

## The Electrical Conductivity of Ammonium Perchlorate Single Crystals\*

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The electrical conductivity of single crystals of ammonium perchlorate has been studied from 25 to 180°C. Plots of  $\log \sigma T$  vs  $1/T$  show two linear regions, one from 25 to 100 and another from 100 to 180°C. Activation energies for the conduction processes in the low- and high-temperature regions are 0.12 and 1.04 eV, respectively. The conduction is a bulk process and not a surface mechanism. Conduction in the low-temperature region is predominantly due to the migration of protons and is sensitive to the concentration of interstitial  $H_2O$  molecules which act as proton donor and acceptor sites. In the high-temperature region, conduction is due to migration of  $NH_4^+$  through cation vacancies. Detailed mechanisms are postulated both for electrical conduction and for the electrode reactions.

Ammonium perchlorate (AP) has been studied extensively because of its use as an oxidizer in solid rocket fuel propellants and in various explosives. Major emphasis has been on the kinetics of the decomposition reaction and comprehensive reviews have been written by Keenan and Siegmund (1) and by Jacobs and Whitehead (2). Proposed decomposition mechanisms showed similarities to proposed electrical conduction mechanisms (3-5) in that proton transfer was involved in both. Therefore, information obtained from electrical conductivity experiments may be useful in a further understanding of the decomposition mechanism. Conductivity studies of single crystals of AP below 200°C have indicated two regions of conduction as reflected by different values of the activation energy,  $E_a$ , obtained from plots of the equation

$$\sigma T = A \exp(-E_a/kT). \quad (1)$$

There is disagreement in the literature as to the conduction mechanism represented by the low- (25 to 100) and high-temperature

(100 to 180°C) activation energies. Also, there is significant variance in the magnitude of the high-temperature activation energy between authors.

Jacobs (5), using ac measurements on both single crystals and pellets, attributed the conductivity from room temperature to 170°C to a proton transfer mechanism and obtained 0.85 eV for the high-temperature activation energy. Maycock (6), using dc measurements on single crystals, obtained 0.18 eV for the region 25 to 92 and 0.54 eV for the 92 to 171°C region. He attributed the 0.18 eV to some unknown surface mechanism and described the high-temperature region as the impurity sensitive region. Owen (7) studied the dc conductivity of single crystals of both rubidium perchlorate (RP) and AP. Since RP has practically identical unit cell dimensions and ion sizes as AP, it is an ideal compound with which to compare conductivity studies of AP. The activation energies for the temperature region 120 to 137°C were 1.1 and 1.2 eV for AP and RP, respectively. Also, the magnitudes of the conductivities were the same, so conduction was attributed to the migration of  $NH_4^+$  ions, since  $Rb^+$  ions are the charge carriers in RP. The apparent inconsistencies between different authors stimulated the present research.

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## Experimental

AP of better than 99.99% purity, obtained from the Fisher Scientific Company, was crystallized three times from water by slow evaporation over a period of several weeks at room temperature. Selected crystals were cleaved to give visually clear specimens of suitable dimensions (several mm on edge). These were stored in a desiccator over silica gel for up to 3 days. Before use the crystal faces were polished with absorbent paper and a 50% aqueous solution of ethanol to give accurately rectangular faces. The dimensions were measured with a micrometer. Since AP has isotropic electrical properties, crystal orientation was not critical. The opposite faces that were to serve as electrodes were painted with high-conductivity silver paint. The crystal was mounted between spring-loaded contacts on a Teflon and porcelain bracket in a glass cell connected to a vacuum line. The cell was contained in an air thermostat that could maintain a preset temperature in the range 24 to 200°C with a stability of  $\pm 0.5^\circ$  for 24 hr. For pretreatment, the crystal was maintained at 118°C and a pressure of 0.1 torr for 24 hr and then allowed to cool to room temperature over another 24-hr period under vacuum. Resistance measurements were then begun using a Keithley Model 610B Electrometer with the vacuum continuously maintained. The temperature was increased at the rate of  $20^\circ/0.5$  hr, and the crystal was subsequently allowed to attain thermal equilibrium for 0.5 hr. The circuit was closed for a standard period of 1 min before reading a resistance. This procedure gave reproducible results (8). Some experiments were performed using a grounded guard ring painted around the periphery of the crystal in order to study surface conductance.

## Results and Discussion

### Confirmation of Low- and High-Temperature Mechanisms

AP crystals with grounded guard rings showed no difference in conductivity from unguarded crystals over the temperature range 25 to 180°C. Therefore, it is concluded that

for the temperature range studied, surface conductance does not contribute significantly to the total conductivity.

Figure 1 shows a typical Arrhenius-type conductivity plot for AP over the temperature range 25 to 180°C. The two slopes evidently indicate two different conduction mechanisms. The average of 14 runs similar to Fig. 1 gave, for the low-temperature region from 25 to 100°C, a value of  $E_a = 0.12 \pm 0.02$  eV. The high-temperature region from 100° to 180°C gave  $E_a = 1.04 \pm 0.11$  eV. Table I shows these

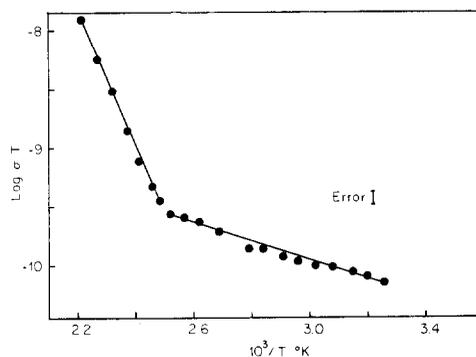


FIG. 1. Typical Arrhenius conductivity plot for single crystal of pure AP,  $\sigma T$  in  $\Omega^{-1} \text{cm}^{-1} \text{K}$ .

TABLE I  
PROTON AND CATION MIGRATION ACTIVATION ENERGIES

Compound	Migration $E_a$ (eV)	Reference and year
I. Proton		
AP	0.12	This work
Pure ice	0.23	10 (1971)
$\text{KH}_2\text{PO}_4$	0.10–0.24	11 (1966)
Ice doped with HF	0.09–0.32	12 (1965)
Ice doped with $\text{NH}_3$	0.11–0.25	12 (1965)
$\text{KHSO}_4$	0.08	13 (1950)
II. Other cation		
AP	1.04	This work
$\text{RbClO}_4$	1.2	7 (1972)
NaCl	0.75	14 (1968)
KCl	0.89	15 (1967)
NaCl	0.73	16 (1967)
KCl	1.21	17 (1964)
NaCl	0.83	18 (1962)

values compared with the results of other authors for known proton conductors and for ionic conductors where the migrating species is a cation other than a proton. The proton conductor values lie in the range 0.08 to 0.32 eV. The other cation conductors lie in the quite different range 0.73 to 1.21 eV. The evidence clearly establishes that in AP in the range 25° to 100°C, the conducting ion is a proton, while in the range 100 to 180°C, the conducting ion is  $\text{NH}_4^+$ . The  $\text{NH}_4^+$  presumably migrates through cation vacancies.

The above mechanisms are supported by such evidence as is available in the literature. Thus, Boldyrev (4), studying the products of electrical conduction through AP crystals below 100°C, detected hydrogen at the cathode in conformity with Faraday's law. He concluded that the charge carriers were protons, but this is not entirely conclusive since the hydrogen may have been a secondary product. Jacobs (5) showed that the conductivity of AP is enhanced by exposure to  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , and reduced by subsequent removal of these species. Owen et al. (7) obtained  $E_a = 1.2$  eV for AP in their rather short high-temperature range of 120 to 140°C. This agrees well with the present value and with their value of 1.1 eV for RP where the charge carrier is necessarily the large cation  $\text{Rb}^+$  rather than a proton. These authors do not report any  $E_a$  nor do they draw any conclusion regarding a carrier in the low-temperature region even though their graph shows a kink at approximately the same temperature as in Fig. 1 of the present work and a low-temperature region of relatively low  $E_a$ .

#### Effects of $\text{H}_2\text{O}$ and Annealing on the Conductivity

Figure 2 illustrates the percent decrease in conductivity of a single crystal of AP over a 50-day period at a pressure of 0.1 torr at 25°C. This crystal was not pretreated at 118°C, and interstitial  $\text{H}_2\text{O}$  is presumably present. If the  $\text{H}_2\text{O}$  molecule acts as a proton site, i.e., as a species that may engage in the association or dissociation of protons, thereby providing a means of proton migration, then the presence or absence of interstitial  $\text{H}_2\text{O}$  would be expected to influence the low-temperature

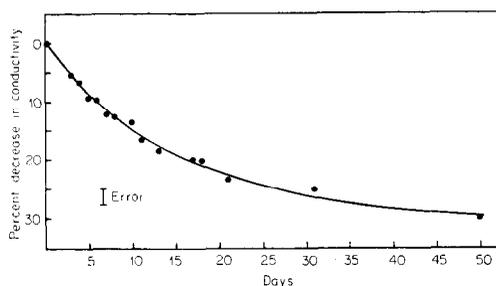
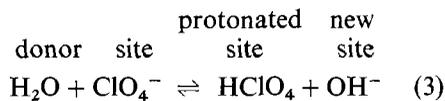


FIG. 2. Change in conductivity with time at 25°C.

conductivity. Keenan and Siegmund (9) studied  $\text{H}_2\text{O}$  content in AP with high-resolution proton magnetic resonance and interpreted their results as involving the following equilibrium.



In this case, the  $\text{NH}_4^+$  is the proton donor or source, the  $\text{H}_2\text{O}$  is the proton site, the  $\text{H}_3\text{O}^+$  is the protonated site, and the  $\text{NH}_3$  is a new proton site. Considering that the only species present in AP are  $\text{NH}_4^+$ ,  $\text{ClO}_4^-$ , and  $\text{H}_2\text{O}$ , three other equilibria may be involved in the proton migration process.



The presence of  $\text{H}_2\text{O}$  is necessary for the first two reactions. Therefore, the decreasing conductivity over a 50-day period in Fig. 2 is attributed to the loss of interstitial  $\text{H}_2\text{O}$  via a gradual diffusion process, thereby diminishing a source of proton donors and decreasing the concentration of proton sites. In a dry crystal of AP, Eq. (5) would represent the sole means of proton migration.

Figure 3 shows the change in conductivity over a 20-hr period at a pressure of 0.1 torr for single crystals of pure AP at four different temperatures between 100 and 180°C. This is the temperature range in which  $\text{NH}_4^+$  ions migrating via cation vacancies dominate the conduction mechanism. Therefore, the presence of interstitial  $\text{H}_2\text{O}$  should have no apparent effect upon the conductivity. The

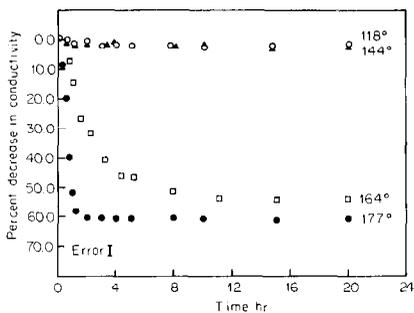


FIG. 3. Change in conductivity with time at various higher temperatures (temperatures in °C).

graphs at 118 and 144°C represent two crystals (no pretreatment) held at constant temperature and a pressure of 0.1 torr for 24 hr. It is reasonable to assume that interstitial  $H_2O$  is diffusing out of the crystal; however, no change in conductivity is observed. At 146°C the conductivity attained equilibrium after approximately 10 hr, and at 177°C it required only 2 hr. Considering the cation vacancy mechanism in this temperature region, these trends may be attributed to an annealing process by which vacancies gradually diffuse out of the crystal. As the concentration of vacancies decrease, the conductivity will also decrease since the conduction mechanism is dependent upon vacancy concentration. Just as  $H_2O$  molecules provide a means by which protons migrate, vacancies provide a means by which cations migrate.

#### Hysteresis Studies

Hysteresis studies were done on crystals that were not pretreated in vacuum at 118°C as in the standard conductivity measurements. Fig. 4 shows the Arrhenius plot for a new crystal that had been stored for 3 days in a desiccator after removal from the crystallization solution. After taking resistance readings in the standard manner from 25 to 180°C, the crystal was maintained at this highest temperature for 1 hr before beginning the decreasing temperature run. Fig. 5 shows the results for an aged crystal that had been stored in a desiccator over silica gel at room temperature for 1 yr. The graphs are plotted with  $\log \sigma T$  as ordinate to be comparable with Fig. 1. However, the variation in  $T$  does not

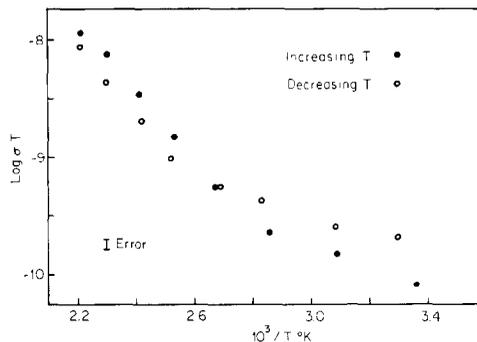


FIG. 4. Hysteresis in a new AP crystal.

change the relative positions of the curves significantly, and the qualitative conclusions to be drawn regarding variation in  $\sigma$  alone are valid.

It is seen that for the new crystal (Fig. 4), there is hysteresis in both temperature regions. On decreasing the temperature, the conductivity is lower in the high-temperature region and higher in the low-temperature region. For the aged crystal (Fig. 5), there is no hysteresis in the high-temperature region, but the hysteresis in the low-temperature region is the same as for the new crystal. These observations are completely in accordance with the model developed so far. If conduction in the high-temperature region is due to  $NH_4^+$  migration through cation vacancies, some of the vacancies in a new crystal would anneal out at the higher temperatures and the conductivity would be lower on the way down. In the case of the old crystal, the vacancy concentration would have annealed out to an equilibrium

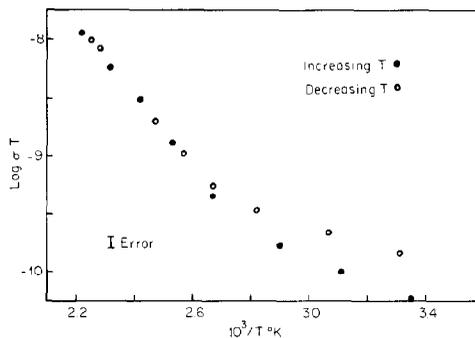


FIG. 5. Hysteresis in an aged AP crystal.

value over the period of 1 yr, and no further detectable annealing occurred during the hysteresis run.

The higher conductivity observed in the low-temperature region for both crystals on decreasing the temperature is attributed to production of water by thermal decomposition while the crystal is being cycled in the high-temperature region. Water is a known product of the decomposition (1) and will, according to the present model, affect the conductivity in the low- but not the high-temperature region. Thermal decomposition of AP at the temperatures in question is slow but not inappreciable. Using average values of the rate constant from the literature (1), it can be estimated that decomposition would occur to the extent of several percent during the high-temperature cycle of the hysteresis run. These conclusions were confirmed further by performing a hysteresis run in which a new crystal was cycled from 25 to 120°C and back. No hysteresis was observed in the low-temperature region in this case. None would be expected since the production of water due to thermal decomposition would be negligible for this temperature range.

Based upon the total picture of the electrical conductivity in AP which has been discussed, the conduction mechanism and electrode reactions of Scheme 1 are proposed.

The electrical conduction mechanism accounts for the observed trends in both the low- and the high-temperature regions. In the low-temperature proton conduction region, the bulk H<sub>2</sub>O concentration is the variable that has significant effect on the magnitude of the conductivity since H<sub>2</sub>O may act as both a proton site and a proton donor. In the high-temperature region, the vacancy concentration is predominant in influencing the conductivity since NH<sub>4</sub><sup>+</sup> ions migrate *via* cation vacancies.

The mechanisms proposed for the electrode reactions result both from a consideration of the work of others already cited and the electrical conduction mechanism proposed in the present work. Proton migration to the cathode results in H<sub>2</sub> evolution in the low-temperature region. Above approximately 100°C, the migration of NH<sub>4</sub><sup>+</sup> ions to the cathode would presumably result in the evolution of both NH<sub>3</sub> and H<sub>2</sub>, but this has not been studied experimentally. The anode

#### Electrical Conduction

Low Temp. (25°--100°C)	donor	site	protonated site	new site	High Temp. (100°--180°C)
Major (proton)	NH <sub>4</sub> <sup>+</sup>	+ H <sub>2</sub> O	⇌	H <sub>3</sub> O <sup>+</sup>	+ NH <sub>3</sub>
	H <sub>2</sub> O	+ ClO <sub>4</sub> <sup>-</sup>	⇌	HClO <sub>4</sub>	+ OH <sup>-</sup>
	H <sub>2</sub> O	+ H <sub>2</sub> O	⇌	H <sub>3</sub> O <sup>+</sup>	+ OH <sup>-</sup>
	NH <sub>4</sub> <sup>+</sup>	+ ClO <sub>4</sub> <sup>-</sup>	⇌	HClO <sub>4</sub>	+ NH <sub>3</sub>
Minor (ionic)	NH <sub>4</sub> <sup>+</sup>	+ □	⇌	□	+ NH <sub>4</sub> <sup>+</sup>
					Major (ionic)

#### Electrode Reactions (M is the metal electrode)

	Low Temp. (25°--100°C)		High Temp. (100°--180°C)
Cathode	Major	2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub>	Minor
	Minor	2NH <sub>4</sub> <sup>+</sup> + 2e <sup>-</sup> → 2 NH <sub>3</sub> + H <sub>2</sub>	Major
Anode	M	→ M <sup>n+</sup> + ne	

SCHEME 1. Electrical conduction and electrode reactions.

reaction is attributed to the dissolution of the metal electrode since there is no experimental evidence on this point.

## References

1. A. G. KEENAN AND ROBERT F. SIEGMUND, *Quart. Rev. Chem. Soc.* **23**, 430 (1969).
2. P. W. M. JACOBS AND H. M. WHITEHEAD, *Chem. Rev.* **69**, 551 (1969).
3. H. WISE, *J. Phys. Chem.* **71**, 2843 (1967).
4. V. V. BOLDYREV, V. V. ALEXANDROV, A. V. BOLDYREVA, V. I. GRITSAN, YU. YA. KARPENKO, O. P. KOROBENITCHER, V. N. PANFILOV, AND E. F. KHAIRETDINOV, *Combust. Flame* **15**, 71 (1970).
5. P. W. M. JACOBS AND WEE LAM NG, *J. Phys. Chem. Solids* **33**, 2031 (1972).
6. J. N. MAYCOCK, V. R. PAI VERNEKER, AND C. S. GORZYNSKI, JR., *Solid State Commun.* **5**, 225 (1967).
7. G. P. OWEN, J. M. THOMAS, AND J. O. WILLIAMS, *J. Chem. Soc. Dalton Trans.* **7**, 808 (1972).
8. L. A. K. STAVELEY AND T. M. HERRINGTON, *J. Phys. Chem. Solids* **25**, 921 (1964).
9. A. G. KEENAN AND R. F. SIEGMUND, *Anal. Chem.* **41**, 1880 (1969).
10. A. VON HIPPEL, *J. Chem. Phys.* **54**, 145 (1971).
11. L. B. HARRIS AND G. J. VELLA, *J. Appl. Phys.* **37** (4), 4294 (1966).
12. S. Y. CHAI AND P. O. VOGELHUT, *Science* **148**, 1595 (1965).
13. S. E. ROGERS AND A. R. UBBELOHDE, *Trans. Faraday Soc.* **46**, 1051 (1950).
14. K. C. KAO, L. F. GILES, AND J. H. CALDERWOOD, *J. Appl. Phys.* **39**, 3955 (1968).
15. C. KITTEL, "Introduction to Solid State Physics," Chap. 18, John Wiley and Sons, New York (1967).
16. N. BROWN AND M. HOODLESS, *J. Phys. Chem. Solids* **28**, 2297 (1967).
17. L. A. K. STAVELEY AND T. M. HERRINGTON, *J. Phys. Chem. Solids* **25**, 921 (1964).
18. R. W. DREYFUS AND A. S. NOWICK, *Phys. Rev.* **126**, 1367 (1962).