

lattice constants  $a = 5.19 \text{ \AA}$ . and  $\alpha = 66^\circ 18'$ , space-group  $D_{3d}^5 - R\bar{3}m$ , 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.

ITHACA, N. Y.

RECEIVED JULY 26, 1943

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

## Microscopic Equilibria in Ampholytes

BY TERRELL L. HILL

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,<sup>1</sup> 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.<sup>2</sup>

In studying the isoelectric point<sup>3-4</sup> 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,<sup>5</sup> which deals with certain aspects of the problem discussed here. Some other aspects have been discussed by Edsall.<sup>1</sup>

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 molecule<sup>6</sup>). 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 ion<sup>7</sup> ( $A_{r_1 r_2 \dots r_k}$ ) 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).

of protons  $r_1, r_2, \dots, r_s$  from A contributed negative charges to the molecule while the dissociation of protons  $r_{s+1}, \dots, r_k$  removed positive charges. In summary, the ion  $A_{r_1 r_2 \dots r_k}$  possesses  $s$  negative charges,  $m - (k - s)$  positive charges, a total of  $m + 2s - k$  charges of both kinds, and a net charge of  $m - k$ .

If the ion  $A_{r_1 r_2 \dots r_k}$  results from the ion  $A_{r_1 r_2 \dots r_{i-1} r_{i+1} \dots r_k}$  by the dissociation of the  $r_i$ 'th proton, the equilibrium constant for the dissociation is written

$$K_{r_1 r_2 \dots r_{i-1} r_{i+1} \dots r_k} = \frac{x u_{r_1 r_2 \dots r_k}}{u_{r_1 r_2 \dots r_{i-1} r_{i+1} \dots r_k}} \quad (1)$$

This notation is used in order to distinguish the different equilibrium constants which may be involved in the formation of the same ion.

We may take as an example an ampholyte containing two acidic groups ( $n=2$ ) and one basic group ( $m=1$ ). In Fig. 1 the various possible ions are represented together with the charges on them and the equilibrium relationships between them. The protons involved in the equilibria are omitted.

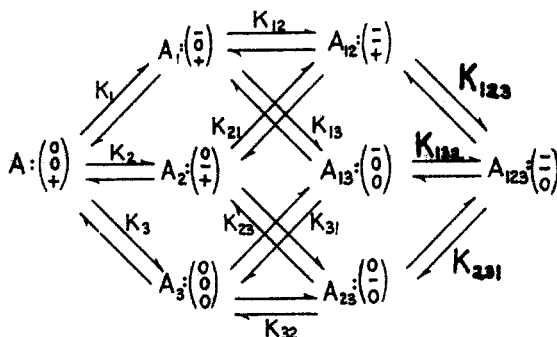


Fig. 1.—Microscopic equilibria for  $n = 2$  and  $m = 1$ . The symbol  $(\bar{\varphi})$  indicates that the ion  $A_1$  has a negative charge at position 1 (due to the dissociation of proton number 1), no charge at position 2 and a positive charge at position 3 (e. g.,  $-\text{NH}_3^+$ ).

It is not difficult to see that in the general case there are

$$\sum_{k=0}^{n+m} \frac{(n+m)!}{k!(n+m-k)!} = 2^{n+m}$$

different ions and

$$\sum_{k=0}^{n+m-1} \frac{(n+m)!}{k!(n+m-k-1)!} = (n+m)2^{n+m-1}$$

different equilibrium constants (of which only

$$\sum_{k=1}^{n+m} \frac{(n+m)!}{k!(n+m-k)!} = 2^{n+m} - 1$$

are independent) to be considered. With the aid of the equation setting the sum of all concentrations equal to a constant  $c$ , each concentration may now be written as a function of  $x$ ,  $c$ , and the necessary equilibrium constants. It proves convenient to use only those equilibrium constants

whose subscripts occur in increasing order. This provides a sufficient number of equations to solve the problem.

We have

$$K_{12 \dots k} = \frac{x u_{12 \dots k}}{u_{12 \dots k-1}} \quad (k = 1, 2, \dots, n+m)$$

whence

$$u_{12 \dots k} = \frac{K_1 K_{12} \dots K_{12 \dots k}}{x^k} u \quad (k = 1, 2, \dots, n+m) \quad (2)$$

Similarly, one can write for any ion  $A_{r_1 r_2 \dots r_k}$

$$u_{r_1 r_2 \dots r_k} = \frac{K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k}}{x^k} u \quad (r_1 < r_2 < \dots < r_k) \quad (3)$$

Putting the sum of the concentrations of all of the ampholyte ions equal to a constant

$$u \sum_{k=0}^{n+m} \left( \frac{1}{x^k} \sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k} \right) = c$$

where  $\sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k}$  represents the sum of  $(n+m)!/k!(n+m-k)!$  terms, each term corresponding to a possible selection of  $k$  different numbers  $r_1, r_2, \dots, r_k$  from among  $1, 2, \dots, n+m$ . Thus

$$\sum_C K_{r_1} = K_1 + K_2 + \dots + K_{n+m} \quad (k = 1)$$

and, if  $n+m = 3$

$$\sum_C K_{r_1} K_{r_1 r_2} = K_1 K_{12} + K_1 K_{13} + K_2 K_{23} \quad (k = 2)$$

To include the case  $k = 0$ , we set  $\sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k} = 1$  for  $k = 0$ .

Then

$$u = \frac{c}{\sum_{k=0}^{n+m} \left( \frac{1}{x^k} \sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k} \right)}$$

and, using equation 3

$$u_{r_1 r_2 \dots r_k} = \frac{c x^{-k} K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k}}{\sum_{i=0}^{n+m} \left( \frac{1}{x^i} \sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_i} \right)} \quad (4)$$

We may now derive the relationships between microscopic and macroscopic equilibrium constants. We have from equation 4

$$K_{(1)} = \frac{x u_{(m-1)}}{u} = \frac{x(u_1 + u_2 + \dots + u_{m+n})}{u} = \frac{\sum_C K_{r_1}}{C}$$

$$K_{(2)} = \frac{x u_{(m-2)}}{u_{(m-1)}} = \frac{\sum_C K_{r_1} K_{r_1 r_2}}{\sum_C K_{r_1}}$$

and in general

$$K_{(k)} = \frac{x u_{(m-k)}}{u_{(m-k+1)}} = \frac{\sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k}}{\sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_{k-1}}} \quad (5)$$

From these

$$\sum_C K_{r_1} = K_{(1)}$$

$$\sum_C K_{r_1} K_{r_1 r_2} = K_{(1)} K_{(2)}$$

and in general

$$\sum_C K_{r_1} K_{r_1 r_2} \dots K_{r_1 r_2 \dots r_k} = K_{(1)} K_{(2)} \dots K_{(k)} \quad (6)$$

Equations 5 and 6 are the desired general ex-

pressions relating microscopic and macroscopic equilibrium constants.

The author is indebted to Professor John T. Edsall for his very helpful suggestions.

### Summary

General expressions are derived relating micro-

scopic and macroscopic equilibrium constants of ampholytes (equations 5 and 6). The concentration of any microscopic ion is given in terms of microscopic equilibrium constants, the hydrogen ion concentration and the total ampholyte concentration (equation 4).

RECEIVED JANUARY 21, 1943

[CONTRIBUTION NO. 31 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, FORDHAM UNIVERSITY]

## Systematic Studies on Palladium-Synthetic High Polymer Catalysts

BY KEVIN E. KAVANAGH<sup>1</sup> AND F. F. NORD

In preceding investigations some applications<sup>2,3</sup> and morphological<sup>4</sup> properties of certain synthetic high polymer-noble metal catalysts, which are highly effective and stable at ordinary pressure and room temperature as well as in acid, neutral and alkaline media, were established. On the basis of their structure as derived from X-ray patterns, it appears to be, however, unpredictable whether *e. g.* PVA, a long chain poly-hydroxy linear polymer,<sup>5</sup> or its derivatives would be preferable in some hydrogenations. It must also be borne in mind that PVA crystallizes readily, whereas polyvinyl acetate (PVAc) exhibits an amorphous pattern, as gum arabic (GA) probably does.

Accordingly, and upon consideration of the reduction of palladium chloride to metallic palladium by means of PVA, it was thought desirable to ascertain whether PVAc and related acetals, in which the acetyl group of PVAc is replaced to varying extent by different aldehydes, may serve as colloidal carriers. Moreover, the fact that the solubility conditions of these products are distinctly different from those of PVA, gave rise to a systematic study of the functioning of these microheterogeneous and multiphase systems in catalytic hydrogenations.

In view of the favorable results recorded in the hydrogenation of cystine,<sup>6</sup> an investigation of the quantitative influence of catalyst poisons, such as thiophene, was undertaken also.

### Experimental

#### Purification of Materials

**Dioxane.**—U. S. P. dioxane<sup>7</sup> was boiled under a reflux condenser for seven hours with 10% of *N* hydrochloric acid

(1) Abridged from a part of the dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate Faculty of Fordham University, 1943.

(2, 3) Louis D. Rampino and F. F. Nord, *THIS JOURNAL*, **68**, 2745, 3268 (1941); **65**, 429 (1943); M. S. Kulpinski and F. F. Nord, *J. Org. Chem.*, **8**, 263 (1943).

(4) Louis D. Rampino, Kevin E. Kavanagh and F. F. Nord, *Proc. Nat. Acad. Sci. U. S.*, **29**, 246 (1943).

(5) E. Dammann, F. E. M. Lange, M. A. Bredig and F. F. Nord, *Biochem. Z.*, **258**, 421 (1936); C. S. Fuller, *Chem. Rev.*, **26**, 163 (1940); R. C. L. Mooney, *THIS JOURNAL*, **68**, 2828 (1941).

(6) Kevin E. Kavanagh, *ibid.*, **64**, 2721 (1942).

(7) A. Weissberger and E. Proskauer, "Organic Solvents," Clarendon Press, Oxford, 1935, p. 140.

to decompose the ethylene acetal present as an impurity, while a slow stream of nitrogen was bubbled simultaneously through the liquid to remove the acetaldehyde formed. The purification of other solvents and acceptors was described previously.

**Preparation of PVAc-Pd Catalyst.**—When alcohol is the solvent used: 125 mg. of PVAc is weighed out and to it is added a volume of absolute ethyl alcohol and then a volume of water which will bring the total volume up to 50 cc., including 1 cc. of PdCl<sub>2</sub> which contains the 10 mg. of Pd. Thus, the volumes of alcohol and water added will vary inversely. As will be pointed out later, there is a definite optimum water concentration. The solution of the PVAc in the alcohol-water mixture, which does not reduce PdCl<sub>2</sub>, will take some time, approximately two hours. However, the preparation of a more concentrated PVAc-alcohol solution, from which less concentrated solutions could be made, is impractical, because PVAc is not very soluble in absolute alcohol, being more soluble in 95% alcohol. Even in this latter medium it is not too soluble, its limit of solubility being about 125 mg. per 50 cc., *i. e.*, 0.25%.

When acetone is the solvent, two procedures are possible. The PVAc may be weighed out for each individual sample of catalyst and then varying quantities of acetone and water added as in the experiments using alcohol as a solvent. The dispersion of the PVAc in acetone is much more rapid than in alcohol. On the other hand, because of the considerable solubility of PVAc in absolute acetone, a 2% solution of PVAc in absolute acetone may be prepared and then from this a volume may be taken which will give the desired amount of polymer. To this are then added varying quantities of absolute acetone and water to give a volume of 49 cc.; the 50th cc. is the 1 cc. of PdCl<sub>2</sub> containing the 10 mg. of Pd.

The catalysts thus prepared by either of the above methods, are introduced into the shaking vessel, reduced by hydrogen for five minutes and the rate of hydrogenation measured after introduction of the acceptor. Because of the limited solubility in alcohol, 125 mg. of PVAc was invariably taken when this solvent was used. A wider latitude in concentration is possible when acetone is the solvent.

**Determination of Rates of Hydrogenations.**—In Fig. 1, the velocities of PVAc-Pd catalysts dissolved in alcohol with varying concentrations of water, are plotted; 1 cc. of nitrobenzene is the substrate in all these cases. Curve A, representing a catalyst with but 1 cc. of water present, which was the volume of the aqueous PdCl<sub>2</sub> solution added, shows a much slower velocity of hydrogen transfer than the other catalysts in which the volume of water present is increased from 1 cc. to 3 cc., then to 5, and to 7 cc. The colloidal Pd solution produced on reduction of the PVA-PdCl<sub>2</sub> is very unstable when only 1 cc. of water is present and the Pd particles aggregate after about five minutes of use. When the volume of water is increased to 3 cc., the tendency to flocculate is nullified and a stable colloid is obtained. From curve B it can be seen that the preparation containing 3 cc. of water produces an excellent hydrogenation.