K. K. EVSTROP' EV and V. A. KHARBUZOV

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

K. K. EVSTROP' EV and V. A. KHARBUZOV

ON THE NATURE OF THE CONDUCTIVITY OF ALKALI-FREE BARIUM SILICATE GLASSES

(Presented by Academician A. N. Terenin, July 4, 1960)

The question of the nature of the conductivity of alkali-free silicate and borate glasses is of both fundamental and practical interest, especially in connection with the needs of electrical-insulation technology. Whereas the ionic character of the conductivity of alkali silicate and borate glasses has been experimentally confirmed and is not in doubt, judgments concerning the nature of the current carriers in alkali-free glasses are contradictory. The most reliable information on the nature of the current carriers in solid glasses is obtained, as is known, by checking the applicability of Faraday' s law by the Tubandt method ([1–3]). However, if in doing so the value of the specific electrical conductivity of the glass under study is small—as is the case in alkali-free glasses of the type indicated—then it does not appear possible to guarantee sufficient sensitivity and reliability of the method.

Many authors ([4–7]) often arrive at contradictory conclusions, basing themselves chiefly on studies of the change of electrical conductivity with composition, which, naturally, cannot resolve the question of the nature of the conductivity—ionic or electronic—of alkali-free glasses.

To establish the type of current carriers, we used a method that had not previously been applied in such cases and that consists in comparing the electrical conductivity measured directly with the electrical conductivity calculated from the Einstein equation ([8,9]) from values of diffusion coefficients determined with the aid of the corresponding radioactive isotopes. It is known that the relation between diffusion and electrical conductivity in the general case is expressed by the following Einstein equation:

$$D = \frac{n\varkappa kT}{N(ze)^2},$$

where D is the diffusion coefficient in $\mathrm{cm}^2/\mathrm{sec}$, $\varkappa$ is the specific electrical conductivity in $\mathrm{ohm}^{-1} \cdot \mathrm{cm}^{-1}$, n is the transport number of the diffusing ion, k is

Fig. 1. Isotherms of the specific electrical conductivity of glasses of the BaO—SiO_2 system

Figure 1: Fig. 1. Isotherms of the specific electrical conductivity of glasses of the BaO—SiO_2 system

Boltzmann' s constant, T is the temperature in $^\circ K$, N is the number of ions in 1 cm^3, z is the valence of the ion, and e is the charge of the electron.

Bloy and Fitzgerald (^{11}), as well as one of us (^{10}), showed that for alkali glasses the differences in the logarithm of the electrical conductivity calculated from the experimentally determined diffusion coefficient of sodium ions and measured directly do not exceed 0.3. Since the ionic character of the conductivity of alkali silicate glasses is not in doubt, then, in the case of agreement between electrical conductivities measured directly and calculated from diffusion in alkali-free glasses, the question of the current carrier can be resolved unambiguously. In the case of electronic conductivity, the values of the specific electrical conductivities calculated under the assumption of ion motion and measured directly should differ by several orders of magnitude, as was observed by us for calcium vanadate glass (18 mol.% CaO and 82% V_2O_5).

Proceeding from all that has been said above, our task included the following. 1. Measurement of the electrical conductivity of selected alkali-free glasses over a wide temperature range. 2. Measurement of the diffusion coefficients of ions —potential current carriers. 3. Comparison of the experimentally measured electrical conductivity with that calculated from the Einstein equation using diffusion measurements, in order to draw a conclusion about the conduction mechanism.

In connection with the task posed, barium silicate glasses were selected for study, since they have a sufficiently broad glass-forming region. Melts of glasses containing 30, 40, and 50 mol.% BaO were made from "pure" grade $BaCO_3$ and separated sand in quartz 6-liter crucibles at 1550° C in a high-frequency furnace.* Measurement of the specific electrical conductivity was carried out by the usual method using an MOM-4 megohmmeter in the temperature range 350–650° C.

Fig. 1. Isotherms of the specific electrical conductivity of glasses of the BaO—SiO_2 system.

The measurement data are presented in Fig. 1. As can be seen from Fig. 1, in the indicated temperature range there is a noticeable increase in the specific electrical conductivity with increasing BaO content in the glass. For one of the glasses (50 mol.% BaO and 50% SiO_2), the diffusion coefficients of Na^+ and Ba^{++} ions were measured at 655°. The choice of the glass and of such a high temperature was not arbitrary, but was dictated by the small diffusion coefficients of the ions under study. The diffusion coefficients were measured by the method of grinding off thin layers of glass (^{12}, ^{13}), using Na^{22} and Ba^{140} as indicators.

Let us calculate what the electrical conductivity of the glass will be under the assumption that the current carriers are only Ba^{++} ions. We rewrite the Einstein equation in the following form

$$\chi_{\mathrm{Ba}} = \frac{4e^2 D_{\mathrm{Ba}} \cdot N_{\mathrm{Ba}}}{kT} = \frac{7.2 \cdot 10^{-15} D_{\mathrm{Ba}} \cdot N_{\mathrm{Ba}}}{T} =$$

$$= \frac{7.2 \cdot 10^{-15} \cdot 1.1 \cdot 10^{22} \cdot (2 \pm 1) \cdot 10^{-12}}{928} = (1.7 \pm 0.8) \cdot 10^{-7}\ \mathrm{ohm}^{-1} \cdot \mathrm{cm}^{-1},$$

where χ_{Ba} is the electrical conductivity of the glass under the assumption that the current carriers are Ba^{++} ions, D_{Ba} is the experimentally determined diffusion coefficient of Ba^{++}, and N_{Ba} is the concentration of Ba^{++} ions in 1 cm^3 of glass.

In an analogous way, let us calculate what the electrical conductivity of the glass should be under the assumption that the current carriers are Na^{+} ions, present in the glass as impurities. According to chemical-analysis data, the amount of $\mathrm{Na_2O}$ did not exceed 0.02 wt.%. Consequently:

$$\chi_{\mathrm{Na}} = \frac{1.8 \cdot 10^{-15} D_{\mathrm{Na}} \cdot N_{\mathrm{Na}}}{T} = \frac{1.8 \cdot 10^{-15} \cdot 1.5 \cdot 10^{19} \cdot (2 \pm 1) \cdot 10^{-12}}{928} =$$

$$= (5.8 \pm 3) \cdot 10^{-11}\ \mathrm{ohm}^{-1} \cdot \mathrm{cm}^{-1}.$$

For glass of composition BaO 50% $-\mathrm{SiO_2}$ 50% (mol.) at $T = 655°$ C, the measured values of the diffusion coefficients of Na^{+} and Ba^{++} and of the electrical conductivity of the glass proved to be the following:

D_{Ba}, $\mathrm{cm^2/sec}$	D_{Na}, $\mathrm{cm^2/sec}$	$-\lg \chi_{\mathrm{Ba}}$	$-\lg \chi_{\mathrm{Na}}$	$-\lg \chi_{\mathrm{exp}}$
$(2 \pm 1) \cdot 10^{-12}$	$(2 \pm 1) \cdot 10^{-12}$	6.8 ± 0.2	10.3 ± 0.3	6.3 ± 0.2

From these data it is evident that the electrical conductivity due to Ba^{++} ions (χ_{Ba}) and the experimentally measured conductivity (χ_{exp}) are, within the limits of experimental error, the same, whereas the electrical conductivity due to Na^{+} ions (χ_{Na}) differs from χ_{exp} by almost 4 orders of magnitude.

* The authors express their gratitude to E. V. Podushko for assistance in the indicated high-temperature melts.

Thus, a joint consideration of the electrical-conductivity values calculated from measurements of diffusion coefficients and measured directly leads to the conclusion that electricity is transported in alkali-free barium silicate glasses by barium ions.

Apparently, the results obtained can also be extended to other alkali-free silicate glasses containing oxides of divalent metals.

Thus, in the present work it has been established that the rate of motion of impurity alkali ions is comparable with the rate of motion of barium ions in alkali-free barium silicate glasses, but the share of alkali ions in the conductivity is immeasurably small because of their low concentration. The carriers of electric current in alkali-free barium silicate glasses are barium ions.

Received
24 VI 1960

REFERENCES

1. G. Ostroumov, ZhOKh, **19**, 407 (1949).
2. K. S. Evstrop' ev, G. A. Pavlova, Tr. Leningr. tekhnologich. inst. im. Lensoveta, issue 46, 49 (1958).
3. O. V. Mazurin, G. A. Pavlova et al., ZhTF, **27**, 2702 (1957).
4. B. I. Malkin, R. L. Müller, ZhFKh, **7**, No. 4, 592 (1936).
5. O. V. Mazurin, E. Ya. Lev, Izv. Vyssh. uch. zav., Fizika, No. 3 (1960).
6. S. W. Strauss, W. H. Harrison et al., J. Res. Nat. Bur. Stand., **56**, No. 3, 135 (1956).
7. G. A. Pavlova, Izv. Vyssh. uch. zav., Khim. i khim. tekhnol., No. 5 (1958).
8. N. Mott, R. Gurney, *Electronic Processes in Ionic Crystals*, IL, 1950.
9. A. V. Lidiard, Handb. der Physik, **20**, issue 20, 246, 1957.
10. K. K. Evstrop' ev, Tr. II Vsesoyuzn. konf. po fizike dielektrikov v Moskve, M., 1960.
11. G. Bley, U. Haven, J. Stevels, Report at the 4th International Congress on Glass in Paris, Inform. Bull. State Optical Institute, No. 7 (30) (1958).
12. P. L. Gruzin, DAN, **89**, 290 (1952).

13. K. K. Evstrop' ev, Tr. III Vsesoyuzn. soveshch., M., 1960.

Note: Figure translations are in progress. See original paper for figures.