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STUDIES OF THE CONDUCTION PROCESS IN GLASS

I. REPLACEMENT OF THE SODIUM BY ALKALI METALS AND AMMONIUM

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Introduction

The conduction of the electric current through glass, involving as it does a very complicated medium, offers an interesting field for the study of electrolytic processes. The medium possesses a very high viscosity, even at temperatures of several hundred degrees. The transport of electricity is almost entirely confined to the cation. The replacement of one ion by another gives rise to significant changes in the nature of the glass. The problem has been studied from various angles by a number of investigators.[1a]

It has been shown that the sodium ions carry practically all of the current. If the anode is immersed in some material capable of supplying ions and making contact with the glass, cations will pass through the glass. This replacement may take place to varying depths in the glass. By using electrolytes containing cations other than sodium, various replacements may be effected.

Description of Apparatus

We have been interested, in this Laboratory, to study the replacement of sodium ions in glass by other ions. For about three years a method has been utilized which possesses several desirable features. The principle has already been noted by several investigators.[2]

An ordinary tungsten filament incandescent lamp is suspended in the electrolytic bath. The filament is lighted by a.c. or d.c. A carbon rod in the electrolytic bath is made the anode of a d.c. circuit of which circuit the filament of the lamp comprises the cathode. When the filament is lighted, thermionic emission across the evacuated space in the lamp completes the circuit, the positive ions passing from the anode through the electrolyte, through the portion of the lamp bulb immersed in the bath to

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[1] *Note by Editor.* A preliminary version of this manuscript was received August 22, 1925.

[1a] Warburg, *Ann. Physik,* **21**, 622 (1884). Tegetmeier, *ibid.*, **41**, 18 (1890). Heydweiller and Kupfermann, *ibid.*, **32**, 739 (1910). Kraus and Darby, THIS JOURNAL, **44**, 2783 (1922). For bibliographies the reader is referred to Clarke, *Glass Ind.*, **2**, 221 (1921). Schumacher, THIS JOURNAL, **46**, 1772 (1924). Sutton and Silverman, *J. Am. Ceram. Soc.*, **7**, 86 (1924).

[2] Pirani and Lax, *Z. tech. Physik,* **3**, 232 (1922); and others. Burt, *J. Optical Soc. Am.*, **11**, 87 (1925).

the interior wall of the bulb. Here union of a cation, ordinarily sodium, with an electron produces an atom, the circuit being thereby completed.

The advantages of this type of procedure are as follows. The products liberated at the cathode are contained in an evacuated bulb. They are easily available for examination and analysis, or they may be kept for some time. We have a number of bulbs which have been kept for over three years. A thin glass wall is available. Any serious weakening of the glass is indicated by the cracking of the bulb.

The composition of glass in the bulbs ordinarily used is given by analysis as follows: silica, 72.44; sodium oxide, 17.06; calcium oxide, 5.02; magnesia, 3.77; alumina, 0.97; ferric oxide, 0.72%; arsenic trioxide, a trace.

Experimental Part

This paper describes the replacement of sodium ions in the glass by sodium, potassium, lithium, silver and ammonium ions. Some data on resistance of the whole system as a function of the temperature of the glass wall were obtained. The following data give the results of a typical run, sodium replacing sodium, each result obtained both by approach from lower and from higher temperatures.

TABLE I

RELATION BETWEEN TEMPERATURE OF GLASS AND RESISTANCE OF THE SYSTEM

Voltage constant, 46.5 v.

Temp., °C.	210	220	230	240	250	260	270	273
Current milliamp.	1.9	2.7	3.9	5.8	8.4	12.5	17.0	19.0
Resistance, ohms	24,400	17,200	11,900	8020	5540	3720	2740	2450

Sodium.—As might be expected, no difficulty was experienced in replacing sodium ions by sodium ions. For the lower temperature range, solutions of sodium chloride and of sodium bichromate were used. The eutectic mixture of sodium nitrate and nitrite extended the range to over 300°. Metallic sodium deposited in the bulb. The glass appeared unaffected at low temperatures; at higher temperatures it became increasingly brownish. Heating the glass to redness in a flame gave no result. Microscopic examination showed no cracking or visible effect except in the vicinity of bubbles in the glass. Bulbs with bubbles were avoided so far as possible. The effect of bubbles in the glass is being further studied.

Potassium.—Solutions of potassium chloride were used up to 105° and fused potassium sulfocyanate up to 265°. Potassium ions penetrated easily, but any considerable depth of penetration resulted in fracture of the glass. No potassium was ever found spectroscopically in the contents of the bulb, that is, in the sodium collected inside.

It was found possible, however, to identify potassium in the contents of a bulb of special potassium glass which had been subjected to the same process.[3]

Lithium.—Fused lithium nitrate was used up to 300°. Replacement of sodium ions by lithium ions proved very difficult. The glass became milky white and cracked if electrolysis proceeded for any length of time. No lithium was found in bulbs which had not been run sufficiently long to crack. It was possible to introduce lithium into a bulb of special lithium glass.

It is interesting to note, however, that with this special glass, and also in the case of the special potassium glass, cracking always resulted in a run of an hour or longer.

Silver.—The results of others were confirmed. Silver was found to penetrate more easily than lithium or potassium. None ever reached the inside. Discoloration of the glass was always shown. Heating this brownish glass produced the silver mirror, observed by others.

Ammonium.—The experiments upon the replacement of sodium by ammonium ion were both gratifying and illuminating. Practically nothing had been done previously on this replacement, and this method has proved ideal for such a study. The electrolytes found most satisfactory were saturated ammonium chloride solution and fused ammonium acetate. Ammonium salts volatilize too rapidly to make the experiment practicable at the higher temperature range.

Ammonia was easily detected in the contents of these bulbs, qualitatively by the odor when the contents were dissolved in water, and quantitatively when the contents were dissolved in dil. hydrochloric acid. Before breaking the bulbs, the bases were removed. The bulbs were carefully washed with both alcohol and water and the tip was broken under dil. hydrochloric acid. Hydrogen was always evolved, due to sodium present. The ammonia was distilled from the hydrochloric acid solution, made alkaline with sodium hydroxide, collected and titrated, rosolic acid being used as the indicator. The largest amount of ammonia found was 0.0075 g. As a check, the contents of bulbs which had been run in sodium chloride were subjected to exactly the same analysis. No volatile alkali was found.

From previous work on hydrides and amides[4] it was concluded that the ammonium radical, formed by the union of an emerging ammonium ion with an electron, would dissociate into ammonia and hydrogen. The sodium present would form sodium amide and sodium hydride. To test this, a special apparatus consisting of an ordinary bulb connected to a vacuum system and a pressure gage was electrolyzed in a bath of fused

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[3] This glass and the special lithium glass were used by courtesy of the Corning Glass Co.

[4] Kraus and Hurd, THIS JOURNAL, **45**, 2559 (1923). Keyes, *ibid.*, **34**, 779 (1912).

ammonium acetate at 120°. After a short time a pressure of 0.2 mm. of mercury was found in the bulb. This pressure was of the order of the pressures of gases in equilibrium over sodium amide and hydride. No other change occurred.

It was considered amply evident that the ammonium ions could traverse the 1mm. thickness of the bulb at a fairly low temperature, 110°, without causing fracture of the bulb. The glass was not discolored. If the run continued for several hours, the glass became first surface-cracked and eventually completely fractured.

Effect of Heating the Glass in Which Ammonium Ions Have Partially Replaced Sodium Ions.—The glass either was smooth or showed surface cracks in an almost perfect spider-web pattern. Heating always caused more cracking. Heating to dull redness caused the appearance of countless bubbles along the cracks. Under the microscope the effect of water on the gas in the bubbles was observed. A portion always dissolved. Dilute methyl orange solutions turned yellowish, though the effect might be due to adsorption. Heating the glass, however, appears certainly to destroy the ammonium compounds present.

Conclusion

Glass appears to have a mesh-like structure in which the cation is able to move under an e.m.f. At higher temperatures, this mesh appears to be more and more elastic. The size of the ion replacing the sodium appears to be the critical condition determining whether or not the glass structure will be destroyed. Sodium ions replace sodium ions with little or no effect. Ammonium ions appear to be of nearly the same size in glass as are sodium ions. No data on the solvation of the ions was obtained.

Summary

1. A method of studying the conductance processes in glass has been described. Replacement of sodium by other ions has been studied. An incandescent lamp bulb was used.

2. Sodium replaces sodium with little effect to the glass.

3. Ammonium ions replace sodium with less serious effect to the glass than any other ions studied. Some of the ammonium ions traversed the 1mm. thickness of glass wall. Even they were found to cause fracture if introduced in sufficient quantity. The resulting glass possessed unique properties.

4. Silver, potassium and lithium were, in the order mentioned, less able to make a substitution.

5. The idea is mentioned that ease of replacement depends upon the size of the sodium ion and the ion replacing it.

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