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Preliminary Proposals for Notations for Solid Phases with Variable Composition ("Berthollides")

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This paper was presented to the Commission for Inorganic Nomenclature of the International Union of Chemistry at the Amsterdam meeting in September 1949. Inorganic Chemists, Metallographers, Mineralogists and others interested in this field are invited to communicate their opinion on Professor Hägg's proposals and possible improvements thereon as soon as possible to Prof. Arne Ölander, University of Stockholm, Sweden. It is intended that notation rules for berthollides be included in a set of Rules for Inorganic Nomenclature, which will be presented to the 1951 Conference of the Union in New York.

A. INTRODUCTION

Solid phases with variable composition, indicating solid solution, occur in non-metallic as well as metallic systems. Consequently, a practical method of notating such phases is of as great importance for chemistry in general as for metallography and mineralogy.

In connection with discussions of solid phases with variable composition the concept *characteristic* (or *ideal*) *composition* is frequently used. A definition of this concept seems to be lacking and as a matter of fact it seems impossible to obtain one single definition. In one case it may be necessary to use a definition based upon lattice geometry and in another to base the definition on the ratio of valency electrons to atoms. Sometimes one can state several characteristic compositions, and other times it is impossible to say whether a phase has a characteristic composition or not.

In spite of these difficulties it seems as if the characteristic composition can be used in its present undefined form when establishing a system of notation for phases of variable composition. It also seems necessary to use the concept even if the characteristic composition is not included in the known homogeneity range of the phase. Thus for the iron oxide commonly written as FeO, this formula so clearly corresponds to a characteristic composition that it must be used as the basis for the phase notation in spite of the fact that it lies outside the homogeneity range hitherto observed.

Many years ago Kurnakow (*Z. anorg. Ch.* **88** (1914) 109, also Kurnakow and Glasunow, *J. Russ. Chem. Soc.* **44** (1912) 1007), proposed the word *berthollide* as a general denomination for such a phase with variable composition, for which no composition could be considered as characteristic. Later, Ölander (*Z. phys. Ch.* **A 165** (1933) 65), proposed that this word should be used for every solid phase with variable composition. This latter proposition seems to be very practical, particularly in view of the above mentioned difficulties of deciding whether a phase has a characteristic composition or not. The word berthollide in the sense proposed by Ölander also is a suitable antipode for the word *daltonide* proposed in the rules of 1940 for phases with a constant composition.

B. GENERAL PHASE NOTATION

1. For a phase where the variable composition is solely or partially caused by substitution, the following two alternatives 1a and 1b are proposed.

a. This is an extension of the notation which has long been in use, especially in mineralogy.

Atoms or atomic groups, which substitute each other are separated by a comma and placed in parentheses. If possible the formula ought to be written so that the limits of the homogeneity range are represented when either of the two atoms or groups are lacking.

Ex. (Cu,Ni) denotes the complete phase from pure Cu to pure Ni. (KBr, KCl) or better yet, K(Br,Cl) comprises the phase from pure KBr to pure KCl.

Substitution accompanied by the appearance of vacant positions (combination of substitutional and interstitial solution) receives an analogous notation. For example $(Li_2,Mg)Cl_2$ (which is probably better than $(Li,Mg_{\frac{1}{2}})Cl$) denotes the homogeneous phase from LiCl to $MgCl_2$ where the anion lattice is constant but where Mg^{+2} is substituted for 2 Li^+ (or more correctly where one vacant cation position appears for every substitution of Mg^{+2} for Li^+). $(Mg_3,Al_2)Al_6O_{12}$ will be the homogeneous phase from the spinel $MgAl_2O_4$ ($= Mg_3Al_6O_{12}$) to γ-Al_2O_3 ($= Al_2Al_6O_{12}$). In this case the phase is unstable at the end of the composition range richest in Al.

The solid solutions between CaF_2 and YF_3, where the cation substitution is accompanied by interstitial addition of F^-, would receive the symbol $(Ca,YF)F_2$. In this case the formal substitution of $(YF)^{+2}$ for Ca^{+2} does not mean that $(YF)^{+2}$ takes the place of Ca^{+2}. It is probably quite clear that Y^{+3} takes the place of Ca^{+2} while at the same time one F^- is added interstitially.

The solid solutions between $LiFeO_2$ and Li_2TiO_3 where $Li^+ + 2\ Ti^{+2}$ are substituted for $3\ Fe^{+3}$ and where the oxygen lattice is constant, can be written $(Li_3Fe_3, Li_4Ti_2)O_6$ in order to show the constancy of the latter. A still better formulation, which shows the mechanism of the cation substitution more directly, seems to be $(Fe_3,LiTi_2)Li_3O_6$.

In many cases the notation may be improved by introducing the charges of the different ions. If several substitutions occur simultaneously it may be desirable to supply additional information or to use certain conventions in order to express the relations correctly. A notation for the phase represented by the plagioclases would be $(Na,Ca)(Si,Al)\ Si_2AlO_8$. Here it is necessary to note that a substitution of Ca^{+2} for Na^+ must be accompanied by a substitution of Al^{+3} for Si^{+4}. There is no proposition made for the notation of this fact.

In many cases the notation proposed above does not give any hints as to the structure of the phase or the function of the different atoms. This is a disadvantage which seems impossible to remedy in any simple way.

b. From a formal viewpoint a much better notation is one which involves a statement of the variables which define the composition. A phase involving simple substitution may be written A_xB_{1-x}, *e. g.* Cu_xNi_{1-x} and KBr_xCl_{1-x}. It is immediately evident that the total number of atoms in the lattice is constant. A combined substitutional and interstitial solution may be written in an analogous way. The homogeneous phase between LiCl and $MgCl_2$ becomes $Li_{2x}Mg_{1-x}Cl_2$. The phase between $MgAl_2O_4$ and Al_2O_3 can be written $Mg_{3x}Al_{2(1-x)}Al_6O_{12}$, which shows that it cannot contain more Mg than corresponding to $MgAl_2O_4 (x=1)$.

Another notation would be $Mg_{3x}Al_{2(4-x)}O_{12} (x \leqq 1)$. The other examples given under 1a will receive the forms $Ca_xY_{1-x}F_{3-x}$, $Li_{4-x}Fe_{3x}Ti_{4(1-x)}O_6$ and $Na_xCa_{1-x}Si_{2+x}Al_{2-x}O_8$ respectively.

The notation 1b evidently is more widely applicable and can give more information (*cf.* the unambiguous notation of the plagioclases) than 1a. It also makes the statement of definite compositions and solubility limits possible. (See below!) Furthermore it is hard to see how for example the γ phase in the AgCd system could be formulated with any notation other than 1b. In this phase, which has the characteristic formula Ag_5Cd_8, the Ag and Cd atoms can replace each other mutually to some extent. The notation would be $Ag_{5\pm x}Cd_{8\pm x}$. Phases of this kind are extremely frequent in alloy systems.

The disadvantage of notation 1b is that the formulae are sometimes more complicated to write than is the case with 1a and that they can not always be so rapidly interpreted as those of type 1a. If the composition is determined by more than one independent variable the expressions tend to be rather bulky. If the three atoms A, B, and C can substitute each other one obtains $A_xB_yC_{1-(x+y)}$. Perhaps the best way is to permit both notations 1a and 1b.

2. A notation, showing the extension of a homogeneity range, generally requires a statement of the corresponding temperature and pressure values. This reduces the practical use of such a notation.

The extension is most easily shown with the notation 1b. For example, the Ag phase in the system Ag—Cd could up to about 400° C be written $Ag_{1-x}Cd_x(x<0.42)$. If it is desirable to show that the variable denoted by x can only attain small values this may be done by substituting ε for x.

With the notation 1a it seems practical to show a limited solubility by means of the letter "p" (= partial) preceding the symbol of the component which is not included in the phase in question.

Ex. The Ag phase (α) in the system Ag—Cd will then be written as (Ag,pCd). The Cd phase (η) in the same system will be (Cd,pAg). The solid solutions of KI in KCl will be K(Cl,pI).

3. Interstitial solutions (whether of the addition or subtraction type) can be designated in a manner analogous to 1b.

Ex. $Fe_{1+x}Sb$, $Fe_{1-x}O$, $Fe_{1-x}S$, $Cu_{2-x}O$, $Na_{1-x}WO_3$ (sodium-tungsten-bronzes), $Mo_{2\pm x}C$. For $x = 0$ these formulae correspond to a characteristic composition. (In the second example the characteristic composition FeO lies outside the homogeneity range.) In several of these examples the range of the variable is small, which may be indicated by writing ε instead of x.

A solid solution of hydrogen in Pd phase can be written PdH_x. A phase of the composition M which has dissolved a variable amount of water (consequently dissolved as "zeolithic" water) can be written $M(H_2O)_x$.

In these cases the solubility limit is frequently determined by the available number of lattice interstices of a certain kind and may consequently be independent of rather large variations of temperature and pressure. In such cases it may be advisable to state the limiting value of x. For example a natrolite phase with 0—2 molecules H_2O for every formula unit can be written as $Na_2Al_2Si_3O_{10}(H_2O)_x(x \leqq 2)$. $A_{1-x}B(x \leqq \frac{1}{2})$ denotes a phase which is homogeneous from AB to $A_{\frac{1}{2}}B$ (AB_2).

4. In many cases (for example if the mechanism of solution is unknown) it may be convenient to have a general sign showing that a phase is a berthollide. In the 1940 rules it was suggested that a variable composition should be denoted by a bar placed above a formula corresponding to a characteristic

composition. A bar is rather inconvenient both in printing and typing and it is suggested here that it should be replaced by the letter "b" (= berthollide) preceding the formula and connected with it by means of a hyphen. Ex. b-Ag_5Cd_8, b-FeO.

5. Sometimes it will be necessary to denote the structure of a phase. This could be done by putting the structural type or some other indication after the formula.

Ex. FeC_x(type A1) or FeC_x(cubic face-centred) in order to indicate the solid solution of C in γ-Fe (austenite). This is a case where it would be appropriate to write FeC_ε.

C. NOTATION OF A CERTAIN COMPOSITION WITHIN THE HOMOGENEITY RANGE OF A BERTHOLLIDE

Using the notations of the type 1b and 3, a certain composition can be indicated by stating the actual value of the variable x. Probably the best way of doing this is to put the value in a parenthesis after the formula as has been done in 2 and 3 above.

Ex. $Li_{4-x}Fe_{3x}Ti_{4(1-x)}O_6$ ($x = 0.35$).

If it is desirable to introduce the value of x into the formula the solution mechanism is more clearly understood if one writes $Li_{4-0,35}Fe_{3\cdot 0,35}Ti_{4(1-0,35)}O_6$ instead of $Li_{3,65}Fe_{1,05}Ti_{2,60}O_6$.

The above proposals have resulted from discussions between Professor S. Claesson, Uppsala, Professor A. Fredga, Uppsala, Professor A. Ölander, Stockholm and the author.

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