

TABLE I. Data on bond distances in OCS.

Constant	Value	Effect of uncertainty on	
		CO distance	CS distance
Atomic weight S ³²	31.9823 ± 0.00030	± 0.00002 × 10 ⁻⁸ cm	∓ 0.00002 × 10 ⁻⁸ cm
Atomic weight C ¹²	12.003861 ± 0.000024	± 0.00005	∓ 0.00004
Atomic weight O ¹⁶	16.0000		
Atomic weight difference S ³⁴ - S ³²	1.9957 ± 0.002	± 0.0047	∓ 0.0038
Mass of atom of unit atomic weight	(1.66035 ± 0.00031) × 10 ⁻²⁴ g	∓ 0.00011	∓ 0.00015
Planck's Constant	(6.6242 ± 0.0024) × 10 ⁻²⁷ erg sec.	± 0.00022	± 0.00030
Calculated values from the observed frequencies:			
Moment of inertia (S ³² molecule)	(137.9540 ± 0.0001) × 10 ⁻⁴⁰ g cm ²	± 0.000009	∓ 0.000005
Moment of inertia difference (S ³⁴ mole - S ³² mole)	(3.4564 ± 0.0003) × 10 ⁻⁴⁰ g cm ²	∓ 0.00075	± 0.00062
Probable error		± 0.0058	± 0.0049

first reported by us at the National Research Council Conference on Insulation in November, 1946.

The frequencies of these two absorption lines have since been measured more accurately by comparison with a harmonic of an oscillator which was heterodyned to zero beat with the 5-megacycle WWV National Bureau of Standards station as used by Good and Coles.⁵ The frequencies of the absorption lines can thus be determined to about one part per million. They are $f(\text{S}^{32} \text{ line}) = 24,325.92 \pm 0.02 \text{ Mc/sec.}$, $f(\text{S}^{34} \text{ line}) = 23,731.33 \pm 0.03 \text{ Mc/sec.}$ Unfortunately, because the nature of the calculation and the uncertainty of other constants necessary, all of this accuracy is not available in the two bond distances which may be calculated from these two frequencies.

In Table I there is a list of all the constants used in the calculation of the bond distances from the frequencies. The values of these constants, together with their uncertainties are given, and the effect of these uncertainties on the calculated bond distances is given. It will be observed that in most cases the effect of the error is in the opposite direction on the two bond distances so that their sum can be calculated more accurately than either separately. It was hoped that this very accurate frequency measurement would give a much more accurate value of the bond distance. An examination of Table I shows that the principal uncertainty is the difference in atomic weight of the sulfur isotopes. This contributes by far the largest amount to the uncertainty of the bond distance. The possible error in the frequency difference between the absorption line of the two isotopic molecules is the next largest uncertainty.

The bond distances C-O, $(1.1612 \pm 0.0058) \times 10^{-8} \text{ cm}$, and C-S, $(1.5604 \pm 0.0049) \times 10^{-8} \text{ cm}$ calculated here are the average interatomic distances in the lowest vibrational state. The atoms are assumed to be point masses and the centrifugal stretching has been approximated from the expressions given by Nielsen⁶ and the vibrational frequencies of Penney and Sutherland⁷ and found to be less than one part per million for the rotational levels involved here. The uncertainty in these bond distances can be reduced to about 0.1 percent when the difference in mass of the two sulfur isotopes is known to be better than

± 0.0001 atomic weight units. The isotope atomic weight values used were obtained from the table of Evans.⁸ The values of interatomic distances given here compare very well with the values obtained by Cross and Brockway from electron diffraction measurements: C-O = $1.16 \pm 0.02 \times 10^{-8} \text{ cm}$, C-S = $1.56 \pm 0.03 \times 10^{-8} \text{ cm}$.

¹ T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **70**, 560 (L) (1946).

² W. D. Hershberger, R.C.A. Review **7**, 422 (1946); J. App. Phys. **17**, 814 (1946).

³ W. E. Good, Phys. Rev. **70**, 213 (1946).

⁴ P. C. Cross and L. O. Brockway, J. Chem. Phys. **3**, 821 (1935).

⁵ W. E. Good and D. K. Coles, Phys. Rev. **71**, 383 (1947).

⁶ A. H. Nielsen, J. Chem. Phys. **11**, 160 (1943).

⁷ W. G. Penney and G. B. M. Sutherland, Proc. Roy. Soc. **156**, 654 (1936).

⁸ R. D. Evans, *Introduction to the Atomic Nucleus* (M.I.T. 1944).

High Energy Ions in Crystal Lattices

A. H. W. ATEN, JR.

Natuurkundig Laboratorium der N. V. Philips Gloeilampenfabrieken,
Eindhoven, Nederland

April 7, 1947

MANY complex anions are known to give rise to a Szilard-Chalmers effect when irradiated with slow neutrons.¹ In the case of a perchlorate, after neutron capture the activity is found entirely in the chloride fraction. This means more than the simple fact that the recoil separates the central chlorine from its surrounding oxygens. It is customary to consider the ClO_4^- ion as having a composition intermediate between the formulae Cl^+O_4 and $\text{Cl}^{7+}(\text{O}^{2-})_4$, but either all the activated chlorine is ejected as negative ions or, if part is ejected with a positive charge or as a neutral atom, it takes up electrons before it can react with any of the oxygen in the lattice. In other cases (e.g., arsenates and arsenites) the radioactivity is found entirely in ions of the same formula as those of which the crystal consists. Thus the capture of a neutron by a nucleus causes either a chemical reduction or it leaves the valency of the activated ion unchanged. Comparison between different reactions of this type is complicated by the fact that both the chemical conditions of atoms ejected by recoil and their chances of subsequent reactions depend on the crystal lattice.

In a note giving some preliminary figures,² it has been pointed out that the position is quite different in case the radioactive nucleus originates from an (n,p) or an (n,α) reaction. If fast neutrons of normal energy are used in such a process the kinetic energy of the recoil of the activated nucleus is very roughly 100 to 1000 times as large as the energy of a nucleus which has captured a neutron. Now this energy is not only sufficient to break the chemical bonds which connect the activated atom with the surrounding oxygens but even to strip it of many of its electrons during a series of collisions with neighboring particles. The highest positive charge which the activated atom attains will depend on the energy it has been given by the nuclear reaction and will be influenced very little by the composition of the lattice. In general, this highly charged ion will be very unstable chemically, and after

losing its excess energy it will settle down in the lowest energy state it can reach in the crystal. Which compound will be formed during this process will depend on the chemical composition of the lattice. This makes it possible to compare the fate of the same activated monatomic ion in different crystals. In general, we may expect to find the products of (n,p) and of (n,α) reactions in a highly oxidized state. Apart from this, a large concentration of oxygen in the lattice will favor the formation of oxygen-rich anions. On the whole, the results of the measurements in Table I are in agreement with these conclusions.

TABLE I. Valency of radiophosphorus from sulfur and chlorine with fast neutrons. Fraction of total radiophosphorus (in phosphate+phosphite+hypophosphite) found in phosphite+hypophosphite in different crystals.

Crystals irradiated	Fraction of P^{32} found in phosphite+hypophosphite
K_2SO_4	0.09; 0.10; 0.10
K_2SO_4 , dissolved in sulfite solution	0.09; 0.10
$Na_2SO_4 \cdot 10$ aq.	0.02; 0.02
$Na_2SO_3 \cdot 7$ aq.	0.50; 0.56
Na_2S hydrate	0.64; 0.78; 0.93; 0.93
$KClO_4$	0.01; 0.01
$KClO_3$	-0.01; 0.01
$MgCl_2$ hydrate	0.07
$MgCl_2$ hydrate dissolved in sulfite solution	0.02
$NaCl$	0.62; 0.68; 0.69

A radium-beryllium neutron source was used, and the irradiated products were dissolved in water containing phosphate, phosphite, and hypophosphite ions, and, in the case of potassium chlorate, ammonia. Separations were carried out as described by Libby, hypophosphite following the phosphite fraction. Although it remains to be investigated in how far the results depend on the time elapsed between the irradiation and the separation and on the temperature of the experiment, the good agreement between duplicates is sufficient proof of the reliability of the figures for comparative purpose (the value -0.01 found for $KClO_3$ was included in the table to give an idea of the degree of experimental accuracy). It is at present an open question whether the phosphate and phosphite ions are formed inside the lattice or whether they adopt their final state at the moment the crystal is dissolved. In this connection it is of interest that the presence of reducing sulfite ions does not influence the result.

In the $NaCl$ crystal the primary product will consist of chlorine-phosphorus complexes, which hydrolyze when dissolved in water. Evidently the presence of oxygen in the $MgCl_2$ hydrate crystal favors the phosphate formation. In the Na_2S hydrate crystal many different types of thiophosphates will be formed which do not hydrolyze as easily as the chloro compounds. Their fate during the chemical separations will depend on absorption processes and will be quite irreproducible, as is seen clearly in the table. These figures for Na_2S hydrate are, of course, without meaning.

¹ W. F. Libby, *J. Am. Chem. Soc.* **62**, 1930 (1940).

² A. H. W. Aten, Jr., *Rec. Trav. Chim. Pays-Bas.* **61**, 467 (1942). Analogous considerations concerning organic compounds have been published by Yankwich, Rollefson, and Norwick, *J. Chem. Phys.* **14**, 131 (1946).

A Note Concerning the Motion of Arc Cathode Spots in Magnetic Fields*

R. L. LONGINI

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

February 17, 1947

A NUMBER of observers¹⁻³ have reported that low pressure arc cathode spots, when in a magnetic field, move in a direction opposite from what one might expect by an application of Ampere's law to the interaction of the magnetic field and arc current. The following explanation is consistent with the field emission theory of cathode spots⁴ which requires a strong electric field at the cathode. This field is due to an excess of ions over electrons in the space between the plasma and the cathode. Electrons carry most of the current but, because of their relatively great velocity, have low density in this transition space⁵ and therefore make only a secondary contribution to the electric field at the cathode. As the field emission increases very sharply with field strength, the cathode-spot position will be that of the peak field. It will be shown that the electron space charge has a significant effect on the position of the field's peak, and therefore influences the cathode spot position.

Quantitative calculations of the effect of magnetic fields on cathode electric field intensity would require a thorough knowledge of space charge distribution. Since this is unknown, only a qualitative discussion will be given here. For simplicity of description, we shall assume independent electric fields at the cathode, one caused by ion space charge (ion field) and one caused by electron space charge (electron field) (ignoring interactions between these). Figure

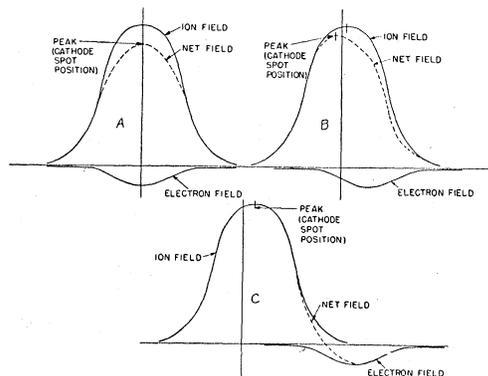


FIG. 1. Qualitative electric fields at the cathode surface. (Magnetic field into Paper.) Figure A—Zero magnetic field. Figure B—Small magnetic field. Shows retrograde motion of the peak field or cathode spot. Figure C—Large magnetic field. Shows the spot moving in the direction of the elementary particles.

1 shows the two fields and their sum, the net field, the peak of which determines the cathode-spot position.

Ions and electrons, having both opposite charges and directions of motion, will be deflected in the same direction by the magnetic field with the electrons being deflected hundreds of times farther than the ions because of their small mass. Thus when a small tangential magnetic field is applied, the average instantaneous position of the ions