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An Electrolysis and Conductivity Study on Ammonium Dihydrogen Arsenate

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Single crystals of ammonium dihydrogen arsenate, $NH_4H_2AsO_4$, were subjected to electrolysis during which hydrogen gas was detected. Quantitative and qualitative determinations were made which indicate that Faraday's law is obeyed for the transport of ions through the crystal. Other single crystals were placed in a vacuum and the conductivity measured as a function of temperature. The activation energy for the conduction was found to be 14.0 ± 0.5 kcal/mole. This value is compared to those obtained for other isomorphous crystals

Introduction

Numerous studies of protonic conduction in solids (*1–4*) resulted in a thorough understanding of proton migration in such crystals as KH_2PO_4, $NH_4H_2PO_4$, and KH_2AsO_4. One crystal which has not been explicitly studied by conductivity methods is $NH_4H_2AsO_4$, ammonium dihydrogen arsenate, which should be considered for the sake of completion of the above list. According to the theory developed, crystals of the type noted above should be protonic conductors. The mechanism of conduction consists of proton jumps from one lattice site to another along a hydrogen-bonded network (*1*, *2*). $NH_4H_2AsO_4$ is an antiferroelectric crystal with a transition temperature of 216°K to the paraelectric state (*5*). It is isomorphic to $NH_4H_2PO_4$ and to KH_2PO_4 above the transition temperature and should display similar conduction properties. A brief study by Adhav (*5*) reported a resistivity at 25°C of 5×10^7 Ω cm.

Experimental

Reagent-grade $NH_4H_2AsO_4$ was recrystallized and filtered numerous times to obtain pure material from which to grow single crystals. Crystals were grown from saturated solutions to a reasonable size to facilitate handling them for the electrolysis and conduction measurements. The average size of the crystals used was $5 \times 3 \times 3$mm. X-ray diffraction was used to determine that pure, single-phase crystals of $NH_4H_2AsO_4$ were always prepared. A coulometer was constructed according to the method of Schmidt (*6*) which traps bubbles of any gas that are evolved during electrolysis. A built-in buret measured the size of the bubbles giving quantitative determinations. Mercury was allowed to come into contact with opposite sides of the crystal and platinum leads were inserted to provide a connection to the potential source. The amount of gas collected in the buret as a function of current and time was recorded. After the completion of this determination the gas so formed was collected in a partially evacuated flask with air and analyzed by mass spectrographic analysis. Other crystals were prepared for the conductivity experiments by coating parallel sides of the crystal with a thin film of gold by evaporation methods. The crystal was then placed in a

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small teflon vise and sealed in a vacuum chamber which could be heated. The temperature was monitered by a platinum resistance thermometer.

Results

During the coulometry experiments a gas did form at the cathode of the Schmidt apparatus. The data from one experiment are plotted in Fig. 1 and show a linear production of gas with coulombs passed through the system after an initial lag. Fig. 1 is typical of results taken from the Schmidt apparatus (*6*). The slope of the line taken after the induction period is 0.1137 ml/C compared to an ideal value of 0.1161 ml/C for totally ionic conduction. The mass spectrometry results gave an analysis of 0.06 V/% of H; the remainder being the component of air introduced during collection and analysis. No other gas was detected. Thus during the electrolysis hydrogen gas was produced. The two analyses prove ionic conduction occurred during the electrolysis and the most likely ion for migration is the proton. The conductivity results are plotted in Fig. 2 for the *C*-axis of the tetragonal $NH_4H_2AsO_4$. As in other studies (*2*, *3*) no anisotropy was found. The activation energy for migration, E_a, is 14.0 ± 0.5 kcal/mole which compares favorably to the other arsenate crystals studied. KH_2AsO_4 has an E_a value of 15.0 ± 0.3 kcal/mole (*3*) whereas the phosphate values range from 12.0 to 13.0 kcal/mole. It is typical of the protonic conductors that the conductivity follows the equation $\sigma T = \sigma_0 \exp(-E_a/RT)$ (*1*, *2*). It has been suggested (*3*) that this higher activation energy for proton migration is due to the larger size of the arsenate tetrahedron and thus a larger jump distance. The room temperature conductivity is 1.1×10^{-8} ohm-cm^{-1} which compares favorably to Adhav's result (*5*).

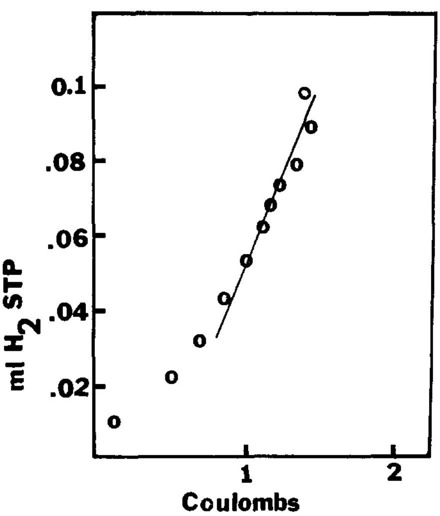

FIG. 1. Volume of hydrogen vs coulombs.

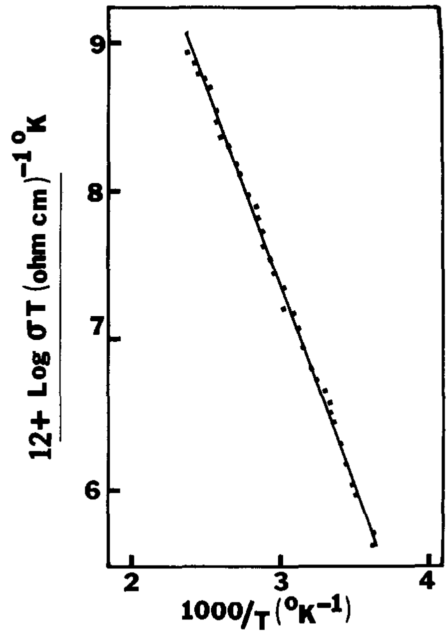

FIG. 2. The conductivity of $NH_4H_2AsO_4$ as a function of temperature.

Conclusion

The indications are strong that $NH_4H_2AsO_4$ is a protonic conductor of the type discussed by Glasser (*1*) and therefore a similar mechanism of conduction prevails. The mechanism of conduction is discussed in papers (*1–4*) and therefore need not be repeated here. The proposal put forth is that $NH_4H_2AsO_4$ is a protonic conductor like the other dihydrogen phosphates and arsenates mentioned above. The results of the electrolysis and conductivity study support this thesis.

Acknowledgments

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