

1. Cuprous nitride is formed by the action of potassium amide on a liquid ammonia solution of cupric nitrate.
2. The ammono basic mercuric bromide, $\text{Hg} : \text{N} - \text{Hg} - \text{Br}$, is formed by the action of potassium amide on an excess of mercuric bromide.
3. Metallic zinc is acted upon by a liquid ammonia solution of potassium amide in a manner analogous to the action of an aqueous solution of potassium hydroxide, to form a well crystallized ammono-zincate of potassium.
4. The same compound is formed by the action of a solution of potassium amide on zinc amide.

This work was carried on in the laboratory of Stanford University at the suggestion and under the direction of Prof. E. C. Franklin. The earthquake of April 18th unfortunately interfered with further investigation upon the formation of the ammono-zincate of potassium.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ALCOHOLS IN LIQUID HYDROGEN BROMIDE.

BY E. H. ARCHIBALD.
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Introduction.

It has been shown by Steele, McIntosh and Archibald¹, that a large number of organic substances dissolve in the liquid halogen hydrides to give solutions which conduct the electric current. In the case of all the substances examined it was found that, as distinguished from aqueous solutions of inorganic substances, the molecular conductivity decreased rapidly as the dilution increased. The results given in the above paper included observations on a typical member of several classes of organic substances, but no attempt was made to study any one class as a whole.

The interesting variation of molecular conductivity with dilution, alluded to above, seemed to warrant a more detailed and somewhat more accurate study of solutions of several classes of these substances, particularly as regards the conductivity of the more dilute solutions. Accordingly a more or less complete study has been made of solutions of the alcohols in liquid hydrogen bromide and the results obtained are described in the following pages.

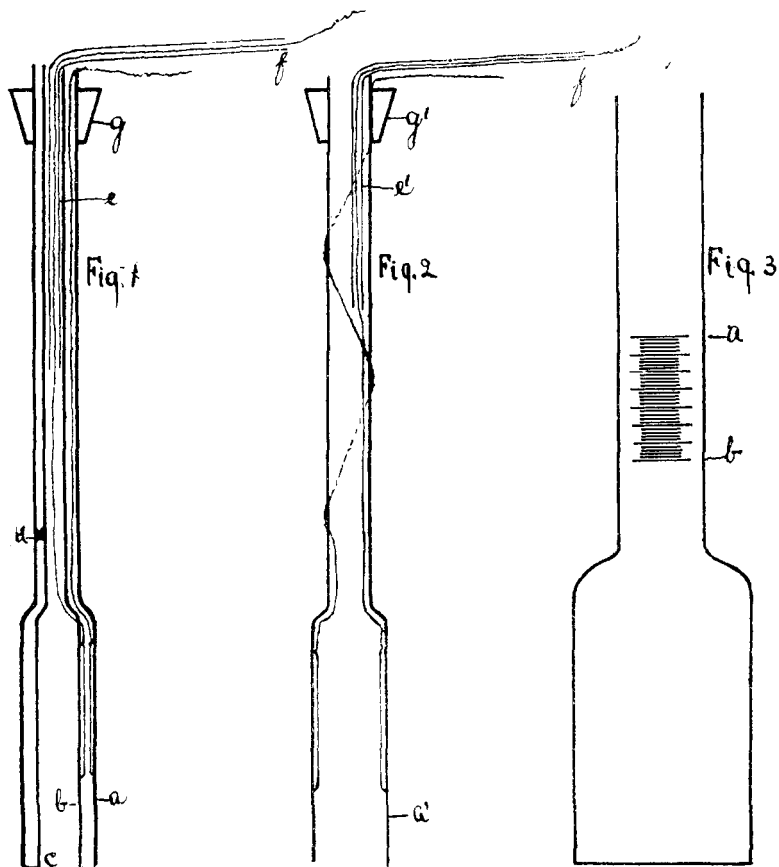
Apparatus.—In order that the conductivity of a dilute solution which had a high resistance might be measured with some degree of accuracy, it was necessary that the electrodes of the conductivity cell should be comparatively large and that the distance between them should be relatively short.

These conditions are secured in the form of cell shown in Figure 1, which is of the ordinary "dip" variety. One electrode is sealed to the out-

¹ Phil. Trans., A. 205, 99 (1905).

side of the inner tube *b*, while the other is sealed to the inside of *a*. The two tubes, *a* and *b*, are then sealed together at *c* and *d*, thereby making any change in the relative position of the electrodes impossible.

Cell No. 2, shown in Figures 2 and 3, was used for the more concentrated solutions, where the resistances were much lower than in the cases referred to above. Here, too, the electrodes are firmly sealed to the sides



Figures 1, II, III.

of the tube so that any change in their relative position is impossible. The conductivity vessel is large enough to allow of working with from 25-30 cc. of the solvent. The stem from *a* to *b* was carefully calibrated with the electrodes in position so that the volume of liquid present could be read off at any time.

A few preliminary experiments showed that the resistance capacity of Cell No. 2 did not change appreciably when the height of the conducting solution, in the conductivity vessel, was raised from *b* to *a*.

When working with solutions which have such high resistances as those in question, great care must be taken to prevent any leak of the current from one lead to the other, outside of the solution. Such a leakage is the more likely to take place, as a thin film of a water solution of the hydrobromic acid will eventually form on the upper parts of the cell, due to condensation of moisture on the colder glass, and to some evaporation of acid from the solution below. A very thin film of this aqueous acid solution may have many times the conductivity of the solution which is being measured. To prevent such a leakage, the small glass tubes, e and e' , surround the inside lead wire from f to f' to a short distance above the solutions.

The stoppers, g and g' , which are movable without difficulty about the tubes a and a' (Figures 1 and 2), serve to keep the water vapor from condensing inside the stem of the conductivity vessel (Figure 3), while the measurements are in progress; for, while water is apparently quite insoluble in the pure liquid hydrogen bromide, it will have a disturbing effect, mechanically at least, if floating about in the solution.

Method of Measuring Resistance.—The method employed of measuring resistance was that of Kohlrausch, using the telephone and alternating current. The minimum point on the bridge, except in the case of the measurements of the pure solvent where the resistances were very high, could be kept quite distinct by careful attention to the platinizing of the electrodes. The "constant" of each cell was determined from time to time and any change in this factor noted.

Materials Used.—The hydrogen bromide was prepared according to the method described in the paper cited above. The interesting facts pointed out by Bailey and Fowler¹, and further verified by Baxter², that hydrobromic and hydrochloric acid gases act to some extent on phosphorus pentoxide forming the corresponding oxychlorides, were kept fully in mind. Solutions prepared with samples of the liquid hydride, which had been dried with phosphorus pentoxide, were compared with other solutions made up with portions which had been dried with anhydrous calcium bromide, as suggested by Richards and Baxter³ and were found to give appreciably the same results. Indeed, the pure liquid solvent which had been dried after the first manner, had as great a resistance as that dried in the second way, and this resistance, as seen below, was very great. This would seem to show that the amount of oxybromide dissolved in the liquid hydride was very small.

The alcohols used were Kahlbaum's preparations, and these were tested and purified, whenever necessary, by fractional crystallization or dehy-

¹ Chem. News, 58, 22.

² This Journal, 28, 770 (1906).

³ Pr. Ann. Acad., 33, 124 (1897).

dration followed by distillation. A constant boiling-point or sharp melting-point indicated the purity of the substance in question.

EXPERIMENTAL PROCEDURE.

The method of procedure adopted in making the measurements was about as follows: The conductivity vessel was filled with the solvent to a convenient point on the stem, the electrodes being in position. The resistance of this liquid was determined, then a weighed portion of the solute was added and the solution well stirred. The volume of the solution was now noted and the resistance measured. This was followed by another stirring and another measurement of resistance, to see if equilibrium had been established. It may be stated here, that the solutions very quickly attained their maximum conductivity, the first stirring being generally sufficient to establish equilibrium. In the case only of the more concentrated solutions of phenol, was there any indication of a time factor of conductivity. Here it required several minutes for the solution to reach the point of maximum conductivity. If, after the second stirring, the resistance still remained as before, more solute was added and the above operations were repeated. This procedure was followed until the solution had reached a concentration beyond which it seemed of little interest to extend the measurements.

In some cases, when the solution had become so concentrated that the resistance had fallen to a comparatively low value, the measurements had to be stopped on account of the difficulty in determining the minimum point, and these measurements would then be supplemented by others made with Cell No. 2, which was more suitable for the concentrated solutions.

In the paper by Steele, McIntosh and Archibald¹, no attempt was made to ascertain the exact value of the specific conductivity of the pure liquid hydrogen bromide. It was shown, however, that the upper limit did not lie above 0.05×10^{-6} in reciprocal ohms. With a cell having a very low resistance capacity, I have attempted to measure the value of this constant with some degree of accuracy. These attempts were not entirely satisfactory. With such high resistances in the bridge, as were here necessary, the minimum point becomes indistinct and cannot be located within several millimeters on the bridge wire. However, portions of the solvent have been repeatedly obtained which had a conductivity not greater than 0.008×10^{-6} in the above units. Franklin and Kraus² have obtained liquid ammonia having a conductivity not greater than 0.005×10^{-6} , while for the purest water the corresponding value is 0.04×10^{-6} .

In the case of the more dilute solutions of a few of the alcohols, where the conductivity value is very low, a correction has to be applied for the

¹ loc. cit., p. 123.

² This Journal, 27, 191 (1905).

conductivity of the solvent. The same rule was followed here as obtains in the case of water solutions, *viz.*, the conductivity of the solvent was subtracted from the conductivity of the solution. As this is a questionable method of procedure under any circumstances and also as the former constant is not very closely defined, the first two or three values of the conductivity in the case of these alcohols may be in error by two or three per cent.

Results.—The results obtained with the alcohols are set forth in the following table. The values in the first column show the number of liters of solution containing one gram molecule, except in the case of resorcinol, where the values refer to one-half a gram molecule. The other columns give the molecular conductivities of the respective substances in reciprocal ohms. These values were obtained from the dilution—molecular conductivity curves obtained by plotting the original observations. These curves will be found below and the points by aid of which they were drawn are indicated on the plates.

In Table II are shown the temperature coefficients of the conductivity expressed as percentage values of the conductivity at -80° . The dilutions of the solutions whose temperature coefficients were measured are given in the first column, while the second column shows the temperatures at which the measurements were made.

If we look at the temperature coefficients in Table II we see that in the majority of cases they are positive, and a little greater than in the case of water solutions of inorganic salts. For a number of the bodies examined, however, the temperature coefficient has a negative sign, and varies considerably with the dilution, but not always in the same direction. Thus for the cresols it is abnormally large and negative for the more dilute solutions, but grows less as the concentration of the solution becomes greater, until, at a dilution of about 1.50, it changes sign, becoming positive, although very small. On the other hand, in the case of α -naphthol the temperature coefficient is positive for the more dilute solutions, and becomes slightly negative for the more concentrated. This would seem to be the case, too, for the thymol solutions; for, although the coefficient is here very small, it is varying in the same direction. Carvacrol, at the dilution examined, seems to give a solution whose conductivity does not vary appreciably with the temperature. Resorcinol solutions have only a very small temperature coefficient.

A change in the conductivity of a solution, due to a change in the temperature, may be due to several causes. As the temperature rises the viscosity of the solution will decrease, and *caeteris paribus* the conductivity should increase. But along with this decrease in the viscosity, we will probably have a decrease in the degree of dissociation of the electrolyte, as well as an increase in the speed of the ions. If the decrease in the con-

ductivity, due to the decrease in the dissociation, is large enough to overbalance the other effects, the conductivity will decrease with rise of temperature. This may be the case with the solutions of the cresols.

Another explanation, however, of these large negative coefficients seems possible. The large amount of heat which is evolved, when the alcohols are added to the liquid hydrogen bromide, leads one to think that chemical union has taken place between the solvent and the solute. In confirmation of this, Archibald and McIntosh¹ have isolated a number of compounds of the halogen hydrides and organic substances, containing a varying number of molecules of solute and solvent. McIntosh² has further prepared a compound of methyl alcohol and hydrogen chloride containing two molecules of hydrogen chloride to three of methyl alcohol; while Steele³ has shown that when solutions of these bodies in liquid hydrogen bromide are electrolyzed, bromine acts as one ion and the organic body as an integral part of the other. It would seem probable then, that in the case of the cresols, as the temperature is raised, the body which is here acting as the electrolyte is partially decomposed, and is therefore no longer present as an electrolyte. In a dilute solution, the decomposition of a small portion of the electrolyte would be sufficient to cause a large change in the conductivity, which might considerably outweigh the changes due to the other causes, and therefore give us a negative temperature coefficient; whereas, in a concentrated solution, where a considerable part of the electrolyte is in the undissociated state, the removal of a portion of this body as an electrolyte, due to decomposition, would produce only a relatively small change in the conductivity, which might not equal the change due to the decrease in the viscosity, or to the increase in the ionic mobility, and therefore give us a positive coefficient.

In the case of the naphthols, the changes in the temperature coefficients with dilution are not nearly so pronounced and may be due to corresponding changes in the viscosity of the solution, the speed of the ions, or the degree of dissociation of the electrolyte.

Negative temperature coefficients of conductivity for solutions in other solvents than water, have been obtained by a number of investigators. Cattaneos⁴ for solutions in ether, alcohol and glycerol, has obtained negative temperature coefficients. Miss Maltby⁵ in the case of ethereal solutions of hydrochloric acid; Franklin and Kraus,⁶ for liquid ammonia solutions at high temperatures, and Hagenbach,⁷ for solutions in sul-

¹ *Ann d. Phys.*, [5], 2, 276 (1901).

² *J. Chem. Soc.*, 85, 919 (1904).

³ *This Journal* 28, 588 (1906).

⁴ *loc. cit.*, p. 138.

⁵ *Rend. Lincei* [5], 2, 1, 295 (1893); [5], 2, 1, 112 (1893).

⁶ *Z. physik. Chem.*, 18, 133 (1895).

⁷ *Am. Ch. J.*, 24, 83 (1900).

phur dioxide at high temperatures have obtained negative temperature coefficients. Kraus,¹ for solutions in methyl and ethyl alcohols, at temperatures of 150° and 100°, respectively, has observed maxima in the conductivity-temperature curves. More recently, Jones and McMaster² have obtained negative temperature coefficients, in the case of solutions of cobalt chloride in mixtures of acetone and ethyl alcohol.

It is interesting, here, to recall the work of Wood,³ Schaller,⁴ Whetham,⁵ Noyes and Coolidge,⁶ Bousfield and Lowry,⁷ and that of Jones and West,⁸ and Jones and Bingham,⁹ dealing with the temperature coefficients of conductivity, in the case of aqueous solutions. Wood concludes from his experiments, that change of temperature has no effect on the dissociation of an electrolyte, if the solution is dilute. Schaller and Whetham both found that dissociation decreased slightly with rise of temperature. The former worked at temperatures between 25° and 100°, and the latter at temperatures between 0° and 18°. Noyes and Coolidge showed that the temperature coefficients of conductivity, for solutions of sodium and potassium chlorides between 18° and 218°, were somewhat higher than those found by other investigators working at lower temperatures. They also obtained maxima in the conductivity-temperature curves, for 0.1 normal solutions of sodium and potassium chlorides, at a temperature of about 280°. Bousfield and Lowry point out, that the effect of change of temperature on conductivity at low temperatures, is chiefly due to a change in the mobility of the ions; while at high temperatures, the decrease in the dissociation is the main factor which influences the conductivity. Jones and his students have ascribed to the change in the dimensions of the atmosphere of solvent which moves about the ion, a considerable share in changing the conductivity, as the temperature changes. This assumption, of an atmosphere of solvent which is associated with, and moves along with every ion, was put forward by Ciamician,¹⁰ and more recently by Kohlrausch.¹¹

We know from the measurements of McIntosh and Steele,¹² that the temperature coefficient of the viscosity of the liquid hydrogen bromide, is relatively small. We might then expect a change of temperature to pro-

¹ Phys. Rev., **18**, 40 (1904).

² Am. Ch. J., **36**, 325 (1906).

³ Phil. Mag., **41**, 117 (1896).

⁴ Z. physik. Chem., **25**, 497 (1898).

⁵ Phil. Trans., A., **194**, 321 (1900).

⁶ Pr. Am. Acad., **39**, 163 (1903).

⁷ Pr. Roy. Soc., **51**, 467 (1902).

⁸ Am. Ch. J., **34**, 357 (1905).

⁹ Ibid, **34**, 481 (1905).

¹⁰ Z. physik. Chem., **6**, 403, (1890).

¹¹ Pr. Roy. Soc., **71**, 338 (1903).

¹² loc. cit., p. 118.

duce only a comparatively small change in the conductivity of a solution in this solvent; at least in so far as it is influenced by the viscosity. Almost all the hydroxy compounds examined were found to dissolve in the liquid hydrogen bromide, and to give conducting solutions. Interesting exceptions were the ortho and para dihydroxy compounds, pyrocatechol and hydroquinone. Apparently, neither of these bodies would dissolve in the least; while the corresponding meta compound, resorcinol, dissolved readily and gave good conducting solutions. In the case of the cresols, too, the meta-cresol is by far the best conductor. It is yet too early in the study of these solutions to advance reasons for this apparently abnormal behavior.

If we compare the conducting power of the solutions of the different alcohols, it will be noticed that the alcohols derived from the paraffin hydrocarbons, do not give as good conducting solutions as those derived from the benzene series of hydrocarbons. That in the case of the former alcohols, the lower members of the series conduct better than the higher ones. Thus,—methyl alcohol conducts better than ethyl, and ethyl better than propyl alcohol—except for the first one or two of the more dilute solutions—the differences becoming greater as the solutions become more concentrated. For the latter series of alcohols—those derived from the benzene hydrocarbons—the opposite is true. Here the alcohol conducts the better, the greater the number of carbon atoms it contains in the molecule. This is in agreement with the results obtained by Carré,¹ for solutions of the phosphoric esters in water, where the molecular conductivity was the higher, the greater the number of carbon atoms in the molecule of the ester.

On looking at the molecular conductivity values of the different alcohols, it will be seen, that, if we except a few cases of the more dilute solutions, the molecular conductivity decreases as the dilution increases and that this decrease is very marked; the values for the dilute solutions, in a number of cases, being less than a fiftieth of the values for the concentrated solutions. This behavior is in entire accord with the results obtained by Steele, McIntosh and Archibald,² for solutions of other organic compounds in this solvent. While several investigators, among them Kabhikoff,³ for solutions of hydrogen chloride in ether and amyl alcohol; Plotnikoff,⁴ for solutions of antimony bromide and phosphorus pentabromide in bromine; Sackur,⁵ for solutions of hydrogen chloride in cineol; Kahlenberg and Rühoff⁶, for solutions of silver nitrate, cadmium

¹ *Compt. rend.*, **141**, 764 (1905).

² *Loc. cit.*, p. 148.

³ *Z. physik. Chem.*, **4**, 429 (1889).

⁴ *J. Russ. Phys. Chem. Soc.*, **34**, 466 (1902); **35**, 794 (1903).

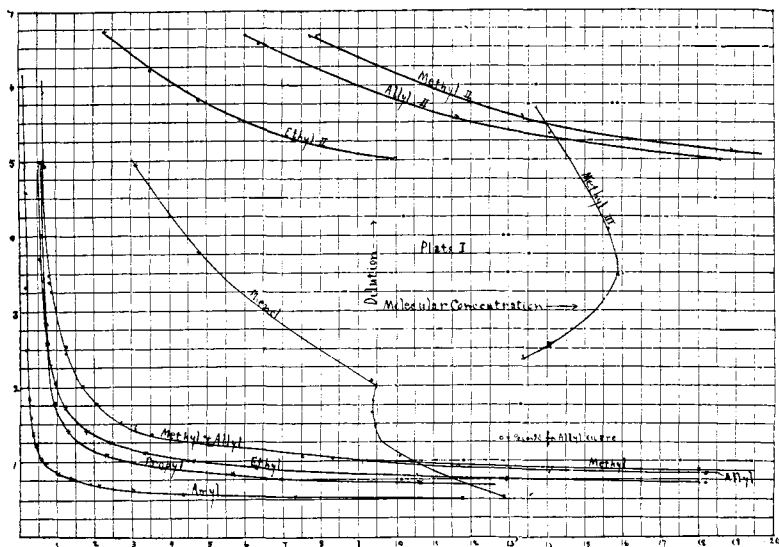
⁵ *Ber.*, **35**, 1242 (1902).

⁶ *J. Phys. Chem.*, **1**, 284, (1903).

iodide and ferric chloride in amylamine; and Walden,¹ for solutions of tetraethylammonium iodide in aldehyde and acetic acid, have pointed out that apparently abnormal results for the molecular conductivity are likewise obtained for solutions in these solvents. In the case, too, of water solutions, a number of instances are on record where the molecular conductivity varies irregularly with the dilution.

In the case of the more dilute solutions of a number of the substances examined, such as methyl, ethyl and propyl alcohol, the molecular conductivity is practically constant, or even increases slightly with the dilution, as in the case of propyl, amyl and allyl alcohol. Here, then, these solutions give us the same variation in the molecular conductivity as we have in the case of water solutions of the ordinary inorganic electrolytes. It would seem probable, too, that if one could carry these measurements to greater dilutions they would show much larger increases in the molecular conductivity.

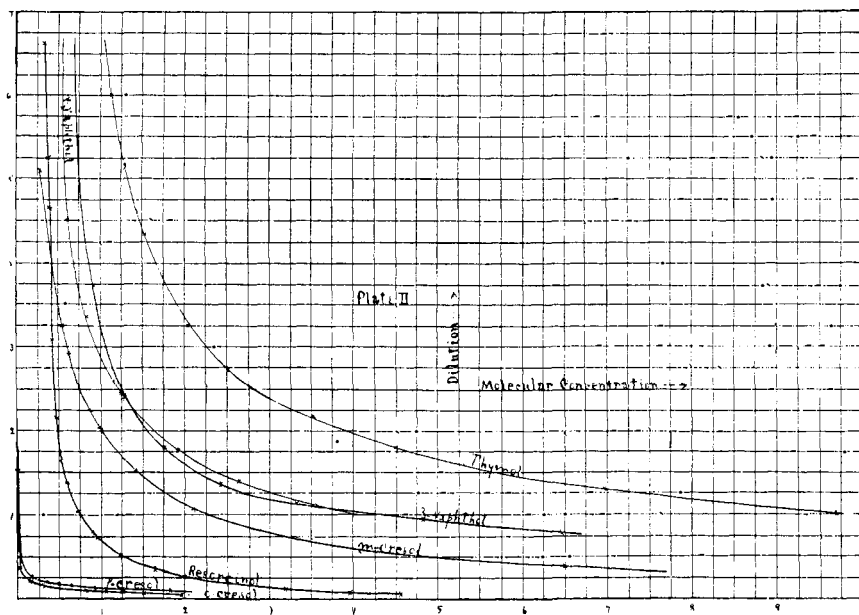
The results given in Table II are shown graphically in Plates I and II, where the abscissae represent the molecular conductivities,



and the ordinates the dilutions. In Plate I the ethyl, propyl, amyl and allyl alcohol curves are broken up into two parts, while in the case of methyl alcohol, where the measurements were carried to greater concentrations than in the other cases, we have three parts to the curve. The curves for the dilute solutions, as well as the curve for phenol, are plotted to the same scale; while those for the more concentrated solutions are

¹ Z. physik. Chem., 54, 131 (1906).

plotted to another scale; and the third curve for methyl alcohol to still another. By extending the curves in this way, one is able to show the



variation in the behavior of the solutions much more clearly.

These curves show plainly the relative conducting power of the different alcohols; the methyl curve lying above the ethyl, the ethyl above the propyl, etc., while the allyl and methyl curves lie very close together, until we come to the more concentrated solutions, where the methyl curve lies somewhat above that of the allyl alcohol. The third part of the curve for methyl alcohol shows, that after a solution of a certain concentration—about 5.85 gram molecules per liter—is reached, the molecular conductivity begins to diminish. This is not thought to be peculiar to the methyl alcohol solutions, but the same behavior would undoubtedly be found in other cases, if the conductivity was followed to sufficiently concentrated solutions.

This behavior must mean, that after a certain proportion has been reached between the solute and solvent, if any more solute is added, it is simply dissolved by the solution, and does not form any more of the electrolytic body. In confirmation of this view, Archibald and McIntosh¹ have pointed out, that after a certain amount of an organic compound, such as an alcohol, has been added to one of the liquid halogen hydrides, the addition of more does not cause the large evolution of heat which is

¹ J. Chem. Soc., 85, 923 (1904).

brought about when the first portions are added. This would be the case, probably, if the solute was simply being dissolved by the solvent.

It will be seen from the position of the phenol curve, that this compound, at least in the more dilute solutions, has a much higher conductivity value than the alcohols of the paraffin series. We seem to have here two distinct curves, meeting at a concentration of about 0.448 gram molecules per liter. It was noticed when making these measurements, that, at about the above concentration, when a fresh portion of the solute had been added and the solution stirred, a quantity of a white powdery substance settled out of the solution. The conductivity, however, was followed a little further, and these measurements gave the points along the dotted curve; but it must be remembered that the true concentrations of the solution are not known for these points. The dilutions here plotted are calculated on the assumption that all the solute added is in solution, which is probably not the case.

The fact noted above, that in the case of the more concentrated phenol solutions, it takes an appreciable time for the solutions to reach their maximum conductivity, is probably connected with the abnormal shape of curve obtained for these solutions. It should be remembered, that in the case of the solutions of these organic compounds in the liquid hydrides, we have to consider not only the solubility of the substance in the hydride, but also, particularly for the concentrated solutions, the solubility of the addition body which is formed, in the excess of solvent. It is probable, that after a certain concentration of phenol is reached, corresponding to the point of saturation of the electrolytic compound in the excess of the solvent, that when more phenol is added to the solution, an addition compound of more complex structure is formed, containing more molecules both of phenol and hydrogen bromide than the compound formed in the dilute solutions, and being more soluble in excess of the solvent. We will then have a state of equilibrium established between this substance of complex structure, the substance formed in the dilute solutions, and the excess of hydrogen bromide. As more of the phenol is added, and more of the second substance is formed, more of the first will be precipitated, removing more and more phenol from the solution. The molecular conductivity curve, for these concentrated solutions, will, therefore, lie below the corresponding curve for the dilute solutions, if this were produced beyond the point where the two curves meet. As we see, this is exactly what takes place in the case of these concentrated solutions. As more of the phenol was added more of the precipitate was formed; while the molecular conductivity curve lies considerably below the curve which would be obtained by producing the corresponding curve for the dilute solutions.

In Plate II we have the curves for ortho, meta and para cresol, α and

β naphthol, thymol and resorcinol, all plotted on the same scale. The greater conducting power of the solutions of the meta, over those of the ortho and para compounds, in the case of the cresols, is clearly shown; while the para solutions are shown to conduct a little better than the ortho. The α and β naphthol curves lie very near together, and considerably above the meta-cresol curve, showing that these bodies give good conducting solutions. Thymol, which belongs the highest in the series of any of the cresols examined, exceeds all the others in conducting power.

As pointed out above, there is considerable evidence in favor of the assumption, that when an alcohol is added to one of the liquid hydrides, an addition compound is formed between the solute and the solvent, and that it is this compound which is ionized, and acts as the conducting body.

In the paper referred to above, Steele, McIntosh and Archibald have shown that in the case of solutions where the electrolyte is a compound containing n molecules of the solute, the concentration of the electrolyte will be proportional to the n^{th} power of the concentration of the dissolved substance; while the molecular conductivity will be given by the expression $\kappa \nu^n$ rather than by $\kappa \nu$; where κ is the specific conductivity, and ν the dilution of the solution in question.

Again, as the conductivity values were always comparatively small, it seemed probable that the concentration of the electrolyte was also small. In such a case, the value of the concentration of the undissociated substance would not differ much from the value of the total concentrations; therefore, in the expression for the equilibrium

$$k(A - nc)^n = k'c$$

where A is the number of gram molecules of the solute dissolved in one liter of solvent, c the number of gram molecules of the electrolytic compound, and n the number of molecules of solute required to form one molecule of the compound, and nc , therefore, the number of molecules of solute used up. We can—according to this assumption—substitute the value of A for the term $A - nc$, and we obtain

$$kA^n = k'c$$

$$\text{or } c = KA^n$$

then, if α is the degree of ionization, and if β ions are formed from each molecule of solute, κ , the specific conductivity, will be proportional to the ionic concentration, or

$$\kappa = k'\beta\alpha KA^n = \alpha K'A^n$$

$$\text{or } \kappa \nu^n = K'a$$

If we make the above assumption in the case of the alcohols and liquid hydrogen bromide, and compute the values for the expression $\kappa \nu^n$, we get the results shown below. Where two molecules of solute combine with one of solvent, the expression becomes $\kappa \nu^2$. Where there are three of solute to one of solvent it becomes $\kappa \nu^3$.

TABLE III. VALUES OF $\kappa\nu^n$

Dilutions	Resorcinol			<i>m</i> -Cresol.		Thymol		α -Naphthol		Methyl Alcohol		Ethyl Alcohol		Allyl Alcohol	
	$\kappa\nu^2$	$\kappa\nu^2$	$\kappa\nu^3$	$\kappa\nu^2$	$\kappa\nu^3$	$\kappa\nu^2$	$\kappa\nu^3$	$\kappa\nu^2$	$\kappa\nu^3$	$\kappa\nu^2$	$\kappa\nu^3$	$\kappa\nu^2$	$\kappa\nu^3$	$\kappa\nu^2$	$\kappa\nu^3$
500.	28.4											
333.3	19.7											
200.0	12.4	5.12	1019.								
125.0	2.47	9.6	1193.	4.67	584.								
100.0	2.68	8.85	885.	4.15	415.								
50.0	1.93	1.47	73.8	6.62	331.	2.90	145.								
40.0	1.63	1.70	68.0	6.59	263.	2.76	110.								
25.00	1.16	1.87	46.9	6.96	174.	3.03	76.								
20.00	0.98	2.05	41.0	7.89	157.	3.29	66.								
12.50	0.80	8.96	112.	3.80	48.	0.00608	0.076	0.00944		
10.00	0.77	2.29	22.9	9.74	97.	4.04	40.	0.00470	0.0470	0.00485	0.049	0.00725	0.073		
7.69	0.69	2.48	19.1												
5.00	0.63	2.46	12.3	0.00342	0.0171	0.00251	0.0123	0.00327	0.0164		
2.00	0.50	3.90	7.8	0.00332	0.0066	0.00200	0.0040	0.00333	0.0067		
1.666	0.45	0.00397	0.0066	0.00218	0.0036	0.00397	0.0066		
1.250	0.00589	0.0074	0.00308	0.0039	0.00564	0.0071		
0.769	0.0291	0.0224	0.00984	0.0076	0.0230	0.0177		
0.714	0.0391	0.0279	0.0129	0.0092	0.0325	0.0232		
0.555	0.0744	0.041	0.0326	0.0181	0.0640	0.0355		
0.500	0.106	0.053	0.0500	0.0250	0.0929	0.047		
0.417	0.140	0.058	0.1125	0.047		
0.357	0.164	0.058	0.1382	0.049		

If we examine the values, shown on the above table, for $\kappa\nu^2$ or $\kappa\nu^3$, we see, that, in the case of the phenol alcohols, we have a regular series of values increasing gradually with the dilution, in the same way as the molecular conductivity varies for solutions of inorganic salts in water.

It is apparent from an examination of the values obtained for $\kappa\nu^3$, in the case of methyl, ethyl, and allyl alcohol, that the expression $\mu = \kappa\nu^2$ is only applicable over a small range of dilution. For, while the molecular conductivity, as given by $\kappa\nu^3$ for the more dilute solutions, increases more rapidly with dilution than would seem possible, in the case of the concentrated solutions, the value for $\kappa\nu^3$ is still increasing rapidly with the concentration. It would seem as if the constitution of the electrolyte varied with the dilution, giving, in the case of the dilute solutions, a molecule and ion of simple structure; but, as the solution became more concentrated, the electrolytic compound became more complex in structure. This would seem not unreasonable in the light of the recent work of Donnan and Bassett¹ on aqueous solutions of cobalt and copper salts, where the constitution of the electrolyte and of the resulting ions is shown to vary with the concentration of the dissolved salt as well as with the temperature of the solution. Such a behavior would also be, in many respects, analogous to the behavior of water solutions of certain inorganic salts, recently studied by Lewis², Jones and Getman³ and Jones and Bassett⁴, Morgan and Kanolt⁵, who have shown by means of certain color changes, determinations of the lowering of the freezing point, conductivity measurements and measurements of the transport numbers, that the constitution of the electrolyte, and of the ions in solution is in many cases very complex, and varies considerably with the concentration of the solution. This assumption would explain too, the fact that in the case of the above alcohols, the more dilute solutions examined behave in the same way as water solutions of the inorganic electrolytes; for here, where the solutions are dilute, the electrolyte has a simple structure, and the molecular conductivity of the solution will be given by the expression $\mu = \kappa\nu$ rather than by $\mu = \kappa\nu^2$ or $\mu = \kappa\nu^3$.

If in the case of some of the above alcohols, we assume that six molecules of solute are present in the molecule of the electrolytic compound, and then calculate the value of the molecular conductivity from the expression $\mu = \kappa\nu^6$, we get a set of values, which, as we would expect, seem impossible for the dilute solutions but vary in a regular manner over perhaps two-thirds of the range of concentration investigated.

¹ J. Chem. Soc., 81, 939 (1902).

² Z. physik. Chem., 52, 224 (1905).

³ Z. physik. Chem., 49, 385 (1904).

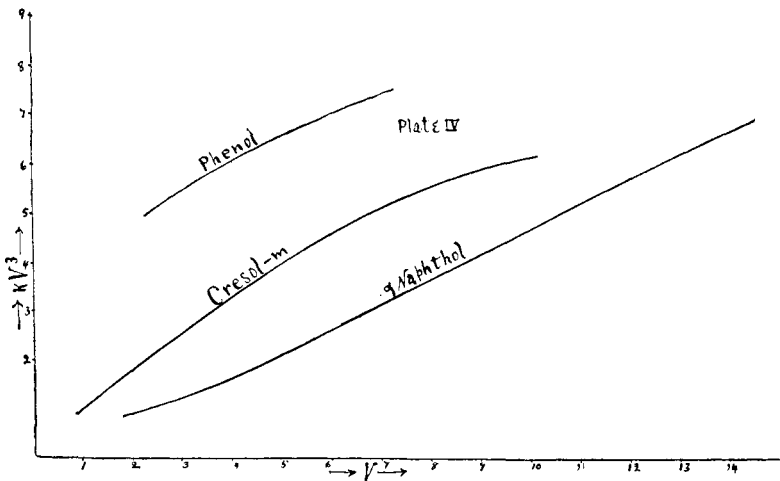
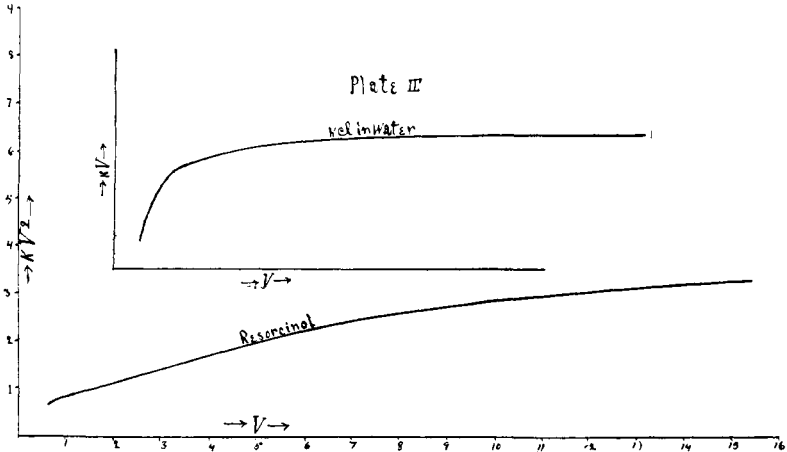
⁴ Ann. Ch. J., 34, 290 (1905).

⁵ This Journal, 28, 572 (1906).

These values have been calculated for methyl, ethyl and allyl alcohol and are given below in table IV.

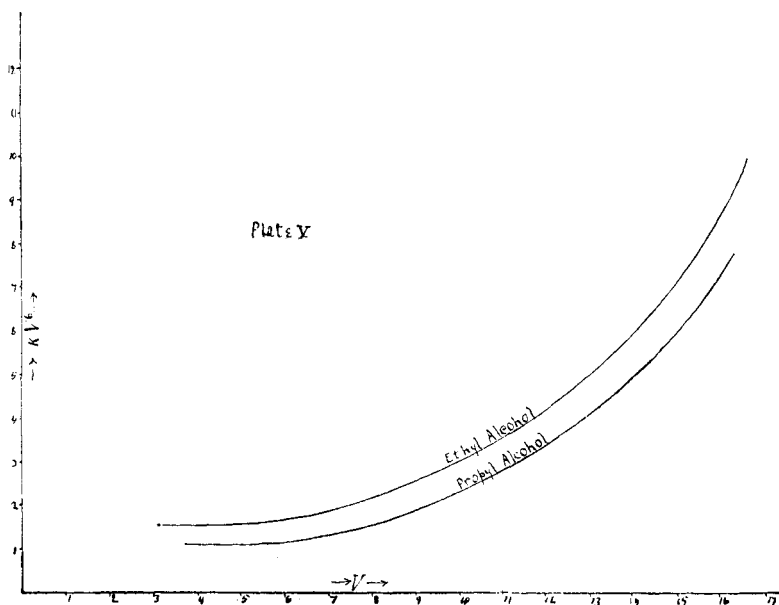
TABLE IV. VALUES OF κV^6

Dilutions		Methyl Alcohol κV^6		Ethyl Alcohol κV^6		Allyl Alcohol κV^6
2.00	0.053	0.0321	0.053
1.66	0.0306	0.0306	0.0306
1.25	0.0144	0.0075	0.0138
0.950	0.0043	0.0091
0.769	0.0102	0.00344	0.0080
0.714	0.0102	0.00334	0.0084
0.555	0.0071	0.00309	0.0061
0.500	0.0066	0.00313	0.0058
0.416	0.0042	0.0034
0.357	0.0027	0.0023



In Plates III, IV and V, the curve obtained by plotting the dilution values as abscissas against the values of κV^2 , κV^3 , or κV^6 , is shown

for a number of cases. Plate III also shows the dilution-molecular conductivity curve for the solution of an inorganic salt—potassium chloride in water.



The curves, in Plates III and IV, are in many respects similar to the curve for potassium chloride in water solutions, but the curves for ethyl and propyl alcohol shown in Plate V, are convex toward the dilution axis, while the dilution-molecular conductivity curve for potassium chloride solutions in water is concave toward this axis. It is probable that in the case of the solutions of these alcohols, the electrolytic compound which is formed is very complex in character, and varies in structure with the dilution, both as regards the number of molecules of solvent and of solute which it contains. This variation apparently takes place so continuously, as the dilution changes, that a simple expression will give the true molecular conductivity, only over a very narrow range of dilution.

SUMMARY.

The results set forth in the foregoing pages show :

- (1) That the greater number of the alcohols dissolve in liquid hydrogen bromide, and give conducting solutions.
- (2) That in the benzene series of alcohols, when the hydroxyl group is in the meta position, the conducting power of the solution is in general greater than when the hydroxyl has the ortho or para position. A case in point being that of the dihydroxy benzenes, resorcinol, hydro-

quinone and pyrocatechol. For while resorcinol dissolves readily to give good conducting solutions, pyrocatechol and hydroquinone apparently do not dissolve at all, and certainly do not give conducting solutions.

(3) That in the paraffin series, the simpler the alcohol—the lower it comes in the series—the greater the conducting power of its solutions. While in the benzene series, the greater the number of carbon atoms in the molecule, the better conductor will the solution of the alcohol be.

(4) That in a very few cases, for two or three of the more dilute solutions, the molecular conductivity increases slightly, or remains practically constant as the dilution increases. But for a majority of the cases examined, and for all the more concentrated solutions, the molecular conductivity decreases rapidly as the dilution increases.

(5) That if we calculate the value of the molecular conductivity from the expression, $\kappa \nu^n$, where n is the number of molecules of solute uniting with one molecule of the solvent to form the electrolytic compounds instead of from the expression $\kappa \nu$, we obtain values which, in the case of the alcohols of the benzene series, vary with the dilution in the same manner as the values for the molecular conductivity of solutions of inorganic salts in water. In the case, however, of the paraffin alcohols, this expression will apply only over a narrow range of dilution.

(6) That the temperature coefficients of conductivity are in some cases positive, in some cases negative, and not infrequently change sign in passing from a concentrated to a dilute solution.

In conclusion, I wish to express my thanks to the trustees of the Elizabeth Thompson Science Research Fund, for a grant which helped to defray the expenses incurred in carrying on this work.

CHEMICAL LABORATORY,
SYRACUSE UNIVERSITY, SYRACUSE, N. Y.

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THE CALCULATION OF SOME CHEMICAL EQUILIBRIA

BY K. GEORGE FALK.

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While assisting Professor W. Nernst in preparing the Silliman lectures which were delivered at Yale University in October, 1906, the writer had occasion to become familiar with the new theory¹ developed by Professor Nernst, which permits the calculation of chemical equilibria from thermal

¹ This theory was published for the first time in the "Nachrichten der K. Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-physikalische Klasse, 1906. Heft 1" under the title "Ueber die Berechnung chemischer Gleichgewichte aus thermischen Messungen." The complete theory so far as it has been developed to the present time has just appeared in book form "Experimental and Theoretical Applications of Thermodynamics to Chemistry" by W. Nernst.