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Electrolysis of Borax, $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

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It was suggested in a preceding communication[1] that protonic conduction may be operative in borax. Coulometric measurements have so far been used twice as evidence for such a mechanism of electrical conductivity. In the case of cetyl alcohol Kakiuchi et al.[2] measured the pressure of the gas evolved on the cathode and verified spectroscopically that it was H_2. Decroly et al.[3] measured the gas volumetrically (in a capillary) on the cathodic side of an ice crystal.

In this work an all-glass apparatus was used, details of which will be given elsewhere. The electrolytic cell, consisting of a borax pellet in contact with mercury on both sides was thermostated to 0.01°C. The evolution of gas on the cathode caused the displacement of mercury in a capillary of 0.4 mm diameter, which was followed by a cathetometer. The pellet obtained in a press at 100 atm was 2 mm thick and 13 mm in diameter. It was cemented to the two cell compartments by Araldite resin cement. The current was continuously recorded on a potentiometric recorder, measuring the potential drop across a resistor in series with the cell.

There are two different temperature regions of the electrical conductivity in borax[1]. The following sequence of measurements was therefore adopted. After the cell was thermostated for an hour at 15.05°C the stabilized voltage rectifier was switched on at the 500 V level and readings were taken for 65 minutes. The practically constant current was about 1 μA. Then the circuit was switched off and the temperature raised to 34.90°C. In this case the current diminished

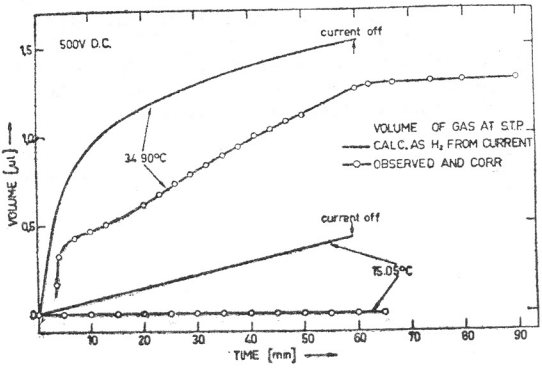

Fig. 1. Electrolysis of borax, $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ at 15° and 35°C. Dependence of the volume of gas (calculated and observed) on time.

exponentially from the initial value of 35 μA to 2 μA. It was graphically integrated at intervals and the obtained quantity of coulombs was converted to μl of H_2 according to Faraday's laws. These data and the measured volume of gas (at s. t. p.) are plotted versus time in Fig. 1.

Two things may be noted. First, there is no evolution of gas at 15°C. Second, permanent evolution took place at 35°C from the very moment of applying the voltage.

One is led to the conclusion that the mechanism of current conduction at 15°C is electronic in nature. It is supposed that this mechanism is still operative at 35°C. Lacking the actual value of this current at any instant in the course of the experiment at 35°C, 1 μA was subtracted from the total current. The results therefore represent the supposed net current involving mass transfer. The ratio of the volume of the evolved gas to that equivalent by Faraday's laws is not constant throughout the experiment. This is attributed to the inadequacies of the experimental technique. However, calculated on a cumulative basis at any point this ratio is always less than unity. The total sums result is equivalent to 86.7% of what is supposed to be protonic conduction. The corresponding result with cetyl alcohol[2] was 89.5%, and for ice[3] 95—100%.

Further experiments are in progress in order to get a more detailed insight into this phenomenon especially with single crystals.

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IZVOD

Elektroliza boraksa, $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$

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Elektrolizom pastile od boraksa u prahu kod 15° i 35°C pod naponom od 500 V utvrđeno je, da se na katodnoj strani kod 35°C razvija plin, dok se to kod 15°C ne dešava. Kod 35°C volumen razvijenog plina odgovara 86.7% H_2 od ukupno moguće količine prema protekloj struji. Ovi su rezultati u suglasnosti s hipotezom, da je mehanizam električne vodljivosti u boraksu kod nižih temperatura elektronski, a kod viših temperatura da postaje pretežno protonski.

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