

the micelle. Sols made in the presence of hydrogen appear to be exceptions; their platinum content was found to be 98.7%. But some data given by Bach and Balaschowa,¹⁸ who studied the electrical properties of these sols, suggest that they are formed by the same mechanism as yields the other types. An arc was passed through water in a hydrogen atmosphere in a cell which permitted the measurement of conductivity. Periodically, the arcing was stopped and hydrogen was bubbled through the liquid. This resulted in a drop in conductivity. Subsequent arcing raised the conductivity, which again decreased when hydrogen was passed through. Since a decrease in conductivity must be associated with a lower concentration of oxidation products, it appears that the effect of hydrogen is to reduce oxides of platinum formed originally by the action of hot particles on water. Pennycuik¹⁵ found that passing hydrogen through air-water sols caused them to lose their acidoid properties, which could be restored by passing oxygen.

If the preparation of stable metallic hydrosols in conductivity water by the Bredig method depends on the formation of small amounts of oxide by the action of hot particles on water, then the free energy of formation of the metallic oxide should be one of the determining factors in the process. Metals whose oxides have positive or small negative free energies of formation should not

(18) N. Bach and N. Balaschowa, *Acta Physicochim.*, U. S. S. R., **3**, 79 (1935).

yield stable sols in pure water. (Such metals may give stable sols in water containing an electrolyte, for then the production of stabilizing compounds other than the oxide is involved.) Thus, gold and silver (Au_2O_3 , $\Delta F = +18.7$ kcal./mole; Ag_2O , $\Delta F = -2.6$ kcal./mole) form stable Bredig sols only in acid, alkaline or salt solutions. Mercury (HgO , $\Delta F = -13.9$ kcal./mole) and copper (CuO , $\Delta F = -30.4$ kcal./mole) give permanent dispersions on arcing under water.¹⁹ In fact, metals like zinc or cadmium, whose oxides have high free energies of formation, give sols consisting largely of the oxide.

Summary

1. Bredig platinum sols have been prepared in water, hydrochloric acid and nitric acid, in atmospheres of air, oxygen and nitrogen.

2. The composition and stability of these sols are only slightly affected by variations in the dispersion medium and in the gaseous atmosphere.

3. There is no change in the platinum content of the micelle on coagulation with acids.

4. Platinum sols prepared by arcing in the gas phase are similar to normal Bredig sols in color, charge, stability and catalytic effect.

5. A mechanism for the formation of Bredig platinum sols is proposed.

(19) Free energy data for the oxides of platinum are not available.

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The Crystal Structure of Boron Carbide

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Upon the basis of X-ray diffraction data, Zhdanov and Sevast'yanov¹ have recently proposed a most interesting and unusual structural type for crystalline boron carbide, B_4C . Although published during 1941, the journal describing their work has not reached our library, and the article was not abstracted until April, 1943. In the meantime we had been investigating the crystal structure of boron carbide as a part of a general program of study of boron² and its compounds being conducted in this Laboratory. We had succeeded in placing definitely nine of the fifteen atoms in the unit of structure when the abstract was published. Through the courtesy of Dr. E. J. Crane of *Chemical Abstracts* we were enabled to see the original article by Zhdanov and Sevast'yanov, and we have now confirmed the structure proposed by these investigators. Be-

(1) G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U. R. S. S.*, **32**, 432-4 (1941) (in English).

(2) A. W. Laubengayer, A. E. Newkirk and R. L. Brandaur, *J. Chem. Ed.*, **19**, 382-5 (1942); Laubengayer, Hurd, Newkirk and Hoard, *This Journal*, **65**, 1924 (1943).

cause of the curious coordination shown by boron and carbon, it seems desirable to publish a brief account of our work, emphasizing that part in which our methods of handling the X-ray data differed from those of Zhdanov and Sevast'yanov and elaborating on some of the unusual features of the structure which were not discussed in detail by these workers.

Earlier work^{3,4} indicated that boron carbide belongs to one of the rhombohedral space-groups, D_{3d}^5 , D_3^7 , or C_{3v}^5 , and contains three molecules of B_4C within the unit cell. We have confirmed these results with Laue, oscillation, and Weissenberg photographs, obtaining for the rhombohedral lattice constants, $a = 5.19 \text{ \AA}$, $\alpha = 65^\circ 18'$, and for the corresponding hexagonal lattice constants, $a = 5.60 \text{ \AA}$, $c = 12.12 \text{ \AA}$. These are in substantial agreement with previous values.

(3) F. Laves, *Zachr. Ges. Wiss. Göttingen, Mathem-Physik Kl.*, Neue Folge **1**, 57-58 (1934).

(4) N. G. Sevast'yanov, *Zavodskaya Lab.* **8**, No. 12, 1317-18 (1939); *Khim. Reprat. Zhur.*, No. 5, 67-68 (1940).

For crystals of composition conforming closely to B_4C we have obtained a density of 2.52 g./cc., likewise agreeing with previous values.^{3,5}

The crystals used in our work were supplied by Dr. Gordon Finlay of the Norton Company and were of two habits: (1) needles twinned on a rhombohedral face and parallel to a hexagonal a axis which coincides with the needle axis and (2) hexagonal plates, to which the c axis is perpendicular. Intensity estimations were made on zero, first, second, and third layer plane equi-inclination Weissenberg copper $K\alpha$ photographs of one of the needle crystals rotated about the needle axis and on zero layer plane Weissenberg molybdenum $K\alpha$ photographs of one of the crystal plates turned about the c axis. $|F|^2$ values were then calculated by dividing by the Lorentz and Polarization factors and by correcting for the position in the layer plane⁶ where necessary.

From the $|F|^2$ values the following series were calculated in the order given: Patterson⁷ projection along the hexagonal a axis on the orthohexagonal (100), Patterson projection on (001), Harker⁸-Patterson series for (001), and Harker-Patterson series for orthohexagonal (100). Very little initial progress was made in interpreting the first projection due, as was discovered, later, to the large number of superpositions of peaks occurring. The second projection seemed to require that the atoms lie in the symmetry planes and led to probable values for some of the hexagonal x and y parameters. These results were substantiated by the first Harker-Patterson series. Complete parameter data for nine of the fifteen atoms of the rhombohedral cell were then obtained by combining these results with the information obtained from the second Harker-Patterson series.

Up to this point the presence of a center of symmetry in the structure had not been assumed as the density distribution on the various plots had not seemed to require it in any obvious manner. It had seemed wise, moreover, to observe caution on this point, as a center of symmetry would require that at least one-third of the carbon atoms could not show tetrahedral coordination. The assumption of a center of symmetry in conjunction with our parameter data would immediately place all of the twelve boron atoms of the unit cell, arranged in the symmetry planes in two sets of six equivalent positions according to the space group D_{3d}^5 . Peaks which would place these additional three atoms in fulfilling the requirements of a center of symmetry were however relatively much weaker in the second Harker-Patterson series than those due to the nine atoms already placed, as a result,

possibly, of incompleteness in the data obtainable with copper $K\alpha$ radiation.

At this point the abstract of the work of Zhdanov and Sevast'yanov appeared. On obtaining the original article, we found that our results, although incomplete, agreed closely with their parameters for boron and that peaks appeared in the second Harker-Patterson series corresponding to their placing of carbon. We proceeded then to check their complete structure against our diffraction data as directly as possible.

Calculation of amplitudes of reflections from the hexagonal forms $\{0kl\}$ based on their complete parameter data resulted in excellent agreement with our observed values and gave an unequivocal assignment of phase. A Fourier projection of relative electron density along a hexagonal a axis on the orthohexagonal (100) was then made (Fig. 1). This projection, except for some slight changes in parameter values, was found to be in complete agreement with the structure of Zhdanov and Sevast'yanov, as determined by the trial and error method. The small undesignated peaks seem, probably, to be due to incompleteness and errors in the data as there does not appear to be enough room in the structure at the indicated places to account for them as being caused by occasional atoms.

Zhdanov and Sevast'yanov used their $\{hk0\}$ amplitude data to make a Fourier projection on the hexagonal basal plane. As a further check we also have made a projection of this type, resulting in a plot very similar to that reproduced in their paper.

As the structural data now seem generally consistent with a center of symmetry, we conclude with Zhdanov and Sevast'yanov that the space-group is $D_{3d}^5-R\bar{3}m$. The twelve boron atoms are in two sets of $6h$ positions.⁹ Two carbon atoms are in $2c$ and the third in $1b$. The hexagonal parameters as determined from our Fourier projections are given with those of Zhdanov and Sevast'yanov in Table I. The

TABLE I

| Position | Parameters from projections | | | Parameters (Z and S) | | |
|----------|-----------------------------|--------|-------|----------------------|--------|-------|
| | x | y | z | x | y | z |
| Boron | | | | | | |
| $6h_1$ | $1/6$ | $-1/6$ | 0.360 | $1/6$ | $-1/6$ | 0.360 |
| Carbon | | | | | | |
| $6h_2$ | 0.106 | -0.106 | 0.113 | 0.106 | -0.106 | 0.110 |
| $2c$ | 0 | 0 | 0.385 | 0 | 0 | 0.38 |
| $1b$ | 0 | 0 | $1/2$ | 0 | 0 | $1/2$ |

differences are only slight, and calculation of several reflection amplitudes using our parameters fails to show much, if any, over-all improvement in agreement with the data.

A reexamination of the Patterson data at this point shows that this structure accounts for

(5) R. R. Ridgeway, *Trans. Electrochem. Soc.*, **66**, 117-33 (1934).

(6) An adaptation of the correction derived in H. Ott, Wien-Harms, "Handbuch der Experimental-physik," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928 Band VII, 2 Teil, p. 160.

(7) A. L. Patterson, *Z. Krist.*, **90**, 517-42 (1935).

(8) D. Harker, *J. Chem. Phys.*, **4**, 381 (1936).

(9) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Erster Band, Gruppentheoretische Tafeln, p. 262.

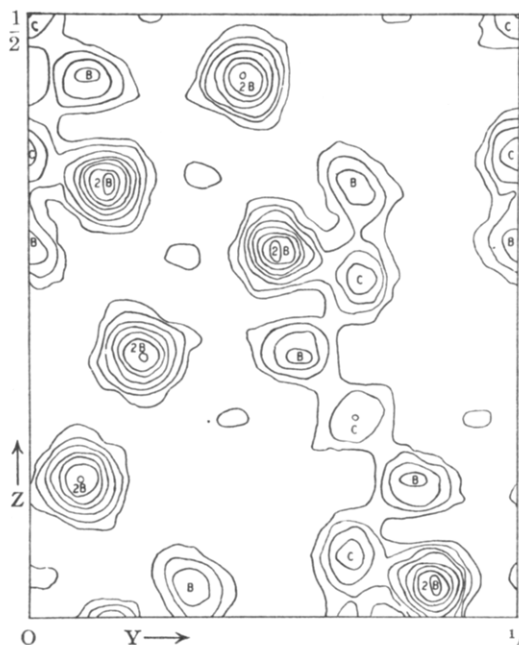


Fig. 1.—Fourier projection of relative electron density along an hexagonal a axis on the orthohexagonal (100).

them rather well. The large peaks in the first Patterson projection are due to superpositions of nearby peaks. Two very large peaks in the second Harker-Patterson series are explainable as superpositions of peaks just off the plane on both sides of a peak in the plane.

As Zhdanov and Sevast'yanov point out, the structure can be represented formally as an approximate NaCl type of structure, referred to rhombohedral axes, with a compact group of twelve boron atoms substituting for Na^+ and a linear group of three carbon atoms for Cl^- . Closer inspection, entailing the construction of a rough model (Fig. 2), reveals, remarkably enough, that the twelve boron atoms of the group are arranged at the vertices of a nearly regular icosahedron. The regular icosahedron is one of the five possible regular solids. It has twenty equilateral triangular faces, twelve vertices, and thirty edges. There are six five-fold axes, ten three-fold axes, fifteen two-fold axes, and fifteen planes of symmetry. Each boron atom has six-fold coordination, being bonded to five others in the icosahedral group and to one other atom outside so as to lie approximately at the center of a pentagonal pyramid. In the case of boron in $6h_1$, the outside atom is carbon in $2c$, and the five atoms in the icosahedral group consist of two $6h_1$ and three $6h_2$ boron atoms; for boron in $6h_2$ the outside bond is to a $6h_2$ boron atom in an adjacent icosahedron, while bonds within the icosahedral group are formed with two $6h_2$ and three $6h_1$ boron atoms. In the carbon chain the two end carbon atoms have four-fold coordination and the center one two-fold coordination.

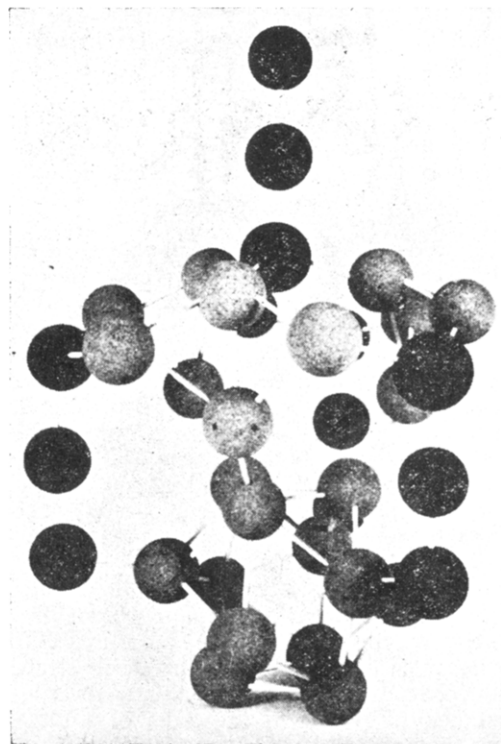


Fig. 2.—Rough model of boron carbide structure showing carbon chains (rhombohedral parameters) at $\frac{111}{222}$, $00\frac{1}{2}$, $0\frac{1}{2}0$, and $\frac{1}{2}00$, a complete boron icosahedron at 000, and partial icosahedra at 001, 010 and 100.

The bond distances calculated from our parameters are: C—C, 1.39 Å.; B—B, 1.74 to 1.80 Å., and B—C, 1.64 Å. From the data of Zhdanov and Sevast'yanov we obtain: C—C, 1.45 Å.; B—B, 1.74 to 1.80 Å.; and B—C, 1.63 Å. More weight, perhaps, should be assigned to our C—C interatomic distance since it was determined directly from our first Fourier projection, made with what are probably our most accurate data. These experimental interatomic distances may be compared with C—C distances¹⁰ of 1.54 Å. (single bond), 1.33 Å. (double bond), and 1.39 Å. in benzene; with B—B distances¹¹ of 1.716 Å. in CaB_6 , 1.73 Å. in AlB_2 , 1.77 Å. in FeB , 1.86 ± 0.04 Å. in B_2H_6 , 1.84 ± 0.04 Å. in B_4H_{10} , 1.81 ± 0.03 Å. in B_5H_{11} , and 1.76 ± 0.02 Å. in B_5H_9 ; and with B—C distances¹¹ of 1.56 ± 0.02 Å. in $\text{B}(\text{CH}_3)_3$, 1.57 ± 0.03 Å. in H_3BCO , 1.57 ± 0.03 Å. in $(\text{BOCH}_3)_3$, and $\frac{1}{2}(1.54) + \frac{1}{2}(1.72)$ to 1.80) = 1.63 to 1.67 Å.

If the x and y parameters for atoms in $6h_1$ are assumed to be correct, a regular icosahedron of boron would have B—B distances of 1.73 Å. and the parameters required for boron would be for $6h_1$: $x = \frac{1}{6}$, $y = -\frac{1}{6}$, $z = 0.358$ and for $6h_2$:

(10) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 172.

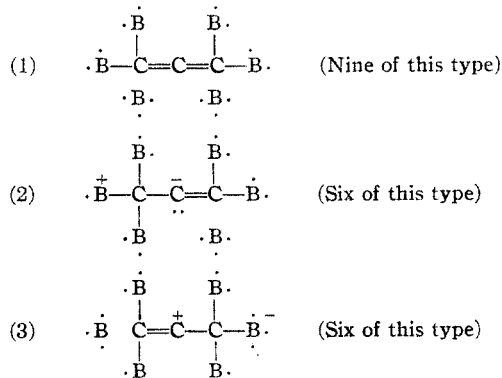
(11) S. H. Bauer and J. Y. Beach, *THIS JOURNAL*, **63**, 1402 (1941).

$x = 0.103$, $y = -0.103$, $z = 0.108$. The B—B distance between two $6h_2$ boron atoms in adjacent icosahedra would be 1.90 Å. Thus the icosahedron is apparently nearly regular.

The three atoms lying on the three-fold axis of the rhombohedral unit are identified as carbon principally through application of the symmetry requirements of the space-group, since the scattering powers of boron and carbon do not differ sufficiently to permit of an entirely definite conclusion on this basis. It is clear, however, that the experimental values for interatomic distances and the coordination types found support this interpretation.

It may be emphasized that the boron atoms, quite apart from carbon, form a continuous three dimensional network extending throughout the crystal. As each boron atom has but three valence electrons while exhibiting a coordination number of six, this network can scarcely be considered to be of the ordinary covalent type. A high degree of resonance leading to a condition not too far removed from metallic binding is presumably of considerable importance in accounting for the stability of the structure. Actually boron carbide shows an appreciable electrical conductivity. At room temperature the specific resistance⁵ of B_4C is of the order of a hundred times that of poly-crystalline graphite, while at 500° this ratio had decreased to around ten. The shining black aspect of the crystals, opaque even in quite thin sections, further indicates the presence of some free electrons.

It is possible also to write various types of electronic formulas for the C_3 group and its immediate neighbors, each of which gives the carbon atom four covalent bonds. The more probable types are perhaps three in number.



The indicated number of formulas of each type is obtained by allowing the double bond and the "no bond" to resonate among the various equivalent positions as required. The second formula corresponds to the C_3 group taking one electron from the boron network while (3) involves a single electron transfer in the reverse direction. This latter in addition has only a sextet of electrons around the central carbon atom, which seems not

improbable in view of the electron deficient character and thus presumably enhanced electron affinity of the boron network.

A superposition of such formulas, as a formal representation of the actual structure, seems consistent with the observed C—C separation. It indicates also that the C_3 groups need not be considered as non-conducting islands distributed throughout a conducting medium. Certainly the presence of the carbon atoms as an integral part of the continuously bonded three-dimensional structure is in part responsible for the remarkable hardness of boron carbide crystals.

Dr. Finlay has reported¹² that even when the B/C ratio is appreciably greater than 4, the excess boron cannot be removed by either nitric acid or aqua regia, reagents which are commonly used to dissolve boron. On the other hand, when the B/C ratio is less than 4, graphite always can be detected. Thus there seems to be evidence that boron goes into solid solution in boron carbide. A possible explanation is the accommodation of extra boron in "holes" in the boron carbide structure. One such set of holes, seemingly allowing enough space for extra boron atoms, is observed on the three-fold axis in $2c$ between the boron icosahedra and the carbon chains. Another dimensionally less probable set occurs in the $6h$ positions. Complete filling of the former set of holes with extra boron would result in a B/C ratio of 4.67. The published density data⁵ are represented in a plot of atomic percentage boron against specific gravity as determined by the pycnometer method for 35 powdered samples of boron carbide material. The plot shows a maximum corresponding to B_4C . It is not certain whether the boron carbide and boron were present as a single phase for B/C ratios greater than 4. Although the analytical procedure for determination of the percentage of boron is somewhat inaccurate, it would seem that the accommodation of much extra boron in holes in the boron carbide structure would require some expansion of the lattice. Our data give no evidence of occasional atoms in these $2c$ holes, but our crystals were very close to the theoretical composition, B_4C .

It would be most interesting to study a series of materials, for which the B/C ratio increased progressively above 4, by a combination of density, analytical, and x-ray data in order to determine if a range of solid solutions of the type discussed actually exists. If so, positions of the "extra" boron atoms could be established in favorable cases by Fourier analysis.

Summary

We have confirmed, by Harker-Patterson and Fourier methods, the interesting structure proposed by Zhdanov and Sevast'yanov for boron carbide. Our data lead to the rhombohedral

(12) Private communication.

lattice constants $a = 5.19 \text{ \AA}$. and $\alpha = 66^\circ 18'$, space-group $D_{2d}^5 - R\bar{3}m$, with three stoichiometric B_4C molecules within the unit cell; the corresponding hexagonal lattice constants are $a = 5.60 \text{ \AA}$. and $c = 12.12 \text{ \AA}$. for a cell containing nine molecules.

The structural units are a linear chain of three carbon atoms and a group of twelve boron atoms arranged at the vertices of a nearly regular icosahedron. These are distributed formally in an approximately NaCl type of structure, the center of the icosahedron substituting for Na^+ and the central carbon for Cl^- . Each boron atom has six-fold coordination, being approximately at the center of a pentagonal pyramid.

Each boron atom is bonded to five others in the same icosahedral group and to either a carbon in $2c$, in the case of boron in $6h_1$, or a boron in $6h_2$ in an adjacent icosahedron, in the case of a boron in $6h_2$. Thus a continuous three-dimensional network of boron runs throughout the crystal. The structure accounts well for the observed physical properties of great hardness and appreciable electrical conductivity. There is apparently room in the structure for the accommodation of additional atoms, a possible explanation for reported indications that commercial boron carbide having a B/C ratio greater than 4 is a solid solution.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Microscopic Equilibria in Ampholytes

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The study of dipolar ions has shown clearly that many molecules carry positive and negative charges, present simultaneously at different points within the molecular structure, where acidic and basic groups are located. Thus it is possible that several ions of an ampholyte may exist which have the same net charge, but which differ in total charge or in the distribution of charges within the molecule. It is of interest, for a number of purposes,¹ to formulate the general equilibrium relationships between such ions. The equations derived will be used in several applications at a later time.

Some attention has been directed to this problem, of course, but there is set forth here a somewhat more general treatment.

We shall employ concentrations throughout, rather than activities. The latter may be introduced with no difficulty if desired.²

In studying the isoelectric point³⁻⁴ it was not necessary to distinguish between "microscopically" different ions possessing the same net charge. Since it will be necessary to make that distinction here, the notation must be changed somewhat. Thus $u_{(r)}$ (rather than u_r) will be written for the total molal concentration of all ions with net charge r , and the equilibrium constant $K_{(r)} = xu_{(m-r)}/u_{(m-r+1)}$ (K_r in references 2, 3 and 4) will be used, where x is the hydrogen ion concentration. The quantities $u_{(r)}$ and $K_{(r)}$ are of course the familiar ones usually written and are the ones of most practical interest. The relationships between these "macroscopic" quan-

tities and "microscopic" concentrations and equilibrium constants will be considered below.

A general treatment of polybasic acids, taking account of microscopic equilibria, has been given by Wyman,⁵ which deals with certain aspects of the problem discussed here. Some other aspects have been discussed by Edsall.¹

We consider an ampholyte which possesses n acidic and m basic groups. The "ampholyte" is an acid if $m = 0$ and a base if $n = 0$. The ampholyte may therefore attain a positive charge of m and a negative charge of $-n$. The ion with charge m (A) may dissociate any one of $m + n$ dissociable protons. We may number these protons $1, 2, \dots, m + n$, listing first those (n of them) belonging to acidic groups (whose dissociation would therefore leave a negative charge on the molecule) and secondly those (m of them) belonging to basic groups (whose dissociation would remove a positive charge from the molecule⁶). It should be realized that the order of numbering the protons has no necessary connection with the order of their tendency to dissociate. If A (whose concentration is u) dissociates the k protons numbered r_1, r_2, \dots, r_k , we denote the concentration of the resulting ion⁷ ($A_{r_1 r_2 \dots r_k}$) by $u_{r_1 r_2 \dots r_k}$, always writing the numbers $r_1 r_2 \dots r_k$ in increasing order.

The ion A has a net charge of m , while $A_{r_1 r_2 \dots r_k}$ has a net charge of $m - k$. Furthermore if s and only s of the k numbers $r_1 r_2 \dots r_k$ are less than or equal to n , the total number of charges on $A_{r_1 r_2 \dots r_k}$, irrespective of sign, is $m + s - (k - s)$ or $m + 2s - k$, since the dissociation

(5) J. Wyman, Jr., see ref. 1, pp. 451-453.

(6) In the terminology of Brønsted, these may be distinguished as uncharged acid groups and cationic acid groups, respectively.

(7) We use "ion" in the general sense, including neutral molecules.

(1) See, for example, E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides as Ions and Dipolar Ions," Reinhold Publishing Corp., New York, N. Y., 1943, Chapters 4 and 20.

(2) T. L. Hill, *J. Phys. Chem.*, **46**, 595 (1942); *ibid.*, **46**, 621 (1942).

(3) T. L. Hill, *ibid.*, **46**, 417 (1942).

(4) T. L. Hill, *ibid.*, **47**, 70 (1943).