S **73**. *Chemical Identity of the Sulphur Formed by the Slow Neutron Bombardment of Alkali Chlorides.*

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The sulphur produced by irradiation of potassium chloride with slow neutrons is shown to be present in the crystal lattice as sulphate ion or as some highly reactive ion which gives rise to sulphate in all aqueous solutions.

E. Buch-Andersen (*Z. physikal. Chem.*, 1936, **32**, *B*, 237) discovered that a long-lived sulphur isotope is formed by the neutron irradiation of carbon tetrachloride. He supposed this isotope to be ^{35}S, formed by an (*n*, *p*) reaction from ^{35}Cl. This assignment has subsequently been confirmed by Kamen (*Phys. Reviews*, 1941, **60**, 537), who compared the yields of ^{35}S obtained by the alternative modes of production ^{34}S (d, p) ^{35}S, ^{37}Cl (d, α) ^{35}S, and ^{35}Cl (n, p) ^{35}S. The same author showed that the latter reaction also occurs with thermal neutrons. Other investigators (Libby and Lee, *Physical Rev.*, 1939, **55**, 245; Levi, *Nature*, 1940, **145**, 588; Hendricks, Bryner, Thomas, and Ivie, *J. Physical Chem.*, 1943, **47**, 469; Henriques, Kistiakowsky, Margnétti, and Schneider, *Ind. Eng. Chem., Anal.*, 1946, **18**, 349; Libby, *Analyt. Chem.*, 1947, **19**, 2; Solomon, Gould, and Anfinsen, *Physical Rev.*, 1947, **72**, 1097; Albert and Wu, *ibid.*, 1948, **74**, 847; Berggren and Osborne, *ibid.*, 1948, **74**, 1240; Cook and Langer, *J. Physical Chem.*, 1948, **73**, 1149) have determined the half-life of the isotope, the absorption of its β-radiation in matter and, latterly, the β-ray spectrum. The isotope has been used (Cook and Langer, *loc. cit.*; Voge and Libby, *J. Amer. Chem. Soc.*, 1937, **59**, 2474; Voge, *ibid.*, 1939, **61**, 1032; Cooley, Yost, and Millan, *ibid.*, p. 2970; Tuck, *J.*, 1939, 1292; Cooley and Yost, *J. Amer. Chem. Soc.*, 1940, **62**, 2474) in a number of studies of the exchange between the sulphur atoms in sulphide, sulphite, sulphate, and thiosulphate ions and with the covalently-combined sulphur in compounds such as carbon disulphide.

The energy released by the nuclear reaction and the range of the protons emitted have been measured (Gibert, Roggen and Rossel, *Portugaliae Phys.*, 1944, **1**, 43). From these the energy of the recoiling sulphur atom can be calculated to be 15 Kev.

Carbon tetrachloride has commonly been used as the target material in the preparation of the isotope and Kamen (*loc. cit.*) showed that whilst some of the product is present as elementary sulphur some can be separated in thiocarbonyl chloride and similar compounds. The identity and distribution of active sulphur in these compounds and the effect of the addition of carbon disulphide have been studied by Edwards and his collaborators (*Nucleonics*, 1948, **2**, No. 6, 54; Edwards, Nesbett, and Solomon, *J. Amer. Chem. Soc.*, 1948, **70**, 1670). However, since solid materials are preferred for irradiation in the pile the alternative production by the irradiation of alkali-metal chlorides is of interest.

Earlier investigators, who prepared ^{35}S from alkali chlorides, record dissolving the target material in water, and oxidizing the solution with nitric acid before determining the active sulphur by precipitation on barium sulphate. More recently it was observed (Willard, Amer. Chem. Soc. meeting, April, 1947, Atlantic City; Edwards, unpublished, see ref. by Edwards and Davies, *Nucleonics*, 1948, **2**, No. 6, 54) that such oxidation was unnecessary since, in its absence, the same amount of activity was found on the barium sulphate. This observation led Edwards to suggest that the active sulphur is present in the alkali-chloride lattice in some form which reacts instantly with aqueous solutions producing sulphate ions.

Libby (*J. Amer. Chem. Soc.*, 1947, **69**, 2523) has singled out the irradiation of potassium chloride with neutrons producing ^{35}S for particular consideration in his analysis of the chemical effect of nuclear recoils. He points out the difference between the slowing-down processes for a recoiling atom and those for an ion. Although the fast-moving ion can become an energetic atom by electron capture, unless the velocity of the recoiling atom is of the same order of magnitude as that of an electron in the lowest energy level in the crystal, self-ionisation will not occur to any appreciable extent (Knipp and Teller, *Physical Rev.*, 1941, **59**, 659; Bohr, *ibid.*, 1941, **59**, 270). Thus for atoms of moderate atomic weight the energy must exceed 100 Kev. before self-ionisation plays an important part in the slowing-down process. Since the sulphur atom has an energy of but 15 Kev., the recoiling fragment, if it is an unchanged atom, will remain so while slowing down.

The slowing-down process for the neutral atom is considered in two stages. In the first, the average energy transferred at each collision is so large that the target atom is moved through the lattice. Libby suggests that this continues until the energy of the recoiling atom is less than half the heat of sublimation of the crystal, *i.e.*, about 5 ev. During this phase the recoiling atom travels through the potassium chloride lattice. Since the sulphur, potassium, and chlorine atoms have all about the same weight the necessary energy loss will require about 10—15 collisions. Thus the recoil atom will travel an average distance of, say, 4 lattice units, from its point of origin during the process. Subsequent cooling takes place more slowly by transfer of energy from the recoil atom to the vibrational energy of the surrounding atoms—a local fusion occurs, but the position of the recoiling atom does not suffer further change. Libby suggests that during this second stage the atom reaches a chemical equilibrium with its surroundings appropriate to the high local temperature.

Further consideration of the forces acting on the intruding active atoms in the lattice lead Libby to suggest that the active sulphur should migrate to the surface of the crystal on heating, so that baking the irradiated crystals might be a novel method of concentration of the activity. He also concluded that the active sulphur should exist in baked irradiated crystals as sulphide ions.

Various features of this model are open to criticism. Since the sulphur atom is recoiling in an ionic lattice, ionisation can occur by means other than self-ionisation, and the slowing-down processes will take place on sulphur ions so that electrostatic forces will play an important part.

Indeed, yet another mechanism for ionisation of the sulphur can be foreseen. If the sulphur were unaffected by the proton emitted at its birth, it would recoil as a S^{2-} ion which might become a neutral atom by ionisation; thus only the initial phase of the slowing-down process would be affected. However, McGee (*Phil. Mag.*, 1932, **13**, 1), Mund, Capron, and Jodogne (*Bull. Soc. chim. Belg.*, 1931, **40**, 35), and others have shown that the recoiling nucleus after α-particle emission carries an average positive charge of two. Thus it appears very possible that the proton emitted by the compound nucleus will give rise to a recoiling S^+ or S^{2+} ion.

When the sulphur atom has slowed down to thermal equilibrium with the surrounding atoms it is still very difficult to predict its ionic state in this condensed phase, especially while the crystal remains in the metastable condition indicated by the purple colour, owing to the *f* centres formed by the ionising radiations accompanying the thermal neutrons (and by the fast neutron flux).

Libby examines the electronic stability of a Sc^+ ion in the potassium chloride lattice. His arguments are probably invalidated for real crystals by the fortuitous presence of stoicheiometrically great excesses of oxidising and reducing agents; these may act as electron donors or acceptors and so permit further ionisation in the case under consideration or increase the negative charge in the case of the sulphur atoms. At the least, such a process might be operative at the temperatures required for relaxation of the *f* centres.

Some estimate of the stability of the various sulphur ions inserted in an ideal potassium chloride lattice can be made by considering cycles such as the following, which refers to the reaction $S^{2+} + Cl^- \rightarrow S^+ + Cl^\circ$ in the lattice. It can be assumed there is no possibility of combination of the chlorine atoms released in this reaction; thus the entropy change will be small and $\Delta F \approx \Delta H$. Let us remove the S^{2+} and Cl^- ions from the lattice, add an electron to the free S^{2+} ion, remove one from the Cl^- ion, and return the S^+ ion and Cl° atom to their original positions in the lattice. ΔH is thus equal to the sum of the energies required to remove the S^{2+} and replace the S^+ ion, the energies to remove the Cl^- ion and replace the Cl° atom, the difference of the first two ionisation energies of the sulphur atom and the electron affinity of chlorine. According to data given by Mott and Gurney (" Electronic processes in ionic crystals," Oxford, 1948), the energy required to abstract the chloride ion is 4·79 ev. (p. 61); the energy required to replace the chlorine atom is about -2 ev. (p. 98); the difference between the ionisation energies of the sulphur ions is -23 ev., the electron affinity of chlorine is $+3{\cdot}75$ ev. (p. 8).

Now the energy required to remove an ion from the lattice is equal to the sum of the electrostatic energy of the ion, the overlap or repulsion energy, and the polarisation energy. The first term is positive and the two latter terms are negative. Thus the energy difference on replacing the S^{2+} ion by a S^+ ion is equal to the difference in electrostatic energies of the two ions plus the difference in overlap and polarisation energies. The first term is about $\alpha_M \mathbf{e}^2/r_{s^+}$ or ~ 7 ev., where α_M is the Madelung constant for the potassium chloride lattice, r_{s^+} is the radius of the S^+ ion and $\mathbf{e}$ is the electronic charge. The second term in the difference is positive, because the repulsion energy depends on the ionic radius and the S^{2+} ion can be assumed to be smaller than the S^+ ion. The third term is negative, because the polarisation due to the S^{2+} is greater than that for the S^+ ion; it is probably greater than the second term by about 1 ev. Thus $\Delta F \approx \Delta H \approx 4{\cdot}8 + 3{\cdot}7 - 2 - 23 + 7 - 1 = \sim -11$ ev., the accuracy of the result being of the order of ± 2 ev. Calculations made for S^{2-}, S^-, S°, and S^+ ions suggest these ions are stable in the lattice, with the possible exception of S°. S^{2+}, S^{3+}, S^{4+}, S^{5+}, and S^{6+} can be shown to be probably unstable by similar calculations.

Such an analysis takes no account of the possible formation of covalent bonds to give complex ions, etc.

The experiments described below lead to the conclusion that the active sulphur is present in the potassium chloride lattice either as sulphate ions or in the form of highly reactive ions which give rise to sulphate ions in all aqueous solutions.

With the former conclusion it is difficult to explain the mode of oxidation of the sulphur: admittedly, even in the high vacuum the residual oxygen is stoicheiometrically sufficient to effect complete oxidation of the active sulphur at the concentrations concerned in these experiments (the irradiated salt contained about 10^{-9} g. of ^{35}S per g. of potassium chloride); but the gaseous oxygen probably does not penetrate the potassium chloride lattice very readily and the homogeneous distribution of activity shown by the photographic-plate experiments proves that the sulphur does not migrate to the surface of the potassium chloride crystals. Traces of inactive sulphur, in the form of sulphate ions, present in the potassium chloride as an impurity ($\sim 10^{-6}$ g. of S per g. of potassium chloride, as sulphate) do not provide any solution to the problem. The relatively low abundance and small capture cross section of the ^{34}S nucleus cause an insignificantly small fraction of the impurity sulphate ions to be activated. Further, it is improbable that the active sulphur atoms will all migrate to, and exchange with, the inactive sulphate ions. No such exchange reactions have been observed with sulphate ions and other sulphur molecules, atoms, or ions in solution, although this does not exclude the possibility of ready exchange between a sulphur atom or ion, possibly unknown in solution, and the sulphate ion under the field condition in the condensed crystal phase. But the low concentration of the impurity sulphate makes it improbable that the active-sulphur atoms would diffuse and exchange as completely as the experiments require.

The alternative conclusion is not readily confirmed or disproved and on the present evidence would appear the more attractive. Moreover, the possibility of a complex ion, involving covalent S–Cl bonds is not excluded.

The significance of the distillation experiments is uncertain, but, if the active sulphur is present as sulphate or converted into sulphate during heating, the effect might be due to the small dissociation pressure of the potassium sulphate at the temperature (~750°) of the sublimation. This hypothesis is supported by the absence of an active distillate when macroscopic quantities of potassium sulphate are added and by the duplication of the effects after dissolution of the salt. It is only at the very low concentration of sulphate represented by the active sulphur and the sulphate impurity ($\sim 10^{-6}$ g. of S per g. of potassium chloride) that an appreciable proportion of the active sulphate dissociates. On this hypothesis the distillate may be expected to consist of sulphur trioxide and possibly dioxide, which is consistent with the observed volatility at room temperature and fixation by potassium chloride.

The heat-treatment experiments fail to reveal any migration effects of the kind predicted by Libby; further, they appear to be without influence on the chemical behaviour of the active sulphur.

A satisfactory explanation of the behaviour of the sulphur in irradiated potassium chloride should also explain the following observation. Kamen (*Physical Rev.*, 1941, **60**, 537) has stated that, when ^{35}S is prepared by the (d, α) reaction from ^{37}Cl in rubidium chloride, 95% of the active sulphur could be removed as hydrogen sulphide by treatment with aqueous hydrochloric acid. The preparation is so closely analogous to that from potassium chloride that any detailed theory of the process should account for this difference.

These experiments are being extended to include the ^{35}Cl (n, p) ^{35}S reaction in all the alkali chlorides and in specially purified materials.

EXPERIMENTAL.

^{35}S was prepared by the irradiation of A.R. quality potassium chloride in the Harwell G.L.E.E.P. Irradiations were for 2 weeks, and the products were stored for more than a month before examination. Radiochemical analysis of the activity produced revealed the presence of only the natural potassium activity and a trace (about 0·1%) of active chlorine, due to the isotope ^{36}Cl.

A study of the absorption of the radiation in aluminium foils showed that barium sulphate obtained in an aqueous solution by direct precipitation of the target material was quite free from contamination by either of the above-mentioned activities after washing twice with warm water.

Measurements were made with a G.M.4 type Geiger–Müller counter with a window thickness of 4·7 mg. per sq. cm. In all the quantitative measurements the ^{35}S was separated on barium sulphate using inactive sodium sulphate equivalent to 3 mg. of barium sulphate as carrier. The precipitate was mounted in a uniform layer of constant area on a flat disc of aluminium foil. The absorption curve, which gave a range of 33·2 ± 1·5 mg. per sq. cm. for the β-radiation of ^{35}S, was in good agreement with that reported by Solomon, Gould, and Anfinsen (*Physical Rev.*, 1947, **72**, 1097).

The half-life was confirmed as 87 ± 0·8 days. Since it was intended that all quantitative measurements should be performed on barium sulphate samples, a self-absorption correction curve for ^{35}S in this material was prepared by precipitating aliquots of the active potassium chloride solution with varying amounts of barium sulphate. The correction curve obtained was in unexpected agreement with that calculated from the external mass absorption coefficient over the middle region of the absorption curve by neglecting back-scattering in the samples $[f = (1 - e^{-dt})/dt]$.

Previous results concerning the absence of exchange between the sulphur atoms in sulphate and sulphite, sulphate and sulphide, and sulphate and aqueous suspensions of sulphur at pH values between 6 and 9 were confirmed, and the extent of the exchange in experiments of 1 week's duration, at room temperature and with ~0·1M-reactants, was limited to less than 0·02%.

The first set of experiments was carried out with target material irradiated in powdered form (~100 mesh) and sealed in an aluminium tube in the presence of air. Identical activities were obtained on precipitating the ^{35}S on barium sulphate from equal aliquots of the potassium chloride dissolved in ordinary water, in de-aerated water with dissolution *in vacuo*, in nitric acid followed by boiling of the solution for 10 minutes (420 ± 5, 416 ± 4, and 421 ± 6 c. per min. per mg., respectively). Oxidation with alkaline hypobromite gave a similar result. The residual solution was in each case devoid of active sulphur. These measurements were made under counting conditions with an approximate efficiency of 2·5% for ^{35}S radiation.

Weighed samples of the potassium chloride were then dissolved in ordinary 0·1M-sodium sulphide and sodium sulphite, sodium sulphate solution equivalent to 3 mg. of barium sulphate was added, and finally the barium sulphate was precipitated by the addition of acidified barium chloride. In each case the barium sulphate precipitate contained substantially all the ^{35}S. In other experiments the solution was treated with phosphoric or hydrochloric acid, and the hydrogen sulphide or sulphur dioxide evolved on heating absorbed in a little bromine and nitric acid. Precipitation of the barium sulphate from this solution proved that less than 0·02% of the ^{35}S had separated in this treatment. The solution experiments were repeated with the dissolution of the potassium chloride in de-aerated sulphite and sulphide solutions *in vacuo*, but the results were the same. In addition, samples of the target material were treated, both alone and after grinding with a few mg. of calcium sulphide, sodium sulphide, and sodium sulphite, with phosphoric acid, and with hydrochloric acid. Treatment of the effluent gases as previously described showed that less than 0·05% of the ^{35}S was removed. Precipitation of copper sulphide from a solution of the irradiated salt in sodium sulphide and sulphate solution did not carry down any appreciable activity.

Samples of potassium chloride were then distilled *in vacuo* in to silica ampoules, which were sealed and irradiated in the pile. The ampoules were broken under solutions containing sulphite and sulphide carriers *in vacuo*, and the series of experiments described above were repeated. The results were the same. Further, the experiments were repeated on large irradiated crystals (about 5-mm. cubes) of potassium chloride, prepared from a potassium chloride melt, without disclosing any difference in behaviour.

The presence of active elementary sulphur was sought by grinding the irradiated potassium chloride with carbon disulphide containing a trace of dissolved sulphur and determining the activity of the solvent. Less than 0·02% of the ^{35}S activity was extracted. A similar result was obtained on solvent extraction of aqueous solutions of the irradiated salt. The experiment was repeated with the large irradiated crystals, an irradiated vacuum-sealed ampoule of the distilled potassium chloride being opened under a carbon disulphide–sulphur solution *in vacuo* and the contents shaken until the potassium chloride was reduced to a fine powder. The results were the same.

The effect of thermal relaxation was examined by heating the irradiated crystals *in vacuo* at 200° until the purple colour due to the *f* centres produced during the irradiation, was discharged. The product was tested for active sulphur, sulphide, and sulphite ions as previously described with the same results. Similarly, 2 hours' heating at 400° was shown to be without effect. The experiments were repeated on the unopened irradiated ampoules, with the same results.

However, by subliming the irradiated potassium chloride *in vacuo* in a silica tube a more volatile sulphur compound was produced. No activity could be removed from the potassium chloride by vacuum-distillation at room temperature; but, when about 90% of the potassium chloride was sublimed just below its m. p. ($\sim$750°) to the cooler end of a silica tube attached to a vacuum apparatus through a trap cooled in liquid nitrogen, about 75% of the active sulphur remained with the residual 10% of the potassium chloride, about 8% was found in the potassium chloride distillate, about 15% of the active sulphur condensed in the liquid nitrogen, and about 2% deposited on the wall of the tube between the chloride residue and distillate. The distribution of the active sulphur between the various fractions varied considerably with the conditions of the experiment, particularly with the rate of heating.

The active condensate in the liquid nitrogen was shown to be volatile at room temperature. When it was treated with solutions of sulphide and sulphate, or of sulphite and sulphate, $\sim$90% of the activity was found in the sulphate fractions. If the volatile material was condensed on finely-powdered sodium chloride or potassium chloride, it combined to give an involatile product. When the potassium chloride was ground with a few mg. of potassium sulphate before distillation, no activity was found in the liquid-nitrogen-cooled trap; nor was any macroscopic concentration of sulphur compounds detectable by oxidation of the contents of the trap with bromine and precipitation as sulphate by barium chloride solution. Similar results were obtained with the vacuum-irradiated material. Further, the same behaviour was observed after dissolution of the potassium chloride in water and evaporation of the aqueous solution to dryness.

The macroscopic sulphate content of the potassium chloride was determined by dissolving 10 g. of the solid in 100 ml. of water, adding 2 ml. of 4N-hydrochloric acid and 2 ml. of 0·4M-barium chloride, keeping the mixture for 24 hours, and comparing with a control mixture. Lack of turbidity or precipitate indicated less than 1 p.p.m. of sulphate.

The distribution of activity in a number of larger irradiated crystals was examined by placing them on a photographic plate. Exposures were made in which the original surface of the crystal was pressed on the plate, and others in which a new surface, prepared by splitting the crystal, was in contact with the plate. In each case the blackening of the plate was quite uniform. Similar results were obtained with thermally relaxed crystals.

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