

in the fact that the kernel of the atom is not uniquely and permanently defined. It seems probable that in these elements there is a possibility of the transfer of electrons either from one part of the kernel to another, or between the kernel and the outer shell, or possibly between two separate outer shells of the same atom, and that electrons which are suspended midway between two such stages are responsible for the absorption of light in these cases.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

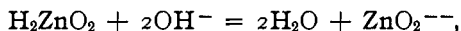
A STUDY OF THE ACTION OF ALKALI ON CERTAIN ZINC SALTS BY MEANS OF THE HYDROGEN ELECTRODE.

BY JOEL H. HILDEBRAND AND W. G. BOWERS.

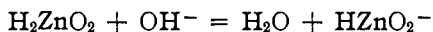
Received January 24, 1916.

The reaction that occurs when zinc hydroxide is dissolved in a strong alkali has been the subject of considerable investigation. Carrara¹ has stated that the alkaline solution contains salts of the type Na_2ZnO_2 , making the hydroxide a dibasic acid. Förster and Günther² have obtained the solid compound $\text{NaHZnO}_2 \cdot 3\text{H}_2\text{O}$, and Comey and Jackson³ a solid compound having the formula $\text{Na}_2\text{Zn}_3\text{O}_5 \cdot 18\text{H}_2\text{O}$. We may mention also the solid alkaline earth zincates of the type $\text{Ca}(\text{HZnO}_2)_2$ reported by Bertrand.⁴ A number of investigators have endeavored to distinguish between the formulas ZnO_2^{--} and HZnO_2^- for the zincate ion. Perhaps the most reliable work is that of Hantzsch,⁵ who concludes that the zinc hydroxide is dissolved mainly as a colloid, but also to a slight extent as HZnO_2^- .

Most of the text-books on general chemistry state that the reaction for the solution of zinc hydroxide in alkali is given by the equation (here written in the ionic form)



in spite of the fact that the reaction represented by



is in much better accord with the evidence, and also with the usual behavior of weak polybasic acids. We find almost invariably that a second hydrogen atom ionizes much less readily than the first, as seen by the ease with which it is possible to prepare acid salts of such acids. It would be very strange, therefore, if the first main product of the neutralization of zinc hydroxide with sodium hydroxide were a solution of Na_2ZnO_2 .

¹ *Gazz. chim. ital.*, 30, II, 35 (1900).

² *Z. Elektrochem.*, 6, 302 (1899).

³ *Am. Chem. J.*, 11, 145 (1889).

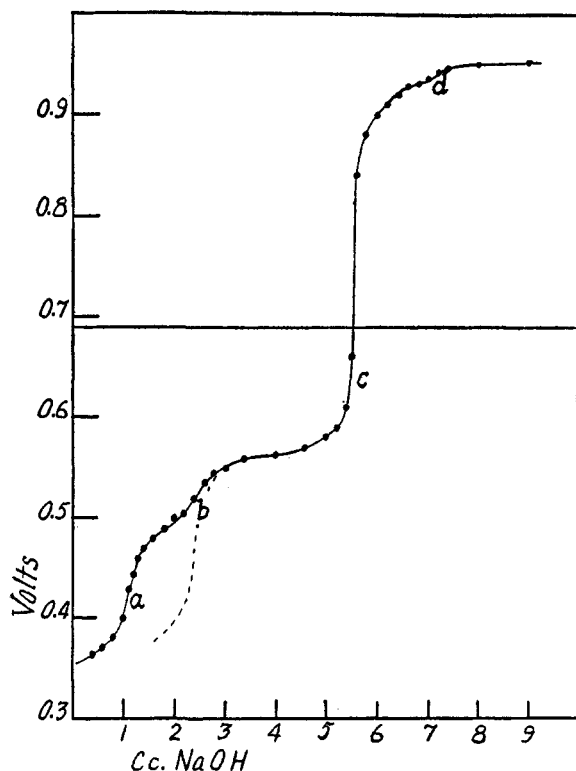
⁴ *Compt. rend.*, 115, 939, 1028 (1892).

⁵ *Z. anorg. Chem.*, 30, 289 (1902).

In a previous publication¹ on the general application of the hydrogen electrode, it was shown how clearly the reaction between aluminum hydroxide and alkali could be followed by this method. Instead of aluminum hydroxide being tribasic in its action towards alkali, as is so frequently stated in the text-books, it was shown to be monobasic.² The success of the hydrogen electrode in dealing with the constitution of aluminates has suggested its application to other amphoteric hydroxides.

The general method of procedure and the apparatus used have been explained in the earlier paper and the description will not be repeated here.

A large number of titrations were made with solutions of zinc halides containing usually an excess of the particular acid, and a few also with



solutions of zinc sulfate. The curves obtained with the solutions of zinc chloride, bromide, and iodide were so concordant that it is useless to repeat them all, and we represent one in the figure which may serve as an illustration of the whole series. At the beginning of the titration the solution had a volume of 100 cc. and contained 0.00044 mol of zinc, and about 0.0008 mol of HBr in excess. This was titrated with 0.287 N NaOH. The big rise in the curve at *c* corresponds to the completion of the precipitation of zinc hydroxide. We were much surprised to note the

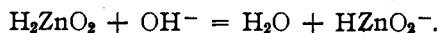
extra inflection during the first portion of the curve at *a*, and found that it was pronounced only when there was an excess of acid in the solution. Furthermore, the portion of the curve from *a* to *b* represents one equivalent of alkali per mol of zinc, and the portion from *b* to *c* repre-

¹ Hildebrand, *THIS JOURNAL*, 35, 847, 1538 (1913).

² See also Blum, *Ibid.*, 35, 1499 (1913).

sents two equivalents. Since but two equivalents of alkali are needed to precipitate zinc hydroxide, and since the precipitate appears just a little before *b*, the only very obvious interpretation of the course of the curve from *a* to *b* is that this represents the neutralization of a weak acid having the composition HZnBr_3 . The presence of the ZnBr_2 makes one equivalent of HBr much weaker than it would otherwise be. Before the point *a* is reached we are neutralizing free HBr , acting as a strong acid, and if all of the excess HBr were free we would expect the curve up to *b* to follow approximately the dotted line in the figure, as was the case when zinc sulfate was used. This same peculiar behavior was found with each of the three halides, so that we feel justified in assuming the existence in solution of HZnCl_3 , HZnBr_3 and HZnI_3 . Confirmation of this conclusion is found in the report by M. R. Engel¹ of solid compounds having the composition $\text{HZn}_2\text{Cl}_5 \cdot 2\text{H}_2\text{O}$ and $\text{HZnCl}_3 \cdot 2\text{H}_2\text{O}$, both of which would fall between *a* and *b* on our curve. Since the position of this portion of the curve is nearly the same in each case, the three complex acids seem to be of about the same strength. The dissociation constant may be inferred roughly from the curve. A point half way from *a* to *b* represents equal concentrations of the acid and its ion, if the latter is not much dissociated into simpler ions, and hence the hydrogen ion concentration at this point equals the dissociation constant. Taking the corresponding e. m. f. as 0.48 volt, the hydrogen ion concentration, and also the dissociation constant, is about $4 \cdot 10^{-4}$.

We will now turn our attention to the portion of the curve from *c* to *d*. Though not very great, a well defined inflection is apparent at *d*. This means that the alkali is not free to exert its full effect in raising the e. m. f. till after *d* is passed, having been acted on before *d* by the zinc hydroxide. Since the amount of alkali used between *c* and *d* corresponds to one equivalent, it is obvious that the reaction here occurring is



The precipitate is not all dissolved at *d*, but this is not surprising, as the acid is so weak that a large excess of alkali must be present in order to make one equivalent of it react. The inflection at *d* can be shown mathematically to indicate that the amounts of acid and base are equivalent, even if neutralization is far from complete. There is no indication of the neutralization of the second hydrogen atom of the zinc hydroxide, and a very large excess of alkali must be necessary for it to take place even to a slight extent.

The solution is far from being clear at *d*, though the zinc hydroxide is usually in suspension at this point. The addition of alkali, therefore, must be regarded as doing two things, just as Hantzsch claims. Part of the alkali is adsorbed, changing the coagulum of zinc hydroxide to a

¹ *Compt. rend.*, 102, 1068 (1886).

suspension, and part of the alkali neutralizes the zinc hydroxide giving the acid zincate. That there is no very great distinction between these processes is evident when we consider that zinc hydroxide, like aluminum hydroxide, silicic acid, etc., is colloidal, so that its formula really is $(\text{H}_2\text{ZnO}_2)_{n,x}\text{H}_2\text{O}$. It is hard to see any great distinction between the adsorption of OH^- by such a molecule, considered as a colloidal particle, on the one hand, and its gradual neutralization, considered as a polyacid, on the other hand. As the neutralization by OH^- (or adsorption of OH^-) proceeds, the molecule (or colloidal particle) becomes progressively smaller, until finally the acid zincate ion is produced. The solid polyzincate, $\text{Na}_2\text{Zn}_3\text{O}_5 \cdot 18\text{H}_2\text{O}$, reported by Comey and Jackson, is evidence in favor of this point of view. A similar relation undoubtedly exists between silicic acid and the silicates.

Summary.

There exists in solutions of zinc chloride, bromide and iodide, each containing an excess of the corresponding acid, a weak acid of the type HZnCl_3 .

Zinc hydroxide acts towards alkali essentially as a monobasic acid.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE EXTRAPOLATION OF CONDUCTANCE VALUES.

By MERLE RANDALL.

Received January 31, 1916.

In connection with researches upon the electrical conductivity of aqueous solutions, a function of the form $\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + K(c\Lambda)^{n-1}$ has been very largely used in order to obtain the equivalent conductance, Λ_0 , at infinite dilution. In the above function Λ is the equivalent conductance at the concentration c , K is a constant, and n is a number which, for aqueous solutions, lies between 1.3 and 1.7. The value of n is so chosen that the graph obtained by plotting the values of $\frac{1}{\Lambda}$ against $(c\Lambda)^{n-1}$ is nearly a straight line, and two other graphs corresponding to neighboring values of n , on opposite sides of the first line, are also drawn so as to aid in determining the most probable point ($\frac{1}{\Lambda_0}$) at which the graphs cut the $\frac{1}{\Lambda}$ axis.¹

While the method outlined above enables one to obtain the best value for the equivalent conductance at zero concentration, the calculations are quite laborious, and unless the data are quite accurate and complete for the very dilute solutions, the result is somewhat uncertain.

¹ A. A. Noyes, *THIS JOURNAL*, 30, 335 (1908); J. Johnston, *Ibid.*, 31, 1010 (1909) discusses the use of the function and gives a plot which shows the general shape of the graphs obtained.