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Low-Field Mobilities of the Negative Ions in Oxygen, Sulfur Hexafluoride, Sulfur Dioxide, and Hydrogen Chloride*

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Measurements of the low-field mobility of the negative ions in O_2, SF_6, SO_2, and HCl are described. The results are 2.46, 0.57, 0.35, and 0.71 cm²/v-sec, respectively, reduced to 0°C and 760 mm Hg pressure. A quantum-mechanical theory of ionic mobility is outlined and applied to the gases investigated experimentally. Comparison of the experimental and theoretical results indicates that the oxygen ion is O_3^-, but attempts to identify the ions in the other gases are inconclusive.

THE first section of this paper deals with negative-ion mobility measurements which were made by one of the authors (E.W.M.) at the Georgia Institute of Technology. The second section provides an analysis of the results of these measurements in terms of the quantum-mechanical mobility theory recently developed by the other author (M.R.C.M.) and his former colleagues[1,2] at the Queen's University of Belfast.

I. EXPERIMENTAL

A. Method and Experimental Apparatus

In the experiments discussed here the ionic mobility is determined by a pulse technique in which a direct measurement is made of the time required for the ions to drift a known distance through the gas under the influence of a uniform electric field of known strength. A polonium alpha source located inside the mobility chamber is used to produce the primary ionization, and the negative ions are formed by the capture of the electrons thus produced by molecules of the gas being studied. Proportional counters are used to time the flight of the ions. The drift time data are displayed on a synchroscope and recorded photographically.

Details of the experimental method used here have been presented in earlier publications.[3,4] The present apparatus differs from that described earlier in that rubber gaskets have been replaced by Teflon and stopcocks by metal valves and that voltage for each electrode is now brought into the chamber through a separate Kovar seal.

B. Electron Capture in Gases

Identification of the ions whose mobility is measured in these experiments is facilitated by knowledge of the mechanism by which negative ions are formed under the conditions existing in our apparatus. Since not only the probability of capture in a given gas but also the type of negative ion formed may depend markedly on the energy of the electrons, it is pertinent first to discuss the mechanism by which electrons are produced in the mobility chamber.

As mentioned in Part A, the primary ionization is produced by the passage of polonium alpha particles through the gas. An alpha particle with initial energy of several Mev produces about 10^5 ion-pairs if it expends its total energy in the gas. The most probable collisions which result in ionization are those in which the ejected electron has low energy, usually less than the ionization energy of the molecule. Some of the ionizing collisions, however, produce electrons of relatively high energy, more than 100 ev in perhaps 10% of the cases.[5] These electrons are very efficient in producing further ionization—in fact, the secondary ionization is roughly two-thirds of the total produced. Thus, when alpha particles produce ionization in a gas, electrons are formed which range in energy from thermal values up to several hundred ev. The fraction of electrons produced with energies over about 10 or 15 ev is probably of the order of 30%. The ejected electrons either execute random motion in the gas and eventually attain thermal equilibrium with it or in the presence of an electric field, the electrons drift through the gas and finally reach an equilibrium condition in which collision losses just balance the energy gained from the field, assuming that they are not first captured to form negative ions. For electrons under conditions prevailing in the mobility chamber, the equilibrium energy is a fraction of an electron volt.[6]

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† On leave at the Georgia Institute of Technology, 1959–60.

[1] Dalgarno, McDowell, and Williams, Phil. Trans. Roy. Soc. (London) **A250**, 411 (1958).

[2] A. Dalgarno, Phil. Trans. Roy. Soc. (London) **A250**, 426 (1958).

[3] E. W. McDaniel and H. R. Crane, Rev. Sci. Instr. **28**, 684 (1957).

[4] E. W. McDaniel, Air Force Office of Scientific Research Document No. TN-58-332, Technical Report No. 1, January 10, 1958 (unpublished).

[5] Bates, McDowell, and Omholt, J. Atmospheric and Terrest. Phys. **10**, 51 (1957).

[6] R. H. Healey and J. W. Reed, *The Behavior of Slow Electrons in Gases* (Amalgamated Wireless Limited, Australasia, 1941).

1. Oxygen

There appear to be three different modes of formation of negative ions by electron impact in oxygen.[7,‡] At electron energies of less than about 1 ev, electrons are reported to be directly captured by oxygen molecules with the formation of O_2^- ions. The excess energy, equal to the kinetic energy of the electron plus the electron affinity of the molecule, is absorbed temporarily by the ion in the form of vibrational energy. Unless the ion is quickly stabilized by collision de-activation, the electron will be ejected from the ion. The cross section for this mode of formation decreases rapidly with increasing electron energy. The second process is that of dissociative attachment to give O^- plus O. This reaction has a threshold of 3.61 ev. A resonance process is involved here, and the reaction occurs with a large cross section. The third process involves the formation of both the O^+ and O^- ions. The threshold of this reaction is 17.22 ev.

It is evident that both the O^- and O_2^- ions should be formed in substantial numbers by electron capture in our oxygen experiment.

2. Sulfur Hexafluoride

SF_6^-, SF_5^-, F_2^-, and F^- ions have been observed in mass spectrographic studies of slow electron impact in SF_6.[8,9] Hickam and Fox[8] have used their retarding potential difference apparatus to study SF_6 at electron energies of less than 2 ev. SF_6^- was observed to be formed in a resonance capture process with an extremely high cross section, estimated to be at least 10^{-15} cm^2. The capture occurred at less than 0.1 ev, and over an energy range of less than 0.05 ev. Hickam and Fox also observed dissociative attachment leading to SF_5^-. The SF_5^- peak maximized at less than 0.1 ev and then decreased to zero at approximately 1.5 ev. The maximum cross section for this process was estimated to be 10^{-17} cm^2. Hickam and Fox did not investigate the formation of F_2^- and F^- ions in their experiment. These ions may have been produced under their conditions, since their formation in SF_6 has been reported by Ahearn and Hannay,[9] but no evidence is at hand regarding this point.

It seems likely that only SF_5^- and SF_6^- ions are produced initially in significant numbers in our experiments. The formation of F^- and F_2^- almost certainly occurs with much lower probability.

3. Sulfur Dioxide

Each of the following ions has been observed to be formed in SO_2 by electron impact: SO_2^-, SO^-, S^-, and O^-.[10,11] As in O_2, the attachment coefficient at very low energy decreases as the electron energy increases, but it rises again at higher energy.[7] The SO_2^- ion presumably is formed by the same process as is O_2^- in O_2, namely attachment with vibrational excitation followed by stabilization by collision. Hickam[10] has studied attachment in sulfur dioxide, and he reports the SO^- ion to be the most abundant of those produced in his apparatus. The SO^- ion appeared at a potential of 4.9 v; the attachment energy range was 0.4 ev wide. Rosenbaum and Neuert[11] have also investigated the negative ions in SO_2. They report the following appearance potentials: O^-, 3.5 ev; SO^-, 3.9 ev; and S^-, 3.6 ev. In their work the O^- and SO^- ions are reported to be formed in fairly large numbers.

Because of the energy spread of the electrons available for capture in our SO_2 experiment, it is likely that all of the above mentioned ions are produced. Estimation of their relative abundances does not appear to be feasible.

4. Hydrogen Chloride

The retarding potential difference method has also been applied by Fox[12] to the study of the formation of negative ions in HCl. Only one ion, Cl^-, is observed, but a plot of ion current *vs* electron energy shows two peaks, indicating that two distinct mechanisms are involved. The low-energy peak occurs at 0.66 ev and corresponds to the formation of ions according to the equation $HCl+e\rightarrow H+Cl^-$. The threshold for the second mechanism is 14.5 ev. The high-energy process is described by the equation $HCl+e\rightarrow H^++Cl^-+e$.

There seems to be no problem in identifying the initially formed negative ion as Cl^- in our experiment, since no other negative ion has been reported in the literature as being produced in HCl.

C. Results

The experimental results on oxygen, sulfur hexafluoride, sulfur dioxide, and hydrogen chloride will now be presented.

1. Oxygen

Four measurements were made on gas taken from a steel tank and one on oxygen from a break-seal glass bulb. The tank oxygen was obtained from the Matheson Company, as were all of the other gases used in the experiments described here. It was certified to be 98.9% pure, containing 0.7% N_2 and 0.4% A. The gas from the glass bulb was "spectroscopically pure." Measurements were made at room temperature in the pressure range of 100 to 130 mm Hg, and the value of E/P ranged from 0.75 to 0.85 v/cm-mm. The results were consistent to within the limit of experimental error, estimated to be 2.4%.

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[7] L. B. Loeb, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 21, pp. 445–470.

[‡] *Note added in proof.*—For the most recent discussion of slow electron attachment in oxygen, see J. B. Thompson, Proc. Phys. Soc. (London) **A73**, 821 (1959).

[8] W. M. Hickam and R. E. Fox, J. Chem. Phys. **25**, 642 (1956).

[9] A. J. Ahearn and N. B. Hannay, J. Chem. Phys. **21**, 119 (1953).

[10] W. M. Hickam (private communication, 1957).

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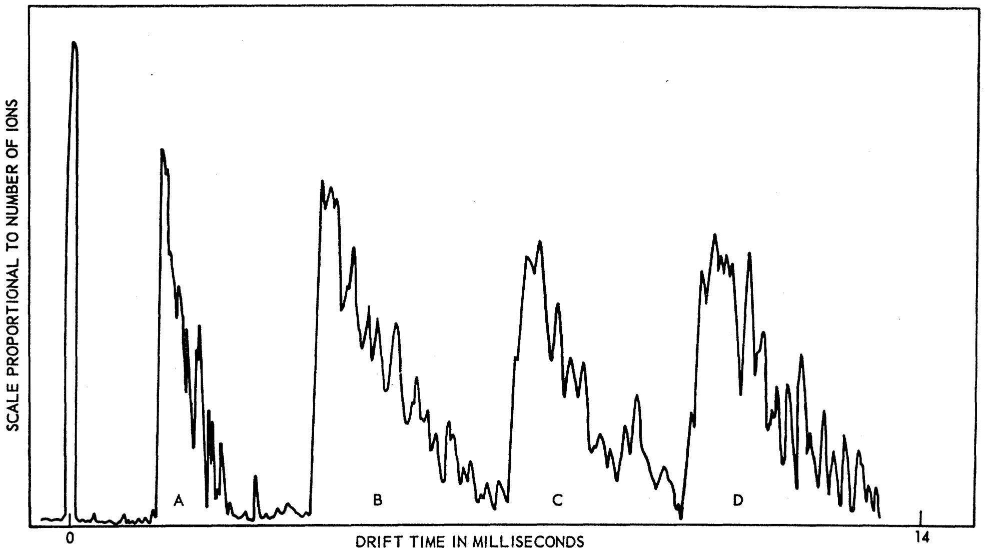

FIG. 1. Drift-time spectra for O_2 at 120.9 mm pressure. 400 events per peak.

A microphotometer plot of a photographic plate obtained with oxygen is shown in Fig. 1. The sharp spike at the origin of the drift time axis corresponds to the production of ionization by the passage of an alpha particle through the gas. The peaks A, B, C, and D represent the distribution of arrival times of the ions at the end of their flight paths for each of four different lengths of flight path. The mobility of the ions forming the sharp edges in the drift time spectra of Fig. 1 was determined to be 2.46±0.06 cm²/v-sec, reduced to 760 mm Hg and 0°C. This ion is identified as O_3^-, based on a comparison of the experimental result with the theoretical predictions of Sec. II of this paper and with the observations of Burch and Geballe.[13]

Burch and Geballe[13] have presented evidence for the presence of three negative ion species in oxygen. Their experiment covered a range of E/P extending from 9 to 50 v/cm-mm Hg and a range of PD from 7 to 26 cm-mm Hg. Here P is the pressure in mm Hg and D is the drift distance in cm. (The range of PD in our oxygen measurements extended from about 600 to 2000 cm-mm Hg.) Three distinct and pressure-independent negative-ion velocities were found, consistent with zero-field mobilities of 3.4, 2.6, and 1.95 cm²/v-sec. The multiplicity of velocities is ascribed to irreversible reactions through which initially formed O^- ions are converted into two slower species, O_3^- and O_2^-, in particular by the $O^- + 2O_2 \rightarrow O_3^- + O_2$ reaction, a chemical process which may be quite rapid.[14] They interpret the species of intermediate mobility (2.6) as O_3^-, and according to their analysis, O_3^- is the ion which would be observed under our conditions. Positive ions were also investigated in their experiments. The initially formed positive ion, thought to be O_2^+, retained its identity as it drifted through the gas. No difference was detected between the mobilities of the O_2^+ and O_2^- ions.

An analysis of the peak shape in our drift time spectrum for oxygen has been presented in earlier publications.[3,4] It was shown[4] that the slope of the leading edge of the spectrum is consistent with the amount of straggling calculated for a single species of ion traveling from a point near the ionization track of the alpha particle to the end of the drift tube. There is no indication of additional straggling due to labile clustering[15] or other type of reaction as the ion drifts down the tube. Thus the ion of maximum mobility (2.46 cm²/v-sec) appears to be a species which remains unchanged after its formation. This does not mean that the ion is of the species initially formed by the capture of the primary electrons by oxygen molecules. In fact, the ion forming the sharp edge is probably produced by some secondary reaction between the initial ion and oxygen molecules. However, if it is a secondary product, it must be one which is formed very near the ionization track and not at an appreciable random distance down the tube. Calculations have shown that reactions of this type may have sufficiently high rate coefficients that the mean free path before formation of the ion of maximum mobility could be a very small fraction of a centimeter under the existing conditions.[16]

The long trailing edge of each peak in the spectrum shows, on the other hand, that the remainder of the initially formed negative ions are converted to one or more species of mobility less than 2.46 by some reaction with oxygen molecules. It has been shown[4] that the

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[13] D. S. Burch and R. Geballe, Phys. Rev. **106**, 183, 188 (1957).

[14] L. M. Branscomb, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1957), No. 9, p. 87.

[15] The term "labile clustering" refers to the formation of clustered ions whose composition changes as the result of the temporary attachment and subsequent detachment of molecules as the ion drifts through the gas.

[16] D. R. Bates, Proc. Phys. Soc. (London) **A68**, 344 (1955).

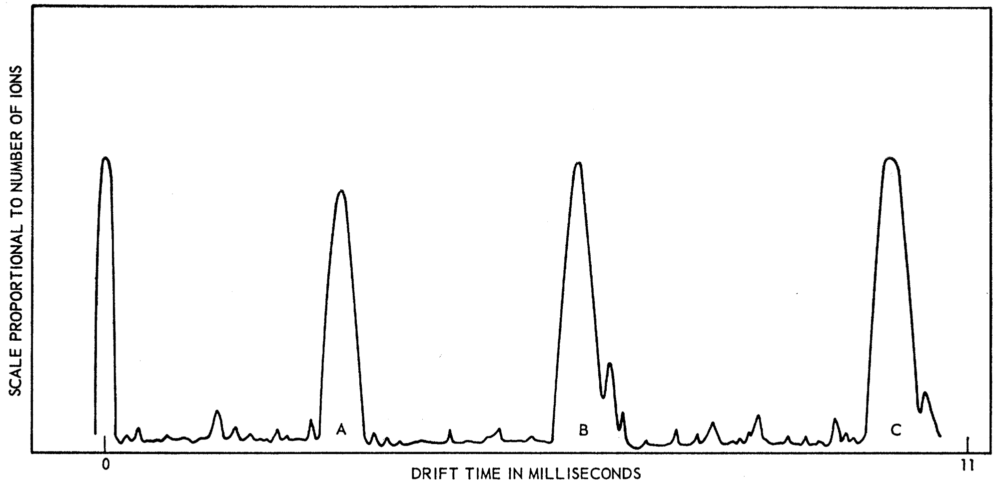

FIG. 2. Drift-time spectra for SF_6 at 35.1 mm pressure. 1800 events per peak.

formation of fixed clusters would produce peaks of a different shape from those observed but that labile clustering or certain other types of reactions could produce peaks of the observed shape.

It may also be of interest to compare the present result of 2.46 cm^2/v-sec for the mobility of the negative ions in oxygen with those obtained by other investigators in addition to Burch and Geballe whose work was referred to above. The first determination was reported by Zeleny,[17] who obtained 1.82 cm^2/v-sec. Franck[18] reported a value of 1.79 cm^2/v-sec, while Bradbury[19] obtained 2.19 cm^2/v-sec. Nielsen and Bradbury[20] also described experiments on oxygen in which they used an electrical shutter technique. They reported that newly formed ions, which they identified as O_2^-, had a mobility of 3.3 cm^2/v-sec and that a strong aging effect was in evidence. The slowest ions observed had a mobility of 2.85. Doehring[21] reported the measurement of the mobility of ions he believed to be O_2^- as 2.68 ± 0.13 cm^2/v-sec. He also used an electrical shutter method. The theory presented in Sec. II indicates that the ions observed by Nielsen and Bradbury were O^-, while those of Doehring were O_3^-. It may be noted, however, that the O_3^- ion has never been reported in any mass spectrographic work.

2. *Sulfur Hexafluoride*

Three mobility measurements were made using SF_6 which, according to the manufacturer, was at least 99.9% pure. (No additional information on the composition of the gas was available.) The runs were made at 35 mm pressure and room temperature, and the electric field strength was 104.9 v/cm.

In each of the runs, a single sharp peak was observed in the drift-time spectrum. Figure 2 shows the superimposed spectra for three different source positions. Analysis of the shape of the spectrum reveals that each peak is narrow enough to be formed only by a single species of ion which preserves its identity all the way down the drift tube.

The mobilities obtained in the various runs are in extremely close agreement, being 0.57, 0.57, and 0.56 cm^2/v-sec, respectively. The accuracy of the SF_6 measurements is estimated to be the same as that of the oxygen measurements, namely 2.4%. Thus our value for the low-field mobility of the negative ions in pure SF_6 is 0.57 ± 0.01 cm^2/v-sec, reduced to 0°C and 760 mm Hg. Comparison of this result with the prediction of the theory of Sec. II indicates that our ion may be the $(SF_6 \cdot SF_6)^-$ or $(SF_5 \cdot SF_6)^-$ cluster.

The only other experimental value of the mobility of the negative ions in SF_6 which is available for comparison appears to be the one resulting from an experiment performed by McAfee.[22] His measurements were made in the range of E/P of 3 to 26 v/cm-mm, and the data extrapolated to $E/P=0$ gave a mobility of 0.45 ± 0.20 cm^2/v-sec. McAfee believed his ion to be SF_6^-. The arguments of Sec. II suggest that his identification was correct.

3. *Sulfur Dioxide*

In the case of SO_2, again only one peak appeared in the drift-time spectrum for a given length of flight path. The shape of the peak was similar to that observed for oxygen, as is apparent in Fig. 3. Analysis of the shape of the peaks in the SO_2 spectrum shows that the sharp front in each case can be produced by a single species of ion, but that the trailing edge must be interpreted in terms of labile clustering or some other type of reaction with SO_2 molecules. Identification of the ion forming the sharp edge is difficult. The theoretical analysis in Sec. II indicates that it may be SO_2^-.

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[18] J. Franck, Z. Physik **12**, 291 (1910).

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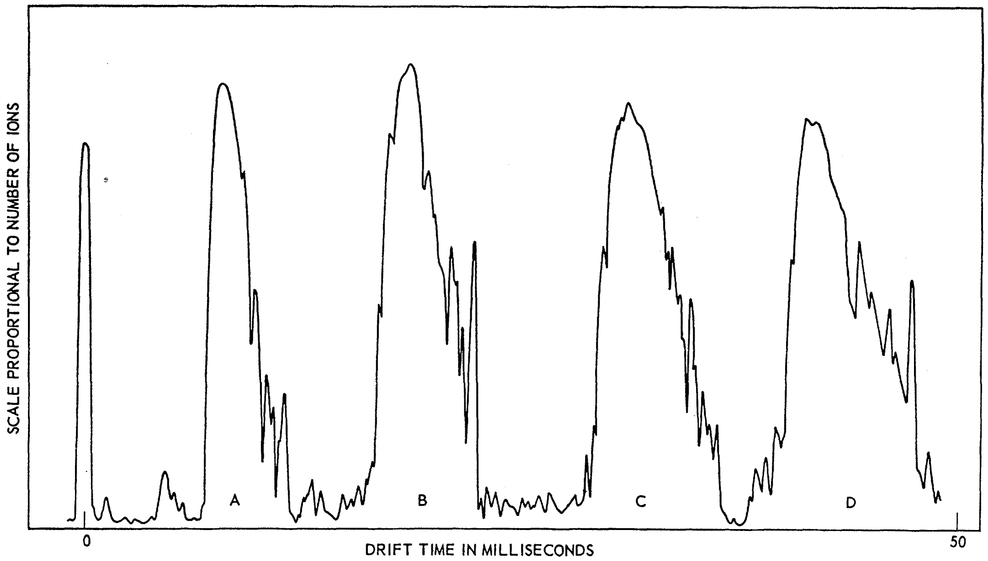

FIG. 3. Drift-time spectra for SO_2 at 53.0 mm pressure. 800 events per peak.

The fact that SO_2^- ions are certain to be formed in our mobility chamber by direct electron attachment may be considered to add plausibility to this interpretation.

The measurements were made at 53.0 mm Hg and a field strength of 86.1 v/cm. The SO_2 was 99.98% pure, containing 0.02% of noncondensable impurities. Each of the three measurements which were made gave a reduced mobility of 0.35 ± 0.01 cm^2/v-sec.

This result may be compared with those reported by other investigators. E. M. Wellish[23] and K. Yen[24] both obtained, in separate experiments, a mobility of 0.41 for the negative ions in SO_2. An experiment performed by DuSault and Loeb[25] gave a value of 0.44. The temperature to which these mobilities refer is not specified in the literature, but it is assumed to be 20°C in each case. This means that each value should probably be multiplied by the factor 273/293 for comparison with our mobility. The values which result are 0.39 and 0.41, respectively.

4. *Hydrogen Chloride*

Three measurements were made on HCl at 85 mm Hg pressure and $E=79.7$ v/cm. The gas was 99.3% pure, containing 0.2% of inert gases and 0.5% of CO_2. A single sharp peak was observed in the drift-time spectrum for each source position, as shown in Fig. 4. Calculations[4] show that the width of the peak is consistent with the assumption that a single ionic species is involved.

The three runs gave reduced mobilities of 0.71, 0.71, and 0.72 cm^2/v-sec, for an average of 0.71 ± 0.02 cm^2/v-sec assuming 2.4% accuracy. Apparently only one other experimental value for the mobility of the negative ions in HCl is available for comparison. Loeb[26] reports a mobility of 0.56 cm^2/v-sec referred to 760 mm Hg and 20°C. This corresponds to a value of 0.52 reduced to standard conditions.

The initially formed ion in our experiment is almost certain to be Cl^-, but an unambiguous interpretation of our mobility data is not possible. It is suggested in Sec. II that the observed ion could be Cl^-, but no great weight can be attached to this interpretation.

II. THEORETICAL

A. General Discussion

Theoretical descriptions of the mobilities of ions in gases, based on elementary kinetic theory, have been developed by Jeans[27] and Loeb.[28] They predict the observed dependence on the reduced mass of the ion-atom system but are only of order of magnitude accuracy in many cases.

A more refined treatment, based on Boltzmann's transport equation and dealing with ions and atoms having an inverse fourth power interaction potential, has been given by Langevin[29] and Hassé.[30] It is a special case of the theory to be presented in this section.

The mobility, K, of an ion in a gas may be represented by the expression[31]

$$K=eD_{12}/kT, \tag{1}$$

where e is the electronic charge, k Boltzmann's constant,

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[23] E. M. Wellish, Phil. Mag. **34**, 33 (1917).

[24] K. Yen, Proc. Natl. Acad. Sci. (U. S.) **4**, 106 (1918).

[25] L. DuSault and L. B. Loeb, Proc. Natl. Acad. Sci. (U. S.) **14**, 384 (1928).

[26] L. B. Loeb, Proc. Natl. Acad. Sci. (U. S.) **12**, 35 (1926).

[27] J. H. Jeans, *Introduction to the Kinetic Theory of Gases* (Cambridge University Press, Cambridge, 1948).

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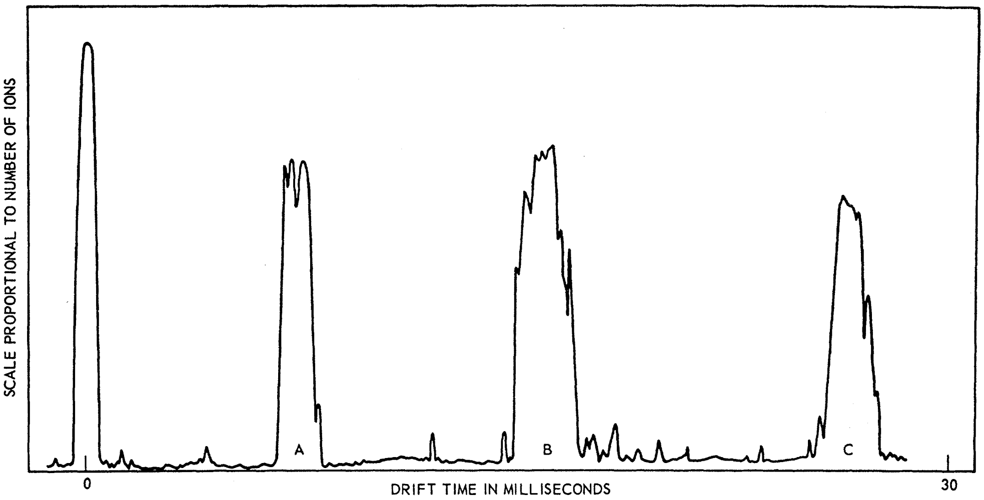

FIG. 4. Drift-time spectra for HCl at 85.0 mm pressure. 1800 events per peak.

T the absolute temperature, and D_{12} the diffusion coefficient. At low field strengths, such that the energy gained from the field per mean free path is small compared with the Maxwellian energy, the diffusion coefficient is given by

$$D_{12}=\frac{3\sqrt{\pi}}{16}\left(\frac{2kT}{\mu}\right)^{\frac{1}{2}}\frac{1+\epsilon_0}{(n_1+n_2)P_{12}}, \tag{2}$$

where

$$P_{12}=\int_0^\infty v^5 Q_D(v)\exp(-\mu v^2/2kT)dv, \tag{3}$$

and

$$Q_D(v)=2\pi\int_0^\infty (1-\cos\theta)p\,dp. \tag{4}$$

Here μ is the reduced mass of the system, n_1 the gas and n_2 the ion number density, and ϵ_0 is a second order correction which is usually less than present experimental errors.[32,33] The diffusion cross section $Q_D(v)$ depends on the detailed nature of the interaction through the impact parameter p and the scattering angle θ and is thus a function of the velocity of relative motion v. The ion number density n_2 is generally much less than n_1 and may be ignored. The second order correction is also neglected for the present purposes.

According to the quantum theory of atomic collisions,[34] if the ion and atom are not of the same species, the diffusion cross section may be expressed in terms of the phase shifts, η_s, as

$$Q_D(v)=\frac{4\pi}{k^2}\sum_{s=0}^{\infty}(s+1)\sin^2(\eta_s-\eta_{s+1}). \tag{5}$$

Here $k=\mu v/\hbar$ is the wave number of the relative motion. If the atom and ion are of the same species, then the interaction potential may arise from states either symmetric or antisymmetric in the nuclei, giving rise to phase shifts β_{2r} and γ_{2r+1}, respectively, where now r is the index in the summation. The situation is more complicated if the atom has nonzero nuclear spin, when account must be taken of the statistics.[2]

Theoretical predictions of the mobilities rest therefore on the evaluation of summations (5), which through the phase shifts depend on a detailed knowledge of the interaction potentials. Owing to the integral over a Maxwell distribution involved in (3) the only values of $Q_D(v)$ important in determining the mobility at temperatures within the normal laboratory range are those at energies in the adiabatic range.[35] We may therefore employ Jeffreys' approximation to the phase shifts,[34]

$$\eta_s=\int_{R_0}^\infty\left[k^2-2\mu V(R)-\frac{s(s+1)}{R^2}\right]^{\frac{1}{2}}dR-\int_{R_0'}^\infty\left[k^2-\frac{s(s+1)}{R^2}\right]^{\frac{1}{2}}dR, \tag{6}$$

where $V(R)$ is the interaction potential and R_0, R_0' the respective outermost zeros of their integrands. It is then convenient to replace the summations by integrations, since a large number of phases enter, and to write (5) as

$$Q_D(v)=4\pi\int_0^\infty p\sin^2\xi(p)dp, \tag{7}$$

where

$$\xi(p)=-\frac{1}{k}\frac{\partial\eta(p)}{\partial p}, \tag{8}$$

and $p=[s(s+1)]^{\frac{1}{2}}/k$. Choosing an impact parameter

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[32] A. Dalgarno and E. J. A. Williams, Proc. Phys. Soc. (London) **A72**, 274 (1958).

[33] E. A. Mason and H. W. Schamp, Ann. Phys. **4**, 233 (1958).

[34] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, 1949).

[35] H. S. W. Massey and E. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, Oxford, 1952).

p^* such that for all $p<p^*$, $\sin^2\xi(p)$ oscillates rapidly and may be replaced by its average value $\frac{1}{2}$, we have

$$Q_D(v)=\pi p^{*2}+4\pi\int_{p^*}^{\infty} p\sin^2\xi(p)dp. \tag{9}$$

The choice of the impact parameter is arbitrary, but $Q_D(v)$ is not unduly sensitive to it, provided p^* is large.[1,36] If this is the case, then s is also large, and the Jeffreys' approximation reduces to the Massey-Mohr approximation,[37] which may be expressed in terms of the impact parameter p as

$$\eta(p)=-\frac{k}{2\mathcal{E}}\int_{p}^{\infty}\frac{V(R)}{[1-p^2/R^2]^{\frac{1}{2}}}dR, \tag{10}$$

where $\mathcal{E}$ is the center-of-mass energy.

The interaction potential between an ion and an atom is, to a good approximation, of the form

$$V(R)=Ae^{-\alpha R}-\frac{C}{R^4}-\frac{E}{R^6}+\cdots, \tag{11}$$

in most cases, so phases are required for potentials of the type $V(R)=Ae^{-\alpha R}$ and $V(R)=C/R^n$. These phases have been calculated.[36,38]

The theory of Langevin[29,30] is obtained by choosing the potential

$$\begin{aligned} V(R)&=\infty \quad (R<\rho)\\ &=-C/R^4 \quad (R>\rho), \end{aligned} \tag{12}$$

where ρ is some cutoff parameter. In this case Jeffreys' approximation may be evaluated analytically,[1] and the diffusion cross section expressed as

$$Q_D=2.210\pi q^2, \tag{13}$$

where $q^4=C/\mathcal{E}$, all quantities being in atomic units.

If the polarizability of the gas is large, only the R^{-4} term of the interaction plays a significant part in determining the mobility. Then, using (11) in (10) but retaining only the R^{-4} term, and carrying out the integrations, the mobility may be expressed in the simple form

$$K=\frac{35.9}{(\alpha\mu)^{\frac{1}{2}}}\text{ cm}^2/\text{v-sec}, \tag{14}$$

where α, the polarizability in atomic units (a_0^3), is related to the parameter C by $C=\alpha e^2/2$. It has been demonstrated in an earlier paper[1] that this result is accurate within the limits of experimental error for ions in A, Kr, Xe, N_2, and H_2, and also rather unexpectedly for the polar gas CO. The interaction between an atomic ion and a heteronuclear polar molecule such as CO presumably includes an R^{-3} term and will be orientation dependent. The success of (14) in this case probably implies that the R^{-3} term vanishes when averaged over all orientations. It should be noted that while (14) predicts, in common with other theories, that $K\propto\mu^{-\frac{1}{2}}$, it disagrees with the usual presentation of the theory in which $\rho\neq 0$ in predicting temperature independence for an R^{-4} interaction, and this prediction is substantiated by the available experimental data.[1,39] It is of interest that the polarizability limit of the classical Langevin theory agrees exactly with (14).

If the interaction is of the more general form

$$V(R)=AR^{-n}, \tag{15}$$

where n is an integer, the theory outlined here predicts that the temperature variation of the mobility will be

$$K=\frac{\text{constant}}{\sqrt{\mu}}T^{(2/n)-\frac{1}{2}}, \tag{16}$$

which agrees with the Langevin result $K\propto T^{-\frac{1}{2}}$ in the limit $n\rightarrow\infty$. It is clear that observations on the temperature variation of mobility could lead to considerable information on ion-atom interactions.[1,33]

When the ion is moving in its parent gas, we must use the modified form of (5) for the diffusion cross section. By a similar analysis,[38,2] it may be shown that Q_D is closely related to the charge transfer cross section Q_T for the process

$$X^+ + X\rightarrow X + X^+, \tag{17}$$

and may be expressed as

$$Q_D=2(Q_T+Q_P), \tag{18}$$

where Q_P is a polarizability correction,

$$Q_P=2\pi\int_{p^*}^{\infty} p\sin^2\left(\frac{3\pi C}{8p^4\mathcal{E}}\right)dp, \tag{19}$$

which has been tabulated by Dalgarno, McDowell, and Williams.[1] The charge transfer cross section Q_T is defined in terms of the phases β_s and γ_s and the impact parameter p as

$$Q_T(v)=2\pi\int_0^{\infty} p\sin^2(\beta_s-\gamma_s)dp. \tag{20}$$

An analysis of the type used to evaluate Q_D [see Eq. (9)] leads to the approximate expression

$$Q_T(v)=\frac{\pi p^{*2}}{2}+\frac{\pi^3 p^*}{16\alpha}, \tag{21}$$

where p^* is given by

$$p^*\exp(-2\alpha p^*)=\pi\alpha\mathcal{E}/(4A^2\mu). \tag{22}$$

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[36] M. R. C. McDowell, Proc. Phys. Soc. (London) **A72**, 1087 (1958).

[37] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A144**, 188 (1934).

[38] A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. (London) **A69**, 615 (1956).

[39] K. Hoselitz, Proc. Roy. Soc. (London) **A177**, 200 (1941).

TABLE I. Mobilities of O_3^- in various gases at a gas number density of 2.69×10^{19} cm^{-3}.

Gas	K_{obs}	α[a]	K_{pol}[b]	90% K_{pol}
He	11.8 ±1.2	1.39	15.8	14.2
Ne	5.14±0.5	2.68	5.85	5.27
A	2.06±0.04	11.0	2.31	2.07
K	1.39±0.07	16.7	1.59	1.43
Xe	0.88±0.10	27.1	1.16	1.04
H_2	11.4 ±1.0	4.3	12.5	11.25
N_2	2.22±0.06	11.9	2.47	2.22
CO_2	1.08±0.03	17.8	1.78	1.60

[a] R. Landolt and R. Bornstein, *Atom und Molekular Physik* (Springer-Verlag, Berlin, 1950), Vol. 1.
[b] K_{pol} is the polarizability mobility calculated from Eq. (14).

Neglecting the second term of (21) when p^* is large, (i.e., at low energies), it is apparent that Q_T is of the form

$$Q_T \rightarrow (\mathcal{A}\log\mathcal{E}+\mathcal{B})^2, \qquad (23)$$

as $\mathcal{E}\rightarrow 0$. In cases when we know the charge transfer cross section experimentally, it is then possible using (23) and (19) to obtain $Q_D(v)$ and hence the temperature variation of the mobility. Previous applications suggest that the method is reliable.[2,40]

B. Identification of the Observed Ions

1. Oxygen

The theory presented above does not differentiate between positive and negative ions. This apparent weakness is due to the use of the Massey-Mohr approximation, rather than the full Jeffreys' approximation, to the phase shift. It is not serious in the case of a polarizability dominated interaction, since only the mass of the ion is concerned, but it might be of importance where charge transfer or other chemical rearrangement reactions take place. There is no experimental information available on slow negative-ion charge transfer of type (17). However, a theoretical study of the simplest case suggests that where the electron affinity is small, the charge transfer cross sections may be very large, and mobilities correspondingly low.[38] It is most unlikely that the mobility of a species X^- in gas X would exceed that of X^+ in X at any temperature owing to the more diffuse structure of the negative ion.

The mobilities of O^- and O_3^- in O_2 predicted by (14) are 3.3 and 2.5 cm^2/v-sec. These should be independent of temperature, and are referred to a constant density of 2.69×10^{19} atoms cm^{-3}. The mobility of O_2^- in O_2 is uncertain, but should be lower than the mobility of O_2^+ in O_2, which may be estimated from the available charge transfer measurements,[41] suitable corrected.[2] Here it is assumed that charge transfer plays a similar role for diatomic molecules as for monatomic ones.

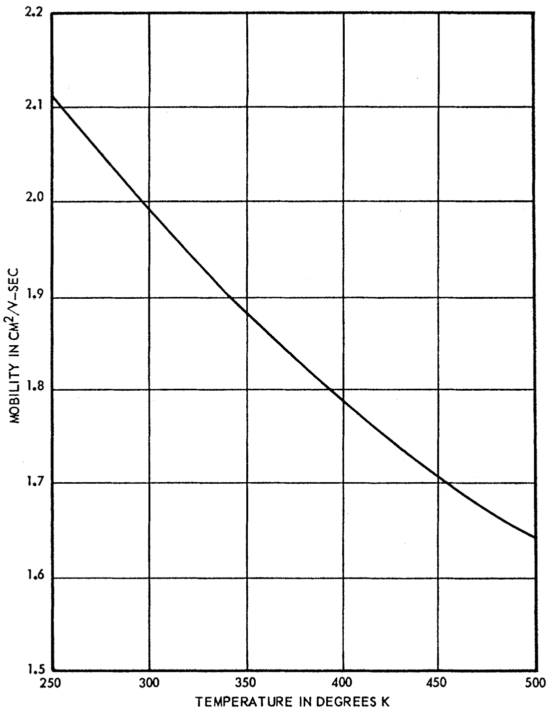

FIG. 5. Theoretical mobility of O_2^+ ions in O_2 as a function of the absolute temperature.

From Eqs. (1)–(3) we have that

$$K=\frac{5.20\times10^3}{\bar{Q}_D\sqrt{T}}\ \text{cm}^2/\text{v-sec}, \qquad (24)$$

where

$$\bar{Q}_D=\frac{\alpha^3}{2!}\int_0^\infty \mathcal{E}^2 Q_D(\mathcal{E})e^{-\alpha\mathcal{E}}d\mathcal{E}, \qquad (25)$$

and α is $(kT)^{-1}$. The results are shown in Fig. 5. The calculated mobility of O_2^+ in O_2 at 293°K is 2.00 cm^2/v-sec.

Burch and Geballe[13] found three types of negative ions present in their oxygen experiments. These have mobilities of 3.4, 2.6, and 1.95 cm^2/v-sec and are assigned to O^-, O_3^-, and O_2^-, respectively. Our analysis substantiates this identification and indicates that the ion observed in the present work, with mobility 2.46 cm^2/v-sec, is O_3^-.

Observations on the mobility of negative ions found in mixtures of oxygen and nonelectronegative gases, over a wide range of oxygen concentrations, have been presented in an earlier paper.[3] The results at 100% oxygen are in agreement with those of the present paper, suggesting that the ion present was O_3^-. Further evidence in support of this contention is forthcoming from observations in He, Ne, A, Kr, Xe, H_2, N_2, and CO_2 in the presence of varying admixtures of O_2. Extrapolation of the results to zero concentration of

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[40] N. Lynn and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A70**, 474 (1957).

[41] Dillon, Sheridan, Edwards, and Ghosh, J. Chem. Phys. **23**, 776 (1955).

TABLE II. Observed and calculated mobilities of ions in their parent gases.

Gas	α^a	μ	K_{pol}	$K_{obs}{}^b$	K_{obs}/K_{pol}
Ne	2.68	10	6.93	4.3	0.62
A	11.0	20	2.45	1.64	0.67
K	16.7	42	1.35	0.90	0.66
Xe	27.1	66	0.85	0.58	0.68
O_2	10.81	16	2.73	1.9	0.69
Hg	34.3	100	0.61	0.29[c]	0.48
CO	13.2	14	2.64	1.6	0.61
SF_6	42.3	73	0.69	0.45[d]	0.65

[a] R. Landolt and R. Bornstein, *Atom und Molekular Physik* (Springer-Verlag, Berlin, 1950), Vol. 1.
[b] References to the observational data are given in our reference 2 unless otherwise indicated.
[c] G. Mierdel, Z. Physik **121**, 574 (1943).
[d] See reference 22.

O_2 yields the data presented in Table I, where they are compared with the theoretical predictions for O_3^- in these gases. The agreement is good but appears to involve a systematic discrepancy of about 10%. It is tempting to suppose that this arises from the rather more diffuse structure of the negative ion, but this supposition is not substantiated by the results in pure O_2. The observed mobility of 11.4±1.0 cm²/v-sec in H_2 is suggestive. Previous work[1,42] indicates that H_2 has an effective polarizability of $4.3a_0^3$. It would then be expected that all ions other than H_2^+ would show mobilities in H_2 exceeding 12.3 cm²/v-sec. Previous data[42–45] support this view. The present result seems to be about 10% too low.

It is interesting to note that the Bristol data[46] on mobilities of positive ions in these gases also show a systematic departure from the theory of about 7%, but in the opposite sense. These discrepancies cannot arise from neglect of second and higher order approximations to the diffusion coefficient, since these vanish exactly for an R^{-4} interaction.[32,33]

The results for He and CO_2 are in no sense anomalous, since the polarizability of He is too small for (14) to apply, and since CO_2 is a polar molecule. The results for Xe should however be treated with some reserve, since Xe has a high polarizability. The measurements in Xe-O_2 mixtures involve an unavoidable extrapolation[3] from 60% O_2 to zero O_2, and the available data do not show as clear a linear dependence on O_2 concentration as do the other gases investigated, where the extrapolation is over a considerably shorter range. The quoted experimental result for Xe may well be too small, apart from any systematic error.

2. *Sulfur Hexafluoride*

The observed mobility of the negative ion in SF_6 was 0.57±0.01 cm²/v-sec. The only other experimental value is that of McAfee,[22] who finds a mobility of 0.45±0.20 cm²/v-sec for negative ions in SF_6 and identifies the ion as SF_6^-. The effective polarizability of SF_6 is $42.3a_0^3$,[47] sufficiently high for Eq. (14) to be applicable, and (14) predicts a mobility of 0.69 cm²/v-sec for $SF_6^\pm$ in SF_6, which is much too high. However, inspection of all the available experimental information on mobilities of ions in their own gases at 300°K suggests that the true mobility is about 65% of that calculated neglecting charge transfer. The data are presented in Table II. This strongly supports McAfee's identification but requires substantiation by observation of the form of the temperature variation. It is most unlikely that the ion observed in our work is SF_6^-. The results of Table II, and the high symmetry of SF_6 suggest that orientation-dependent forces will be relatively unimportant.

Solving Eq. (14) for the reduced mass gives $\mu=93.8\pm3.5$ and hence the mass of the ion is $m_2=262\pm30$. The discussion of Sec. IB indicates that the only ions likely to be seen with mass in this range are the clusters $(SF_6\cdot SF_6)^-$ and $(SF_5\cdot SF_6)^-$, with $m_2=292$ and 273, respectively. We therefore suggest that either or both of these clusters may be present in our experiment.

3. *Sulfur Dioxide*

The most probable ion in this case would seem to be SO_2^-. Since the interaction is not of the R^{-4} type, application of (14) and the 65% criterion must be unreliable. However, the polarizability is very large,[48] $\alpha\approx200a_0^3$; it must therefore play a considerable part in determining the mobility in spite of the occurrence of orientation-dependent dipole-dipole interactions. In the absence of charge transfer, the theoretical value of the mobility of SO_2^- in SO_2 suggested by Eq. (14) is 0.46 cm²/v-sec. Application of the 65% criterion yields a mobility of 0.30 cm²/v-sec. It is possible that S^- or O^- ions might be present. They would have mobilities of 0.55 and 0.71 cm²/v-sec on the assumption of an R^{-4} interaction.

The single ion observed had a mobility of 0.35 cm²/v-sec. Other workers[23–25] have obtained mobilities of 0.39 and 0.41 cm²/v-sec for negative ions in SO_2^-. It is tempting to identify our ion as SO_2^-, but a detailed study of the temperature dependence would be necessary before doing so.

4. *Hydrogen Chloride*

As in the previous case, it seems unlikely that the interaction is of the R^{-4} type. As was noted in Sec. I,

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[43] A. V. Hershey, Phys. Rev. **56**, 908 (1939).

[44] K. B. Persson, *Proceedings Sixth Annual Conference on Gaseous Electronics* (Washington, 1953).

[45] E. J. Lauer, J. Appl. Phys. **23**, 300 (1952).

[46] A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, Cambridge, 1938).

[47] Calculated from the dielectric constant D, i.e., $\alpha(a_0^3)=2.07\times10^4(D-1)$, so as to include the contribution, to the R^{-4} term, of the permanent dipole moment.

[48] *Smithsonian Physical Tables*, Smithsonian Institution (1954).

the only negative ion which has been identified in HCl by previous workers is Cl^-. Charge transfer would not be expected to play a significant role if this were the ion in our experiment. The observed value of 0.71 ± 0.02 cm^2/v-sec is to be contrasted with that of 0.88 expected if Eq. (14) is applicable. This suggests that an orientation-dependent R^{-3} interaction is important in this case, so that the mobility should vary as $T^{1/6}$. If, however, these forces averaged out, so that only the R^{-4} term contributed, then the observed mobility of 0.71 ± 0.02 cm^2/v-sec would be accounted for by the presence of $(Cl\cdot 2HCl)^-$ clusters. We must also allow for the possibility that the initial Cl^- ions might form permanent clusters with highly polarizable impurities, such as water vapor, since it is impossible to achieve a high degree of gas purity by baking our apparatus. Information on the temperature dependence would clarify the situation.

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Cross Sections for the $Li^7(n,\gamma)Li^8$ Reaction

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The neutron radiative capture cross section of Li^7 was measured for neutron energies between 40 and 1000 kev and at thermal energy. The reaction was detected by observing the beta decay of Li^8 in a natural LiI crystal exposed to a flux of monoenergetic neutrons. The cross sections for the $Li^7(n,\gamma)Li^8$ reaction were obtained relative to the known cross sections for the $Li^6(n,t)He^4$ and the $I^{127}(n,\gamma)I^{128}$ reactions which also took place in the crystal. The $Li^7(n,\gamma)$ cross section decreases from a value of 50×10^{-6} barn at 40 kev to 5×10^{-6} barn at 1000 kev. A maximum in the cross section was found at 250 kev, corresponding to a known level in Li^8 at 2.28 Mev. The observed radiation width of this level was 0.07 ± 0.03 ev.

INTRODUCTION

RADIATIVE capture of neutrons by Li^7 leads to an unstable isotope, Li^8, which decays with about a 0.9 sec half-life by emitting electrons with a maximum energy of 13 Mev.[1] The residual nucleus, Be^8, further decays into two alpha particles in about 10^{-15} second. Since the spin and parity of the ground state of Li^8 are 2, even,[2] and the spin and parity of the ground state of Li^7 are $\frac{3}{2}$, odd, the excited state of Li^8 formed by *s*-wave neutron capture in Li^7 will decay to the ground state by electric dipole emission. Calculations of the cross section for this process have been made by Thomas[3] and his results predict a cross section which decreases smoothly with increasing neutron energy. However, a maximum in the capture cross section might be expected near 250 kev because of a resonance in the total cross section of Li^7 at this energy.[4] The 2.28-Mev state in Li^8, which is responsible for this resonance, has spin 3 and even parity and may decay to the ground state by magnetic dipole or electric quadrupole transition. Observation of an enhanced capture cross section in this energy region will give a measurement of the radiation width of the 2.28-Mev level in Li^8.

Capture of thermal neutrons by Li^7 was observed by Hughes, Hall, Eggler, and Goldfarb,[5] who obtained 33 ± 5 mb for the cross section and 0.89 ± 0.02 sec for the half-life of the Li^8 product nucleus. In a more recent experiment a cross section of 42 ± 10 mb for capture of thermal neutrons was reported by Koltypin and Morozov.[6] These authors also attempted to observe capture of fast neutrons and placed an upper limit of 0.25 mb on the cross section at 275 kev.

EXPERIMENTAL PROCEDURE

Monoenergetic neutrons were produced by bombarding solid lithium and gaseous tritium targets with protons from a 3-Mev Van de Graaff generator. With the lithium target, measurements at energies between 150 kev and 1000 kev were made with neutrons emitted in the forward direction, whereas the neutrons emitted at 120° to the incident proton beam were used below 150 kev. At neutron energies above 656 kev, the $Li^7(p,n)Be^7$ reaction produces a second group of lower energy neutrons. Corrections, which were always less than 10%, were made for the second group contribution to the counting rates. The $H^3(p,n)He^3$ reaction was

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