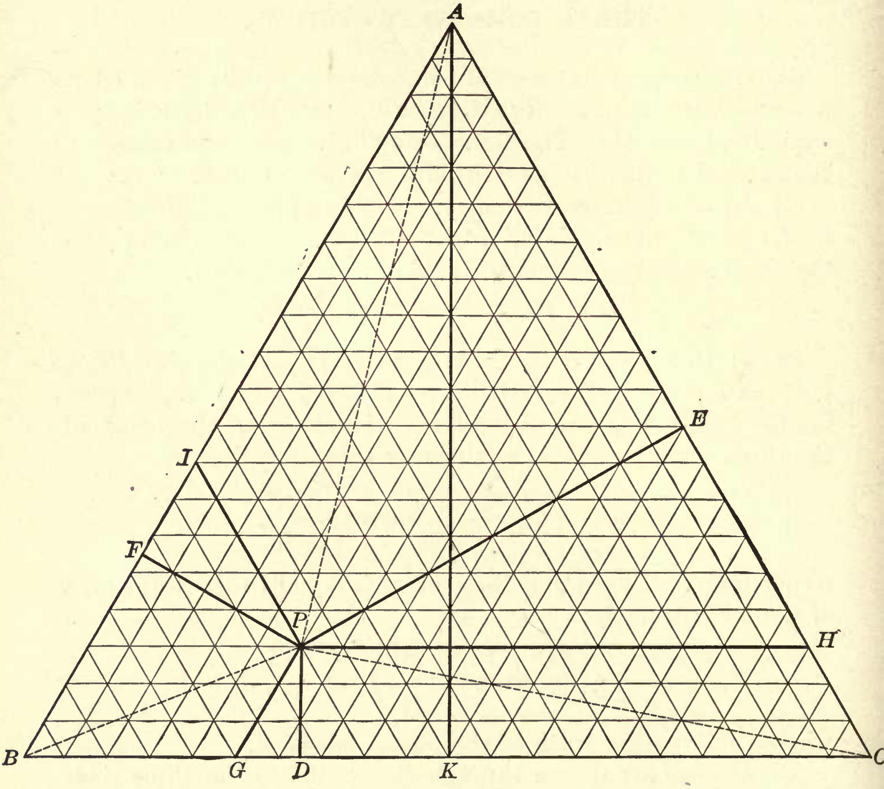

Fig. 99.

The corners *A*, *B* and *C* are intended to correspond to the pure components *A*, *B* and *C*. We associate a point *P* with each mixture such that its vertical distance

PD from the side *BC* denotes the *A*-content,
PE from the side *AC* denotes the *B*-content and
PF from the side *AB* denotes the *C*-content of the mixture.

Since $PD + PE + PF = h$, we obtain the content in percentage figures by using $\frac{h}{100}$ as a unit of measure.

It follows from Theorem 2 that distances PG, PH and PI, which are parallel to the individual sides, may be used as well in locating the composition of a mixture corresponding to the point P of the diagram. Since the sum of these three distances is equal to s, we must choose $\frac{1}{100}$ of s as unit of measure for percentage figures in this case. The relationship,

$$PD : PE : PF = PG : PH : PI,$$

shows that both methods of representation lead to identical results, *i.e.*, the point P corresponds to the same mixture in either case.

The points A, B and C correspond to pure substances as noted above. Therefore, these points are 100 units distant from the opposite (respective) sides. The sides AB, BC and AC correspond to binary mixtures of A and B, B and C, and A and C, respectively.

We perceive that the melting-point diagram of a ternary system cannot be drawn on a plane surface, but requires a third dimension for its construction. To this end, we imagine the temperature axis drawn at right angles to the plane of the paper. We then obtain a spacial model of prismatic form, the three sides of which are formed by the two component systems A–B, B–C and C–A.

§1. THE LIQUID STATE IS CHARACTERIZED BY COMPLETE MISCIBILITY; THE CRYSTALLINE STATE BY COMPLETE IMMISCIBILITY.

A. *The Components do not Unite to Form a Chemical Compound.*

When a molten alloy consisting of three components which bear the mutual relationship given in the above heading is allowed to cool, crystallization usually begins with the separation of a single material. Let this be the substance A in the present instance. After a time, separation of the second substance B begins, and finally that of the third substance C. From this time on, the melt is saturated with its three constituents and solidifies at a minimum constant temperature without change in composition, as ternary eutectic, just as we have observed in the case of binary eutectic crystallization. The cooling curve of a ternary alloy will, then, in general, show two breaks *a* and *b* (Fig. 100) and a halting point *cd*. During separation of the component *A*, the quantitative relation between the two components *B* and *C* in the melt remains unchanged. The compositions of such mixtures as show constant proportion between their *B*- and *C*- contents, in connection with changing *A*- content, are given by the points of a straight line drawn through *A*. (Proof of this is taken from Fig. 101. Similarity of the triangles AP_1D_1 and AP_2D_2, on the one hand, and of the triangles AP_1E_1 and AP_2E_2, on the other hand,

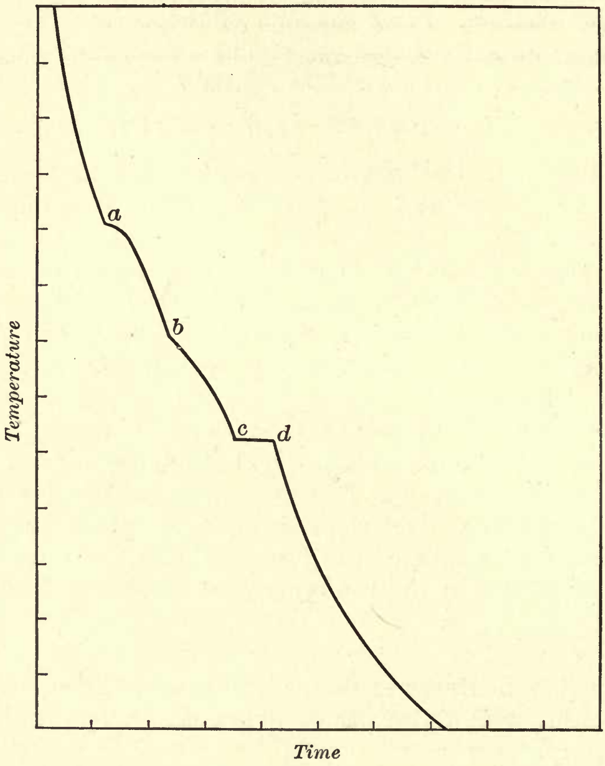

FIG. 100.

gives rise to the proportions $\frac{P_1D_1}{P_2D_2} = \frac{P_1A}{P_2A} = \frac{P_1E_1}{P_2E_2}$, from which the truth of the above assertion, *i.e.*, that $\frac{P_1D_1}{P_1E_1} = \frac{P_2D_2}{P_2E_2}$, is at once evident.)

Thus, the change in concentration of the melt is defined when it is known which constituent at first separates, as long as this crystalline variety alone separates. In order to become familiar with subsequent change in concentration, the concentration of the ternary eutectic must first be ascertained. Let this be given by the point E in Fig. 102. This is the concentration at which the melt is saturated with all three substances, as we have seen above, and on this account is definitely fixed, while here the alloy possesses a minimum freezing point. Moreover, let E_1, E_2 and E_3 represent the concentrations of the binary eutectics composed of A and B, A and C and B and C, respectively. Now, for example, addition of C to the eutectic E_1, composed of A and B, will occasion a lowering of the melting point of this eutectic, as well as, in general, a change in the proportion of A to B in the A- and B-saturated melt. The concentration change sustained by a melt which is already saturated with two components, when increasing amounts of the third component are added, is given by the respective curve E_1E, E_2E or E_3E. These three curves must meet at the ternary eutectic point, which represents a melt saturated with all three components. When the positions of these

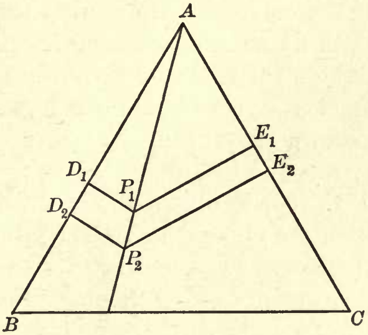

FIG. 101.

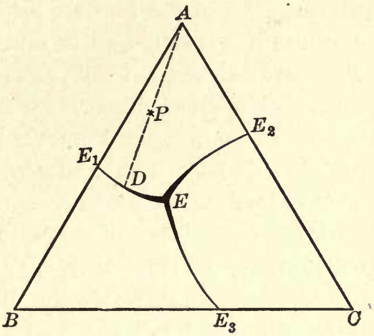

FIG. 102.

three curves are known, we are able to fully determine the concentration changes which a melt of composition corresponding to a point *P* (Fig. 102) will undergo. Along the line *PD*, obtained by prolongation of *AP*, the crystalline variety *A* separates from the melt. At *D*, this line meets the curve E_1E, giving the composition of melts which are saturated with the two varieties *A* and *B*, and simultaneous separation of *A* and *B* follows, with concentration change along the curve *DE*, until, at *E*, the remainder of the melt solidifies without further concentration change to ternary eutectic. The direction of falling temperature is indicated in Fig. 102 by increasing thickness in the corresponding curves. As to the relative amounts of eutectic, we note that the maximum is reached at *E*, and that a linear decrease occurs from *E* toward the sides of the triangle, where the zero value is reached, there being only one or two components present in these localities. These amounts might be shown graphically by using a pyramid of base *ABC* and apex *E*.

A spacial model, as given in Fig. 103, is obtained when the initial temperatures of crystallization are entered at right angles to the plane of the paper. The three corners *A*, *B* and *C* of the prism, correspond, as regards height, to the melting points of the pure components. The lateral walls represent three binary systems, showing eutectics at the three concentration-temperature points E_1, E_2 and E_3. The three curves E_1E, E_2E and E_3E which begin at these eutectic points correspond to incomplete equilibrium of two concurrent crystalline varieties with the melt. All three run at constantly decreasing temperature from the outside points into the ternary eutectic point *E*, which, as we have seen, corresponds to complete equilibrium of the three crystalline varieties with melt. At all temperatures below *E*, the melt is completely crystallized. The three curves E_1E, E_2E and E_3E, along which a given pair of crystalline varieties are in equilibrium with the melt, represent the lines of intersection of a respective pair of surfaces, each of which characterizes the equilibrium between a single crystalline variety and melt. Thus, the variety *A* separates primarily at some point upon the surface AE_1EE_2, the variety *B* at some point upon the surface BE_1EE_3 (separated from the former surface by the curve E_1E), and the variety *C* at some point upon the surface CE_2EE_3 (separated from the foregoing surfaces by the curves E_2E and E_3E, respectively). The concentration changes sustained by a melt on cooling have already been discussed. We observe that the curves in Fig. 102 represent projections of the corresponding spacial curves (in Fig. 103) upon the concentration plane.

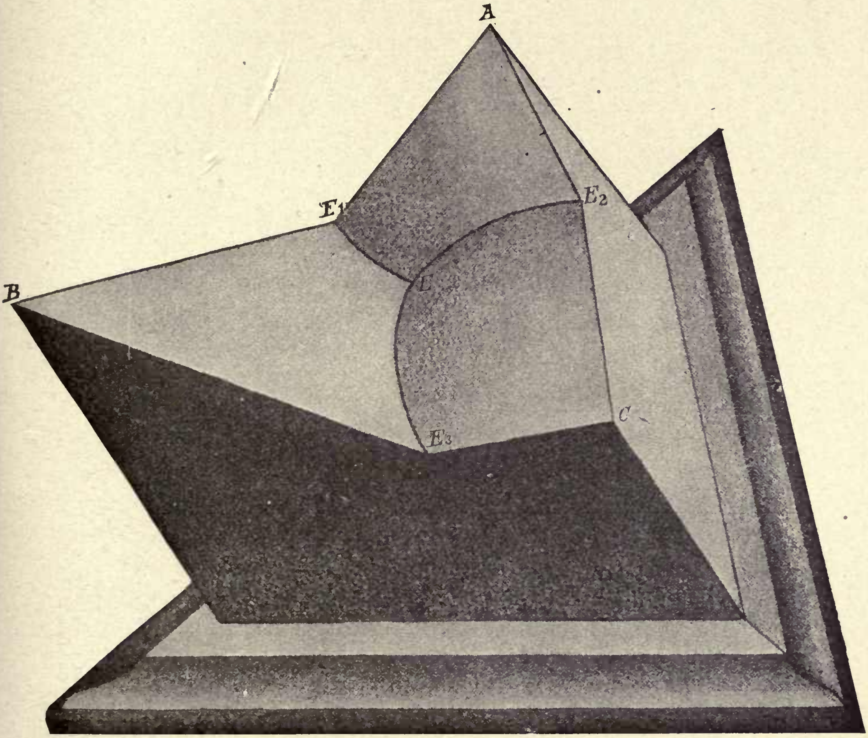

Fig. 103.

Certain deficiencies are recognized in the use of a spacial model as a means of representing solidification processes in a three component system, notwithstanding the general view of associated details which it offers. In particular, the distortions of certain regions which are inevitable when such a figure is represented upon a plane surface often prove annoying. An exact two dimensional representation of the experimental results may be effected by means of supplementary plane sections passed through the three dimensional figure parallel or perpendicular to the temperature axis. The latter method alone will be discussed briefly here. For information relative to the form of sections parallel to the temperature axis, reference may be made to papers by Stoffel[1] and Sahmen and v. Vegesack.[2] Consider that the

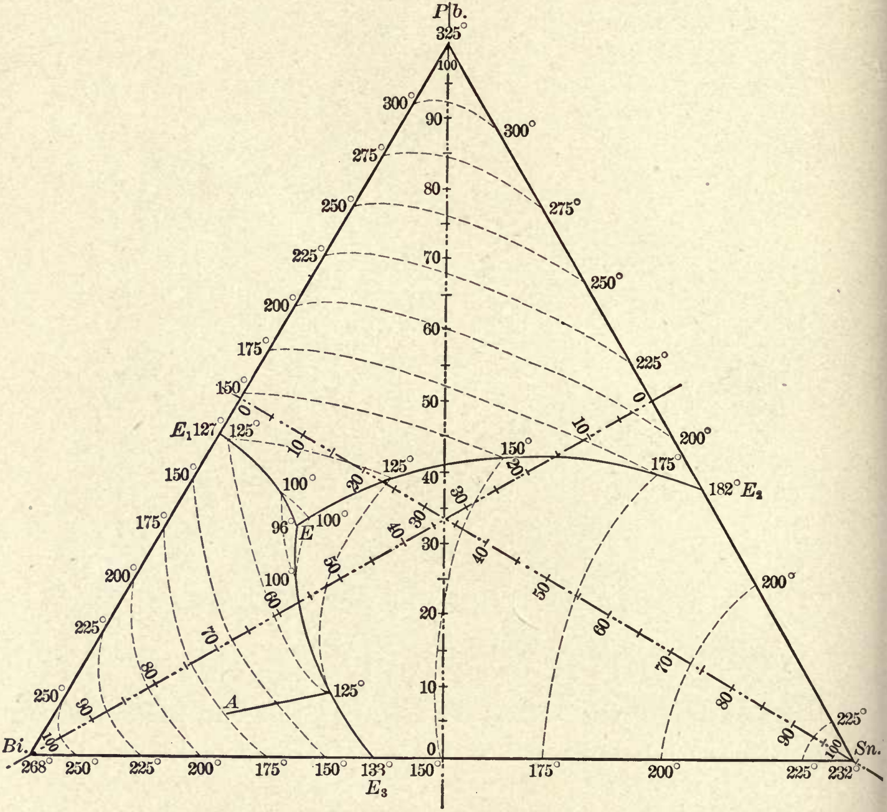

Fig. 104. Fusion Diagram of the System Pb-Bi-Sn, according to Charpy.

model shown in Fig. 103 be cut by horizontal planes at various heights, and that the intersecting lines be projected upon the concentration plane. The diagram given in Fig. 104 is constructed

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[1] Stoffel, Z. anorg. Chem., 53, 156ff. (1907).

[2] Sahmen and v. Vegesack, Z. phys. Chem., 59, 257, (1907)

in this manner and constitutes a fusion diagram of the system Pb-Bi-Sn as determined by CHARPY.[1] The dotted lines are lines of intersection of the horizontal planes with the surface of the spacial model, each joining concentrations of the same temperature of solidification. Hence, they are called isotherms. The temperature of each isotherm is given by associated figures. Each of the crystalline varieties A, B and C is in equilibrium with an unlimited number of melts containing A, B and C at any one temperature, as indicated by each respective isotherm. Projections of the curves EE_1, EE_2 and EE_3 (Fig. 103) appear in Fig. 104 as lines joining the points at which two isotherms corresponding to different crystalline varieties intersect. The eutectic point E lies at the concentration

$$32\% \text{ Pb} - 15.5\% \text{ Sn} - 52.5\% \text{ Bi}$$

and at the temperature 96 degrees. This ternary eutectic is the well known Rose's metal.

Binary and ternary (particularly the latter) alloys of Cu, Sn, Sb, Pb, and Zn are much used in the arts as so-called bearing metals. The friction of metal on metal during rotation of a shaft in its bearings is not completely obviated by the use of lubricating preparations. An ideal bearing metal must possess two leading characteristics. First of all, its coefficient of friction must be small, *i.e.*, it must be hard. At the same time it should adapt itself to the contour of the revolving shaft, *i.e.*, it must be soft or plastic. Obviously a unit material cannot possess these contradictory properties. These special demands may, however, be met by choosing alloys which consist of hard grains embedded in a soft ground mass. Charpy (l. c.) was able to specify the concentration limits within which an alloy is suitable as bearing metal, by means of microscopical examination in connection with determinations of compressibility and brittleness.

B. *The Components when Fused in Conjunction Unite to Form a Chemical Compound which Melts without Decomposition.*

When the two components A and B form a compound A_mB_n which melts without decomposition, the corresponding side wall of the fusion figure will possess the general form given in Fig. 16c

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[1] CHARPY, Contribution à l'étude des alliages (1901), p. 203.

(p. 78). The concentrations of both eutectica are represented by the points E_1 and E_1', respectively, in Fig. 105. Obviously, it is permissible to regard the system, Compound A_mB_n — Component C, as a binary system. Concentrations in this system are located along the connecting line A_mB_n–C. The eutectic A_mB_n–C is at E_4. Each curve in Fig. 105 corresponds to equilibrium between two crystalline varieties and melt. The direction of falling temperature is again denoted by increasing thickness of the lines. Two ternary eutectica must be observed in this case — at E and E'. The former corresponds to the three crystalline varieties A, A_mB_n and C; the latter to B, A_mB_n and C. In the light of the above information, it will not be difficult to construct a special model covering this case. In line with the fact stated on p. 78 that a compound A_mB_n corresponds to a more or less rounded maximum on the melting-point curve rather than to a sharp maximum, the surface of the fusion figure along A_mB_n–C shows a more or less rounded ridge, sinking from A_mB_n to E_4, and then rising again towards C. As C is approached, this ridge rises more sharply, culminating in a sharp point at C. The melting-point diagram may be separated into two independent parts by division along the line A_mB_n-C. Each part corresponds to a three component system without compounds, formed from the components A_mB_n, A, C and A_mB_n, B, C, respectively. According as the initial concentrations of the melts lie above or below the line A_mB_n-C, the compositions of all phases which appear during crystallization remain inside either one or the other of the triangles $(A_mB_n)C\ A$ or $(A_mB_n)C\ B$. On this account, A_mB_n-C may be called the impassable (unüberschreitbar) line. In case the concentration of the melt corresponds to a point upon this line, the same also holds for the phases which appear on cooling (see above).

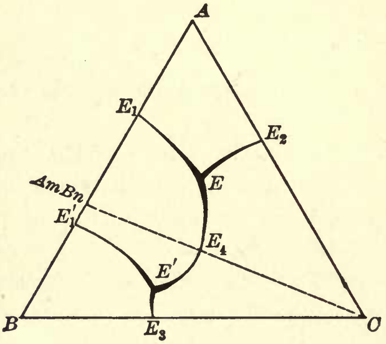

Fig. 105.

A ternary compound will not correspond to a ridge in the fusion figure, but rather to an isolated conical elevation with a more or less rounded off summit, according as the dissociation of the fused compound is more or less marked. When, in addition, binary compounds occur in large or small number, the surface of the fusion figure may appear extremely complicated. Thus far, investigation of ternary systems has not been very comprehensive. Two ternary inter-metallic compounds, viz., $NaKHg_2$ and NaCdHg, have recently been discovered by Jänecke.[1]

§2. Both the Liquid and Crystalline States are Characterized by Complete Miscibility. — Here, we will limit ourselves to the case wherein the solidification curves of the three binary systems correspond to Type I, according to Roozeboom. If then, the three side walls of our prism (Fig. 106) show this type (given in Fig. 56, p. 169), a surface passing through the three *l*-curves will give the initial temperatures of crystallization. Let us now imagine another surface passed through the dotted *s*-curves. Then we have before us the location of temperatures (corresponding to each concentration) at which the alloys become completely solidified (assuming that equilibrium is established with sufficient rapidity). In the region enclosed by the two surfaces, crystals and melt may exist side by side. On cutting the surfaces by a horizontal plane, two isotherms *ab* and *cd* are obtained. Obviously, the former gives the concentrations of melt and the latter the concentrations of mixed crystals. Special experiments are necessary here in order to show in what manner the points of both curves are associated with one another, in contradistinction to the relations presented by the two component system, where, in principle, at least, the equilibrium concentra-

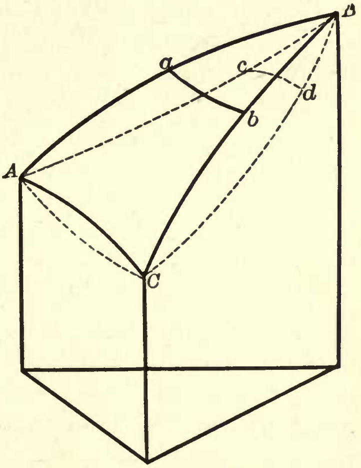

Fig. 106.

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[1] Jänecke, Z. phys. Chem., 57, 507 (1906).

tions are ascertained by simple determination of the beginning and end of crystallization (see p. 172).

No example for this case is known. Boeke[1] has constructed the melting-point diagram for the system, sodium sulphate, -molybdate, -tungstate; but the behavior of these substances does not correspond to the simple conditions discussed above, owing to appearance of a minimum and isodimorphism, as well as to transformations in the crystalline state, whereby the construction of the fusion figure is quite complicated. We are indebted to Schreinemakers[2] for a thorough theoretical treatment of mixed-crystal relations in ternary system.

Finally an investigation by Sahmen and v. Vegesack[3] on the occurrence of mixed crystals in ternary system may be cited.

§ 3. Supplementary. The Phase Rule. — We were able, in case of the ternary system, to make the discussion concise, since no fundamentally new points of view were involved. The behavior of an heterogeneous system, *i.e.*, one composed of several phases, on addition or abstraction of heat, leads to recognition of two sorts of equilibrium, just as before. Either incomplete heterogeneous equilibrium or complete heterogeneous equilibrium may result, according as enforced change in the heat content of the system does or does not bring about temperature change. We have seen that the former condition is realized when at least one of the phases changes its composition,[4] and that the latter condition results when the composition of every phase remains unchanged. In case of the one component system, it was noted that heterogeneous equilibrium is invariably complete, *i.e.*, the temperature at which a unit crystalline material is in equilibrium with its melt is unchangeable at constant pressure, since abstraction of heat, for example, causes only an increase in the amount of material forming the crystalline phase, and a decrease in the amount of material forming the liquid phase, but no change in the composition of either phase. On the other hand, a unit crystalline material is not in complete heterogeneous equilibrium with a melt which is com-

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[1] Boeke, Z. anorg. Chem., 50, 355 (1906).

[2] Schreinemakers, Z. phys. Chem., 50, 169 (1905); 51, 547 (1905); 52, 513 (1905).

[3] Sahmen and v. Vegesack, Z. phys. Chem., 59, 265 (1907).

[4] Compare in this connection the discussion on p. 213.

posed of two substances. We have met with many examples of this condition.

It may be deemed sufficient, in this connection, to refer again to the earlier discussion (*cf.* p. 38 *et seq.*) relative to the freezing of a solution of common salt. Abstraction of heat effects concentration of the solution, at least at the start, owing to separation of ice, and attendant lowering of the freezing temperature. This persists until the temperature has fallen to its eutectic value, at which point salt crystals separate in common with ice crystals. Hereby, the solution is compelled to solidify without change of composition. Thus we see that, while two phases are sufficient for institution of complete heterogeneous equilibrium in a one component system, three are necessary in case of a two component system.

Again, we perceive on further consideration of this example that the appearance of a new phase lessens the possibilities under which the system may be realized, and, therefore, has an effect just opposite to that caused by the entrance of a new substance into the system (the possibility of realizing the particular equilibrium in question being greater, in the latter case). The two-phase system, Ice-Water, is realizable at 0 degrees only, under atmospheric pressure. The system, Ice-Common Salt solution, is realizable between the limits 0 degrees and − 22.4 degrees, under atmospheric pressure. This is a two-phase system, as is the former, but contains one more substance, common salt. The system, Ice-Crystalline Salt-Salt solution, on the other hand, can exist at one temperature only, − 22.4 degrees, under atmospheric pressure. The general limitation of the range of existence of a system, following the appearance of new phases, is brought out very plainly in the ternary system shown in Fig. 81. Each surface corresponds to equilibrium between one crystalline variety and melt. Thus, on the surface AE_1EE_2, we have equilibrium between crystalline A and melt. Such systems may be realized at all temperatures between the limits A and E in all concentrations which are defined by projection of the surface upon the concentration plane. For constant temperature, the concentration of the melt is in no way fixed, but may vary at random (see p. 275) within the values given by the corresponding isotherm (Fig. 104).

If a new phase, for example, the crystalline variety B, is added, the range of existence of the system is reduced to the concentrations and temperatures given by a curve — in the current example, by E_1E — which represents the line of intersection of two surfaces (each corresponding to equilibrium between a single crystalline variety and melt). Here, as well, the equilibrium, A crystals-B crystals-Melt, is realizable at all temperatures between E_1 and E, and yet the concentration of the melt is unequivocally fixed (under constant pressure), on specification of the temperature, since this curve is cut at only one point by a horizontal plane.

The curve of incomplete equilibrium E_1E, along which three phases in the three component system are in equilibrium, corresponds to incomplete equilibrium in a two component system consisting of two phases: also given by a curve (see, for example, Fig. 9b). If our three component system sustains addition of the crystalline variety C as fourth phase, its range of existence under constant pressure is limited to the concentration and temperature of the point E, the point of intersection of three curves defining the equilibrium between a single crystalline variety and melt. Thus, at a given pressure, the temperature and concentration of each phase of the system are unequivocally fixed, *i.e.*, complete heterogeneous equilibrium obtains. In the same manner, the binary eutectic is to be regarded as the point of intersection of two curves of incomplete equilibrium between a single (respective) crystalline variety and melt.

To summarize then: when we aggregate the phases which are sufficient in number to determine complete heterogeneous equilibrium in the separate systems, we obtain:

For a one component system	2 phases,
For a two component system......	3 phases,
For a three component system.....	4 phases,

and we conclude that $n + 1$ phases are sufficient in an n-component system for the production of complete heterogeneous equilibrium.[1]

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[1] Under certain conditions (see p. 165 *et seq.*), it is possible for complete heterogeneous equilibrium to occur in a two component system, for example, when only two phases are present. Such a system is therefore to be regarded as a one component system throughout the temperature and concentration ranges in question (*cf.*, in this connection, p. 34 *et seq.*).

These equilibria which we have considered have been limited, for the most part, to such as are made up of liquid or crystalline phases. Change of pressure has relatively little influence upon such equilibria, and we are therefore justified in neglecting the effects of not too great pressure changes. This has been done by regarding the pressure as constant. If, however, we vary the pressure within wide limits — by hundreds or thousands of atmospheres — the resulting effect upon the melting temperature, for example, will be quite considerable. Hence, such complete heterogeneous equilibrium is not immune from all possibility of change, inasmuch as we may change the pressure exerted upon the system, and thereby effect a simultaneous change in the equilibrium temperature. We know from previous experience that the appearance of a new phase invariably limits the range of existence of the system, and we find ourselves in agreement with both theory and practice when we urge that for an n-component system which consists of $n + 2$ phases the pressure is definitely fixed and that, in consequence, the system is not open to alteration, or, more accurately, that any change must cause disappearance of a phase. Since the range of existence of such a completely defined system with respect to pressure, temperature and composition of the separate phases is the smallest imaginable, any further limitation of this range, such as would characterize appearance of another phase, cannot be effected. Thus we see that, in an n-component system, not more than $n + 2$ phases can exist side by side. Indeed, these are capable of coincident existence only at a certain defined temperature and under an equally specific pressure, as has been said before.

Equilibrium between the three states of aggregation of a pure substance, for example, water, may be cited as a simple example of equilibrium in an n-component system, consisting of $n + 2$ phases. We know that under atmospheric pressure the equilibrium temperature for Ice-Liquid Water is 0 degrees, and that the melting point of ice is *lowered* by increase in pressure at the rate of 0.0077 degrees per atmosphere (see p. 7). Thus, the freezing temperature of water under a pressure of 100 atmospheres will be -0.77 degrees. The complete heterogeneous equilibrium, Ice-Liquid Water, may, therefore, be realized at various temperatures, provided the pressure attains a corresponding value. The pressure becomes definite on specification of the temperature, and the temperature on specification of the pressure. If, however, water vapor is included as an additional phase, the above possibility of change is no longer admissible. Ice, liquid water and water vapor are capable of coexistence at the one temperature, + 0.0077 degrees, and under the one pressure, 4.57 mm. (the pressure of saturated water vapor at this temperature). (The insignificance of this pressure in comparison with normal atmospheric pressure is responsible for the fact that the equilibrium temperature rises practically as far above 0 degrees as would correspond to a pressure change of one atmosphere.)

Evidence contradictory to the above statements seems to lie in the observation that the equilibrium Ice-Liquid water-Water Vapor may be realized in a (non-evacuated) space filled with an indifferent gas — air, for example — under a pressure of one atmosphere — moreover, at the temperature 0 degrees in this case, corresponding to the current pressure value of one atmosphere. This apparent contradiction finds an explanation in the fact that air takes part in the equilibrium not only in the gas phase, but also in the crystalline and liquid phases. The ice, as well as the liquid water, will have dissolved quantities of each gas present, in proportion to the partial pressures of these gases, whereby we must of necessity recognize as many independent constituents (components), in addition to the water, as there are gases present. Thus, on these grounds, there is no such thing as an indifferent gas, *i.e.*, one whose presence may be entirely neglected.

This explanation indicates that, before making general application of deductions from the phase rule, certain idealisms must be made regarding our experimental appointments, provided the fusion experiments are not carried out in a vacuum, but in open crucibles (which communicate freely with the atmosphere), as is usually the case. Two assumptions may be made in this connection. The first is that the presence of air be neglected, and that we work in a vacuum, whereby the system must exist strictly under the pressure due to its own vapor. If, for example, we have a solidifying eutectic mixture of two metals in our vessel, there is present, besides the three phases, Crystalline A, Crystalline B and Melt, a fourth or gas phase, and we perceive that, according to the rule previously given, in this system where $n = 2$, a greater number of phases cannot be present at the same time. Pressure (equal to the sum of the partial pressures of the substances concerned), temperature and individual composition of the several phases are completely fixed, according to the above, and cannot be altered, unless accompanied by the disappearance of one of the phases. Such a system is frequently termed a "non-variant system" in the literature, for obvious reasons.

In terms of the second assumption bearing upon this question, we imagine the surface of the melt to be protected from contact with the atmosphere by means of a perfectly articulating and impervious piston. The atmospheric pressure, which operates upon the piston from above, may then be regarded simply as mechanical pressure directed against the system. Thus, the gas phase is assumed to be entirely absent. Previous conclusions have been based upon this conception. Considering the binary eutectic from this standpoint, we see that equilibrium is complete. There are n (= 2) + 1 = 3 phases participating, namely, Crystalline A, Crystalline B and Melt. A definite mechanical pressure is exerted upon the system, change of which within certain limits causes a shifting of the equilibrium temperature, without coincident disappearance of any phase from the system.

Both conceptions "idealize " *i.e.*, they presume other experimental conditions, than those which areactually observed. Nevertheless, the data to be obtained under actual working conditions differ so slightly from those which would be realized under the strictes tpossible adherence to one or the other of the ideal procedures that we need pay no attention to the above imaginary restrictions in considering experimental results. When possible, experiments are conducted in the medium of a gas which is practically without chemical action upon the melt. It has already been stated (on p. 7) that a change of more than 0.03 degree in melting point per atmosphere pressure change has not as yet been observed.

We have thus arrived at the result that, *neglecting the gas phase*, the greatest number of phases which may be present in an n-component system is $n + 1$. If they are all present at the same time, addition or abstraction of heat under constant pressure can occasion no temperature or concentration change, but merely change in the respective amounts of the several phases. Not until a phase is completely exhausted does further change in the heat content of the system effect concentration change — in at least one phase — accompanied by change in the equilibrium temperature. It is clear that adequate appreciation of these relations effectually simplifies the study of equilibrium conditions. Thus we are able, even though unfamiliar with the actual process of crystallization, to affirm that simultaneous separation of two crystalline varieties from a melt consisting of both substances (eutectic crystallization in a two component system) must proceed at constant temperature, since here, n $(= 2) + 1 = 3$ phases, namely both crystalline varieties and melt, are in equilibrium. We also see that crystallization at constant temperature will not result in a three-component system until four phases are in equilibrium with one another, as is true during the solidification of a ternary eutectic. In the case representing incomplete miscibility in the liquid state and complete immiscibility in the crystalline state (discussed on p. 149), complete heterogeneous equilibrium, viz., constant temperature, must result at the time when a crystalline variety appears in the presence of the two liquid phases. But it is never possible for two crystalline varieties to appear in the presence of both liquid phases, since, in such event, the number of hypothetical coexistent phases would be one too great.

Knowledge of the above principles aids us materially in criticising the structure of solidified alloys. Coexistence of $n+1$ liquid or crystalline phases is possible only at the temperature of equilibrium under the prevailing pressure. If the system is existent at a lower temperature, one of the phases must have become exhausted. Thus, a two component system in equilibrium in the solid condition can show *in maximo* two crystalline varieties; a three component system, three varieties. If more are present, we are dealing with abnormal structure, due to incomplete reaction (see pp. 134, 138). Equilibrium is not at hand in such a system. An exception to the above could obtain only when the temperature at which the sections were under examination chanced to coincide with a temperature of complete heterogeneous equilibrium. This conjecture might be tested, omitting from consideration, however, the circumstance that in general no further changes in the sections occur at ordinary temperature, on the grounds that slight cooling or heating would of necessity cause the disappearance of one or two structure elements.

The relations which have been outlined above are special cases of a general law developed by GIBBS[1] on theoretical grounds; the so-called Phase Rule, according to which the number of Degrees of Freedom (= possibilities of change) F, the number of components n, and the number of phases P, corresponding to equilibrium in a given system, are mutually related as follows:

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

We see, on consideration of this equation, that the appearance of a new phase robs this system of one possibility of change, or Degree of Freedom. Since F cannot assume a negative value, the greatest possible number of coexistent phases (inclusive of the gas phase) is $n + 2$. The above relation holds under an assumption that the system is in equilibrium, whereby a sufficiently rapid rate of reaction throughout all transformation is presumed.

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[1] GIBBS, Thermodynamische Studien (German translation by Ostwald), Leipzig, 1892 P. 115. Trans. Coun Acad., iii, 1875-8.

PART II.

PRACTICE.

CHAPTER I.

THERMAL INVESTIGATION.

§ 1. MEASUREMENT OF TEMPERATURE.

THE use of thermometers based upon the expansion of liquids is not considered in this connection. Thermo-elements, or thermoelectric couples, are best suited to temperature measurement in metallographical work. Small dimensions may be chosen at will in their construction. Thus, they are more sensitive than mercury thermometers in small masses of material on account of their less rapid conduction of heat away from the surrounding mixture. For this reason, they are preferable to thermometers in which a liquid column is used, even at temperatures which are low enough to permit application of the latter type.

Thermo-electric temperature measurement is based upon determination of the electromotive force between the free ends of two metallic wires of different composition, the other ends being fixed in secure contact and heated to the questionable temperature. The junction is usually in the form of a small bead of metal, obtained by fusing the ends of the wires together. The difference in temperature between the junction and the free ends bears a functional relation to the observed electromotive force. If this relation is known, together with the temperature of the free ends, measurement of the electromotive force supplies the data necessary for calculation of the temperature of the junction. For the temperature interval between − 200 degrees and + 600 degrees, thermo-elements giving relatively large electromotive forces for small temperature differences may be advantageously used. A couple consisting of copper or iron joined to a constant is often used for this purpose. For measurements between + 200 degrees and + 1600 degrees the LeChatelier thermo-element, in which one wire is of pure platinum and the other of a platinum-rhodium alloy (platinum 90 per cent — rhodium 10 per cent), is almost universally used. (A thermo-element of pure iridium and an alloy of iridium with 10 per cent ruthenium may be used up to about 2000 degrees). Thermo-elements with accompanying tables giving the electromotive force as function of the temperature, determined at the Physikalisch-Technische Reichsanstalt, are on the market at the present time. The relation between electromotive force and temperature of the junction for a LeChatelier thermo-element, the free ends of which were maintained at 0 degrees, is shown graphically in Fig. 107 according to measurements by Holborn and Day.[1] The horizontal axis is graduated in centigrade temperatures, the vertical axis in millivolts. It may be observed that the electromotive force is not directly proportional to the temperature, on the contrary, its increase per 100

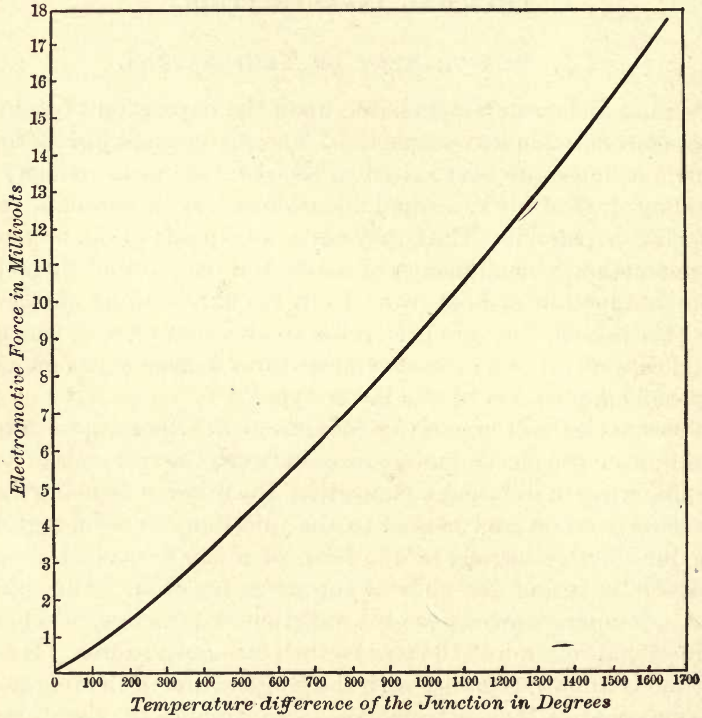

FIG. 107.

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[1] Holborn and Day, Drude's Ann., (2) 505 (1900).

degrees temperature difference is about twice as great at higher temperatures as at lower temperatures. Between 250 degrees and 1100 degrees Holborn and Day (l. c.), were able to represent the relation between electromotive force and temperature with great accuracy by means of a quadratic interpolation formula. Temperatures were measured with an air thermometer up to 1130 degrees. Above this point, no determinations were made, the further course of the curve as represented resting upon the assumption that their interpolation formula remain accurate outside of verified limits. LUMMER and PRINGSHEIM[1] uphold this assumption as a result of their investigation on the laws of black body radiation.[2]

Electromotive forces are measured with a galvanometer, the scale of which is advantageously graduated in degrees centigrade corresponding to the LeChatelier thermo-element with free ends at 0 degrees, as well as in millivolts. This arrangement is extremely convenient, as it obviates considerable calculation. Since the deflection of the needle is proportional to the *electromotive force,* the divisions on the *temperature scale* become larger as the temperature increases. The requisites of an instrument of this sort are rapid adjustment, extreme sensitiveness, and large internal resistance, in comparison with which the resistance in the outside circuit is negligible. The millivoltmeters constructed for this purpose by the firm of SIEMENS and HALSKE, Berlin, possess an internal resistance of approximately 400 ohms and a sensitiveness of 0.1 millivolts per degree (= 0.8 mm.), deflection. These are DEPREZ-D'ARSONVAL galvanometers, consisting of a spool, through which the current to be measured flows, suspended in the field of a strong magnet. The instrument (Fig. 108) is levelled by means of the three-foot screws upon a support which should be free from vibration. After releasing the needle arrest, the pointer should register 0. Trifling variations from the 0 point may be corrected by manipulation of the

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[1] LUMMER and PRINGSHEIM, Physik. Z., 3, 98 (1901).

[2] The validity of this extrapolation is questioned in a recent paper by HOLBORN and VALENTINER, Drude's Ann., (4) 22, 1 (1907). These authors have made direct use of the air thermometer in connection with the thermoelement up to 1600 degrees. Since their results necessitate a revision of the generally accepted value of one of the radiation constants (in Wien's equation), they are not considered here.

adjusting screw at the head of the suspension. If the variation is greater than two scale divisions, proper adjustment is no longer possible, and the instrument must be repaired. Before transportation, care must be exercised that the needle is in arrest. Only when the instrument is in use, should the needle remain in suspension. The zero point is affected by temperature changes. If readings must be made in close proximity to a source of heat, the galvanometer should be protected as far as possible by several sheets of asbestos.

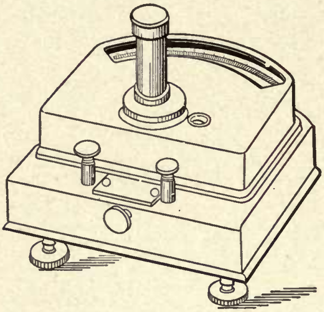

FIG. 108.

Quite recently, the firm of Siemens and Halske has placed a modified form of instrument on the market, which is adapted to a larger range of temperature measurement. This is secured by introducing two separate resistances of approximately 400 and 130 ohms, respectively, either of which may be used by changing the connection. A temperature scale for each connection is given, and the millivolt graduations are omitted.

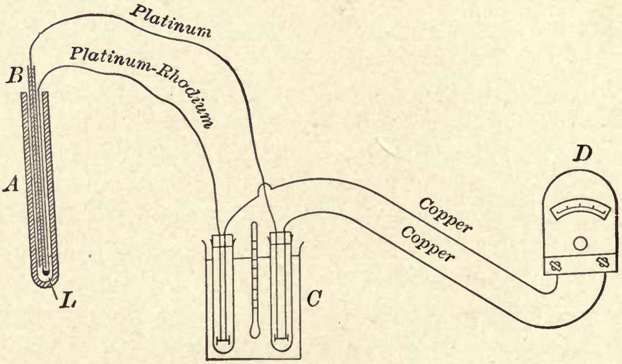

FIG. 109.

A small oxy-hydrogen flame is most satisfactory for joining the two ends of the LeChatelier thermo-element. The junction is shown at *L* in Fig. 109. In the Goettingen laboratory, thin thermo-element wires (of 0.2 mm. diameter), are used, partly on account of reduced expense, and partly by reason of the minimum heat conduction from the melt which can be secured in this way. The thermo-element junction is protected from contact with the molten metal by placing it in a small tube of unglazed porcelain (inside diameter 1.7 mm., outside diameter 2.5 mm., length 15 cm.) closed at the lower end by fusion in the oxy-hydrogen flame. This material may be obtained from the Royal Porcelain Manufactory in Berlin. For temperatures below 800 degrees this tube may be made of difficultly fusible glass, *e.g.*, Jena combustion tubing. (A tube of this sort, which hinders heat transfer between melt and thermo-element, is undesirable except when absolutely necessary. For work with non-metallic substances which do not attack the thermo-element wires, it may often be omitted). Insulation of the two wires inside the protecting tube is conveniently effected by means of thin mica strips. A better arrangement is obtained by enclosing one of the wires with a capillary tube of porcelain, or of other refractory material. Material manufactured for use in the Nernst lamp has served this purpose in the Goettingen laboratory. Short pieces of 0.3 mm. inside and 1 mm. outside diameter in sufficient quantity to perfect insulation inside the protecting tube are very satisfactory.

Both free ends of the thermo-element are connected with heavy copper wires by means of binding posts. These copper wires lead to the voltmeter *D*. The binding-post connections are enclosed in test tubes and placed in a beaker *C* containing water. A thermometer measures the temperature of the bath (free ends of the thermo-element), which may be varied at will, or maintained at 0° C. by adding ice. Attention has been called to the fact that the electromotive force measures the temperature difference between the junction and the free ends of the thermo-element. Consequently, the voltmeter registers the true temperature of the junction only when the free ends are maintained at 0 degrees. If the temperature of the free ends is *t* degrees (measured by the temperature of the water in the beaker *C*), the electromotive force corresponding to the difference between 0 degrees and *t* degrees must be added to the reading from the instrument to obtain the total electromotive force corresponding to the true temperature of the junction. It is more convenient to use the following table prepared by Vogel:[1]

TABLE 7.

Temperature reading of the voltmeter in degrees.	ρ
0	1
100	0.89
200	0.76
300	0.65
400	0.59
500	0.56
600	0.54
700	0.52
800	0.51
900	0.50
1000	0.49

The temperature of the free ends is observed, multiplied by the factor ρ, taken from Table 7, and added to the temperature reading of the voltmeter. This gives the actual temperature of the junction. The decrease in value of the factor ρ corresponds to the increase in electromotive force per degree (Fig. 85) with rising temperature. At temperatures above 500 degrees, sufficient accuracy is obtained by placing $\rho = \frac{1}{2}$. This correction applies to the LeChatelier thermo-element only. Corrections for the copper-constantan thermo-element may be made by adding the total temperature of the free ends to the observed temperature, since with this element the electromotive force is approximately proportional to the difference in temperature between the free ends and the junction throughout its whole range of usefulness.

It is necessary to standardize the thermo-element before use. Where wires as small as 0.2 mm. thickness are used in its construction, as is often desirable in metallographical work, standardization is not undertaken at the Physikalisch-technische Reichsanstalt. Moreover, since it is essential that the readings of the instrument be frequently tested for accuracy, a short description of the method of calibration is hereby presented. For this pur-

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[1] Vogel, Z. anorg. Chem., 45, 13 (1905).

pose, the melting points of the following metals (in pure condition) are used as fixed points:

Lead	326.9[1]
Antimony	630.6[1]
Gold	1064.[1]
Nickel	1451.[2]
Palladium	1541.[3]

Lead, antimony and nickel of adequate purity may be obtained from the firm of *C. A. F. Kahlbaum*, Berlin. The melting points are determined in the usual manner by taking cooling curves. This method may also be chosen for the gold and palladium calibrations. On account of the attendant expense, however, the so-called wire method[1] is usually preferred. This procedure consists in fusing a short piece of the metal in question between the two wires of the thermo-element, in place of the ordinary junction, heating this part gradually up to the fusing temperature of the wire, and continually observing the temperature up to the point where contact is broken by fusion. This temperature is the melting point sought. It sometimes happens that the molten drop of metal remains suspended between the wires for a short time, keeping the circuit closed after fusion, and failing to drop away until a temperature higher than the temperature of fusion has been reached. This method is applicable to none but the noble metals, which are not oxidized in air, and not even to these if their melting points are lowered by the material of the thermo-element. In any case, if a sufficient quantity of material (approximately, 20–30 g.) is at hand, the crucible method (by which cooling curves are taken in the usual manner) is to be preferred, since, aside from added certainty and accuracy, no separation of the two ends of the thermo-element is required.

Results agreeing within 5 degrees may be regarded as satisfactory. It may also be noted in this connection that the use of copper for calibration purposes cannot be highly recommended,

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[1] Holborn and Day, Drude's Ann. (4), 2, 535 (1900).

[2] Ruer, Z. anorg. Chem., 51, 225 (1906).

[3] Nernst and v. Wartenberg, Verhandlungen der deutschen physikalischen Gesellschaft, 8 (1906), p. 48.

since, according to Heyn,[1] the molten metal dissolves copper suboxide (formed when air is incompletely excluded), thereby forming an eutectic which is fusible some 20 degrees lower than the true melting point of the pure metal. According to Callender and Heycock and Neville silver melts and solidifies in an oxidizing atmosphere at a lower temperature than in a reducing atmosphere.[2] The melting points of lead, antimony and gold may be regarded as very definitely fixed. The above determination of the melting point of nickel (1451 degrees) is based upon the palladium melting point, 1541 degrees. The recent measurements of Holborn and Valentiner place this point at 1575 degrees. Acceptation of this figure forces a rejection of the previously used interpolation formula, based upon thermo-electric measurements, and necessitates the introduction of extremely inconvenient corrections. Until this question is settled beyond controversy, it seems desirable to use the value 1541 degrees for the palladium point. The temperature interval above 1100 degrees, as defined by the above fixed points, is, therefore, subject to possible revision on the basis of future work.

The metals chosen for calibration of the thermo-element obviously depend upon the temperature range throughout which it is to be used. Corrections throughout the whole range become approximately linear if the palladium point is placed at 1546 degrees; consequently, two fixed points suffice in the preparation of a complete correction table — perhaps supplemented by an additional point for extra control. A thermo-element may be adequately tested for accuracy by determination of a single fixed point. The gradual decrease in length to which a thermo-element is subjected through long-continued usage (accident, etc.) is itself responsible for a certain variation in the temperature corresponding to a given electromotive force, if the instrument is constructed of thin wires, as described above. The resistance of such a thermo-element, each wire of which measures 1 meter, is approximately 9 ohms at ordinary temperature. If the thermo-element is reduced to half length, its total resistance will have

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[1] Heyn, Mittheilungen der Koenigl. Technischen Versuchsanstalt, Berlin, 315 (1900).

[2] Heycock and Neville, Jour. Chem. Soc., 1895, p. 160, 1024; Holborn and Day, Drude's Ann. (4), 2, 528 (1900)

decreased one-half, whereby, in a circuit, the total resistance of which measures 450 ohms, an increase in the observed electromotive force (and consequently in the observed temperature) of about 1 per cent is attained. Nevertheless, it seems that this is not the only reason for the well-recognized variation in electromotive force which is incident to renewal of the junction.[1] It is apparently difficult to prepare such exceedingly thin wires in a state of perfect homogeneity.

Certain gases such as sulphur vapor, phosphorus vapor, etc., attack the thermo-element strongly, rendering it brittle and unreliable in its registry. This applies, as well, to the effect of hydrogen at temperatures above 1200 degrees. On this account, use of hydrogen to guard against oxidation, above this temperature, cannot be recommended, since diffusion through the porcelain protecting tube is sure to result with attendant damage to the thermo-element. On the other hand, when nitrogen is used it is difficult, without taking especial precautions, to prevent access of air and consequent oxidation of a melt easily susceptible to this sort of chemical action. This disadvantage is unusually troublesome when the resulting oxide, as in the case of manganese and silicon, attacks porcelain strongly. In such cases, the porcelain protecting tube is usually destroyed. LEVIN and TAMMANN[2] protect the thermo-element with a layer of magnesia. This material cannot be placed directly in contact with porcelain, since an easily fusible compound will then be formed at high temperatures. Accordingly, the protecting tube is first covered with a thin layer of nickel or platinum upon which the magnesia mass, consisting of magnesia and a quantity of ground porcelain, made into a paste with a solution of tragacanth and dextrine, is placed, leaving the upper part of the nickel or platinum foil free. This tube is dried in the air and ignited to approximately 1400 degrees before use. The tube, protected in this manner, lasts through one or more experiments, but we are here confronted with the disadvantage of imperfect heat transfer between the heavily enveloped thermo-element and melt, which renders the reading of temperature less sensitive and definite than is to be desired. The use of nitrogen, and intro-

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[1] HOLBORN and DAY, Drude's Ann. (4), 2, 540ff. (1900).

[2] LEVIN and TAMMANN, Z. anorg. Chem., 47, 136 (1905).

duction of the thermo-element, protected in the usual manner, at the last moment before taking the cooling curve will be found practicable in most cases. Thus far, tubes of pure magnesia have not given satisfaction.

§ 2. HEATING APPARATUS FOR THE PREPARATION OF FUSED ALLOYS.

A. *For Temperatures up to* 1100 *Degrees.*

Small Hessian crucibles are used as receptacles whenever possible, owing to their cheapness. In general, individual experiments should require about 25 g. material, less often 50 g., which amount may be conveniently handled in a crucible approximately 5 cm. high and 3 cm. wide at the top. The English crucibles made by the firm of *Morgan*, Battersea Works, London, are less porous, extremely durable, but rather expensive. Since these crucibles show practically no tendency to absorb melt, they are to be

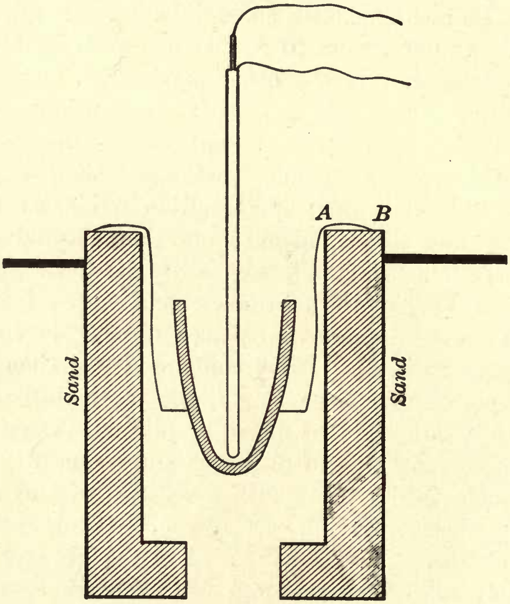

FIG. 110.

especially recommended for work with the more expensive metals. Graphite crucibles may be used to hold melts which react strongly with silicates.

The crucible rests in a wire or clay triangle which is surrounded by a mantle to prevent rapid heat radiation (Fig. 110). The latter is about 10 cm. high and consists of two clay cylinders, *A* and *B*, of 5 and 8 cm. diameter, respectively, which are wrapped with asbestos and fitted together by means of a sand filling. The outside cylinder is bound with heavy iron wire suitably bent to support the apparatus on an ordinary iron ring stand (used in chemical laboratories). Some form of bunsen burner or blast lamp is used as a source of heat. After removal of the heating apparatus, the top opening of the mantle is closed with an asbestos plate, and the bottom opening with an iron saucer filled with sand. In this way, rapid cooling by means of air currents is avoided. To render the cooling curves of various concentrations strictly comparable, care must be exercised that cooling invariably take place under similar conditions, and that the position of the thermo-element in all melts be uniform as far as is possible. The last condition is best guaranteed by maintaining the protecting thermo-element tube in a vertical position touching the bottom of the crucible. A small binding clamp attached to the iron stand serves to hold the tube in this position.

Melts which are susceptible to oxidation may often be adequately protected by means of a layer of ground charcoal at the top of the crucible. A mixture of potassium chloride and sodium chloride, or of potassium chloride and magnesium chloride, serves the same purpose.[1] Nevertheless the best plan in such cases is to make use of a reducing atmosphere as outlined below (C).

B. *For All Temperatures.*

The electric current offers the best means of obtaining temperatures above 1100 degrees. Carbon resistance furnaces heated by means of an alternating current of low voltage are used at the Goettingen Laboratory. Direct current at 220 and 440 volts enters the laboratory, where it is rendered suitable for heating purposes by transformation into alternating current at 5 to 10

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[1] ZEMCZUYNYJ, Z. anorg. Chem., 49, 386 (1906).

volts. The first transformation is effected by means of a rotary transformer, a small model having the capacity of about 3 kilowatts, and furnishing single-phase alternating current at 150 volts. This current traverses the primary winding of the second transformer, which is connected in series with a rheostat for regulation purposes. The secondary winding delivers 300 to 600 amperes at 5 to 10 volts. Copper bus bars carry the current from the secondary transformer circuit to the furnace. An ammeter indicates the strength of current entering the primary winding, and a voltmeter registers the voltage in the secondary circuit. This small model is very convenient in manipulation for furnace work requiring temperatures in the vicinity of 1500 degrees. Used in connection with the furnace of dimensions described below, there is no danger of fusing the porcelain receptacle holding the melt, since, under the most favorable conditions, the highest temperature attainable can scarcely exceed 1600 degrees. Two larger models operating on the 440-volt circuit are in use at the Goettingen Laboratory. One of these has a maximum capacity of 8 kilowatts, the other of 10. Both deliver alternating current at 310 volts. These machines are connected to the alternating current transformer described above, which furnishes at 6 to 10 volts, in the one case, current of 1200 to 700 amperes, in the other case of 1500 to 900 amperes.[1]

A top view and a vertical section of the resistance furnace are shown in Fig. 111. The resistor tube *A* is of retort carbon (from *Conrady*, Nuremberg) of the following dimensions: length, 13 cm., inside diameter, 2 cm., outside diameter, 3 cm. Two semicircular carbon plates *B*, 2 cm. in height and 9 cm. in outside diameter, are fitted to each end of the tube *A*, and clamped securely by means of the bent copper bars *C*, 2½ cm. high and 0.7 cm. thick, which are extended to a convenient length for terminal connections with the bus bars. For protection against rapid heat radiation from the interior of the furnace, the clay cylinder *D* is clamped between the carbon plates *B*. The space between this clay cylinder and the carbon tube *A* is filled with ignited charcoal. The furnace rests upon an iron saucer filled with sand. In setting

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[1] The above apparatus was supplied by the firm of *Ruhstrat Brothers*, Goettingen. If alternating current is directly available, there is obviously no call for a direct current-alternating current transformer.

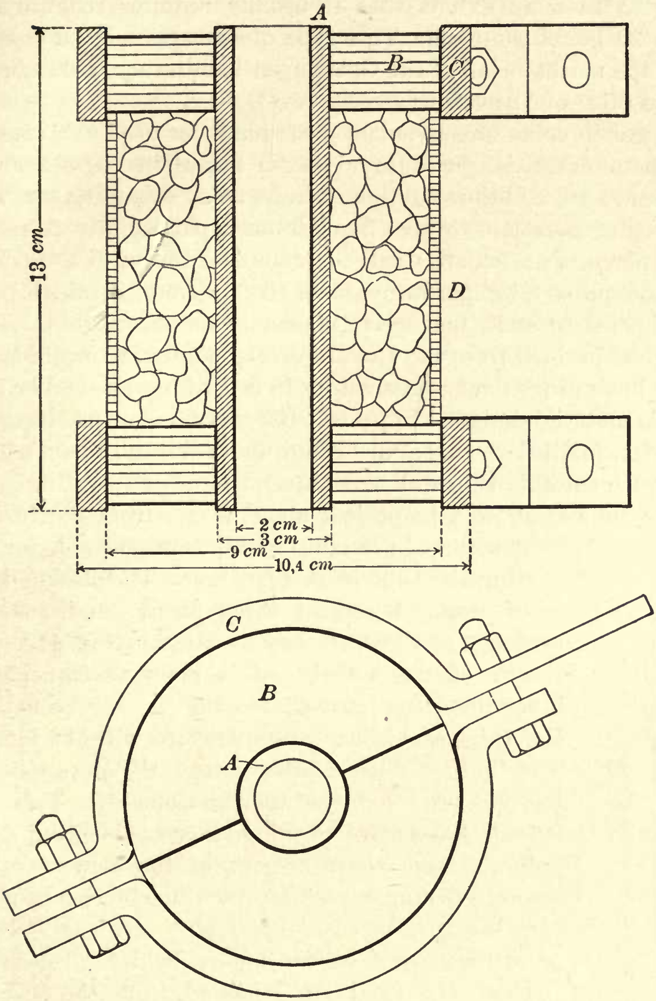

FIG. 111.

up this apparatus, a paste made of tar and graphite powder is used to insure good conduction of the articulating parts. Before use, the furnace must be gradually heated to expel volatile matter. When volatilization has ceased at 1000 degrees, the operation may be considered complete. During use, the resistor tube *A* deteriorates to such an extent that it usually requires renewal after some 20 hours' running. This type of furnace may be obtained from the mechanician of the Goettingen Laboratory, *Ernst Beulke*, at the price of 11 marks.

Porcelain tubes of convenient dimensions for use in this furnace are manufactured by the Royal Saxon Porcelain Manufactory of Meissen. In addition to those made from the ordinary white variety of porcelain, others made from a particularly refractory gray porcelain mass are used. If complete fusion of the components requires a temperature above 1600 degrees, at which porcelain begins to melt, magnesia tubes may be substituted. These may be obtained from the Royal Porcelain Manufactory of Berlin. They have proven very satisfactory in use, although smaller tubes of this material designed to protect the thermo-element, have not, thus far, fulfilled the necessary condition of durability (in connection with suitably thin wall substance).

The tube is allowed to project about 2 cm. from the furnace. Fragments of arc lamp carbons are suitable for supporting the tube in this position. The closing device is of brass, bored in three places, and generally arranged as shown in cross section in Fig. 112. The length of this metal cap is about 4 cm., and its inner diameter is so chosen that it may be fitted to the tube at ordinary temperature without binding. The borings must readily admit the porcelain protective tube for the thermo-element. This tube enters the central opening, thereby insuring a consistently central placement of the element. The second opening serves for the introduction of a tube carrying gas, in case experiments are conducted in a nitrogen (or other non-oxidizing) atmosphere. Traces of oxygen are removed from the ordinary nitrogen which is delivered in steel cylinders under pressure by passing it through an alkaline solution of pyrogallic acid, after which the gas is dried by means of sulphuric acid. The third opening is used to admit a stirrer, in order that a possible contingency of supercooling may be avoided. Sometimes it is desirable to use the thermo-element tube for this purpose. Porcelain

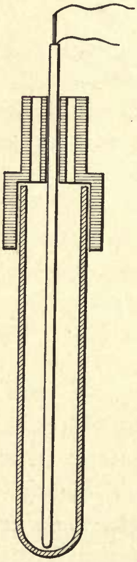

FIG. 112.

tubes identical with those used to protect the thermo-element are, in general, suitable for purposes of stirring and introducing the neutral gas.

If the components possess very different melting points, the most difficultly fusible one is placed in the lower part of the tube, since a higher temperature is attained in this region. The above described method of fusion is applicable to all temperatures between some 300 degrees and an upper limit approximating 2000 degrees.

When a considerable source of electrical energy at low voltage is not available, metal resistance furnaces may be used. For high temperatures, platinum furnaces alone are suitable. The tubes used in the construction of these furnaces are composed of some refractory material such as magnesia, Marquand mass, etc. They are wound with platinum wire, or, according to Heraeus, best of all with platinum foil, which carries the current and must accordingly possess a resistance corresponding to the nature of current used. Since these refractory tubes commence to conduct electrolytically at about 1500 degrees, and therefore bring about gradual deterioration of the platinum, furnaces of this type are not suited to continuous running above this temperature. Aside from this disadvantage, they are generally inferior to carbon resistance furnaces: *e. g.*, they require very carefully handling and it is difficult to repair them.

C. *For Temperatures up to* 800 *Degrees and* 1100 *Degrees, Respectively, in a Protective Atmosphere.*

If fusion is to be effected in a protective atmosphere, it is desirable to reject the use of crucibles, even when heating is other than electrical in nature, and to make use of an arrangement sketched in Fig. 112, wherein tubes of porcelain, or of other material, are substituted. The mantel shown in Fig. 110 is desirable in this case, provided temperatures up to 1100 degrees must be attained. For temperatures not exceeding 800 degrees, tubes of difficultly fusible glass, *e. g.*, of Jena combustion tubing, are excellent, if not attacked by the melt. The admirable arrangement used by GRUBE[1]

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[1] GRUBE, Z. anorg. Chem., 44, 117 (1905).

in investigating magnesium alloys, is shown in Fig. 113. The glass melting tube *A* is contained in a cylindrical iron sand bath *B*, which is heated by means of a powerful combination of four burners, thus avoiding local overheating. The sand bath is surrounded by an asbestos mantle *C*, which is closed above by a mat of the same material, and also below, during cooling, by a shallow iron dish filled with sand. The glass tube is fitted with a cap *D*, similar to that pictured on p. 302. Through the three openings in this cap, a stirrer *F*, gas leading in tube *G*, and a glass protective tube *E*, enclosing the thermo-element, are introduced. Grube used an atmosphere of hydrogen, which was found to operate at 800 degrees without injury to the thermo-element (cf. p. 297).

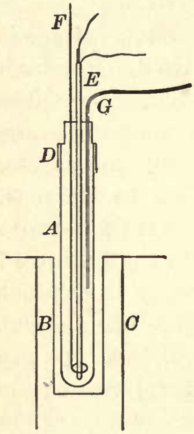

Fig. 113.

§ 3. The Determination of Cooling Curves, and Heating Curves, Respectively.

In opening the investigation of a binary alloy, it is desirable, for the purpose of obtaining a general survey, that the determination of cooling curves proceed regularly (from concentration to concentration), throughout the whole concentration range, at intervals of 10 per cent.[1] The amount of material necessary for an individual determination may vary from 20–30 g., according to the specific weight of the metals in question. The metals are heated until completely melted, and stirred until a uniform mixture is attained. Immediately after direct heating has been discontinued, some further elevation in temperature is observed. This is due to a certain delay attending transfer of heat from the walls of the vessel to the thermo-element. Furthermore, this condition causes a rate of cooling which is less than normal to ensue directly after the temperature has reached a maximum and has started to

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[1] Concerning the logical choice of concentrations in the investigation of a three component system, compare Sahmen and Vegesack, Z. anorg. Chem., 59, 262 (1907).

fall. On this account, it is desirable, if possible, to heat the mixture some 50 degrees above the temperature at which primary observation is to be made. In determining a cooling curve, the temperature of the cooling melt is noted at regular intervals, usually from 10 to 10 seconds, sometimes from 5 to 5 seconds as indicated by a suitable (stop) watch, and this collection of temperature observations is plotted against the time, as described on page 4.[1]

Melts frequently tend to supercool. This condition is rendered evident in most cases by the appearance of a sudden elevation in temperature when the melt finally begins to crystallize. If we are dealing with solidification of a mixture, this elevation will in no case reach the temperature at which normal crystallization of one variety occurs. Therefore, we always seek to eliminate supercooling. This may usually be effected by thorough stirring. When stirring fails to establish normal conditions, it is necessary to inoculate the melt with a particle of solid material obtained from a previously cooled melt. Introduction of the solid material should be opportune, *i. e.*, it should take place at a moment (ascertained by preliminary experiment) when the temperature of the melt is only a few degrees above the value which normally determines crystallization, and it should be accompanied by vigorous stirring.

Determination of a heating curve, following that of the cooling curve, is most advisable, since it offers a most reliable check on the latter data. Addition of heat must obviously be made with the greatest possible uniformity; a result easily attained by the aid of electrical apparatus. Pure metals and their pure compounds are not subject to superheating. But superheating may well be encountered in the case of mixtures, since here the melting point of one component is not reached at the time of fusion, and we are obviously dealing with a solution process. Nevertheless, resulting complications are not, as a rule, prevalent. Particularly when supercooling occurs in a melt which is already partially solidified and is consequently not amenable to stirring or to inoculation, determination of heating curves is frequently our only means of explaining the crystallization processes.

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[1] Another graphical method consists in representing the rate of cooling, or its reciprocal value, as a function of the temperature.

Self-registering pyrometers which are based upon the use of mirror galvanometers and photographically depict the deflection of the galvanometer needle as a function of the time, have been described by ROBERTS-AUSTIN,[1] SALADIN and LECHATELIER,[2] and KURNAKOW.[3] A self-registering instrument without mirror suspension is manufactured by the firm of *Siemens and Halske.*[4]

§ 4. CONSTRUCTION OF IDEALIZED COOLING CURVES AND HEATING CURVES, RESPECTIVELY.

The form of an experimentally determined cooling curve differs in many respects from that developed in our theoretical discussion. This is due to the fact that certain assumptions which we made relative to the behavior of substances in general and to the method of experimentation are never completely (often, indeed, most incompletely) realized. Since we are, as a rule, fully cognizant of the reasons underlying such deviation, it is not difficult to construct altered or "idealized" curves, based upon the actual curves, which shall closely correspond to a full realization of our preliminary hypotheses. The cooling curve of a pure substance (silver) is given in Fig. 114, I, as determined with the aid of a carbon resistance furnace. Divisions on the time axis correspond to 100 seconds, those on the temperature axis to 100 degrees. Since no supercooling has resulted, the beginning of crystallization is sharply indicated on the curve. No equally marked change in direction of the curve shows the time at which crystallization has ceased; on the contrary, the temperature began at the point *f* to fall slowly, thereupon falling more and more rapidly as far as the point *c*, which constitutes a point of inflection, and finally falling off at a constantly decreasing rate, as shown by the portion *cde*. The reason for this phenomenon, which is associated with all experimental cooling curves, is defined by TAMMANN[5] as follows: Flow of heat takes place not only from the surface of the melt outwards, but also through the thermo-

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[1] ROBERTS-AUSTIN, Five notes to the Institute of Mechanical Engineers, Proceedings, 93, 95, 97, 99 (1891).

[2] SALADIN and LECHATELIER, Revue de metallurgie, February (1904).

[3] KURNAKOW, Z. anorg. Chem., 42, 184 (1904).

[4] Zeitschr. f. Instrumentenkunde, 25, 273 (1905).

[5] TAMMANN, Z. anorg. Chem., 47, 291 (1905).

metric apparatus. Furthermore, the previously assumed good heat conductivity (*cf.* p. 17), which would preclude the existence of measurable temperature differences within the system, is not

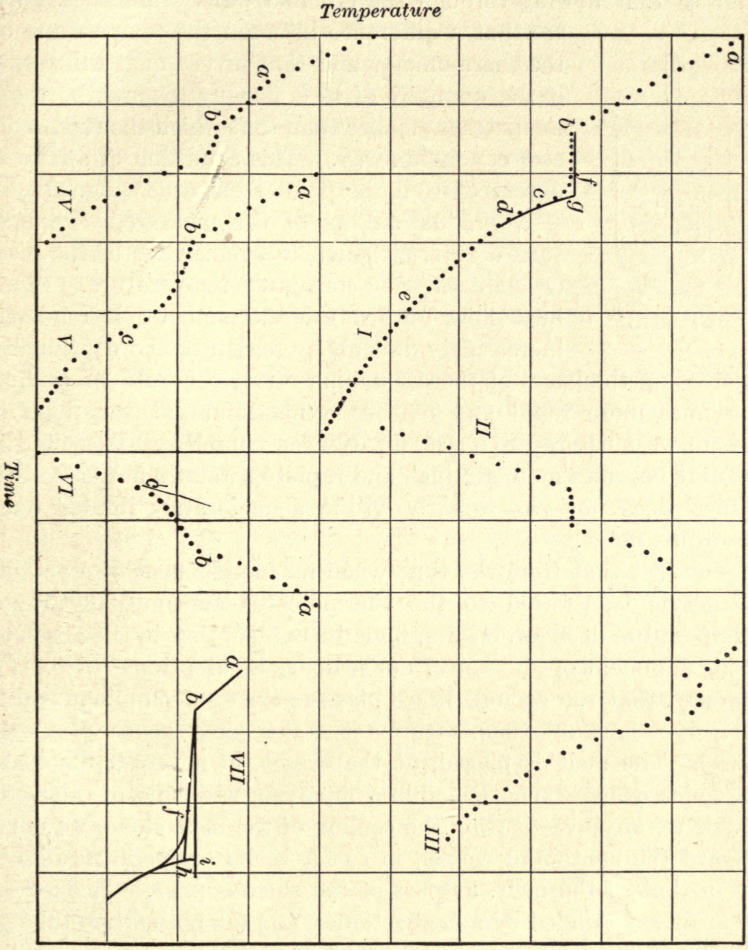

Fig. 114.

completely realized. When a melt in the crucible *A* (Fig. 115), containing a centrally located thermometer *B*, cools off, a crust of crystals is deposited, not only on the crucible walls, but also around the thermometer. The final remainder of the melt therefore crystallizes in the space *CCC*, the distance of which from the thermometer *B* will become less, in proportion as the relation between the heat quantity passing away through the thermometer to that flowing through the crucible walls diminishes. We see that a difference between the temperature of the thermometer and that of the melt will result if the quantity of heat flowing toward the thermometer is smaller than that which the thermometer conducts away. This condition of affairs is observed from the point *f* onwards (Fig. 114, I) — a gradual falling of the measured temperature occurs, although the remainder of the melt crystallizes at constant temperature. Since heat flow toward the thermometer is rendered increasingly difficult by reason of the continually increasing thickness of the crystalline crust, the rate of cooling becomes more rapid and reaches a maximum at the point *c*, where we must regard crystallization as complete. Henceforth, cooling becomes more gradual, and rapidly attains a normal value, which does not vary greatly within a moderately limited temperature range.

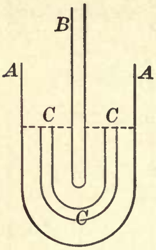

FIG. 115.

The fact that from the time when no further heat of crystallization is transferred to the thermometer an unusually rapid temperature decrease ensues, finds its explanation in the absolute non-fulfillment of another of our primary assumptions (*cf.* p. 17), namely, that the cooling takes place against surroundings which preserve constant temperature (constant convergence temperature). The melt is placed, at the outset, in a vessel, the mass of which cannot be neglected in comparison with that of the melt. Since we are investigating the cooling of the melt alone, we must regard the containing vessel, in so far as its temperature differs from that of the melt, as part of the surroundings. This vessel is again surrounded by a heat retainer, *i.e.*, the hot carbon tube of the furnace with its own further heat insulation, or a clay mantle, etc. These surroundings also gradually cool off. Thus, the melt cools in the presence of surroundings which themselves possess variable, gradually decreasing temperature. In general, no particularly obvious deviation from the theoretical form of cooling curve, such as might result from these modifying influences, is actually observed: the experimental curves actually show the logarithmic form (or a very similar form) developed on page 12 *et seq.*, and illustrated in Fig. 3 (p. 14). We obtain a quite different result, however, when the melt is maintained at constant temperature for a certain length of time through the agency of an internal source of heat. During this time, the immediate surroundings cool off unhampered, the temperature difference between them and the melt increasing until a maximum difference is reached at the moment the above-mentioned heat source becomes exhausted (when crystallization of the melt is completed). An increased rate of cooling will be indicated by the thermo-element until this temperature difference has again reached the normal value. Conditions of this sort are observed at the points *c* and *d* (Fig. 114, I).

Now, in order to deduce the approximately theoretical form of cooling curve, let us reflect that the portions *ab* and *de* of the experimentally determined curve (Fig. 114, I) are themselves sufficiently accurate to stand. By prolonging the portion *de* continuously over *d* as far as the point of intersection *g* with the horizontal drawn through *b*, we construct an idealized cooling curve *abgde*, which coincides above *b* and below *d* with the experimental curve.

Fig. 114, II, gives a heating curve of the same material (pure silver). This was also obtained with the aid of the electric furnace. Here, fusion commenced at the walls of the vessel, and, consequently, flow of heat toward the thermo-element was most hindered in the beginning, becoming more perfect as the crystalline layer melted away from the thermo-element. In accordance with the conditions just noted, there is no constant temperature to be observed on the heating curve, corresponding to the beginning of fusion, but rather a very gradual rise in temperature. When all of the alloy has melted, an abrupt change in the rate of temperature increase is observed — the temperature begins to rise at a rapid rate, whence a change in the direction of the curve ensues at this point. The construction of an idealized heating curve may be carried out as described above relative to the cooling curve.

Fig. 114, III gives the cooling curve of pure palladium. Supercooling has taken place in this case.

Fig. 114, IV gives the cooling curve of an alloy composed of 70% Pd and 30% Pb. First, a single crystalline variety separates for a time, beginning at *a*. Then, from *b* onwards, eutectic crystallization follows. In all of these cases, "idealized" curves may be derived from the experimental curves.

We have seen in the theoretical part of this book how important knowledge of the relative amounts of eutectic at various concentrations is with respect to determination of the constitution of the alloy. Now, the heat quantity liberated during crystallization of the eutectic is proportional to the amount of eutectic present. Thus, on comparing equal weights of alloys of different concentrations, these heat quantities are proportional to the relative amounts of eutectic in the several cases. If cooling were to occur in an ideal manner (according to the description beginning on p. 17), then, under similar conditions and for the same quantities of melt of different concentrations, the periods of eutectic crystallization would be proportional to the heat quantities liberated and consequently to the relative amounts of eutectic in the different alloys. We would, therefore, possess in this method of procedure a means for determination of the relative amounts of eutectic. Since, when the concentration axis is made to show weight per cent (see p. 107) the relative amounts of eutectic decrease lineally from their maximum of 1 towards both zero points, a linear decrease would be expected relative to the duration of eutectic crystallization.

Experience fails to completely substantiate this conclusion, as we have seen. We find in addition to a linear decrease in eutectic periods, as represented in Fig. 116 (shown by verticals drawn in proportion to the periods of eutectic crystallization in the various concentrations), a too gradual decrease (Fig. 116, II), and a too rapid decrease (Fig. 116, III). Too gradual decrease may be readily explained on the basis of our experimental conditions. We have seen that while the temperature of the melt is kept constant by the influx of heat of crystallization, the material adjacent to the melt continues to cool down. Since the heat quantity dissipated in a unit time, *ceteris paribus*, is proportional to the temperature difference between melt and adjacent material, it follows that the heat quantity necessary to maintain constant temperature is greater in proportion as this period lengthens. On this account, when the amount of eutectic is doubled, the corresponding eutectic period (of constant temperature), will be less than twice that before.

The frequently observed too rapid decrease (Fig. 116, III), is probably due to a tendency of the substance towards supercooling. When a large amount of eutectic is present, and separation of two crystalline varieties has begun at any one point, a large number of crystalline particles may be regularly disposed throughout the main quantity of melt by stirring, whereby orderly crystallization, regulated alone by the flow of heat throughout the material, may ensue. Quite different results are to be expected when the amount of eutectic is small, and that which still remains molten towards the end of crystallization is situated in different parts of the mixture between masses of crys-

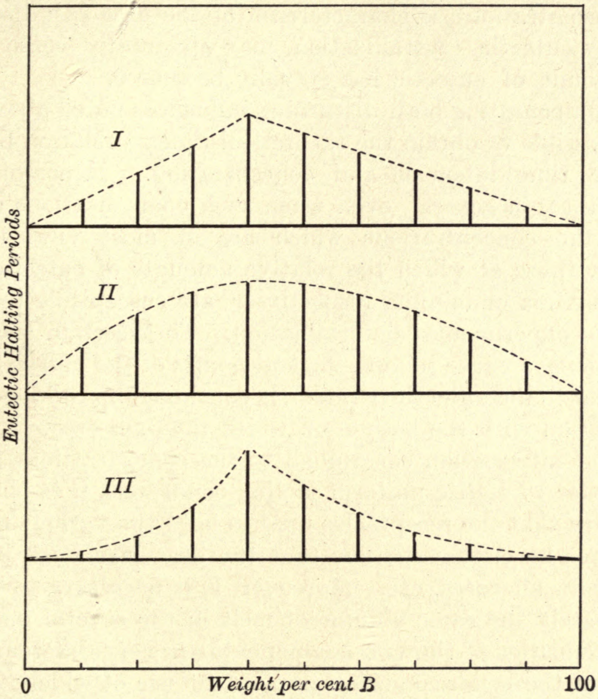

FIG. 116.

talline material (too much solid material being present to admit of stirring). In such a case, separation of eutectic in these different localities may take place at unequally retarded rates, and the temperature, instead of remaining constant during crystallization, may vary more or less. It is possible that the resulting change in the course of the cooling curve may be sufficiently slight to escape observation when the experimental results are plotted. Thus, a too rapid decrease in the eutectic period (with the concentration) is characteristic of the case just discussed, whereby eutectic crystallization, may apparently cease before the amount of eutectic has actually become 0.

By compensating both disturbing influences noted above, it is often possible to obtain the theoretical (linear) relation between eutectic time intervals and concentration. Experience has shown that, in general, even when such compensations are not made, the concentrations which are of most vital interest namely, those at which the relative amounts of eutectic reach their maxima or minima respectively, are susceptible to rather accurate experimental determination. To ascertain such concentrations, a curve joining the end points of the verticals (proportional to the eutectic periods), is continued up to its points of intersection with the base upon which they are erected. These points of intersection correspond to the concentrations sought.

In order to realize uniform cooling conditions, it is obviously necessary that the receptacles used to hold the various melts in the series be closely similar; that the heat insulation be comparable in all cases, etc. Moreover, it is necessary to use approximately the same volume of melt in the several instances. If the densities of the two components are very different, realization of the latter condition implies the use of widely varying weights of material in the different concentrations. In such cases, the observed eutectic periods of crystallization must be divided by the weights of the corresponding melts, in order that numbers which shall apply to a definite weight of melt may be obtained. Since, according to equation 4, p. 15, the product of rate of cooling and specific heat is constant under the same conditions of cooling, a uniform rate of cooling in the various melts is to be expected only when the specific heat does not vary with the concentration.

When the components form mixed crystals with one another, the temperature at which crystallization ceases is usually very imperfectly indicated on the cooling curves. This is illustrated in Fig. 114, V. The cooling curve refers to a mixture of 90 per cent silver and 10 per cent palladium. Only the beginning of crystallization is quite apparent (at *b*) on examining the curve. The point of inflection *c* is used, according to the procedure of Tammann, in ascertaining the end of crystallization. At this point, the rate of cooling is most rapid, and crystallization is to be regarded as complete. It would, however, be incorrect to consider the whole temperature interval *bc* as the crystallization interval $I_{10\%\ \mathrm{Pd}}$. For, on this basis, a similar crystallization interval *bc* (Fig. 114, I) would of necessity pertain to pure silver, which must crystallize at constant temperature. Therefore, a certain quantity ΔI, which could be obtained by determining the apparent crystallization interval corresponding to crystallization of a *pure* substance at the same temperature under the same cooling conditions, must be deducted from the apparent crystallization interval $I_{10\%\ \mathrm{Pd}}$ to render the latter correct.

Tammann uses an indirect method wherein calculation of the quantity ΔI is made from the apparent crystallization intervals of both components by applying the rule of mixture. If I_{A} and I_{B} are the apparent crystallization intervals for the components A and B, respectively, and if the corresponding concentration in weight per cent B is x — whence the alloy contains $x\%$ B and $(100 - x)\%$ A — then the quantity,

$$\Delta I = \frac{1}{100}\left[(100 - x) \,.\, I_{\mathrm{A}} + xI_{\mathrm{B}}\right],$$

must be deducted from the apparent crystallization interval I.

In many cases, the crystallization interval may be recognized at once upon the *heating curve.* Thus, Fig. 114, VI, shows the heating curve for the same mixture, 90 per cent Ag + 10 per cent Pd, for which Fig. 114, V, gives the cooling curve. The beginning of fusion, at the point *c*, where, owing to very gradual heating, a rather marked deviation of the heating curve from its previously linear course occurs, is here very clear, although not so sharply marked as the end of fusion at *b*. The value to be deducted in this case for the apparent interval of a pure substance is comparatively small, as is evident on comparison of the curves, Fig. 114, I and II, and may be regarded as constant (to within 5 degrees under present conditions).

If the crystallization interval is very small, the following procedure may be suggested for determining it.[1] In normal cases, *i.e.*, when an excessive quantity of heat is not conducted away by the thermometer, the point *f* (Fig. 114, I) at which the thermometer begins to register a fall of temperature during crystallization of a pure substance lies in the last third of the period of crystallization. Therefore, if the point *b*, which indicates the beginning of crystallization, is joined to the point *f*, which corresponds to some two-thirds of the period of crystallization, a straight line is obtained in the case of a pure substance. If, however, we are dealing with mixed crystals (Fig. 114, VII), *bf* is inclined to the time axis. An extension of the straight line *bf* to the point *h*, which corresponds to the end of crystallization, then yields the required crystallization interval *hi*.

We see from the above that the determination of a crystallization interval through the agency of cooling curves is comparatively uncertain in the case of mixed crystals, the difficulty pertaining to location of the end point of crystallization. At this juncture, we may cite the method of HEYCOCK and NEVILLE,[2] according to which, in their investigation of copper-tin alloys (bronzes), the end points of crystallization were ascertained by quenching the alloys at various temperatures, and subjecting polished sections of the resulting material to microscopical examination. The separating crystals are larger in proportion to the slowness with which they crystallize. Hence, those crystals which have separated before quenching are readily distinguished by reason of their larger size from those which have formed after quenching. If small crystals are entirely absent in the section, quenching has occurred after all the material has crystallized. In this manner, it is possible to determine the end points of crystallization in the several concentrations with considerable accuracy. Such accurate determination of the crystallization interval is obviously of value only when it is certain that the concentration balance (see p. 173) necessary for realization of equilib-

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[1] RUER, Z. anorg. Chem., 49, 379 (1906).

[2] HEYCOCK and NEVILLE, Phil. Trans., 202, 1 (1903).

rium has reached a degree approximating perfection, since, in such cases alone, does the curve joining the final temperatures of crystallization coincide with the *s*-curve. Finally, it may be stated that a faint break in the cooling curve appears most plainly when the latter is drawn so as to incline about 45 degrees toward the axes.[1]

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[1] Boeke, Z. anorg. Chem., 50, 358 (1906).

CHAPTER II.

INVESTIGATION OF STRUCTURE.

CONTINUED reference to the importance of microscopical investigation of polished sections for the purpose of regulating and supplementing the results of thermal investigation has been made in the theoretical part of this text. The task of harmonizing the results of both methods of investigation proves in many cases extremely difficult, and severely taxes the experience of workers in the metallographical field. Particularly when the existence of mixed crystals is indicated by thermal investigation are we likely to obtain results on microscopical examination which are more or less at variance with those to be expected. We have already noted (on p. 180) how it may be shown in such cases that inhomogeneous structure of reguli finds its explanation purely in incomplete concentration balance between crystals and melt during solidification. In the main, we are indebted to SORBY, MARTENS, HEYN, BEHRENS,[1] OSMOND,[2] WEDDING, and LECHATELIER[3] for the development of microscopical methods of investigation.

§1. PREPARATION OF SECTIONS.

To serve the purposes of microscopical investigation, a chosen section of the cold regulus is usually brought to a mirror-like surface, several square centimeters in area, by cutting and polishing. The manner of obtaining this result varies according to the properties, in particular, the hardness, of the alloy in question. In case of a soft alloy, it may be unusually difficult, or indeed

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[1] BEHRENS, Das mikroscopische Gefüge der Metalle und Legierungen, Hamburg and Leipzig, 1894.

[2] OSMOND, Methode générale pour l'analyse micrographique des aciers au carbone. Contribution à l'étude des alliages, Paris, 1901, p. 277. German translation of the same by L. Heurich, under the title, Mikrographische Analyse der Eisen-Kohlenstofflegierungen, Halle, 1906.

[3] LECHATELIER, Contribution à l'étude des alliages, p. 421.

impossible, to obtain a surface which will show no polishing scratches under the microscope. Since we are in a position, after some practice, to distinguish such scratches from striations which may be characteristic of the structure of the crystals themselves, the above limitation does not constitute an absolute hindrance to the progress of microscopical work.

It is, nevertheless, of great importance that the composition of the alloy in its different parts be uniform. If the crystals which first separate are widely different from the mother liquor, as regards specific weight, they readily collect in the upper or lower part of the melt and are thus open to dissimilarity in their general make-up. Microscopical investigation may then easily lead to false conclusions. Frequently, the external appearance of the section alone indicates that the upper and lower parts have been formed under unlike conditions, as above. In other cases, microscopical examination of a longitudinally cut section must be undertaken in order to determine whether or not this effect has occurred. If evidence of a tendency toward "segregation," as such phenomena are named, has accrued, too slow cooling of the melt should be avoided and the additional safeguard of vigorous stirring should be brought into requisition.[1]

If the regulus under investigation is hard (hardness 4 and over), and is composed of material of a sufficiently cheap variety, it may best be brought to a smooth surface by grinding on emery or carborundum wheels. In this operation, the sample is passed from the coarser to the finer wheels by degrees. At the Goettingen Institute, a small electric motor running at about 1800 revolutions per minute is used as a polishing machine by attaching the polishing plates directly to its revolving (horizontal) axis. Obviously, hand polishing stones may be used as well. Care should be taken that the reguli do not become hot during their manipulation, since this may bring about changes in structure. To avoid any such possibility, they may be dipped into water from time to time during the course of the grinding and polishing. Further treatment of the sections is carried out with graded sizes of emery cloth. Osmond (l. c.) requires the following of an emery cloth: the grain must be uniform; the emery powder must adhere to the backing so firmly that it does not

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[1] Compare, also, p. 138 and following pages.

become detached on rubbing; the powder must wear away in streaks but not in spots, as is the case when it adheres loosely; finally, the cloth (or paper) and the glue themselves must not score soft iron. Since the commercial article satisfies these demands only infrequently, he adds directions relative to the preparation of satisfactory emery cloth, and concerning which the reader is referred to the original. The so-called French emery paper, manufactured by the firm of *Georg Voss & Co.*, Deuben, Dresden, Germany, is used at the Goettingen Institute. This is prepared in the grainings, 3, 2, 1, 0, 00 minutes, and, furthermore, 0, 1, 2, 3, 5, 10, 15, 20, 30 and 60 minutes. In general, six varieties, *e.g.*, 3, 1, and 10, 20, 30 and 60 minutes, will be found adequate.

The emery cloth is tacked on right angled wooden blocks (about 30 × 15 cm.), upon which the section is then rubbed back and forth. Polishing on each separate number of emery cloth should be so carried out that the lines of abrasion run in a definite direction. On passing to another number, the operation is continued in a direction at right angles to these lines, until the latter are completely obliterated, *i.e.*, replaced by a new series. Thus, it develops that the scratches from the last number of emery cloth, even though they may fail to disappear completely on subsequent polishing, are, nevertheless, hardly distinguishable as such, since they preserve the same direction over the whole surface. Such direction is indeed likely to be that corresponding to the general disposition of the crystal polygons. Finally, polishing is finished most effectually with a revolving felt or leather disc bearing metal-polishing wax upon its surface. In case use is made of a wax preparation in grinding the regulus, great care should be taken that none of this reaches the polishing disc, since the latter may be ruined in this way for polishing purposes.

The reguli of especially brittle alloys may be broken into pieces from which selection of those showing smooth surfaces may be made with a view to further mechanical treatment.

Emery or carborundum wheels should not be used on soft alloys, in order that serious contamination of the latter with foreign metallic particles be avoided. Coarse and fine files in succession are best used in working such material into shape. Further treatment with emery cloth follows in the manner described above. Eventually, they are polished on a piece of felt or soft leather which is stretched over a smooth block and used in connection with Vienna chalk and polishing oil (stearin oil). According to Behrens (l. c.), certain alloys which are troublesome by reason of their softness and friability assume an excellent polish when rubbed on fine whetstones moistened with a trace of kerosene — a drop of kerosene is rubbed into the stone with the finger, vigorously wiped with a cloth and rubbed with the ball of the hand until the stone appears quite dry. Osmond uses English red — the variety known as jewelers' red — for polishing soft iron-carbon alloys. He advises that the commercial preparation be washed before use, or, still better, that the material be prepared by the user, whereby as low a temperature as is practicable should be maintained in firing it. He obtained especially favorable results with the oxalate red (English red made from iron oxalate) which is employed in mirror factories. If aluminium oxide is used in polishing (LeChatelier), much more rapid results are obtained. The polishing machine used by Osmond was constructed by *Fuess* of Steiglitz, near Berlin. A piece of short fibered cloth is stretched upon its smoothly machined horizontal revolving plate, and sprinkled with polishing powder.

Alloys which are composed of costly material should be neither ground nor filed, but are most economically shaped by sawing.

§ 2. DEVELOPMENT OF STRUCTURE.

If the separate structure elements of an alloy differ in color, the structure of its section is evident at a glance. A good example of this condition is to be found in the gold-lead series investigated by VOGEL.[1]

In case the different structure elements vary considerably in hardness or elasticity, it is possible for reliefs to appear in the finished section, owing to more rapid wearing off of the softer material on grinding and polishing. In general, it is desirable to avoid this effect, since the difference in height between the several structure elements after the section is prepared may be great enough to prevent sharp focusing under the microscope. The method of grinding and polishing outlined above is capable of

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[1] VOGEL, Z. anorg. Chem., 45, 11 (1905).

producing level surfaces if carried out properly. There are, however, methods which make use of these differences between the several structure elements with respect to mechanical properties, in the development of structure. They are, namely, "grinding in relief,"[1] and "relief polishing."[2] The latter method has proven valuable in the investigation of iron-carbon alloys (compare Table 6, p. 237) and is based upon the use of an elastic polishing foundation, *e.g.*, of parchment, which will readily adjust itself to the resulting irregularities in the surface of the section. In polishing, the ordinary polishing materials (such as jewelers' red) are used with water. Relief polishing may be combined with feeble chemical action ("Etch-polishing").[2] Quite notably, solutions may be used in this connection which ordinarily fail to attack iron, for example, extract of licorice, ammonia water, or, best of all, a 2 per cent solution of ammonium nitrate. Etch-polishing is carried out in the same manner as relief polishing: one of these solutions replacing water.

In the main, the goal is most quickly reached when the differing chemical properties of individual structure elements are observed in the development of structure. Thus, the section is "etched," *i.e.*, it is treated with reagents which attack the different structure elements variously. The portions which are most strongly attacked by the etching agent suffer loss of their property of reflecting light, which was due entirely to their high polish, while the more or less unattacked parts retain their brilliancy. In order that an etching agent may attack the material uniformly, it is essential that the latter be well wet by the liquid. Therefore, the section must first be freed from all fatty material. This condition is secured by dipping in alcohol, ether, or chloroform, etc., after which a clean cloth is used to wipe away the liquid. Some consider it more advisable to remove grease by dry rubbing with Vienna chalk or tin ash, which material may be applied on a clean cloth or a piece of fine grained wood.

What etching agent is suitable for a given alloy and how long it should be allowed to act are matters which must be determined by experiment. For this purpose, a drop of the liquid to be tested is placed on the alloy and left for a moment. It is then washed

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[1] Behrens, l. c., p. 10.

[2] Osmond, Contribution à l'étude des alliages, p. 280.

off and the section examined — eventually under the microscope. If either very slight action or none at all is observed, etching is allowed to continue in the same spot. If too pronounced etching is noticed, the reagent is allowed to act for a shorter period in another spot, or it is further diluted. It is frequently difficult to find a proper etching agent. Sometimes the structure is developed very beautifully by over etching the section and then lightly repolishing the etched spot.

Etching agents which are commonly used are the ordinary acids: nitric acid, sulphuric acid and hydrochloric acid, in concentrated form, as well as variously diluted. Solutions of the acids in amyl alcohol operate very slowly, but withal very evenly. In this connection, 4 per cent solutions of nitric acid or of picric acid in amyl alcohol are of service in the investigation of alloys containing iron. After etching with picric acid, the section should be rinsed with absolute alcohol and wiped with a soft flannel cloth. Solutions of the various acids in ethyl alcohol have also been extensively used. Etching with aqua regia, variously diluted, frequently yields satisfactory results in the case of alloys of the noble metals.

Reference has already been made to the use of tincture of iodine in the investigation of iron-carbon alloys (p. 237). According to Osmond, this mixture should not be prepared with absolute alcohol. The tincture ordinarily used in medicine is of the proper concentration. He applies it gradually with the finger until about a drop per square centimeter has been added. Etching proceeds until the color of the tincture disappears. If necessary, the process is repeated. When etched sufficiently, the section is rinsed with alcohol and dried with a fine dry linen cloth. A blast of air is even better for drying.

An aqueous solution of copper-ammonium chloride has also been used largely for etching — *e.g.*, in the investigation of antimony-bismuth alloys by Hüttner and Tammann. They were able in this way to distinguish the antimony rich crystals (only slightly attacked in the cold by a dilute solution as above) from the bismuth rich crystals (much more strongly attacked by this etching agent).

In other cases, etching by means of alkaline solutions brings about the desired end. Thus, Vogel obtained good contrasts in the case of gold-antimony alloys of high gold concentration by long continued action of sodium hydroxide solutions. Again, in the cases of zinc alloys, aluminium alloys and silicium alloys, this etching agent has been used to good effect.

Ammonia should be tried on copper alloys. Addition of hydrogen peroxide hastens its action as a rule.

LeChatelier[1] uses the electric current for etching, in that the alloy under investigation is made the anode in a circuit. Operating under a current density of 1/1000 to 1/100 amperes per square centimeter, only the least resistant structure elements are etched in from 1 to 10 minutes. A lesser current density is to be chosen in proportion as the different structure elements approach one another in their tendency to become etched. It is not advisable, however, to use a current density of less than 1/1000 amperes per square centimeter, since, otherwise, non-uniform distribution of the current over the surface of the section is likely to result. An aqueous salt solution which does not attack the alloy when no current is passing is used as electrolyte. In most cases ammonium nitrate was chosen by LeChatelier. Now and then, etching appeared very plainly when a salt giving a precipitate with the metal in question was added to the electrolyte — for example, in the case of copper, potassium ferrocyanide or potassium thiocyanate.

In many cases a section becomes etched simply on standing in the air, *i.e.*, it "tarnishes." Obviously, such ready oxidation of an alloy considerably hinders investigation of its structure. Sometimes it is impossible to polish the section. Oxidation of a single constituent of the alloy may occur, and even that may require moisture. Such sections are preserved, after being etched sufficiently on exposure to the air (which always contains water vapor), by enclosing them in a desiccator.

If oxidation does not proceed with sufficient rapidity at ordinary temperature, it may be hastened by heating. The section, dry and free from grease, is heated upon an iron plate or sand bath until the desired surface colors (interference colors caused by thin layers of oxide) appear. It is then cooled off with all possible rapidity. Some practice is necessary in order to properly carry out this process.

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[1] LeChatelier, Contribution à l'étude des alliages, p. 67.

§ 3. MICROSCOPICAL INVESTIGATION.

Metallic sections are capable of investigation in reflected light alone, owing to their opacity. If light is allowed to fall in an oblique direction upon a perfectly mirrored surface, no rays will enter a microscope, the optical axis of which is perpendicular to the reflecting surface (Fig. 117, *a*), *i.e.*, the latter will appear dark. In order that the reflecting surface may appear bright, it is necessary to adjust the optical axis of the microscope obliquely to it in the direction of the reflected rays (Fig. 117, *b*). On the other hand, if the rays of light fall perpendicularly upon the reflecting surface, the latter will appear light through a microscope, the optical axis of which is perpendicular to the surface (Fig. 117, *c*). On directing light upon a diffusely reflecting surface, a rather unchangeable fraction enters the microscope, however the latter may be arranged with respect to the direction of the original beam. Relative to the appearance of a section which, although originally polished to a mirror-like surface, has lost its luster in certain places through etching, the following may be said: Under the arrangement given in Fig. 117, *a*, no light enters the microscope from the "mirrored" portions, but the "non-mirrored" portions send diffuse light into the microscope. The portions which have not been etched appear dark, and those which have been etched appear light. Under the arrangements shown in Fig. 117, *b* and *c*, all of the light which falls upon the unetched (completely reflecting) portions enters the microscope, and these portions consequently appear lighter than the diffusely reflecting

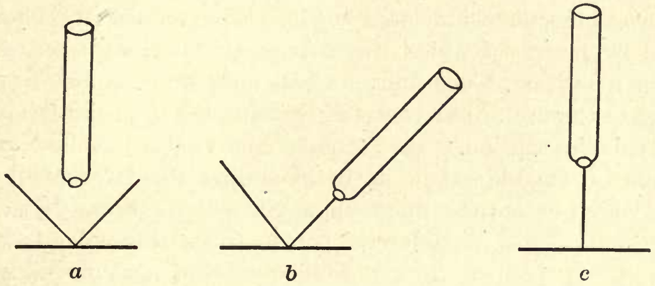

FIG. 117.

portions, although the sum total of light which enters the microscope from the latter source is about the same as under the arrangement given in Fig. 117, *a*.

An arrangement such as that indicated in Fig. 117, *a*, is readily attained with ordinary appliances. A common microscope with a rigid stand may be used in making observations. The oblique bundle of light rays may be obtained by means of a simple or compound lense properly set up. Since very little light, namely, only that which comes from the diffusely reflecting portions of the section, enters the microscope, low magnifications must be used.

The arrangement indicated in Fig. 117, *b*, requires a microscope stand by means of which the instrument may be placed in any inclined position. The Martens ball microscope stand, so called owing to the use of ball joints in securing the requisite flexibility, is of this description. This arrangement is also unsuited to high powers of magnification, notwithstanding the large amount of light which enters the microscope, since the varying distance of different parts of the illuminated surface from the objective (on account of its inclination to the axis of the instrument) precludes all possibility of a sharp focus with objectives of short focal distance. Obviously, the arrangement indicated in Fig. 117, *c*, may be realized with the Martens stand.

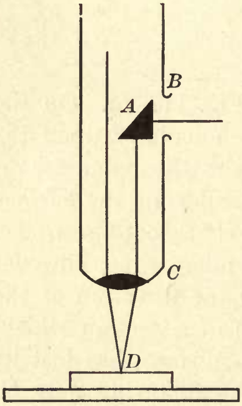

FIG. 118. Vertical Illuminator.

It is thus evident that for higher magnifications the arrangement shown in Fig. 117, *c*, which assigns a vertical position to the microscope and perpendicular incidence to the light rays, is alone open to consideration. The latter is effected by means of a vertical illuminator. This consists essentially of a glass prism *A* (see Fig. 118) placed between objective and ocular in such a way that its extreme (inside) edge reaches only to the optical axis of the microscope. A given ray from a beam of light which enters on the side at *B* and is cut down to the requisite size at this point by an iris diaphragm is totally reflected downwards through the prism, deflected by the objective *C* so that it falls upon the object

D under investigation, reflected from the surface of the object, and deflected again by the objective, whence it proceeds to the ocular in a direction parallel to the optical axis.

The construction of a microscope for this purpose calls for nothing unusual and is governed by the desired magnification and sharpness of image. The microscope used at the Goettingen Institute was constructed at the optical works of *R. Winkel* at Goettingen for magnifications of 18, 60, 140, 310 and 640 times.

§ 4. PHOTOGRAPHY.

Metallic sections may be photographed by removing the ocular from the microscope and substituting a suitable photographic camera. Naturally, the section is first placed to advantage, as regards the portion of the surface to be photographed, by direct test observations under the ocular. The frequent exchange of ocular and camera which is necessary under these conditions, becomes a burden and is dispensed with in the arrangement given by LECHATELIER.[1] This arrangement consists in a combination of ocular *A* and camera *B* (Fig. 119, *a*), the optical axes of which are both horizontal and stand at right angles to each other, with a single objective *C*, the optical axis of which is vertical. The latter axis is therefore at right angles to the first two axes, and the three optical axes are disposed in such a way as to constitute a right angled coördinate system. The necessary deflection of

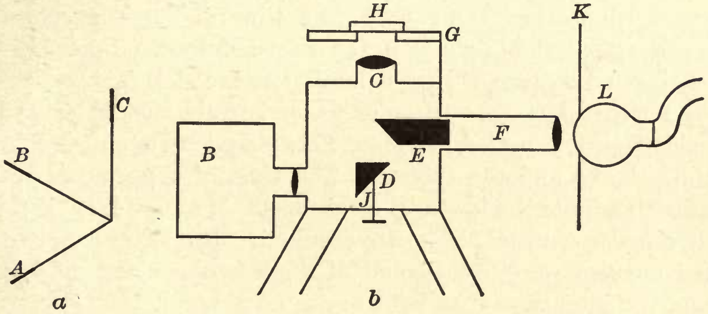

FIG. 119. Microscope according to LeChatelier.

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[1] LECHATELIER, contribution á l'étude des alliages, p. 431.

the light rays is effected by two total reflecting prisms *D* and *E*, which are so placed in Fig. 119, *b*, that light would enter the camera *B*. A ray of light which is passed through the illumination tube *F* in a direction parallel to its axis falls upon the prism *E*, in which it is totally reflected upwards. In this manner, it reaches the objective *C*, where it is deflected to fall upon the lower side of the object *B*. At this point, it is reflected and again deflected on repassing *C*. The ray is now directed at right angles towards the prism *D* (below), where it is totally reflected in the direction of the camera *B*. If the prism *D* is now turned 90 degrees around the vertical axis *J*, it directs the light ray toward the ocular *A*, which is situated at right angles to *B*. The latter course cannot be followed on the diagram since it is at right angles to the plane of the paper (*A* is not shown in Fig. 119, *b*). The perforated object table *G* is adjustable. For photographing, a section is placed on the object table with its prepared surface downwards. The prism *D* is turned so that light enters the ocular, and a suitable part of the surface of the section is sought out. Then the light rays are directed into the camera by turning the prism.

The ordinary methods of photography are carried out in the present connection. Obviously, the time of exposure depends upon the strength of light from the source of illumination. At the Goettingen Institute, a Nernst lamp (large model) *L* is preferably used for this purpose. In order to obviate the disturbing action of side lights, a perforated plate *K* is placed between the illuminating source and the tube *F*. The time of exposure approximates 10 minutes under these conditions. If an arc lamp is used, only a few seconds exposure are required. The latter is not to be recommended since, on account of the irregular action of such a lamp, the intensity of its light varies considerably.

After exposure, the plate is developed in the usual manner, fixed in an acid fixing bath, thoroughly washed, and then used for preparation of a positive. In case the contrasts in the object to be photographed are very delicate, Vogel-Obernetter's eosine plates (prepared by *Otto Perutz*, Muenchen), which are very sensitive to colors, will be found very serviceable. Contrasts appear best on short exposure. Glossy paper is most satisfactory in printing from the negative. If contrasts are not well marked in the negative, good prints may be made on "Rembrandt" paper, which should be printed to a dark bronze color. Directions for drying and fixing accompany the different brands of printing paper.

CONCLUSION.

In conclusion, we will introduce a few remarks relative to the practical significance of the methods described in this book, and the results obtained by their use. In estimating the service which METALLOGRAPHY has rendered in the realm of its application, we must not fail to recognize that the time during which metallic alloys have been used without any particular need of inquiring into their constitution has been incomparably long as opposed to the few years during which successful scientific revision of this field has taken place. If, therefore, we are unable to report, at this juncture, any revolutionary innovation in the metal industry field due to metallographical investigation, yet the advancement along technical lines which has already been brought about by this infant branch of science seems worthy of consideration in the highest degree. METALLOGRAPHY first of all furnishes us with a means for judging a product in cases where chemical analysis fails of application, and is, in consequence, a valuable agent in the testing of materials and in the regulation of factory products. We have seen, in discussing the iron-carbon diagram, how much the properties of two alloys of the same chemical composition may differ from one another. To one acquainted with the structure of iron-carbon alloys, microscopical investigation of a section is capable of showing at once whether the material in hand possesses the desired properties or not.

If the properties of the various structure elements composing a system are known, a glance at the perfected diagram serves to indicate how one should proceed to vary the properties of an alloy of given composition within possible limits — also shown by the diagram. We are already close upon this goal in the especial case of iron-carbon alloys. The temperature to which a variety of iron of definite carbon content should be heated, the temperature range within which it should be held for a time on cooling, and that through which it should be conducted with all possible rapidity in order to obtain this or that variety of steel — all this information may be taken directly from the diagram, which embraces the results of our experience in these matters in the most concise and clear manner. The enhanced trustworthiness of manufacture when managed on such a basis will not be held cheaply by any technical worker.

Again the rationally progressive investigator in this field will scarcely be able to do without a knowledge of the constitution of metallic alloys, whether he has the intention of realizing processes which are already current with cheaper materials or by cheaper methods, or is aiming to adjust new demands to a certain kind of material. The melting-point diagram shows him the predominant concentrations, such as limits of miscibility, eutectica, etc., whence it is merely necessary for him to investigate the properties of alloys corresponding to these and to several intermediate concentrations in order to learn whether a certain course entered upon may be expected to realize the end in view or not. Thus, well directed experimental effort is substituted for aimless probing and testing. Charpy's investigation of bearing metals, which was mentioned on page 275, furnishes a standard illustration of this.

The metallic alloys of greatest technical importance are radically those, the components of which are appreciably miscible in the crystalline condition. Experience teaches us that a metal which in the crystalline condition contains a dissolved amount — even though small — of another substance, frequently exhibits properties — hardness, tensile strength, conductivity, etc., which are quite widely at variance with those of the pure metal. Experiments dealing with the quantitative aspect of these effects are already on record. C. BENEDICKS[1] arrives at the conclusion that different elements when dissolved in equivalent quantities in iron raise its specific conductivity to the same extent. Concerning the influence of dissolved material on the hardness of iron, somewhat similar, although less simple, relations were found.

Although we stand at the present time on the threshold of a process of development, it may, nevertheless, be held most probable that technical progress in the metallic alloy field will proceed henceforth lesser in an empirical manner than on the basis of exact knowledge of their constitution.

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[1] BENEDICKS, Recherches physiques et physico-chimiques sur l'acier au carbone. Upsala, 1904.

Collection of references to Binary Fusion Diagrams of the Metallic Elements, covering such elements as have received more or less extended attention in this respect (all of the common metals and many which, although not rare, are commercially unimportant).

1. Sodium.

1. Na-K. Kurnakow and Puschin....Z. anorg. Chem., 30, 109, (1902).
2. (Na-Cu).
3. (Na-Ag).
4. (Na-Au).
5. Na-Mg. Mathewson..............Z. anorg. Chem., 48, 191, (1906).
6. Na-Zn. Mathewson..............Z. anorg. Chem., 48, 101, (1906).
7. Na-Cd. Mathewson..............Z. anorg. Chem., 50, 171, (1906).
8. Na-Hg. Schüller..................Z. anorg. Chem., 40, 3, (1904).
9. Na-Al. Mathewson..............Z. anorg. Chem., 48, 191, (1906).
10. Na-Tl. Kurnakow and Puschin....Z. anorg. Chem., 30, 86, (1902).
11. (Na-Si).
12. Na-Sn. Mathewson..............Z. anorg. Chem., 46, 94, (1905).
13. Na-Pb. Mathewson..............Z. anorg. Chem., 50, 171, (1906).
14. Na-Sb. Mathewson..............Z. anorg. Chem., 50, 171, (1906).
15. Na-Bi. Mathewson..............Z. anorg. Chem., 50, 171, (1906).
16. (Na-Cr).
17. (Na-Te).
18. (Na-Mn).
19. (Na-Fe).
20. (Na-Co).
21. (Na-Ni).
22. (Na-Pd).
23. (Na-Pt).

2. Potassium.

24. (K-Cu).
25. (K-Ag).
26. (K-Au).
27. K-Mg. Smith.....................Z. anorg. Chem., 56, 109, (1907).
28. K-Zn. Smith.....................Z. anorg. Chem., 56, 109, (1907).
29. K-Cd. Smith.....................Z. anorg. Chem., 56, 109, (1907).
30. K-Hg. Jänecke....................Z. phys. Chem., 58, 245, (1907).
31. K-Al. Smith.....................Z. anorg. Chem., 56, 109, (1907).
32. K-Tl. Kurnakow and Puschin.....Z. anorg. Chem., 30, 86, (1902).
33. (K-Si).
34. K-Sn. Smith.....................Z. anorg. Chem., 56, 109, (1907).
35. K-Pb. Smith.....................Z. anorg. Chem., 56, 109, (1907).
36. (K-Sb).

37.	K-Bi.	Smith	Z. anorg. Chem., 56, 109, (1907).
38.	(K-Cr).		
39.	(K-Te).		
40.	(K-Mn).		
41.	(K-Fe).		
42.	(K-Co).		
43.	(K-Ni).		
44.	(K-Pd).		
45.	(K-Pt).		

3. Copper.

46.	Cu-Ag.	Heycock and Neville	Trans. Royal Soc., 189, 25, (1897).
		Friedrich and Leroux	Metallurgie, 4, 293, (1907).
47.	Cu-Au.	Kurnakow and Zemczuznyj	Z. anorg. Chem., 54, 149, (1907).
48.	Cu-Mg.	Sahmen	Z. anorg Chem., 57, 1, (1908).
49.	Cu-Zn.	Shepherd	J. Phys. Chem., 8, 421, (1904).
		Tafel	Metallurgie, 5, 343, (1908), *et seq.*
50.	Cu-Cd.	Sahmen	Z. anorg. Chem., 49, 301, (1906).
51.	(Cu-Hg).		
52.	Cu-Al.	Gwyer	Z. anorg. Chem., 57, 113, (1908).
53.	Cu-Tl.	Doerinckel	Z. anorg. Chem., 48, 185, (1906).
54.	Cu-Si.	Rudolfi	Z. anorg. Chem., 53, 216, (1907).
55.	Cu-Sn.	Shepherd and Blough	J. Phys. Chem., 10, 630, (1906).
56.	Cu-Pb.	Hiorns	J. Soc. Chem. Ind., 25, 616, (1906).
		Friedrich and Leroux	Metallurgie, 4, 293, (1907).
57.	Cu-Sb.	Baikow	J. Russ. Phys. Chem. Soc., 36, 111 (1905). Bull. soc. encouragement, 200, (1903); C. B., 1905 (1), 665.
58.	Cu-Bi.	Jeriomin	Z. anorg. Chem., 55, 412, (1907).
59.	Cu-Cr.	Hindrichs	Z. anorg. Chem., 59, 414, (1908).
60.	Cu-Te.	Chikashige	Z. anorg. Chem., 54, 50, (1907).
61.	Cu-Mn.	Wologdine	Revue de Met., 4, 27, (1907).
		Sahmen	Z. anorg. Chem., 57, 1, (1908).
		Zemczuznyj, Urasow and Rykowskow	Z. anorg. Chem., 57, 253, (1908).
62.	Cu-Fe.	Sahmen	Z. anorg. Chem., 57, 1, (1908).
63.	Cu-Co.	Sahmen	Z. anorg. Chem., 57, 1, (1908).
64.	Cu-Ni.	Guertler and Tammann	Z. anorg. Chem., 52, 25, (1907).
		Kurnakow and Zemczuznyj	Z. anorg. Chem., 54, 149, (1907).
65.	Cu-Pd.	Ruer	Z. anorg. Chem., 51, 223, (1906).
66.	Cu-Pt.	Doerinckel	Z. anorg. Chem., 54, 333, (1907).

4. Silver.

67.	Ag-Au.	Roberts-Austin and Kirke Rose	Chem. News, 87, 2, (1903).
68.	Ag-Mg.	Zemczuznyj	Z. anorg. Chem., 49, 400, (1906).
69.	Ag-Zn.	Petrenko	Z. anorg. Chem., 48, 347, (1906).

70. Ag-Cd. Rose.................... Proc. Royal Soc., 74, 218.
71. (Ag-Hg).
72. Ag-Al. Petrenko.................. Z. anorg. Chem., 46, 49, (1905).
73. Ag-Tl. Petrenko.................. Z. anorg. Chem., 50, 133, (1906).
74. Ag-Si. Arrivant.................. Z. anorg. Chem., 60, 436, (1908).
75. Ag-Sn. Petrenko.................. Z. anorg. Chem., 53, 200, (1907).
76. Ag-Pb. Petrenko.................. Z. anorg. Chem., 53, 200, (1907).
Friedrich and Leroux..... Metallurgie, 4, 293, (1907).
77. Ag-Sb. Petrenko.................. Z. anorg. Chem., 50, 133, (1906).
78. Ag-Bi. Petrenko.................. Z. anorg. Chem., 50, 133, (1906).
79. Ag-Cr. Hindrichs................. Z. anorg. Chem., 59, 414, (1908).
80. (Ag-Te).
81. Ag-Mn. Hindrichs................. Z. anorg. Chem., 59, 414, (1908).
82. Ag-Fe. Petrenko.................. Z. anorg. Chem., 53, 212, (1907).
83. Ag-Co. Petrenko.................. Z. anorg. Chem., 53, 212, (1907).
84. Ag-Ni. Petrenko.................. Z. anorg. Chem., 53, 212, (1907).
85. Ag-Pd. Ruer...................... Z. anorg. Chem., 51, 315, (1906).
86. Ag-Pt. Doerinckel................ Z. anorg. Chem., 54, 333, (1907).

5. Gold.

87. (Au-Mg).
88. Au-Zn. Vogel..................... Z. anorg. Chem., 48, 319, (1906).
89. Au-Cd. Vogel..................... Z. anorg. Chem., 48, 333, (1906).
90. (Au-Hg).
91. Au-Al. Heycock and Neville....... Trans. Royal Soc., 194 (A), 201, (1900).
92. Au-Tl. Levin..................... Z. anorg. Chem., 45, 31, (1905).
93. (Au-Si).
94. Au-Sn. Vogel..................... Z. anorg. Chem., 46, 60, (1905).
95. Au-Pb. Vogel..................... Z. anorg. Chem., 45, 11, (1905).
96. Au-Sb. Vogel..................... Z. anorg. Chem., 50, 145, (1906).
97. Au-Bi. Vogel..................... Z. anorg. Chem., 50, 145, (1906).
98. (Au-Cr).
99. (Au-Te).
100. (Au-Mn).
101. Au-Fe. Isaac and Tammann..... Z. anorg. Chem., 53, 281, (1907).
102. (Au-Co).
103. Au-Ni. Levin.................. Z. anorg. Chem., 45, 238, (1905).
104. Au-Pd. Ruer................... Z. anorg. Chem., 51, 391, (1906).
105. Au-Pt. Doerinckel............. Z. anorg. Chem., 54, 333, (1907).

6. Magnesium.

106. Mg-Zn. Grube.................. Z. anorg. Chem., 49, 72, (1906).
107. Mg-Cd. Grube.................. Z. anorg. Chem., 49, 72, (1906).
108. (Mg-Hg).
109. Mg-Al. Grube.................. Z. anorg. Chem., 45, 225, (1905).

110.	Mg-Tl.	Grube	Z. anorg. Chem., 46, 76, (1905).
111.	Mg-Si.	Vogel	Z. anorg. Chem., 61, 46, (1909).
112.	Mg-Sn.	Grube	Z. anorg. Chem., 46, 76, (1905).
113.	Mg-Pb.	Grube	Z. anorg. Chem., 44, 117, (1905).
114.	Mg-Sb.	Grube	Z. anorg. Chem., 49, 72, (1906).
115.	Mg-Bi.	Grube	Z. anorg. Chem., 49, 72, (1906).
116.	(Mg-Cr).		
117.	(Mg-Te).		
118.	(Mg-Mn).		
119.	(Mg-Fe).		
120.	(Mg-Co).		
121.	(Mg-Ni).	Voss	Z. anorg. Chem., 57, 34, (1908).
122.	(Mg-Pd).		
123.	(Mg-Pt).		

7. Zinc.

124.	Zn-Cd.	Hindrichs	Z. anorg. Chem., 55, 415, (1907).
125.	Zn-Hg.	Puschin	Z. anorg. Chem., 36, 201, (1903).
126.	Zn-Al.	Shepherd	J. Phys. Chem., 9, 504, (1905).
127.	Zn-Tl.	Vegesack	Z. anorg. Chem., 52, 30, (1907).
128.	(Zn-Si).		
129.	Zn-Sn.	Heycock and Neville	J. Chem. Soc., 383, (1897).
130.	Zn-Pb.	Spring and Romanoff	Z. anorg. Chem., 13, 29, (1897).
		Heycock and Neville	J. Chem. Soc., 71, 383, (1897).
131.	Zn-Sb.	Mönckemeyer	Z. anorg. Chem., 43, 182, (1905).
		Zemczuznyj	Z. anorg. Chem., 49, 384, (1906).
132.	Zn-Bi.	Spring and Romanoff	Z. anorg. Chem., 13, 29, (1897).
		Heycock and Neville	J. Chem. Soc., 71, 383, (1897).
133.	Zn-Cr.	Hindrichs	Z. anorg. Chem., 59, 414, (1908).
134.	(Zn-Te).		
135.	(Zn-Mn).		
136.	Zn-Fe.	Vegesack	Z. anorg. Chem., 52, 30, (1907).
137.	Zn-Co.	Lewkonja	Z. anorg. Chem., 59, 293, (1908).
138.	Zn-Ni.	Tafel	Metallurgie, 4, 781, (1907) and 5, 343, (1908) *et seq.*
		Voss	Z. anorg. Chem., 57, 34, (1908).
139.	(Zn-Pd).		
140.	(Zn-Pt).		

8. Cadmium.

141.	Cd-Hg.	Bijl	Z. Phys. Chem., 41, 641, (1902).
		Jänecke	Z. Phys. Chem., 50, 399, (1907).
142.	Cd-Al.	Gwyer	Z. anorg. Chem., 57, 113, (1908).
143.	Cd-Tl.	Kurnakow and Puschin	Z. anorg. Chem., 30, 86, (1902).
144.	(Cd-Si).		
145.	Cd-Sn.	Stoffel	Z. anorg. Chem., 53, 137, (1907).

146.	Cd-Pb.	Stoffel	Z. anorg. Chem., 53, 152, (1907).
		Jänecke	Z. Phys. Chem., 50, 399, (1907).
147.	Cd-Sb.	Treitschke	Z. anorg. Chem., 50, 217, (1906).
		Kurnakow and Konstantinow	Z. anorg. Chem., 58, 1, (1908).
148.	Cd-Bi.	Stoffel	Z. anorg. Chem., 53, 137, (1907).
		Portevin	Revue Met., 4, 389, (1907).
149.	Cd-Cr.	Hindrichs	Z. anorg. Chem., 59, 414, (1908).
150.	(Cd-Te).		
151.	(Cd-Mn).		
152.	Cd-Fe.	Isaac and Tammann	Z. anorg. Chem., 55, 58, (1907).
153.	Cd-Co.	Lewkonja	Z. anorg. Chem., 59, 293, (1908).
154.	Cd-Ni.	Voss	Z. anorg. Chem., 57, 34, (1908).
155.	(Cd-Pd).		
156.	(Cd-Pt).		

9. MERCURY.

157.	Hg-Al.		
158.	Hg-Tl.	Kurnakow and Puschin	Z. anorg. Chem., 30, 86, (1902).
159.	(Hg-Si).		
160.	Hg-Sn.	Van Heteren	Z. anorg. Chem., 42, 129, (1904).
161.	Hg-Pb.	Fay and North	Am. Chem. J., 25, 230, (1901).
		Puschin	Z. anorg. Chem., 36, 209,(1903).
		Jänecke	Z. Phys. Chem., 50, 399, (1907).
162.	(Hg-Sb).		
163.	Hg-Bi.	Puschin	Z. anorg. Chem., 36, 201, (1903).
164.	(Hg-Cr).		
165.	(Hg-Te).		
166.	(Hg-Mn).		
167.	(Hg-Fe).		
168.	(Hg-Co).		
169.	(Hg-Ni).		
170.	(Hg-Pd).		
171.	(Hg-Pt).		

10. ALUMINIUM.

172.	Al-Tl.	Doerinckel	Z. anorg. Chem., 48, 185, (1906).
173.	Al-Si.	Fraenkel	Z. anorg. Chem., 58, 154, (1908).
174.	Al-Sn.	Gwyer	Z. anorg. Chem., 49, 311, (1906).
175.	Al-Pb.	Gwyer	Z. anorg. Chem., 57, 113, (1908).
176.	Al-Sb.	Tammann	Z. anorg. Chem., 48, 53, (1905).
177.	Al-Bi.	Gwyer	Z. anorg. Chem., 49, 311, (1906).
178.	Al-Cr.	Hindrichs	Z. anorg. Chem., 59, 414, (1908).
179.	(Al-Te).		
180.	Al-Mn.	Hindrichs	Z. anorg. Chem., 59, 414, (1908).

181.	Al-Fe.	Carpenter and Edwards	Engineering, 83, 253, (1907).
		Gwyer	Z. anorg. Chem., 57, 113, (1908).
		Curry	Metallurgie, 5, 540, (1908), detailed abstract with fusion diagram.
182.	Al-Co.	Gwyer	Z. anorg. Chem., 57, 113, (1908).
183.	Al-Ni.	Gwyer	Z. anorg. Chem., 57, 113, (1908).
184.	(Al-Pd).		
185.	(Al-Pt).		

11. Thallium.

186.	Tl-Si.	Tamaru	Z. anorg. Chem., 61, 40, (1909).
187.	Tl-Sn.	Kurnakow and Puschin	Z. anorg. Chem., 30, 86, (1902).
188.	Tl-Pb.	Kurnakow and Puschin	Z. anorg. Chem., 52, 430, (1907).
		Lewkonja	Z. anorg. Chem., 52, 452, (1907).
189.	Tl-Sb.	Williams	Z. anorg. Chem., 50, 127, (1906).
190.	Tl-Bi.	Chikashige	Z. anorg. Chem., 51, 328, (1906).
191.	(Tl-Cr).		
192.	Tl-Te.	Pelabon	Cr., 145, 118, (1907).
193.	(Tl-Mn).		
194.	Tl-Fe.	Isaac and Tammann	Z. anorg. Chem., 55, 58, (1907).
195.	Tl-Co.	Lewkonja	Z. anorg. Chem., 59, 293, (1908).
196.	Tl-Ni.	Voss	Z. anorg. Chem., 57, 34, (1908).
197.	(Tl-Pd).		
198.	(Tl-Pt).		

12. Silicon.

199.	Si-Sn.	Tamaru	Z. anorg. Chem., 61, 40, (1909).
200.	Si-Pb.	Tamaru	Z. anorg. Chem., 61, 40, (1909).
201.	Si-Sb.	Williams	Z. anorg. Chem., 55, 1, (1907).
202.	Si-Bi.	Williams	Z. anorg. Chem., 55, 1, (1907).
203.	(Si-Cr).		
204.	(Si-Te).		
205.	Si-Mn.	Doerinckel	Z. anorg. Chem., 50, 117, (1906).
206.	Si-Fe.	Guertler and Tammann	Z. anorg. Chem., 47, 163, (1905).
207.	Si-Co.	Lewkonja	Z. anorg. Chem., 59, 293, (1908).
208.	Si-Ni.	Guertler and Tammann	Z. anorg. Chem., 49, 93, (1906).
209.	(Si-Pd).		
210.	(Si-Pt).		

13. Tin.

211.	Sn-Pb.	Stoffel	Z. anorg. Chem., 53, 137, (1907); *cf.* also Puschin, C. B., 1907, (2), 2027.
212.	Sn-Sb.	Williams	Z. anorg. Chem., 55, 1, (1907).
213.	Sn-Bi.	Stoffel	Z. anorg. Chem., 53, 137, (1907).
		Lepkowski	Z. anorg. Chem., 59, 285, (1908).
214.	Sn-Cr.	Hindrichs	Z. anorg. Chem., 59, 414, (1908).

215.	Sn-Te.	Fay	J. Am. Chem. Soc., 29, 1265 (1907).
		Pelabon	Cr., 142, 1147, (1906).
216.	Sn-Mn.	Williams	Z. anorg. Chem., 55, 1, (1907).
217.	Sn-Fe.	Isaac and Tammann	Z. anorg. Chem., 53, 281, (1907).
218.	Sn-Co.	Lewkonja	Z. anorg. Chem., 59, 293, (1908).
		Zemczuznyj and Belynsky	Z. anorg. Chem., 59, 364, (1908).
219.	Sn-Ni.	Guillet	Revue de Met., 5, 34, (1907).
		Voss	Z. anorg. Chem., 57, 34, (1908).
220.	(Sn-Pd).		
221.	(Sn-Pt).		

14. LEAD.

222.	Pb-Sb.	Gonterman	Z. anorg. Chem., 55, 419, (1907).
223.	Pb-Bi.	Stoffel	Z. anorg. Chem., 53, 137, (1907).
224.	Pb-Cr.	Hindrichs	Z. anorg. Chem., 59, 414, (1908).
225.	Pb-Te.	Fay and Gillson	Am. Chem. J., 27, 81, (1902).
226.	(Pb-Mn).		
227.	Pb-Fe.	Isaac and Tammann	Z. anorg. Chem., 55, 58, (1907).
228.	Pb-Co.	Lewkonja	Z. anorg. Chem., 59, 293, (1908).
229.	Pb-Ni.	Portevin	Rev. de Met., 4, 814, (1907).
		Voss	Z. anorg. Chem., 57, 34, (1908).
230.	Pb-Pd.	Ruer	Z. anorg. Chem., 52, 345, (1907).
231.	Pb-Pt.	Doerinckel	Z. anorg. Chem., 54, 333, (1907).

15. ANTIMONY.

232.	Sb-Bi.	Huttner and Tammann	Z. anorg. Chem., 44, 131, (1905).
233.	Sb-Cr.	Williams	Z. anorg. Chem., 55, 1, (1907).
234.	Sb-Te.	Pelabon	Cr., 142, 207, (1906).
235.	Sb-Mn.	Williams	Z. anorg. Chem., 55, 1, (1907).
236.	Sb-Fe.	Kurnakow and Konstantinow	Z. anorg. Chem., 58, 1, (1908).
237.	Sb-Co.	Lewkonja	Z. anorg. Chem., 59, 293, (1908).
238.	Sb-Ni.	Lossew	Z. anorg. Chem., 49, 58, (1906).
		Kurnakow and Podkopajew	J. Russ. Phys. Chem. Soc., 37, 1280, (1905).
239.	(Sb-Pd).		
240.	Sb-Pt.	Friedrich and Leroux	Metallurgie, 6, 1, (1909).

16. BISMUTH.

241.	Bi-Cr.	Williams	Z. anorg. Chem., 55, 1, (1907).
242.	Bi-Te.	Monckemeyer	Z. anorg. Chem., 46, 415, (1905).
243.	Bi-Mn.	Williams	Z. anorg. Chem., 55, 1, (1907).
244.	Bi-Fe.	Isaac and Tammann	Z. anorg. Chem., 55, 58, (1907).

245. Bi-Co. Lewkonja..............Z. anorg. Chem., 59, 293, (1908).
246. Bi-Ni. Voss....................Z. anorg. Chem., 57, 34, (1908).
247. (Bi-Pd).
248. (Bi-Pt).

17. CHROMIUM.

249. (Cr-Te).
250. (Cr-Mn).
251. Cr-Fe. Treitschke...............Z. anorg. Chem., 55, 402, (1907).
252. Cr-Co. Lewkonja...............Z. anorg. Chem., 59, 293, (1908).
253. Cr-Ni. Voss....................Z. anorg. Chem., 57, 34, (1908).
254. (Cr-Pd).
255. (Cr-Pt).

18. TELLURIUM.

256. (Te-Mn).
257. (Te-Fe).
258. (Te-Co).
259. (Te-Ni).
260. (Te-Pd).
261. (Te-Pt).

19. MANGANESE.

262. Mn-Fe. Levin and Tammann.....Z. anorg. Chem., 47, 136, (1905).
263. (Mn-Co).
264. Mn-Ni. Zemczuznyj, Urasow and
Rykowskow ....Z. anorg. Chem., 57, 253, (1908).
265. (Mn-Pd).
266. (Mn-Pt).

20. IRON.

267. Fe-Co. Guertler and Tammann.. Z. anorg. Chem. 45, 205, (1905).
268. Fe-Ni. Guertler and Tammann...Z. anorg. Chem., 45, 205, (1905).
269. (Fe-Pd).
270. (Fe-Pt).

21. COBALT.

271. Co-Ni. Guertler and Tammann...Z. anorg. Chem., 42, 353, (1904).
272. (Co-Pd).
273. (Co-Pt).

22. NICKEL.

274. (Ni-Pd).
275. (Ni-Pt).

23. PALLADIUM.

276. (Pd-Pt).

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