

ON THE THEORY OF DALTONIDES AND BERTOLLIDES

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ABSTRACT

In the present article an attempt has been made to generalize all the various cases of variable composition phases by approaching them from one standpoint, and in this way to create an atom-structural basis for the conceptions, which have proved to be most fruitful both scientifically and practically, that were introduced into science 50 years ago by N. S. Kurnakov. This part of chemistry is known at present as the theory of daltonides and bertollides.

We believe this essay to be a further step in the development of the said theory.

INTRODUCTION

1. In 1900 N. S. Kurnakov and his assistants began an experimental investigation of chemical relation between metals (1939). It appeared that chemical compounds, formed out of two (and more) metals, differed considerably from ordinary inorganic and organic compounds. The first peculiarity of these compounds was that it did not always prove possible to isolate them in their pure form; secondly, these compounds had a composition, which varied within wide limits. In contradistinction to most of the ordinary inorganic substances, it was difficult to characterize them by a definite composition.

For the purpose of overcoming these difficulties Kurnakov began to investigate equilibrium systems consisting of metal components by applying the method of physico-chemical analysis and drawing composition-property diagrams that were subsequently analysed.

While investigating the Cu-Au system Kurnakov discovered a new phenomenon (Kurnakov *et al.*, 1914, 1915, 1916). It appeared that the properties of the samples depend on their history. This peculiarity revealed the essential difference existing between intermetal substances and ordinary inorganic ones. An inorganic salt, no matter how it is prepared, usually possesses the same properties. But it is altogether different with a sample of intermetal.

It appeared that tempered and annealed samples of the same composition possess different properties and that this is not connected with polymorphism. Kurnakov drew correct conclusions to the effect that in this particular case (Cu-Au system) intermetal compounds (Cu-Au and Cu_3Au) are obtained out of a solid solution. These processes have been now thoroughly studied for many systems and have been given the name *processes of ordering*.

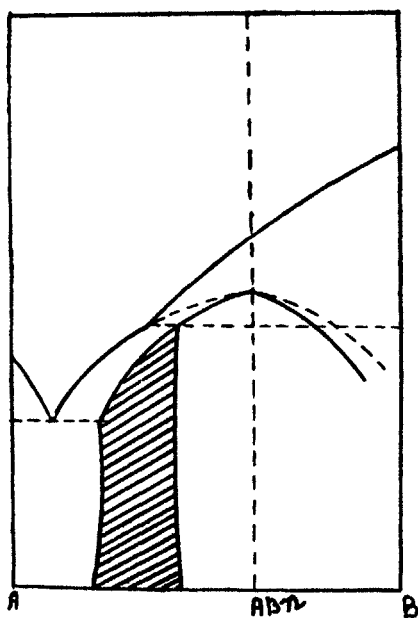
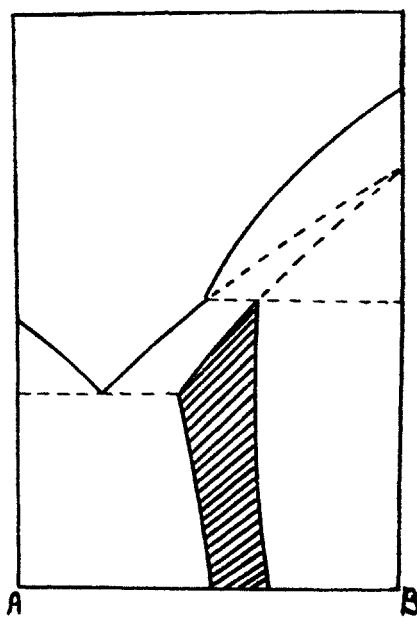
The study of melting diagrams of double metal systems has revealed that some solid phases are characterized by the absence of a maximum on the liquidus and solidus curve, whereas others have a maximum. Solid phases, characterized by a maximum, may also be divided into two groups. In one group the distectid point is governed by the law of composition constancy, in the second, some deviations from this law are observed. Kurnakov gave the phases of the second group the name of 'indefinite compounds' (Kurnakov and Pushin, 1900, 1906, 1907a, 1907b) to distinguish them from the 'definite' ones (first group). He pointed out that in both groups of compounds in a solid state a variability of composition takes

place (Kurnakov and Jemchujny, 1906); in this they differ from 'compounds of constant composition'.

In the case of definite compounds, specific 'singular' points corresponding to the rational composition (Kurnakov and Jemchujny, 1912*a*, 1912*b*) appear on the isotherm of composition-property diagrams.

In the case of phases without a maximum on the liquidus curve and in the case of indefinite compounds, the composition-property diagram will be of a 'non-singular type'. The maximum on the composition-property curves in the case of indefinite compounds will be displaced, that is, changed in point of composition, if the equilibrium factors are changed. Kurnakov suggested that the phases of the last two types should be called 'bertollides' (1940*a*) so as to distinguish them from 'daltonides' or definite compounds (1940*b*). In his later works, when trying to comprehend the nature of these phases, Kurnakov went on distinguishing bertollides with a maximum from bertollides without a maximum [(1928), p. 549, Figs. 50-52].

For this purpose he used the concept of a *labile compound* or a compound which does not exist in its pure form, or of a polymorphous modification of a substance, which is a component of the system. Such substances, by dissolving the second component or the second compound, have a certain sphere of existence, the compounds of rational composition, on the basis of which this phase has been formed, not being found within its limits. These compounds or modifications have been later given the name of 'imaginary' (Figs. 1*a* and 1*b*).

FIG. 1*a*FIG. 1*b*

The terms 'daltonides' and 'bertollides' have been introduced by Kurnakov into science in memory of the historic argument of Dalton and Proust with Berthollet and his followers on the nature and composition of chemical compounds.

2. Kurnakov and his followers investigated the problem of daltonides and bertollides in the course of a number of years. Ageev (1935, 1941), Makarov (1940-41) and Ageev and Makarov (1943) worked at the problem of imaginary compounds. The latter, however, repeatedly made critical remarks in the press

concerning the conception of imaginary compounds in chemistry (Makarov, 1947, 1949, 1950), and Ageev, on the basis of the investigation of bertollides, formed a wrong conception of 'variability and continuity of changes of atom valency in a crystal' (Ageev, 1952).

Mikheeva (1944*a*, 1944*b*), Kurnakov and Mikheeva (1938*a*, 1938*b*, 1940*a*, 1940*b*) and recently Petrov (1953) did much work in order to throw light on the nature of daltonides and bertollides.

All these investigations are somewhat one-sided, for the authors tried to penetrate into the essence of the concepts in question on the basis of a purely phenomenological approach to the problem. It was Makarov who tried to get out of this tangle by supposing that daltonides are characterized by one kind of structural types, and bertollides by others (Makarov, 1949). Later on, however, he himself proved that from the point of view of structure there is no difference between daltonides and bertollides.

This conclusion has always seemed natural to me, since the continuous transition of daltonides into bertollides was an established fact. Kurnakov himself (1936, 1940*c*) used to write about the possibility of such transitions. They were realized in several systems (see, for instance, system Fe-Sb-Ni), that have been investigated by Ageev and Makarov (1943).

Thus, Makarov's attempt has not proved successful either.

3. Nevertheless the solution of the problem of the nature of daltonides and bertollides is not so hopeless as it may seem. A correct solution of the problem may, possibly, lie in a combination of data, obtained by means of phenomenological methods with atom-structural conceptions of modern crystallo-chemistry.

In the first place let us elucidate the essence of the concept of an 'imaginary compound' or 'imaginary modification'. Kurnakov wrote about the nature of phases, whose field of expansion does not extend to pure components (Fig. 1): 'The experimental discrimination between these two possible cases presents many difficulties and may be achieved only approximately (presumably) by means of comparison with corresponding systems, in which the singular ordinate AB_n (Fig. 1*a*) or the second modification of components B (Fig. 1*b*) are open to direct observation' (Kurnakov, 1928, p. 549).

What seemed very difficult, and in a number of concrete cases even impossible, if we make use only of methods of physico-chemical analysis, may be solved rather easily if we use for this purpose atom-structural data.

Solid phases of variable composition are of the solid solution type of displacement or incorporation. From the point of view of structure the common feature they have is, that the change of composition in both cases, as a rule, occurs within the limits of one correct system of points.* In case of solid displacement solutions the atoms of elements displacing each other alternate in this CSP, whereas in case of solid incorporation solutions the atoms of the element, whose quantity changes in the phase, do not occupy all the points of CSP, but only some of them; in other words the atoms of this element alternate with the vacant places in the given CSP.

If in some concrete case the process of displacement or incorporation of CSP as a result of unfavourable physico-chemical conditions finishes without having reached the limit, that is, without a complete filling of this CSP with atoms of a certain element, then such a phase will not reach a limit rational composition. This will take place in both cases of Fig. 1. Nevertheless we can always extrapolate till a complete filling of the CSP. The composition of the phase in this case will have a simple definition and we shall be able to distinguish easily case (a) from case (b). The limit composition will be always governed by the law of composition constancy, as the CSP multiples are always integral figures. In this way the

* Further on the term 'correct system of points' will be denoted by CSP.

crystallo-chemical analysis of facts always allows us to determine on principle the composition of the imaginary compound or to prove that the limit is an imaginary modification.

To illustrate case 1a, we may take the E-phase in system Fe-Sb, stable from 42 to 48 at. % Sb (II), the limit composition of which is FeSb; or the β -phase in system Na-Pb, the limit composition of which is Pb_3Na (Zentlu and Horden, 1931). As an example of 1b may be taken the β -phase in system Cu-Zn, whose region of homogeneity varies within the limits of Cu-Zn 0, 7-1, 4. The limit of the phase will be the non-existent modification of copper with the structure of cubic body-centered packing (type L-Fe).

4. Such crystallo-chemical approach of the problem allows us to raise a wider question than the one raised in the physico-chemical analysis, and to solve it in many cases.

In the examples that have been analysed above (Figs. 1a and 1b) Kurnakov raised the question of one limit—namely that of the imaginary compound or modification. Now we may raise a more general question and limit the phase by all the possible limits of composition. Evidently for phases in two-component systems there are two limits of that kind, for three-component systems, three, etc.

In the analysed example of the Cu-Zn system the non-existing cubic body-centered modification of zinc will be the second limit of the β -phase. The components, however, will not always be the limits, and the limits are not always conditioned by purely structural characteristics. The valency of elements may impose its restrictions. For the E-phase of the Fe-Sb system, for instance, the composition Fe_3Sb_2 will be the second limit, as the excess of iron in the phase is caused by the fact that not all the atoms of iron are in a trivalent state, part of them are in a divalent state; therefore a larger quantity of iron atoms than that of Sb atoms is observed in the phase. Thus if we proceed from purely structural considerations, we should arrive at a limit composition of Fe_2Sb -phase (Ni_2 in type), but the valency of elements, out of whose atoms the given phase is formed, puts the limit earlier.

Thus in many concrete cases it is possible to find all the composition limits for the phases of variable compositions, that is, its imaginary compounds or modifications.

The crystallo-chemical approach of the problem not only proves the rationality of introducing into science the notion of an imaginary compound, but also supplies us with a method of determining its composition in concrete cases.

5. We have analysed here the essence of one of the bertollide types from the atom-structural point of view; now let us turn to the essence of daltonides. If we are to denote by the term daltonide a compound of strictly constant composition, then from the atom-structural point of view it is characterized by the fact that in the crystal structure different CSP's are occupied by atoms of various chemical elements (for instance $NaCl$, K_2PtCl_6 and others). In some cases the atoms of one chemical element may occupy several CSP's, but even in that case they occupy the latter completely.

All these phases in double systems will be expressed on the composition-temperature diagram by one ordinate and, consequently, in these cases no composition-property diagrams can be built in one-phase regions.

N. S. Kurnakov's theory was most fruitfully applied to phases, which have a definite homogeneity region depending on its composition, this being characteristic, as has been mentioned above, of systems formed of metals. If such a phase on the composition-property diagram has a singular point, it is called a daltonide, to distinguish it from a bertollide that has no such point. Some authors apply the term daltonide only to a substance, corresponding to a singular point, whereas the whole variable composition phase that contains a daltonide, they call a daltonide phase (see, for instance, Makarov, 1940-41). This may make the concept

of a daltonide somewhat more precise, but its drawback is that it does not allow this notion to be contrasted to that of a bertollide.

These arguments are mostly of a terminological character and we are not going to dwell on them. In the present article the terms 'daltonide' and 'bertollide' will imply phases, exactly as it follows from the spirit of Kurnakov's theory. In both cases these are variable composition phases. If we try to analyse from the point of view of the atom-structure the structure of a daltonide (to be more exact, of a daltonide phase) then our attention will be attracted by the fact that within the interval from the border line of the phase to the dalton point the composition change occurs in one CSP, and from the dalton point to the other border line, in another CSP (see, for instance, the Ni-Sb system, Makarov, 1947). In the case of a bertollide (without a maximum on the composition-property curves) that has been analysed above, the change of composition occurred in one CSP.

So long as the composition change occurs in one CSP, the phase properties, depending on the composition, change smoothly. In some cases such a curve, showing the dependence of properties on the composition, may have a maximum or a minimum but it will always be very slightly inclined and will not correspond to a definite compound, as it takes place, for instance, on the liquidus and solidus curve in some double systems with a continuous row of solid solutions (see system Cu-Au).

As soon as the composition in another CSP begins to change, the nature of the change in the dependence of properties on the composition becomes different. As a result of it the property curve shows a sudden breaking. Two tangents drawn in this point to two curves (dependence of properties on the composition, connected with a change in two CSP) will not coincide; the phase of such a type will be a typical daltonide.

If the process of displacement or filling a CSP, as a result of unfavourable physico-chemical conditions, ends without having reached the limit (that is, a complete filling of CSP) such a phase will have no maximum on the property curve and will be a bertollide.

6. The most difficult case is presented by solid phases, which have a maximum on the property curves, but this maximum does not strictly correspond to stoichiometric composition and, depending on various conditions, its position may change along the abscissae axis. This is a special bertollide case (Kurnakov, 1928, p. 549). Probably such a case may be properly comprehended if such a displacement of the maximum will be accounted for on the basis of atom-structural peculiarities of variable composition phases and a knowledge of regulating processes.

The necessary explanation of the phenomenon may be given, if we accept the hypothesis that in such solid phases the process of composition change before ending in one CSP has already begun in another CSP. Such processes actually take place in solid phases. This may be seen from the example of the Fe-Al system, where the regulation processes were investigated in great detail by applying the Rentgen method (Bradley and Jay, 1932).

To explain the properties of solid phases of this type we suggest using a method that may be called a method of cycles.

Fig. 2 represents 3 CPS's: (a) and (b) with multiple 4¹ and (c) with multiple 8 in the Fm3m Fedorov group. If all the three CPS's are occupied by atoms of one element, then we obtain a structure with Jm3m Fedorov group of the L-Fe type, that corresponds to A composition on Fig. 3. If positions a and b are occupied by atoms of the second component and c by atoms of the first component, then we have composition AB and a structure of the CsCl type (the Pm3m Fedorov group). If among these two four multiple positions only one is occupied by atoms

¹ By CPS multiple we mean the number of points to one elementary structure cell (unit).

of the second component (for instance (a)), and (b) and (c) are occupied by atoms of the first component, then we have an A_3B composition and a structure of the Fe_3Al type.

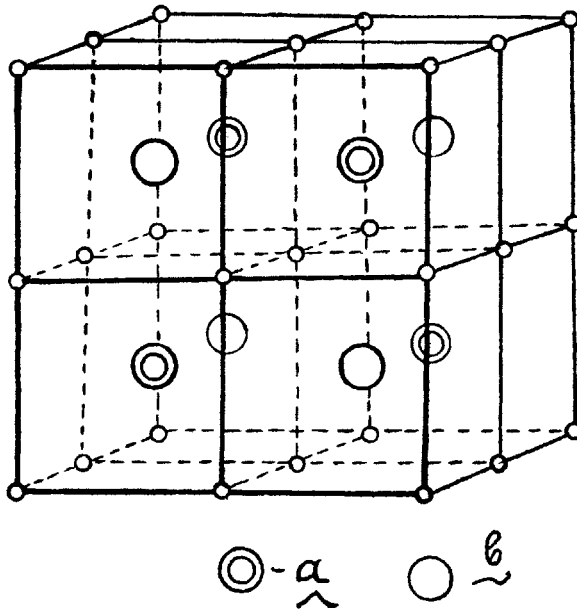


FIG. 2

Let us go back to Fig. 3. In case of uninterrupted (continuous) solid solutions from A to AB, the phase properties will be expressed by curve CDEF. But if the regulation begins at once in positions (a) and (b), the phase properties will be different. They will be expressed by curve CGLH.

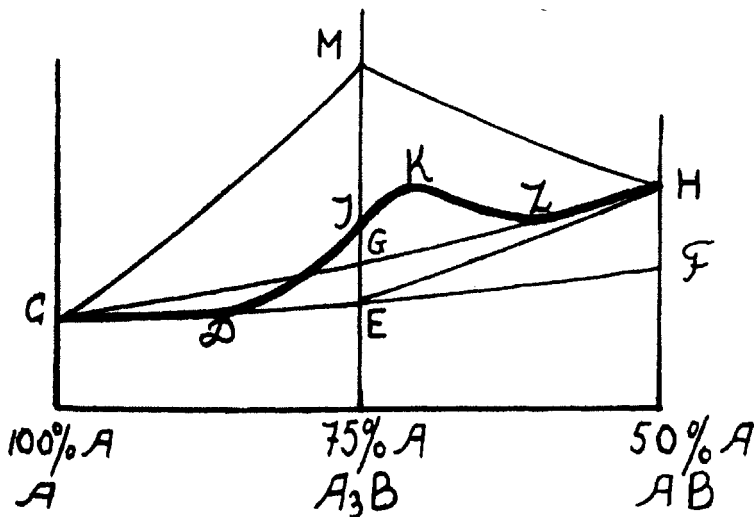


FIG. 3

As can be seen from experiment (Bradley and Jay, 1932), tempered alloys in the Fe-Al system are accordingly regulated not from the very beginning, but approximately starting with the 25% B composition, that is from point E on our diagram (Fig. 3). If the regulation process takes place parallel with the change of composition then the property curve will be EH. But if the redistribution of atoms begins also in system (c), the composition answering point E, that is, atoms of the B-component, will begin to move so as to assume positions (a) and (b). Then, in the case of a complete shift of that kind, the property curve will suddenly change from point E to point G, and will then change in the direction of GLH. Evidently the actual process will take place along some curve, lying in the interval between EH and GH, but will end in point H. Since both these curves are sufficiently close to each other, it is probably rather difficult to find experimentally the details of the process. Evidently the regulating process in the Fe-Al system in tempered alloys follows approximately the CGEGLH way.

All the transitions from one curve to another are represented on Fig. 3 by sudden breakings (see, for instance, points E and G, and also D and L).

In fact these transitions, evidently, are much more smooth owing to the fact that one process has not yet ended, when another begins.

If we imagine the regulation process in a manner where from the very beginning of it atoms of the B-component will be arranged only in system (a) or only in system (b), then the phase properties on Fig. 3 will be expressed by curve CM. When the CPS (a) is filled (this will take place when we have composition A_3B) then, with a further growth of the amount of the B-component, its atoms will begin to fill the second four multiple position (for instance (b), if (a) was occupied first, and vice versa). The process is bound to end in point H, as in this case positions (a) and (b) will be fully occupied by atoms of component B, and again we shall have the AB compound, whose structure is of the Cs-Cl type. Here the cycle comes to an end. The M point will always be the singular point, that strictly corresponds to the composition A_3B , in other words we shall have a typical daltonide. It is impossible to prolong the property curve CM beyond the M point, as all the places in this CPS are already filled by the atoms of the B-component; therefore in order to be more exact, we shall call point M 'special', but not singular.

If we turn again to experimental data in the Fe-Al system (Bradley and Jay, 1932) and investigate the regulating processes in annealed alloys we shall find that the regulating process does not begin at once in point C, but it starts when we have a composition, corresponding to 18 at. % Al, which on our diagram (Fig. 3) answers point D. Thus the section of the CD curve answers the properties both of tempered and annealed alloys. Further, the regulating process begins in annealed alloys, that is, atoms of the B-component assume position (a) and the property curve lies in the DI direction. The inclination of this curve with regard to the CM curve may be more or less steep, owing to the degree of redistribution in other CPS, that is in systems (b) and (a). On Fig. 3 the DI curve is shown as more or less parallel to curve C. No matter how it is inclined it will cross at a certain moment the ordinate of composition A_3B ; on Fig. 3 this takes place in point I. The composition of the phase in this point strictly corresponds to the A_3B formula, but, unlike point M, CPS (a) is not wholly occupied by atoms of the B-component; in other words, at the beginning of the process, part of the B-component atoms section placed themselves on the CD section not only in (a) position, but also in (b) and (c) positions. For this reason the process of filling points in the CPS (a) will continue further, on the IK section, which is the continuation of the DI curve. When all the places in this CPS are occupied (point K) the composition of the phase will contain more B-component than A_3B . Only after this will the curve change its direction and follow the KL line. The inclination of the KL curve with regard to the MN curve may also be different, depending on the atom redistributions of the

B-component in (a) and (b) positions. The last section of the experimental curve LH coincides with curve CH. It corresponds to a complete filling of both CSP's, with a multiple 4, and in H point brings the phase to a 100% regulated C_3Cl type.

It is evident that the maximum on this K-curve does not correspond to stoichiometric relation of components and its position may change along the abscissae axis depending on the conditions of crystallization, for instance, on the rate of cooling. The length of the IK section depends on the length of the CD section. The latter, in its turn, characterizes the size of the homogeneity sphere of the α -phase, that is of partly solid solution of B-component in A.

In many intermetal systems the α -phases have a large sphere of homogeneity. Its size is determined by many factors, such as: identical type of structure of both components, chemical relationship of elements, relative valency, electron concentration, etc.

The character of the maximum in point K will be the smoother, the further it is away from point M. If point H, however, is situated higher than point M, then, instead of a maximum, we shall have a singular breaking in point M, and a non-singular one in point K.

Summing up what has been said above it is possible to state that the displacement of a maximum on the property curve in relation to the composition axis will be observed in such phases where the process of filling one (or several) CPS's is not completed, whereas in another CPS (or in other CPS's) a similar process has already started. It is this case that characterizes the bertollide with a maximum.

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