

the generation of the high-frequency oscillations is disturbed and modified by the pulverization process which takes place in the same circuit and across the same discharge gap. These two processes are separated in the Tesla coil. In this investigation, a low-voltage type of Tesla coil has been used as a source of damped high-frequency oscillations for the pulverization of cadmium into various liquids. Rates of pulverization, sediment formation and decomposition of the medium have been studied. Parallel studies have been made with a modified Poulsen circuit and with a transformer circuit. It has been shown that the Tesla coil is superior to the other types of circuits studied for the production of colloid solutions with minimum decomposition of the medium, and therefore with maximum purity. A discussion of the possible causes underlying the various behaviors of the different circuits has been given. Particular emphasis has been placed upon the influence of the character of the condenser discharge upon the nature of the oscillatory current produced, and therefore upon the pulverization process.

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## THE ELECTROLYSIS OF SODA-LIME GLASS. I EVOLUTION OF GAS AND ITS RELATION TO SORPTION AND CONDUCTIVITY

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Our meager knowledge of the nature of the conduction process in glass has been well indicated by the recent work of several investigators. Poole,<sup>1</sup> for example, found that Ohm's law is not obeyed at moderate temperatures and this would seem to indicate at these temperatures a different process of conduction from the purely electrolytic one occurring at higher temperatures.<sup>2</sup> Results have also been obtained by Bush and Connell<sup>3</sup> which may be interpreted as indicating that the sorbed gases are primarily responsible for the conduction process at ordinary temperatures. We have, therefore, carried out several series of experiments for the purpose of clearing up if possible some of the chemical aspects of the problem and in particular those aspects which have a bearing on the probable behavior of glass in vacuum apparatus such as is now used for many electrical purposes.

Our work has shown that under certain conditions of electrolysis, gas is evolved and this gas is related to the sorbed water. The present paper is

<sup>1</sup> Poole, *Phil. Mag.*, **42**, 488 (1921).

<sup>2</sup> This has been pointed out by C. A. Kraus, "Properties of Electrically Conducting Systems," Chemical Catalog Co., 1922, p. 352.

<sup>3</sup> Bush and Connell, *J. Franklin Inst.*, **194**, 231 (1922).

intended to cover the phenomena connected with this gas evolution. Since these phenomena offered a new avenue of approach to the problem of sorption of moisture by glass, results bearing on this problem have also been included. In a later paper the electrical conductance and polarization phenomena will be dealt with in detail; only those resistance measurements having a direct bearing upon sorption will be mentioned in this paper.

### Evolution of Gas

**General.**—When a tube of ordinary soda-lime glass is filled with mercury and subjected to electrolysis by applying a potential difference between the mercury and a suitable external conductor such as a liquid electrolyte, a coating of gas bubbles forms between the mercury and the glass when the mercury is cathode. Drying both the mercury and the glass previous to filling the tube with mercury does not prevent bubble formation, nor does filling the tubes by distillation in a good vacuum.<sup>4</sup> When, however, the tubes are annealed, or baked out in a vacuum for many hours at high temperatures, little or no gas develops. Once the gas has formed it may be made to disappear by reversing the potential. An adequate explanation for these and other curious facts which we observed was the main problem before us.

**Apparatus and Method.**—The tubes used in the qualitative experiments were of the form shown at A, attached to the filling still, Fig. 1.

The larger portion of the tube was usually 6 cm. long, 1 cm. in diameter, and with a wall thickness of about 0.7 mm. The end and joints were made thicker than the wall of the tube. Usually the glass tubing was cleaned with a cleaning mixture of sulfuric acid and dichromate, washed with distilled water and dried with warm air prior to making into tubes. They were filled with mercury by distillation at known low pressures. When it was desired to bake out a tube, a small tubular furnace was placed around the tube while the latter was connected to the vacuum pumps and McLeod gage.

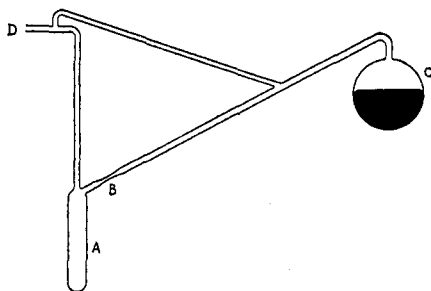


Fig. 1.—Apparatus for filling bulbs by distillation.

carried out by merely setting the tubes in the furnace. A temperature of 350° was usually employed in the two latter operations. When the level of the mercury had reached the side tube B (see Fig. 1) it was sealed off and the distillation continued until the smaller tube was filled for 2 or 3 cm. above the main tube. In this way the trapping of residual air was practically avoided. The pumps and gage were attached at D and the bulb C contained redistilled mercury.

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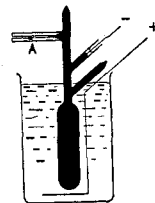


Fig. 2.—A bulb set up for gas production. The electrolysis

<sup>4</sup> The production of gas by means of an electrical discharge in mercury vapor in glass bulbs has been noted by N. R. Campbell, *Phil. Mag.*, **41**, 690 (1921).

of most of the tubes was carried out by setting them in test-tubes which contained dil. sodium hydroxide solution for the outer conductor and which were suspended in a heating medium. For the carefully controlled experiments an electrically operated thermostat was used, the bath liquid being connected to the outer conductor, and always grounded. This proved to be a very convenient arrangement, since the source of electrolyzing current was a d. c. 3-wire grounded system. Fig. 2 shows the type of tube used in the rate experiments.

The glass used in these experiments was analyzed according to the method of Sullivan and Taylor<sup>5</sup> with the following results: SiO<sub>2</sub>, 71.08%; Na<sub>2</sub>O, 18.85%; CaO, 6.22%; MgO, 3.38%; small amounts of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and ZnO.

### Qualitative Experimental Results

Space will not permit detailed accounts of the many experiments which were carried out to settle essential points as they came up. These experiments were qualitative in the sense that they lead to no definite numerical results, but were nevertheless made under carefully determined conditions. The following points were, however, definitely established.

1. Gas was not formed when mercury-filled glass bulbs were heated to 100° immersed in liquids such as aqueous solutions of salts, mercury, oils or glycerol, or in air, although the gas pressures during the filling were as high as 0.1 mm. The slight variations which occurred in cleaning the glass did not affect this result.

2. At temperatures above 200° simple heating caused quite noticeable gas evolution.

3. Electrolyzing with mercury cathode gave rise to gas. At 94° with voltages equal to or above 1.3 volts between the mercury and the external conductor a noticeable gas layer formed in about 20 hours. No gas was produced in several days under similar conditions with potential differences of 1.0 volt. At the same temperature a minute suffices for the formation of a microscopically visible layer of bubbles with a potential difference of 110 volts. At room temperature the same potential difference gave rise to a visible layer of bubbles in 20 hours.<sup>6</sup>

4. No gas was produced when the mercury was the anode. The quantity of current flowing fell off rapidly in this case, but when a fresh tube was connected in series (with mercury as cathode) with a tube that had been electrolyzed for some time with 110 volts at 90° there was a sufficient difference of potential across the new tube to form gas even though the first tube had been electrolyzed for 60 hours.

5. No gas was produced by 110 volts a. c. (60 cycle) in 24 hours at 90° to 100°.

<sup>5</sup> Sullivan and Taylor, *J. Ind. Eng. Chem.*, **6**, 897 (1914).

<sup>6</sup> The resistance of our glass at 20° was approximately  $5.6 \times 10^{11}$  ohms. A potential difference of 110 volts would in 20 hours cause the passage of a quantity of electricity which, assuming that Faraday's law was obeyed, would liberate 0.02 cu. mm. of gas per sq. cm. This amount of gas is readily seen under the microscope. The formation of gas at room temperatures has been independently checked by Mr. M. J. Mulligan.

6. Gas once produced was made to disappear by reversing the potential. This has been observed in a number of cases. For example, practically all of the gas produced in 120 hours at  $75^\circ$  with an unannealed tube disappeared in this way in 138 hours.

7. No gas was produced in tubes which were annealed or baked in a vacuum at  $350^\circ$  for many hours. Such a tube annealed for 30 hours did not develop gas when electrolyzed for 40 hours at  $94^\circ$  and 100 volts.

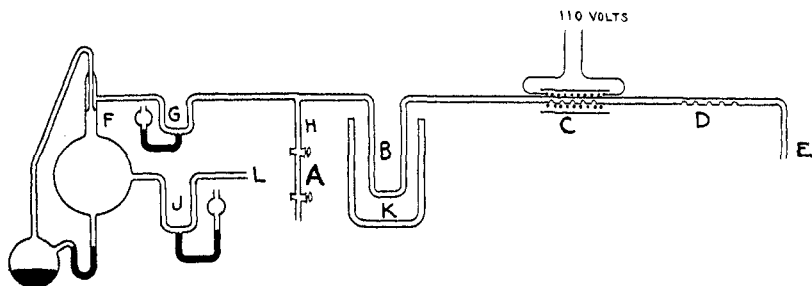


Fig. 3.—Gas analysis apparatus.

Short annealing (or baking out) allowed some gas to form; the longer the treatment, the less the gas.

**Composition of Gas.**—Samples of gas were prepared by electrolyzing tubes at  $90^\circ$  with a potential gradient of 1200 volts per cm. for 20 hours. The few cubic millimeters of gas obtained were transferred to an analyzing

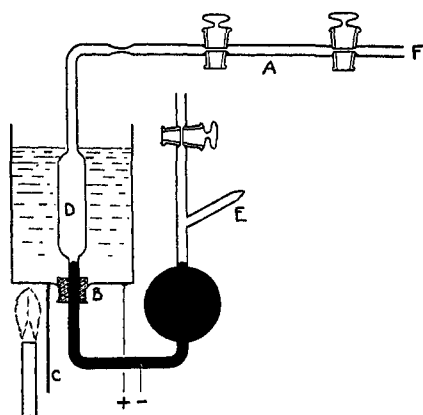


Fig. 4.—Apparatus for collecting gas sample for analysis.

apparatus (Fig. 3) consisting of a McLeod gage connected at E, a liquid air trap B, a copper oxide tube C, and a phosphorus pentoxide tube D. The gas-collecting apparatus is shown in Fig. 4. Pressure changes (if any) were noted when the copper oxide was heated and when liquid air was placed around the trap. The permanent disappearance of practically all the gas after heating the copper oxide indicated that the gas was hydrogen or a mixture of hydrogen and oxygen with the former at least twice the latter in volume.

Another sample was heated in a tube with copper wire. The volume change in this case corresponded to 18% oxygen.

In carrying out the analysis careful attention was given to such sources of error as gas evolution from the copper oxide and copper oxide contamina-

tion of the copper wire. The gas may therefore be said to be hydrogen and oxygen with the former predominating.

**Alkali Observations.**—Since the evolution of gas takes place only when the mercury is cathode, and since at high temperatures the current is carried entirely by the sodium ions which migrate to the cathode,<sup>7</sup> the formation of gas seemed to be connected with the passage of sodium in some way. The mercury in the tubes and the tubes themselves were leached with neutral distilled water and titrated with dil. acid. After short periods of electrolysis alkali was detected only in the water used to rinse the inner walls of the tube, but after longer periods of electrolysis both the extract of the tube and of the mercury were alkaline. Experiments were then made to see whether mercury containing traces of sodium would produce gas when heated alone. It was found to do so. Enough so-

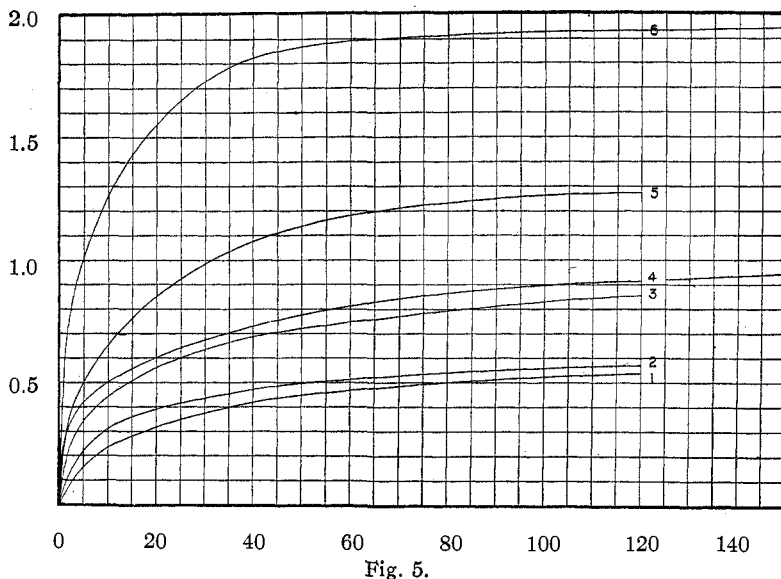


Fig. 5.

dium was contained in mercury which had been in contact with sodium amalgam to effect this evolution. Gas produced by mercury containing sodium disappeared when the tubes were electrolyzed with the mercury as anode, although the rate of disappearance at  $94^\circ$  was very slow.

**Rate of Formation of Gas.**—The rate at which gas was produced was measured by noting the rise of the mercury in a capillary arm attached to the tubes (Fig. 2). The coating of bubbles was not displaced during the electrolysis and no difficulty resulted from gas escaping measurement by floating out of the heated part of the bulb. The freshly blown parts

<sup>7</sup> Le Blanc and Kerschbaum, *Z. physik. Chem.*, **72**, 468 (1910).

of the bulb, namely the ends, evolved no gas. The rates of evolution of gas for a series of experiments are shown in Fig. 5. The ordinates represented the volumes at standard conditions in cubic millimeters of the gas evolved per square centimeter of glass surface for the times in hours given by the abscissa. The experimental conditions are given in Table I.

TABLE I  
EXPERIMENTAL CONDITIONS FOR CURVES IN FIG. 5

Curve.....	1	2	3	4	5	6
Potent. grad., v. per cm.....	780 <sup>a</sup>	1170 <sup>a</sup>	1720 <sup>a</sup>	1540 <sup>b</sup>	3620 <sup>a</sup>	Hg cont. Na <sup>b</sup>
Applied voltage.....	50	75	110	100	226	.....

<sup>a</sup> At 75°.

<sup>b</sup> At 94°.

The falling off of the quantity of gas evolved is not due to a decrease in the current flowing. In one experiment at 75° with a potential gradient of 1720 volts per cm. the gas evolution became inappreciable after 100 hours, although the current had fallen but 10% of its initial value. This decrease in the current is largely accounted for by polarization phenomena, a matter to be taken up in a later paper.

When, after the gas evolution has ceased at one temperature, the source of potential is disconnected and the temperature raised, more gas develops. Since at this stage the mercury must contain quite a quantity of sodium, the effect of temperature upon the gas evolved with mercury containing sodium and without a difference of potential was investigated. Curve 6 (Fig. 5) shows that at a single temperature the gas evolution follows a somewhat similar course to that obtained by electrolysis. Raising the temperature in such a case in which the gas evolution has apparently ceased immediately causes the evolution of more gas. Since the rate of gas production falls off rapidly with time, although the current flowing does not do so, there can be no general relation between current and gas formation. However, it seems reasonable to suppose that at the beginning of the electrolysis the formation of gas might follow Faraday's law. Upon the assumption that one Faraday produces 11.2 liters of gas, the theoretical rates have been calculated. These rates and the observed rates are given in Table II. The latter were obtained graphically and are necessarily only approximate values.

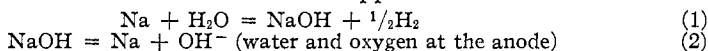
TABLE II  
OBSERVED RATES AND FARADAY'S LAW  
Rate in cu. mm. per sq. cm. per hour<sup>a</sup>

Curve.....	1	2	3	4	5
Calcd.....	0.063	0.094	0.14	0.48	0.29
Obs.....	.04	.08	.16	.45	.30

<sup>a</sup> Resistance of glass in ohms per cc. at 75° =  $52 \times 10^8$ ; at 94° =  $13.4 \times 10^8$ .

**General Theory.**—The experimental evidence favoring the view that the gas is derived from water may be summed up as follows: (1) the gas consists of hydrogen and oxygen; (2) if the gas-evolving properties of the glass be destroyed by suitable heat treatments such as are known to remove water from the glass, this property may be restored by exposure to water vapor or liquid water; (3) the experiments with mercury containing sodium parallel to some extent the phenomena obtained during electrolysis and one cannot readily find a source of the gas so evolved other than the water held by the glass.

The phenomenon is not a simple electrolysis of a water film, since the gas does not contain hydrogen and oxygen in the requisite proportions and is only obtained with the mercury cathode. This latter observation and the facts that at higher temperatures the current is carried entirely by sodium ions, that in all cases of appreciable gas evolution the aqueous extracts of the tubes tested were found to be alkaline and that somewhat similar phenomena may be produced with the mercury containing sodium without the use of an electric current, all point to the conclusion that sodium plays a major role in the production of the gas. The principal reactions involved would therefore appear to be



In our calculation based upon Faraday's law we assumed the first reaction to be involved. Some justification for this is to be found in the fact that a voltage as low as 1.3 produces a noticeable gas bubble film at 94° in 24 hours. This voltage includes a contact potential, to be overcome of at least 0.1 volt, so that 1.2 volts is evidently above that required to just produce gas. This voltage is lower than one would expect for Reaction 2 or for Reaction 3:



The presence of some oxygen in the gas is in qualitative agreement with the observations of Pirani and Lax<sup>8</sup> who obtained a deposit of tungstic oxide upon the walls of a lamp bulb through which they had electrolyzed sodium at 450°. They assumed that the sodium had displaced the sorbed water and that the latter attacked the filament. Their work appears to be the only previous experimental work upon this problem.

The total quantity of gas obtained in a given case depends upon both the temperature and the voltage used. Experiments with mercury containing sodium show that the quantity of gas thus obtained is also dependent upon the temperature and the concentration of the sodium in the mercury. Another important factor is the diffusion of the water to the surface of the glass.

**Sorbed Water.**—Our knowledge of sorbed water upon glass has been

Pirani and Lax. *Z. tech. Physik*, [3] 23, 2 (1923).

derived from two methods of attack. The older method consists of weighing the glass before and after exposure to moisture; the newer method consists of measuring the gas evolved by heating in a vacuum, glass which has previously had a known treatment. In general, the water is thought to be dissolved in the glass. This viewpoint is mainly supported<sup>9</sup> by the facts that the amount of water obtained from glass is far too great to be accounted for by our present day theories of adsorption and that this amount may be greatly reduced by heat treatments.<sup>10</sup>

Harris and Schumacher<sup>11</sup> and others consider adsorbed gases those liberated readily at temperatures below 300° and the absorbed gases to be those liberated readily only at higher temperatures. According to Dushman, Sherwood's results with soda glass indicate an adsorbed layer of moisture about four molecules deep. The electrolysis of glass appeared to offer an independent method of differentiating between adsorbed and absorbed water. Accordingly a tube was half filled by distillation with mercury immediately after it had been annealed and cooled in the atmosphere. The upper unfilled half was allowed to stand exposed to the air of the room for about 80 hours and the tube was then evacuated and completely filled with mercury in the usual manner. Upon electrolysis of the tube at about 100° and with a potential difference of 110 volts the upper half of the tube became coated with a layer of very evenly spaced bubbles of such a size that they could be counted and measured by means of a microscope and a hemocytometer. The lower half of the tube showed a few patches of bubbles involving not more than 5% of this surface, but on the remaining 95% there were parts where no bubbles at all were visible and other parts where they were so small as to be just visible with a magnification of 160 diameters. The lower half of the tube was thus a good blank determination for comparison with the upper half of the tube which evolved gas as a result of exposure to moist air. When the upper halves of the tubes were exposed to dry gases similar results were obtained on both portions of the tube; that is, exposure to dry gases caused no subsequent evolution of gas. A tube exposed to the atmosphere for 4200 hours developed upon electrolysis about as much gas as would have been obtained from unannealed glass under the same electrolyzing conditions. Further experiments showed that this renewal of the gas-evolving condition was dependent upon the time of exposure.

The taking up of moisture under these conditions was thus shown to be a slow process. It was thought, however, that wetting the surface with liquid water should saturate the surface instantly, and so a tube was

<sup>9</sup> See Saul Dushman, "High Vacuum," *General Electric Review*, 1922, p. 155. W. D. Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 18.

<sup>10</sup> Sherwood, *THIS JOURNAL*, 40, 1645 (1918).

<sup>11</sup> Harris and Schumacher, *Ind. Eng. Chem.*, 15, 174 (1923). This article contains a bibliography.



prepared in this manner and subjected to electrolysis as quickly afterwards as the operations of removing the water from the upper half of the tube, evacuation (drying) and completing the filling with mercury, would allow. The liquid water was in contact with the glass not longer than five minutes. Upon electrolysis at about 100° and 110 volts, a visible film of gas bubbles developed in several hours and gradually increased until at the end of 200 hours the evolution appeared to cease. The quantity of gas estimated by independent observers was 0.185 cu. mm. per sq. cm. of glass surface. This quantity is in agreement with that obtained by Sherwood.<sup>12</sup>

To the naked eye the upper half of the tube appeared as a mat silver surface, while the lower half seemed unchanged. Such an experiment, therefore, furnishes a very striking visible demonstration of the phenomena of sorption of moisture by glass.

Qualitative experiments indicate that the longer the exposure to water, the greater the gas evolved upon electrolysis until the gas-evolving property has been restored to that of unannealed glass and that this renewal may be accomplished within a few hours.

Further experiments bore out the fact that under similar conditions of wetting and electrolysis somewhat differently annealed tubes evolved the same amount of gas and after 24 hours electrolysis this amounted to 0.02 cu. mm. per sq. cm. The electrolysis of an unannealed tube under the same conditions would have given rise to about 0.5 cu. mm. of gas per sq. cm.<sup>13</sup>

The slow rate of evolution of the gas from wetted tubes raises the question as to whether the truly adsorbed water is not less than that indicated by the total volume of gas obtained. In an electrolysis of an unannealed tube the rate of gas evolution is greatest at the beginning of electrolysis and corresponds approximately to the rate of production of hydrogen from water according to Faraday's law, and this would seem to indicate that the adsorbed water is decomposed at a more rapid rate than the absorbed water diffuses to the surface. Applying the same method of reasoning to the case of wetted tubes and assuming that the adsorbed water is decomposed in 24 hours, the latter corresponds to 0.02 cu. mm. per sq. cm., or about one-half a unimolecular layer (assuming cubic molecules). The differentiation of the water from wetted tubes into adsorbed and absorbed water is somewhat obscured by the fact that during the early stages of the electrolysis the water may be diffusing into the glass. Were the water merely adsorbed at the start one would not look for an

<sup>12</sup> If one assumes that (a) the gas is all hydrogen; (b) the molecules of water are cubes and (c) their diameters are  $2.9 \times 10^{-8}$  cm.—this quantity of gas corresponds to a layer of water 4.8 molecules deep. A unimolecular layer in this case would be equivalent to 0.036 cu. mm. of gas.

<sup>13</sup> The resistance of an annealed tube being about 2.5 times an unannealed one at the temperature of this electrolysis.

appreciable diffusion, so that one is forced to the conclusion that the water obtained is partly adsorbed and partly absorbed and that the latter in all probability accounts for an appreciable quantity of that found.

**Sorption and Conduction.**—Bush and Connell's results using Pyrex glass (Corning G 702) were interpreted by them as evidence in support of the view that the conductivity of this glass was markedly affected by the sorbed gases. In particular they found that the resistance was greatly increased by the baking-out process and that exposure to the atmosphere of the room tended to restore its original conductivity. If their conclusions are sound one might expect that the conductivity of a glass such as soda-lime glass, which is well known to have a greater sorption capacity for gases than the glasses used by Bush and Connell, would also be affected to a much greater degree by the sorption of gases. In the many experiments which we have carried out with unannealed glass in which gas was produced by electrolysis the reduction of the water content of the glass, as has been previously mentioned, did not materially affect the conductance of the glass. However, the conductance of the glass does markedly decrease upon annealing or baking out, a point which will be further elaborated in a subsequent paper, but when such treated glass (in the form of tubes) is totally immersed in water and later dried, its conductance when measured is found to be not noticeably different from that measured prior to the water treatment. For example, a tube whose resistance, measured at  $94^{\circ}$ , was increased from  $13.4 \times 10^8$  to  $27.5 \times 10^8$  ohms/cc. by annealing for 24 hours, still retained the latter resistance after subjecting it to total immersion in water at  $20^{\circ}$  for 114 hours. Since we have shown that immersing in water was a much more effective method of restoring the gas-evolving property to glass than exposure to the atmosphere, and since the gas-evolving property appears to be directly connected with the sorbed water and also since the restoration of the gas-evolving property is not accompanied by a noticeable decrease in resistance we must conclude that sorbed water does not affect the conductance of soda-lime glass, and that the increase in resistance brought about by annealing or baking out is due to other factors than the removal of sorbed gases, although the removal of sorbed gases may simultaneously bring these other factors into play. Further evidence of the negligible influence of sorbed gases on the conductance was obtained from tubes whose increased resistance, due to annealing, had not decreased, as far as could be detected, by more than 4000 hours' exposure to the laboratory atmosphere.

**Miscellaneous Experiments.**—The work of Harris and Schumacher and others has pointed to a relation between the alkali content of the glass and sorbed gases. The effect of treating annealed tubes with acid and alkaline solutions was therefore determined. Tubes were filled with water, acid and sodium hydroxide solutions and held in a thermostat at  $94^{\circ}$  for

18 hours, then emptied of their respective liquids, washed quickly with distilled water, dried by evacuation, distilled full of mercury and electrolyzed. Another set of tubes was treated similarly except that while resting in the thermostat a potential (100 volts) was applied so as to make the liquids in the tubes anode. With water the gas obtained was 0.48 cu. m. per sq. cm. and 0.52 cu. mm. per sq. cm., respectively; with sodium hydroxide solutions 0.047 *N*, 0.094 *N* and 1 *N* after electrolysis, somewhat less gas was evolved than without electrolysis, but the volume obtained was not greatly different from the amounts just mentioned for pure water in the latter case. With acid solutions of the same normality without electrolysis nearly twice the amount of gas was obtained as with water, while with electrolysis the amount was still greater. In the case of these solution treatments without electrolysis the quantity of gas evolved in the final electrolysis was not much dependent upon the strength of the solution, while in the case of electrolysis during the treatment there was a slight but noticeable increase in the quantity of gas, as the strength of the acid decreased, and *vice versa* for the alkali solutions.

These results do not indicate that the sodium ions carry with them into the glass any water, but do on the other hand suggest that hydrogen ions may be adsorbed on or may migrate into the glass. The idea that hydrogen ions are adsorbed upon glass is strengthened by the fact that glass electrodes may be used for electrometric titrations, and under certain conditions function very similarly to hydrogen electrodes.<sup>14</sup> Certainly, washing the glass with alkaline solutions followed by distilled water does not increase the tendency of the glass to absorb moisture.

**General Observations.**—In their study of the conduction process in soda-lime glasses Kraus and Darby<sup>15</sup> found that alkali amalgam electrodes were troublesome because they gave rise to gas and this they were unable to prevent by careful drying and handling of the amalgam. Our results show that this gas was probably due to a reaction between alkali in the amalgam and moisture in the glass. Annealing the glass for long periods of time would probably have prevented its formation. The formation of gas by alkali metals in this manner may have some technical importance if the use of apparatus such as sodium vapor thermionic valves becomes at all general.

Dushman has summarized much of the information extant upon the complicated process included under the general heading of "electrical clean-up of gas in vacuum apparatus." The role that electrolysis of the glass may play in these phenomena is somewhat uncertain, especially since the electrolytic processes are so little understood. It is therefore interesting to note that at 94° voltages as low as 1.3 volts will cause the

<sup>14</sup> Hughes, *THIS JOURNAL*, **44**, 2860 (1922). Bovie, *J. Opt. Soc. Am.*, **8**, 149 (1924).

<sup>15</sup> Kraus and Darby, *THIS JOURNAL*, **44**, 2785 (1922).

production of appreciable amounts of gas and since with higher voltages, such as 110 volts, gas is readily produced at room temperature in less than 24 hours there seems to be no *a priori* reason why, given time, the smaller voltages would not also do so at these temperatures. In other words, in considering such problems, one may deal with appreciable effects without thinking in terms of the great potential differences such as the high resistance of glass might predispose one to consider. A somewhat practical application of the results of this study may be made to the laboratory electric thermoregulator. Regulators made of soft glass containing mercury often slowly accumulate gas when there is a potential difference between the mercury and the bath liquid and the former is cathode. This gas may be especially troublesome at temperatures above 50°. The formation of gas may be prevented by annealing or by an electric screen around the regulator when the latter is connected to the mercury in the bulb or by making the mercury the anode. The combination of a screen and annealing of the regulator bulb prior to filling is the most satisfactory method; we have had such a regulator in continuous use at 94° for five months without formation of gas, and have also had an annealed regulator function satisfactorily at 160° for 24 hours without a screen or without paying any attention to the polarity of the mercury.

Thanks are due Mr. M. J. Mulligan for the assistance he gave us with some of the experiments.

### Summary

1. The reversible phenomena of gas evolution which takes place during the electrolysis of glass under proper conditions has been shown to be due probably to the action of sodium upon the sorbed water and the simultaneous electrolysis of the hydroxide formed.
2. Appreciable gas evolution may be obtained with voltages as low as 1.3 volts.
3. Results are given which indicate that sorption of water does not affect the resistance of soda-lime glass.
4. A new method for the study of the sorption of water by glass is presented.
5. The possible adsorption of hydrogen ions by glass and also their electrical migration into glass is indicated.
6. A number of related phenomena are also discussed.

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