

tesimal aqueous film surrounding the fat globules, and that anything which increases the degree of peptization of the fat, and hence the amount of interface exposed, accelerates the hydrolysis.

9. The mechanism of the hydrolysis of benzene-sulfone-chloride was found to be similar in practically every respect to that of mustard gas, except that it was apparently catalyzed in the aqueous phase by the presence of hydroxyl ions, and showed no evidence of reversal in acid solutions. Acid solutions of various colloids showed a similar accelerating tendency in cases where benzene-sulfone-chloride was soluble in the colloidal phase.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 22]

A STUDY OF THE CONDUCTION PROCESS IN ORDINARY SODA-LIME GLASS

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Introduction

While the fact that glass is a conductor of the electric current was known at a very early date, none of the earlier investigators seems to have had a clear notion of the nature of the conduction process.

It was Warburg¹ who, for the first time, showed definitely that this process in glasses is an electrolytic one, and that the passage of the electric current through glass is due to the motion of sodium present in the glass. On passing a direct current through glass, using mercury electrodes, he found that a thin layer of very high resistance is formed at the anode.

Le Blanc and Kerschbaum² repeated Warburg's work using a mercury anode. They concluded that conduction is due entirely to the motion of the sodium present in the glass and that the glass is ionized to the extent of about 80% at 250°, the temperature at which they carried out their experiments. They also observed the formation of the poorly conducting layer at the anode. In this layer, Ohm's law does not hold, the current apparently varying as the square of the resistance. According to these writers, the passage of the current through this layer is not accompanied by a transfer of matter. They give the migration velocity of the sodium ion in glass as 1×10^{-8} cm. per sec. at the temperature in question. They showed, too, that at the anode the original glass may be regenerated by reversing the current, while, if a sodium amalgam is employed as anode, the layer is not formed.

Warburg and Tegetmeier³ studied both glass and quartz crystals, using amalgams and, in some cases, coatings of plumbago or gold. They showed that in these substances conductance is due to the presence of sodium. Tegetmeier⁴ worked with both sodium and lithium amalgams. He states that lithium may be completely electrolyzed through quartz and glass, the metal appearing at the cathode. The glass is brittle and goes to pieces easily. The passage of lithium through glass could be followed by the

¹ Warburg, *Ann. Physik*, **21**, 622 (1884).

² Le Blanc and Kerschbaum, *Z. physik. Chem.*, **72**, 468 (1910).

³ Warburg and Tegetmeier, *Ann. Physik*, **35**, 455 (1888).

⁴ Tegetmeier, *ibid.*, **41**, 18 (1890).

translucent appearance of the glass into which the lithium had penetrated. This glass is milk-white, and is porous and may be stained with a fuchsin solution. He ascribes this porosity to the difference in specific volume existing between the sodium and lithium atoms. We shall later have occasion to refer to this conclusion. Tegetmeier found it impossible to electrolyze potassium into glass from an amalgam, nor could he electrolyze such metals as calcium, magnesium, aluminum, tin, bismuth, zinc and gold into glass from their amalgams. Assuming that 1 sodium ion is replaced by 1 lithium ion, the amount of sodium affected by the passage of the current through the glass is approximately 60%. Heydweiller and Kopfermann⁵ worked with soda-lime glasses, using fused salts as electrolytes. They investigated the action of salts of sodium, potassium, barium, strontium, tin, lead, copper, iron, cobalt and silver. Gold, platinum and uranium apparently do not enter glass under the action of the current. In a number of instances they observed pronounced color effects which they attributed to a colloidal condition of the metal. Examination under the microscope bore this out. They found that the conductance of the glass varied as electrolysis proceeded. They considered this to be due to a change in the actual value of the conductance of the glass as a result of the replacement of sodium ions by ions of other metals. They also found that various metals could be introduced into glass by diffusion from a fused salt.

The diffusion of metals into glass was studied somewhat in detail by Schultz⁶ who worked with silver nitrate. Warburg⁷ examined the results of Schultz's experiments and developed the equations for the diffusion process.

None of the investigations referred to gives sufficient information regarding the condition of the sodium present in glass, and it appeared desirable, therefore, to carry out a series of experiments in an attempt to determine to what extent the sodium in glass is subject to the action of the electric current. Le Blanc and Kerschbaum state that a layer of measurable thickness is obtained when glass is electrolyzed between mercury electrodes. However, by their method, it was not possible to obtain a layer of sufficient thickness to permit of accurate measurement. It was accordingly determined to attack the problem by means of the replacement of the sodium contained in glass by another metal, the depth of whose penetration into the glass could be measured. This virtually constitutes a transference experiment in glass by means of the moving boundary method.

Preliminary Experiments

Lithium.—As was shown by Tegetmeier, lithium may be electrolyzed into glass from its amalgam, while from the investigation of Heydweiller and Kopfermann it is to be expected that it may likewise be introduced from its fused salts. Accordingly a series of experiments was carried out in which lithium was used as an electrode, both in the form of an amalgam and of the fused salt. The lithium amalgams were prepared by electrolysis and filtered in a vacuum and stored. They were introduced into the cell in a vacuum, after which the cell was sealed. Using dil. amalgams, however, there was only a slight effect on the glass. The resistance was found to increase rapidly and the penetration was found to be very small.

⁵ Heydweiller and Kopfermann, *Ann. Physik.*, **32**, 739 (1910).

⁶ Schultz, *ibid.*, **40**, 335 (1913).

⁷ Warburg, *ibid.*, **40**, 327 (1913).

One difficulty which arises in the use of amalgams is the formation of bubbles of gas on the surface of the glass. Even after prolonged heating in a vacuum and after boiling and partial distillation of the amalgam, gas bubbles slowly appear on the walls of the tube during electrolysis.

Solid amalgams, likewise, were prepared and manipulated in a manner similar to that employed with the liquid amalgams. In transferring, the solid amalgam was filtered and allowed to cool, after which the tube was broken and the needle-like crystals of amalgam were removed from the liquid. These were separated from excess mercury by pressing and were then stored in a vacuum over phosphorus pentoxide. The solid crystals are comparatively stable in dry air and may be transferred to the electrolytic cell without difficulty.

When electrolysis was carried out with the fused solid amalgam, a marked increase in the resistance was not observed as electrolysis proceeded. Even with the solid amalgams, however, the process of electrolysis was found to proceed very slowly, requiring 24 to 30 hours at a temperature of 350° with a potential of 500 volts in order to produce a measurable result. The glass tube into which the amalgam was electrolyzed had a thickness of approximately 1.5 mm.

Fused lithium salts are much more convenient to handle than the amalgams and the time necessary in order to carry out an electrolysis is greatly lessened. Lithium nitrate was prepared from *c. p.* carbonate and dehydrated in a vacuum. The nitrate is stable in air and fuses at a sufficiently low temperature to allow its use in a pure state. The greater portion of the work with lithium was, therefore, carried out with the fused nitrate.

As a means for determining the relative amount of sodium concerned in the conduction process, lithium proved a complete failure. It is unquestionably true that on electrolysis lithium enters the glass, but the resulting product does not appear to be a definite homogeneous material. Indeed, the glass is completely disintegrated. This disintegration of the glass is more complete when a fused salt is used than when an amalgam is employed. The difference, however, is purely one of degree. Even with dil. amalgams, fine cracks could readily be observed running across the surface of the glass. When more concentrated amalgams were used, the number of these cracks increased greatly—so much so that the glass had a milky appearance. Finally, when a fused salt was used, the glass was broken into minute particles which adhered to one another but which crumbled between the fingers. In fact, the substance was no longer a glass. That actual disintegration occurs is further shown by the fact that a marked loss in weight occurs when electrolysis is carried out with a lithium anode. This loss is much greater than corresponds to the relative weights of the lithium and sodium atoms. Observed with the naked eye, the boundary

of the affected layer appears to be fairly sharp, but when viewed under a high-power microscope it is seen that the boundary is ragged and that the glass presents a granular structure. On heating the glass, the milky appearance entirely disappears, showing that the effect is a purely mechanical one. Lithium likewise diffused into glass without the action of the electric current, yielding a product which appears to be identical with that obtained by electrolysis.

Sodium.—Sodium enters glass with the greatest ease, both from the amalgam and from the fused salt. Apparently, an unlimited amount of sodium may be electrolyzed through glass without causing any change in its properties. In one case, as much as 0.5 g. of sodium was electrolyzed through a tube without noticeable change in the weight of the tube. Faraday's laws are obeyed, the amount of sodium in the cathode being equivalent to the quantity of electricity passing.

Potassium.—Potassium enters glass readily from the fused nitrate. The glass, however, is very unstable and flies into minute pieces on cooling. Heydweiller and Kopfermann state that the glass shows a violet color, but this was not observed in the case of the glasses employed in the present investigation.

Copper.—When copper is electrolyzed from an amalgam, no effects are noted in the glass. Apparently, a poorly conducting layer is formed at the anode surface. From the fused salts, copper may be electrolyzed into glass, but disintegration occurs and quantitative measurements cannot be carried out.

Lead.—Lead may be electrolyzed into glass, replacing the sodium. As most lead salts have too high a melting point for this purpose, it was found advantageous to use a eutectic mixture of the iodide and bromide. This method is preferable to that of Heydweiller and Kopfermann, in which a lead salt is dissolved in a mixture of sodium and potassium nitrates. The glass formed on replacing sodium by lead is unstable. It breaks easily and in most cases disintegrates on cooling, even though carefully annealed. The glass has a milky appearance, resembling that of the glass obtained with lithium, but the disintegration is not so marked.

Zinc.—With zinc amalgams, a poorly conducting layer is formed at the anode. Evidently zinc does not enter the glass from an amalgam. With zinc chloride, however, the current passes readily, but the resulting glass disintegrates. It was found impossible to obtain a tube which would remain intact long enough to be weighed.

Silver.—Silver is by far the most satisfactory element for introduction into soda glass in place of sodium. Furthermore, it is readily handled, both as amalgam and as the fused nitrate. With silver amalgam, the process of electrolysis proceeds slowly and a long time is required to complete an experiment. With silver nitrate, however, the process of elec-

tolysis proceeds rapidly and the tubes remain intact, even though the silver penetrates to a considerable depth. When silver enters glass, whether from the amalgam or from the fused salt, a sharp boundary is formed between the sodium and the silver. Up to a certain point, the strains introduced, due to the substitution of sodium by silver, are not sufficient to crack the glass, but with a tube having a length of 55 mm., a thickness of 1.5 mm., and a diameter of 10 mm. it was not found possible to introduce more than 0.05 g. of silver into the glass without danger of the ultimate cracking of the tubes. In this case, however, there are no signs of disintegration of the glass, which remains transparent throughout. Accordingly, experiments were carried out to determine the relative amount of sodium present in soda glass which could be replaced of silver.

Apparently when silver enters the glass from the amalgam or from the fused nitrate an atom of silver replaces an atom of sodium. This is shown by the gain in weight of the tube and by the presence of sodium in the mercury which serves as cathode. The amount of sodium replaced may be determined by analysis of the amalgam and this may be checked by the change in the weight of the tube.

At the temperatures at which the experiments were carried out, 250–350°, the glass turns a light amber color; on heating to higher temperatures, it passes from deep red to brown. Heated nearly to redness in a free flame, a metallic mirror is formed on the surface. These effects appear to be due to the precipitation of silver in the metallic form. If the process of heating is carried out rapidly, there is no appreciable alteration in the depth of penetration. If, however, the heating is continued for a considerable period of time, the boundary between the salt and the sodium is displaced as a result of diffusion.

Quantitative Experiments

Apparatus.—The temperature coefficient of the conductance of glass is relatively high and it is, therefore, necessary to control the temperature within reasonable limits. This is a factor to which earlier investigators have paid very little attention. For the purpose of this investigation, an air thermostat was constructed which could be operated between 200° and 350°, and with which the temperature could readily be maintained constant within 0.5° and, for shorter periods of time, within much narrower limits.

A small direct-current generator served as a source of electromotive force. The voltage of this generator could be varied between 150 and 600 volts by means of a field rheostat.

In order to avoid various experimental difficulties, all electrolyses were carried out with glass tubes having a diameter of 1 cm. and a wall thickness of approximately 1.5 mm. The interior of the tube was filled to a height of 12 or 15 cm. with mercury, which served as cathode, while on the outside it was dipped into a bath of silver nitrate to a depth of approximately 5 cm. The silver nitrate was contained in a tube of special glass which was little affected by silver nitrate at the temperatures employed in this investigation. Contact was made with the electrodes by means of iron wires. A copper coulometer placed in series with the electrolyzing circuit served to measure the quantity of electricity flowing through the cell.

Conductance measurements were likewise made, using a drum-wound bridge 3 m. long, with a telephone as indicating instrument and a Vreeland oscillator as source of alternating current. A resistance box of the Curtis type was employed.

Materials.—The glass used was a soda-lime glass of American manufacture. It was analyzed according to the method developed by Sullivan.⁸ The results of two analyses are given in the following table.

TABLE I
ANALYSES OF SODA-LIME GLASS

	I	II	Mean
	%	%	%
Calcium and lead as oxides.....	11.28	11.20	11.24
Aluminum and iron as oxides.....	2.31	2.39	2.35
Sodium as oxide.....	16.85	16.95	16.90
Sodium as metal.....	12.50	12.46	12.48

The silver nitrate employed was a C. P. product, obtained on the market, which was not further purified.

Procedure.—The tube to be electrolyzed was carefully annealed, placed in the thermostat, and allowed to come to temperature. It was then placed in the cell containing the fused silver nitrate and centered so as not to come in contact with the walls of the tube. Mercury was then introduced into the tube to serve as cathode. The level of the cathode mercury was always higher than that of the fused salt as, otherwise, a correction for the relative expansions of glass and mercury would have been necessary in calculating the amount of affected surface. The cell was then connected to the generator through the coulometer and the current passed for periods of time varying from 30 minutes to 15 hours. After completing a run, the glass tube was quickly annealed. It was then cut into sections and the penetration of the silver layer was measured by means of a high-power micrometer microscope. At temperatures below 290°, the color of the glass after electrolysis was comparatively faint, and in order to bring out the line of division it was necessary to heat it slightly for a short period of time. The diameter of the tube and the height of the affected surface, that is, the depth of immersion in the nitrate bath, being known, the volume of the affected portion could be calculated from the depth of penetration, assuming the tube to be of uniform dimensions throughout. Knowing the density of the glass and the original percentage of sodium metal in the glass, the total amount of sodium in the affected portion could be calculated. When the amount of copper deposited in the coulometer is known, the total quantity of electricity passing through the circuit was also known, and therefrom the amount of sodium electrolyzed from the glass and of silver electrolyzed into the glass could be determined. The relative amount of sodium taking part in the conduction process could then be calculated from the ratio: $i = p/g$, where p is the amount of sodium electrolyzed out and g is the total amount of sodium initially present in the affected region.

⁸ Sullivan, *J. Ind. Eng. Chem.*, 6, 897 (1914).

Experimental Results.—It is necessary to show that every atom of silver entering the glass replaces an atom of sodium leaving the glass. This may be done in two ways. First, there should be a gain in weight of the tube which is equal to the difference in weight of silver introduced and of sodium extracted. The amount of silver and sodium affected may be determined from the quantity of electricity passing through the circuit, which is determined by means of the coulometer. Second, the amount of sodium electrolyzed out of the glass and which enters the cathode to form an amalgam may be determined by titration.

In Table II are given the results obtained by the first method. In the first column is given the number of the experiment; in the second, the amount of copper deposited; in the third, the gain in weight of the tube, calculated from the amount of electricity passing; in the fourth, the measured gain in weight; in the fifth, the elapsed time; and in the sixth, the temperature. Excepting No. 18, in which an amalgam was used, the electrolyses were carried out with silver nitrate as anode.

TABLE II
COMPARISON OF OBSERVED AND CALCULATED GAIN IN WEIGHT OF GLASS TUBE ON
ELECTROLYSIS WITH SILVER ANODE

No.	Cu deposited G.	Gain in weight		Time Hrs.	Temp. ° C.
		Calc. G.	Observed G.		
18	0.0127	0.0339	0.0347	4 $\frac{1}{2}$	350
21	0.0145	0.0396	0.0416	2	350
118	0.0269	0.0732	0.0762	$\frac{1}{2}$	343
131	0.077	0.0209	0.0209	$\frac{1}{2}$	343

In Table III are given the results obtained by the second method. In the first column is given the number of the experiment; in the second, the amount of copper deposited in the coulometer; in the third, the amount of sodium transported, calculated from the amount of copper deposited; in the fourth, the amount of sodium as determined by titration of the cathode mercury; in the fifth, the temperature; and in the sixth, the length of time elapsed during the run. Run No. 19 was carried out with amalgam as anode.

TABLE III
COMPARISON OF OBSERVED AND CALCULATED AMOUNT OF SODIUM ELECTROLYZED INTO
CATHODE MERCURY FROM GLASS

No.	Cu G.	Na		Temp. ° C.	Time Hours
		Calc. G.	By titration G.		
118	0.0269	0.0194	0.0222	343	$\frac{1}{2}$
19	0.0612	0.0442	0.0426	350	8
21	0.0145	0.0105	0.00886	350	2

Owing to the difficulty of titrating accurately the small quantities of alkali present, the first method is the more reliable.

As may be seen from the inspection of Tables II and III, there is as close an agreement between the observed and calculated results as might well be expected. It is clear, therefore, that the process of electrolysis consists in the replacement of sodium by silver in the layers of glass in contact with the fused silver nitrate or amalgam. As the process of electrolysis proceeds, the boundary between the silver and the sodium ion remains sharp and moves through the matrix of the remaining material, which must be negatively charged, at a fixed rate, depending upon the potential gradient existing in the path of the ions.

The first experiments on the determination of the amount of sodium transported in the conduction process were carried out with a potential of 500 volts. On measuring the current at the instant of starting and at various intervals of time thereafter, it was found to increase to a constant value considerably higher than the initial one. On again shutting off the current and allowing the cell to stand for a short time, it was found that, on applying the potential, the current had returned to its initial value. This procedure could be repeated without variation. This effect is undoubtedly due to the temperature rise of the conducting medium, as a result of the Joule effect. Since it was proposed to determine the influence of temperature upon the relative amount of sodium concerned in the conduction process, the potential was lowered to a point where the heating effect became negligible.

TABLE IV
RESULTS OF ELECTROLYSES OF GLASS WITH SILVER NITRATE ANODE

No.	Duration		Copper deposited G.	Penetration Mm.	Height Mm.	Diameter Mm.	Ionization %
	H.	M.					
<i>t</i> = 278°							
142	14	44	0.0135	0.0225	54.0	10.25	75.4
143	9	..	0.0056	0.015	53.5	9.46	71.2
144	13	30	0.0061	0.013	50.0	9.8	77.6
<i>t</i> = 295°							
145	10	55	0.0220	0.056	50.5	9.6	77.2
146	21	15	0.0274	0.076	50.0	9.6	76.4
<i>t</i> = 323°							
148	8	14	0.0290	0.061	51.5	9.92	78.4
149	4	54	0.0207	0.050	51.0	9.95	75.7
150	5	1	0.0249	0.060	48.5	9.05	84.0
<i>t</i> = 343°							
137	2	12	0.0291	0.057	59.5	10.15	82.6
138	2	50	0.0249	0.0582	55.0	10.00	73.5
139	2	29	0.0202	0.040	53.0	9.82	82.0
141	4	7	0.0290	0.060	54.0	10.00	82.4
140	4	..	0.0272	0.052	54.0	10.07	84.5

In Table IV are given the results of a series of determinations of the relative amounts of sodium transported through the glass and replaced by

silver at various temperatures. The number of the experiment is given in the first column; the duration of the run, in the second column; the amount of copper deposited in the coulometer, in the third column; the penetration of the silver, in the fourth column; the height of the tube, affected in the fifth column; the diameter of the tube, in the sixth column; and the degree of ionization of the sodium, that is, the fraction of sodium electrolyzed out of the glass, in the last column. The temperatures at which the experiments were carried on are indicated in the table.

The density of the glass employed in these measurements was found to be 2.044. The experiments were carried out with an applied potential of 200 volts. In determining the volume of the tube affected, it was assumed that the tube consisted of a cylinder and a hemisphere. The mean value obtained for the ionization of the sodium from all experiments is given in the following table.

TABLE V

IONIZATION AND RESISTANCE OF GLASS AT DIFFERENT TEMPERATURES

Temperature.....	278°	295°	323°	343°
Ionization, %.....	74.4	76.8	79.4	81.0
Resistance, ohms.....	72800	35000	14200	6600

Although there is considerable variation in the values found for the ionization in the different experiments carried out at a given temperature, there can be no question but that, as the temperature increases, the relative amount of sodium affected by the current likewise increases. The increase, however, is not great.

The resistance of the glass was likewise measured at the same temperatures. The measurements were made by employing a sodium nitrate bath both as cathode and as anode with iron wires. The form of the cell and its dimensions were the same as those of the specimens employed in the electrolysis experiments.

Since the ionization varies but little with the temperature, it follows that the depth of penetration at different temperatures should vary directly as the conductance of the glass at those temperatures, provided the potential gradient is the same. These conditions were approximately fulfilled in the experiments, the data for which are given in Tables IV and V. The mean depths of penetration per hour, according to the data of Table IV, are 0.00153, 0.00439, 0.00983 and 0.0160 mm. at 278°, 295°, 323° and 343°, respectively. The ratio of the depth of penetration at the last 3 temperatures to that at 278° is 2.88, 6.41 and 10.40, respectively. For the same temperatures, the resistance ratios are 2.08, 5.12 and 11.08, respectively. It is evident that the depth of penetration is very nearly proportional to the conductance of the glass.

Shift of the Boundary.—Since the boundary of the silver layer penetrates farther into the glass as the duration of the process of electrolysis

is continued, and since it consists essentially in a replacement of sodium ions by silver ions, it was to be expected that the reverse phenomenon would likewise take place, namely, that the direction of motion of the boundary would be reversed on reversing the applied potential. If the potential were maintained in the original direction for a sufficient length of time, the silver would ultimately penetrate the entire tube and pass into the mercury which serves as the cathode. It is not possible, however, to carry this out, since the glass is unstable and shatters before this process can be completed. Accordingly, a tube was prepared by first introducing silver from the fused nitrate, allowing the tube to cool, and then replacing the silver nitrate anode with one of sodium nitrate. The current was then again allowed to flow in the original direction. After a period of time, the tube was again cooled, after which it was sectioned, and the depth of penetration measured. As in the preceding experiments, a copper coulometer was connected in series with the cell.

In one of these experiments, a silver nitrate anode was used for 30 minutes during which 0.0224 g. of copper was deposited, corresponding to a penetration of 0.05 mm. at 334°, the temperature of the cell. Silver nitrate was then replaced by sodium nitrate and the current passed for 3 hours, when the copper deposited amounted to 0.1334 g. The tube was then cooled and sectioned and the depth of penetration measured. The depth was found to be 0.260 mm. In other words, when the amount of electricity was equal to 5.92 times that passed in the first half hour, the depth of penetration was 5.02 times that usually obtained for the first 30 minutes. Because the precise depths of penetration in the first 30 minutes cannot be determined with great precision, the agreement of the above values is as close as might be expected. As, in this experiment, the boundary was not shifted to the cathode surface when the silver nitrate was replaced by sodium nitrate as anode, it follows that the weight of the tube should have remained constant. This was found to be the case. It is evident that both boundaries between the silver and the sodium ions may be shifted through the tube. Correspondingly, on reversing the applied potential, the boundary may be shifted back and silver electrolyzed out of the glass. Before introducing the sodium nitrate as anode, the tube weighed 28.2835 g. and after 3 hours' running with the sodium nitrate anode the weight of the tube was found to be 28.2798 g. As the tube was slightly etched, the loss in weight may be ascribed to this cause.

On attempting to reverse the process and electrolyze the silver out of the glass, it was found that this could not be carried out completely. When the tube was sectioned, it was found that the color characteristic of the presence of silver remained to approximately the depth of the original penetration of silver. Apparently, a portion of the silver is precipitated, presumably in colloidal form, and this cannot be subsequently removed by electrolysis.

Change of Resistance Due to Substitution of Sodium by Silver.—Heydweiller and Kopfermann mentioned the fact that, as the process of electrolysis continues with the silver nitrate anode, the current increases. They found that this increase was very marked at lower temperatures, where the conductance increased more than 100-fold in a few minutes. From the results mentioned above, relative to the increase of conductance due to the heating effect, it is to be expected that the phenomenon observed by Heydweiller and Kopfermann is due to the same cause. In order to determine whether the decrease in resistance is due to heating or to a change of resistance because of the presence of silver in the glass, the resistance before and after electrolysis with silver nitrate was measured. The results are given below.

	I	II
	Ohms	Ohms
Resistance of tube before running.....	1,650	1,590
Resistance of tube after running.....	1,450	1,440
Fall in resistance.....	200	150
Resistance after standing for 30 minutes.....	1,649	1,590
Temperature, 343°	Amount of copper deposited, 0.0264 g.	
Potential, 300 volts	Time of run, 1½ hours	

It is evident from these results that, while the resistance decreases as the current flows, the decrease is not a permanent one and that, under the same thermal conditions, the resistance of the glass containing silver is practically identical with that of the original glass.

Ionic Mobilities.—Le Blanc and Kerschbaum from their measurements give the value of the speed of the sodium ion in glass as 1×10^{-8} cm. per second under unit potential gradient at 350°. In order to check this value the ionic velocity of sodium when replaced by silver at various temperatures was calculated from the data given above. It is here assumed that the speed of the boundary accurately represents the speed of the sodium ion, since it has been shown that 1 atom of silver replaces 1 of sodium and that the speed of the boundary is dependent on the speed of the sodium ion as long as the silver layer has not penetrated to any considerable depth. Calculating on this basis, the velocities of the sodium ion at 278°, 295°, 323° and 343°, are found to be 4.52×10^{-8} , 1.46×10^{-7} , 3.26×10^{-7} and 5.9×10^{-6} , respectively.

It will be seen that these values lie considerably above that obtained by Le Blanc and Kerschbaum. It appears very probable that the method which they employed for determining the velocity of the sodium ion is not a satisfactory one.

Discussion

The foregoing experiments show clearly that only a fraction of the sodium present in ordinary soda-lime glass is concerned in the conduction process. Glass may be considered as a mechanically rigid, undercooled, fused salt

mixture. At higher temperatures, where the glass is fluid, such a mixture is undoubtedly in a state of equilibrium. The equilibrium in the system, at lower temperatures, in a mechanically rigid state, must correspond approximately to that at a higher temperature, which has, so to speak, been frozen and which is maintained at lower temperatures. The results given in the foregoing sections, therefore, show that the major portion of the sodium present in glass is in an ionic condition, as it is capable of taking part in the conduction process. Between the temperatures of 278° and 343° , the ionization, that is, the fraction of sodium taking part in the conduction process, increases from 74% to 81%. This is a comparatively small change and does not greatly exceed the experimental error. Nevertheless, the results obtained for the ionization show an unmistakable upward drift as the temperature increases, indicating that at higher temperatures a relatively larger proportion of the sodium takes part in the conduction process. In interpreting the results of the present investigation, therefore, we may be in error in assuming that the values found actually represent the true degree of ionization of the sodium in the glass. It is possible that all the sodium present is in an ionized condition, but that some of the ions are rigidly held in position by interatomic forces. It should be noted, however, that if a sodium ion is capable of moving at all, it apparently moves with a fixed velocity which is determined solely by the temperature. Otherwise, it would be difficult to account for the sharp boundary obtained between the sodium and the silver ions. Our knowledge of mechanically rigid systems is still too meager to enable us to hazard a guess as to the true nature of the equilibrium existing in systems of this kind. In any case, however, by far the greater proportion of the sodium in glass is present in a condition in which it is capable of conducting the current, and it may be inferred, therefore, that other similar systems will be in a similar condition. In view of the fact that the apparent ionization increases with the temperature in the case of glass, it may be inferred that ordinary salts are highly ionized in the fused state.

The above experiments, as well as the experiments of earlier investigators, further show that a charged sodium atom may function as an ion. In solutions in electrolytic solvents, the ions do not consist of simple charged atoms, but rather of such charged atoms in association with the molecules of the solvent medium. It may be concluded, however, that in salts of strongly electropositive metals the association between the charged atoms and the solvent molecule is of a secondary nature so far as the ionization process is concerned.

One of the striking properties of glasses, as of many other rigid electrolytic systems, is the great increase of conductance with increasing temperature. Since the ionization of glass varies only little with the temperature, it follows that the increased conductance must necessarily be due to the

increased speed of the ions at the higher temperatures. The influence of temperature on the conductance of a glass, therefore, is of the nature of a viscosity effect. In interpreting the results, however, it must not be concluded that a direct relation exists between the mobility of the conducting ions and the elastic constants of the medium. The measurements of Winkelmann⁹ show that the elastic properties of glasses do not vary greatly until a little below the softening temperature. It may be inferred, therefore, that the increased speed of the sodium ion at higher temperatures is not directly related to the elastic constants of the glass. Conversely, it may be inferred that the elastic properties of a glass are not primarily due to the sodium ions. In a glass, the current is carried solely by the positive ion. The negative ions, therefore, must be a part of, or must constitute, a rigid system to which, ultimately, the mechanical properties of the glass are due.

Since the sodium in glass, even in a rigid condition, is for the most part in a conducting state, it follows that a glass is to be looked upon as a mixture of electrolytes. In treating the properties of glasses at the present time, it is customary to relate these to their composition in terms of their content of acidic and basic oxides. If the constituents of glasses are in fact salts, as they unquestionably are, then it would appear that this procedure is not accurate, for it is difficult to see how the content of sodium oxide, for example, can be a controlling factor in the case of a given property, when the sodium is present not as oxide but as a more or less complex silicate, in which the sodium functions as an ion. At the present time, however, it would be difficult to interpret the properties of glasses in terms of their ionic constituents, since we have but little definite knowledge as to the nature of these constituents. In addition to sodium, lime glasses contain a considerable amount of calcium. In what condition the calcium exists in glasses we cannot, at the present time, state. In view of the strongly electropositive nature of calcium, it appears improbable that calcium is present otherwise than as calcium ion. If such is the case, then the calcium ions must form a rigid system in the glass. In the case of a rigid mixture of ionic constituents, we should perhaps consider that each ionic constituent forms a more or less definite system.

In many respects, the glasses resemble crystalline salts, which have been shown to conduct the current by a similar process; that is, by one in which the charge is carried solely by the positive or the negative constituent of the salt in question.¹⁰ In the case of most salts, the current is carried by the positive constituent, but in that of lead chloride¹¹ the current is carried by the negative constituent. The mechanical properties of solids of the

⁹ Winkelmann, *Ann. Physik*, **61**, 105 (1897).

¹⁰ Tubandt and Lorenz, *Z. physik. Chem.*, **87**, 513 (1914).

¹¹ Tubandt, *Z. Elektrochem.*, **26**, 358 (1920).

electrolytic type must therefore be due, primarily, to a single constituent, usually the negative constituent. At any rate, this is the case at temperatures approaching the melting point. The conductances of many salts near their melting points have very high values. In these regions, therefore, the rigidity of the salt must be due to the constituent whose position is fixed.

Only a few metals do not enter glasses from their fused salts or from their amalgams. It is interesting to note that many metals, which enter glass readily from the fused salts, enter glass only with difficulty from their amalgams. This is not true of sodium, which enters glass comparatively readily from its amalgam. The more dilute the amalgam, the greater the difficulty with which the metal enters the glass. If the concentration falls below a certain value, a poorly conducting layer is formed at the anode, and the conductance of the glass falls to a very low value. Apparently, the formation of this poorly conducting layer is due to the removal of carriers from the layers of glass in immediate contact with the anode surface. In other words, the phenomenon is one of polarization. In order that the current should pass continuously, it is necessary that the ions removed from the surface of the glass in contact with the anode shall be replaced by ions present in the anode medium. If the density of the positive ions in the anode medium is much lower than that of the positive ions in the glass, then it may be expected that polarization will occur; all of the sodium ions will be electrolyzed out of the glass in the immediate neighborhood of the anode surface. The fact that many metals enter glass much more readily from their fused salts than from their amalgams indicates that the concentration of the ions of the metal in the amalgam is relatively much lower than in the fused salt. Thus, zinc enters glass readily from the fused salt but only with difficulty from a concentrated amalgam. While the total concentration of zinc in the two cases is comparable, it is evident that the concentration of the zinc ions in the two cases is not. It follows, therefore, that the concentration of normal zinc ions in a zinc amalgam is below that of the total zinc in the amalgam. The behavior of amalgams may be accounted for by assuming that the metal is present in the form of a compound rather than in that of an ion.¹² At the present time, however, we do not have sufficient data on this point to warrant drawing any very definite conclusions.

Summary

1. The replacement of sodium ions in soda-lime glasses by ions of other metallic elements has been studied. Although the sodium ions may be replaced by the ions of many other metals under the action of a potential, from their amalgams as well as from their fused salts, replacement takes place more readily from the fused salts than from the amalgams. In

¹² Compare Kraus, *THIS JOURNAL*, **44**, 1216 (1922).

most instances, the glass formed on replacement is not stable. In some cases, the glass is completely disintegrated and in others the glass cracks on cooling. Sodium may be replaced by silver to a depth of approximately 0.1 mm. without cracking.

2. On replacing sodium by silver under the action of a potential, a sharp boundary is formed between the sodium and the silver ions. From the rate of motion of the boundary, the speed of the ions under a unit potential gradient has been determined. The speed of the ions increases greatly with increasing temperature, corresponding to the increased conductance of the glass with increasing temperature.

3. The fraction of the total sodium present in the glass, which takes part in the conduction process, has been determined from the depth of penetration of the boundary and from the amount of electricity passing, as well as from the change in the weight of the tube. It has been found that from 74% to 82% of the total sodium present in an ordinary soda-lime glass takes part in the conduction process. The remainder of the sodium is either not in a charged state or otherwise the ions are held in fixed position. The fraction ionized, as defined in this way, increases slightly with the temperature between 278° and 343°.

4. The results obtained are discussed and some inferences are drawn relative to the nature of rigid substances of the electrolytic type.

WORCESTER, MASSACHUSETTS

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THE INTERFACIAL TENSION BETWEEN GELATIN SOLUTIONS AND TOLUENE¹

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In a technical paper² on "Colloidal Fuels" one of the authors made a suggestion as to the emulsoid colloid state, which was developed more fully in a letter to *Nature*.³ The essential feature of the hypothesis put forward was that the micelles, or multimolecular units of such colloid systems, are formed, and their growth and aggregation determined by "the orientation of definite atom groups, entirely in the sense of the theory of molecular orientation due to structure proposed for surface and interfacial tension phenomena by W. B. Hardy,⁴ W. D. Harkins⁵ and I. Langmuir."⁶

¹ Paper read at the Birmingham meeting of the American Chemical Society, April, 1922.

² Sheppard, *J. Ind. Eng. Chem.*, **13**, 37 (1921).

³ Sheppard, *Nature*, March 17, 1921, p. 73.

⁴ Hardy, *Proc. Roy. Soc.*, **81A**, 610 (1912).

⁵ Harkins, Davies and Clark, *This Journal*, **39**, (a) 354, (b) 541 (1917).

⁶ Langmuir, *ibid.*, **39**, 1848 (1917).