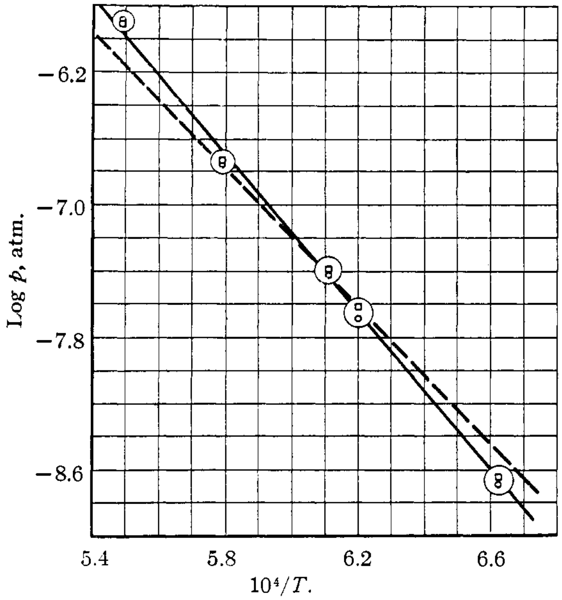

Fig. 1.—Vapor pressure of titanium: O, resistance change; □, weight loss; large circles, ±10° temperature. The full curve is that of Equation (7). The dashed curve is from Equation (6) of Carpenter and Reavell.

and the free-energy functions for titanium vapor as given by Latimer,[12] lead to vapor pressures which may be expressed to within 2.5% by the equation

$$\log p \text{ (atm.)} = 6.255 - (22{,}110/T)$$

The calculated boiling point is 3535°K.

It has been observed in this Laboratory that at the temperatures encountered in the present work, oxygen and nitrogen diffuse very rapidly into titanium, forming solid solutions. This fact greatly reduces the possibility of an error encountered with many metals using the Langmuir technique, *i. e.*, a lowering of the rate of evaporation by surface oxide or nitride films. The impurities in solid solution with the titanium used in the present work, a maximum of 0.005 mole-fraction, would reduce the vapor pressure of pure titanium, and might yield observed values roughly 99.5% of the true values. This difference is insignificant relative to experimental error.

Acknowledgment.—It is with gratitude that the authors acknowledge the financial aid of the Iodine Educational Bureau, Inc., in carrying out this work. The interest of Mr. A. C. Loonam[13] is gratefully acknowledged. His independent interpretation of the vapor-pressure data resulted in a ΔH_0^0 value but 160 cal. above that of the authors.

Summary

The vapor pressure of solid titanium has been determined in the range 1500–1800°K. by measuring the rates of evaporation of titanium wire using the Langmuir technique. The data fit the thermodynamic requirements quite well and yield heats of sublimation of 111,000 cal. at 0°K. and 111,700 at 298.2° K. The resulting equation for the vapor pressure of solid β-titanium, valid over the range 1200–2000°K., is $\log p$ (atm.) = 7.782 − $(24{,}275/T) - 0.230 \times 10^{-3}\, T$.

The data may be extrapolated to yield an equation for the vapor pressure of the liquid: $\log p$ (atm.) = $6.255 - (22{,}110/T)$, leading to a normal boiling point of 3535°K.

The data agree over a limited range with the incomplete experimental results of Carpenter and Reavell. Their equation for the rate of evaporation of titanium has been shown to be inconsistent with other available thermodynamic data.

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(12) Wendell M. Latimer, "Tables of Free-Energy Functions for Elements and Compounds in the Temperature Range 2000–5000°K." MDDC-1462, U. S. Atomic Energy Commission, Sept. 10, 1947, p. 4.

(13) Deutsch and Loonam, Consultants, 70 E. 45th Street, New York 17, N. Y.

Columbus 1, Ohio Received June 6, 1949

[Contribution from the Department of Chemistry, The Johns Hopkins University]

The State of Oxidation of S^{35} Formed by Neutron Irradiation of Potassium Chloride

By W. S. Koski

When potassium chloride is irradiated with thermal neutrons the following is one of the reactions that takes place

$$Cl^{35} + n \longrightarrow S^{35} + H' + Q$$

The Q of this reaction as estimated from the masses is 0.63 mev. From simple considerations of conservation of energy and momentum, one can estimate the energy of the recoiling sulfur fragment as equal to 17.6 kev. Since it is believed[1,2] that ionization by a rapidly moving particle is probable only at velocities comparable to the effective velocities of free electrons, the recoiling sulfur fragment will produce no appreciable ionization by the process of electron ejection and capture. However, the irradiated chlorine is an ion in the crystal lattice, and the proton on leaving the compound nucleus will reduce the nuclear charge by +1 leaving the residual sulfur fragment with a double negative charge. This charge may be reduced by electron capture by the proton as it moves through the electronic field of the sulfur fragment. Such

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(1) H. A. Bethe, *Rev. Mod. Phys.*, **9**, 262–265 (1937).

(2) J. Knipp and E. Teller, *Phys. Rev.*, **59**, 659 (1941).

considerations would lead one to believe that the sulfur activity should be present as sulfide ion or possible elementary sulfur. This seems to be contrary to observation,[3] since it has been reported that the sulfur activity appears in its highest state of oxidation rather than in its lowest. We thought it might be of interest to investigate this apparent contradiction, especially since this information was very pertinent to another problem that we have under investigation.

Experimental Details

Materials.—All of the chemicals used in this work were of a C. P. grade, and unless otherwise stated were used as commercially available with no further purification. The water that was used as a solvent was freshly distilled, having a specific conductance of 1-2 × 10^{-6} mho. The alcohol was absolute and taken from a freshly opened container and no further attempts were made at purification.

Preparation of Carbonyl Sulfide.—The carbonyl sulfide that was used in this work was prepared[4] by the reaction of carbon monoxide with an excess of sulfur at 425° for sixteen hours. The carbon monoxide was prepared from oxalic and concentrated sulfuric acids. The water and carbon dioxide were removed with liquid nitrogen.

Separation of Carriers.—During the course of this work it was necessary to separate various combinations of carriers. Mixtures of sulfide and sulfate or sulfite and sulfate ions were separated by acidifying the solutions and distilling the resulting hydrogen sulfide or sulfur dioxide, and whenever necessary the gas samples were collected and oxidized with bromine and nitric[5] acid and precipitated as barium sulfate. Whenever mixtures of sulfide, sulfite and sulfate ions were used they were prepared just before use and always in alkaline solutions in order to avoid complications by reactions between sulfides and sulfites. In these cases the separations were performed by precipitating the sulfide by adding appropriately acidified copper chloride solution. The resulting copper sulfide was oxidized to the sulfate and the sulfate precipitated as barium sulfate. The sulfite ion was separated by distillation, collected, oxidized and precipitated as barium sulfate. In addition to using copper for the sulfide separation, lead acetate was used following the procedure of Bassett and Durrant,[6] thus enabling us to make the separation directly in the 2 *N* sodium hydroxide solution. The same results were obtained with both methods of separation.

Pre-irradiation Treatment of Potassium Chloride.[7]—In view of the nature of this experiment it was considered desirable to remove as much oxygen and water from the potassium chloride sample as possible. The potassium chloride was put into a quartz container and attached to a high vacuum system. The sample was then heated to a temperature of approximately 700° for sixty hours. The system was pumped on with an oil diffusion pump backed by a suitable mechanical pump, and at the conclusion of the heating treatment the pressure in the system with the heat on was better than 10^{-5} mm. The sample was permitted to cool, and then 15 cm. of purified carbon monoxide was admitted, the container was sealed and the sample was irradiated in the Oak Ridge pile.

Treatment of the Irradiated Samples.—The quartz vessel containing the irradiated potassium chloride sample was sealed on to a vacuum system. A portion of the carbon monoxide atmosphere in which the potassium chloride was bathed was put into a gas counter and tested for activity. The gas was radioactive but none of it was condensable in liquid nitrogen. A portion of this carbon monoxide was then mixed successively with sulfur dioxide, carbonyl sulfide and sulfur monochloride, and on separation of the condensable gases with liquid nitrogen only traces of activity were found in the condensed gases.

The potassium chloride container was then opened in a dry nitrogen atmosphere and some of the crystals were dissolved in water containing traces of carrier ions or, if necessary, in carrier-free alcohol. The various experiments discussed were performed with 5-cc. portions of these solutions.

Preparation of Radioactive Samples for Measurements.—All the sulfur samples that were measured for radioactivity were oxidized to the sulfate and precipitated as barium sulfate. The precipitates were then collected on one-inch filter papers in a Hirsch funnel, washed with water, acetone, dried, mounted and examined for activity with a Geiger–Müller counter. In all cases the amounts of sulfate present were adjusted so that all of the samples compared had the same amount of barium sulfate.

The activities of gaseous samples were measured by fitting a small gas cell over the mica window of the counter. This cell was pumped out, and then the gas to be tested was admitted and measured for activity.

Discussion of Results

Untreated Potassium Chloride Samples.—When a sample of potassium chloride which has had no outgassing treatment is irradiated with neutrons and then dissolved in a water solution containing sulfide, sulfite and sulfate ions as carriers, it is found that on separation of the carriers practically all of the activity is present as sulfate. This observation is in agreement with the results of Willard mentioned earlier.

One of the most obvious ways of oxidizing sulfur is by reaction with atmospheric oxygen. However, experience with reactions of macro amounts of sulfur and oxygen indicate that the tetravalent state of sulfur should be expected. This, however, is not a serious objection since the sulfur formed in the body of the crystal is in an unusual habitat, and it might well undergo oxidation to the hexavalent state through a heterogeneous catalytic process. Furthermore, the S^{35} at the moment of its creation is in a high state of electronic excitation and may well react with any oxygen present to form sulfur trioxide.

During the course of irradiation of the crystals elementary chlorine is formed and the sulfur fragments would be oxidized through the formation of such compounds as sulfur mono- and dichlorides. On hydrolysis, however, these compounds lead to sulfite rather than sulfate ions.

There is, of course, the possibility that some of the free chlorine formed during the irradiation may bring about oxidation of the sulfur when the sample is brought into solution. Experimental results that will be cited later indicate that very little of the oxidation is actually brought about by this mechanism.

If one tentatively takes air oxidation as the explanation for the presence of hexavalent sulfur it remains to be shown that potassium chloride

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(3) John E. Willard, Conference on the Chemical Effects of Nuclear Transformations at Brookhaven National Laboratory, August 19, 20 (1948).

(4) G. N. Lewis and W. N. Lacey, THIS JOURNAL, **37**, 1976 (1915).

(5) Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, 1937, New York, N. Y., p. 320.

(6) H. Bassett and R. G. Durrant, *J. Chem. Soc.*, 1401 (1927).

(7) This phase of the work was carried out at Brookhaven National Laboratory in collaboration with Dr. V. W. Cohen.

crystals can occlude reasonable amounts of foreign gaseous substances. Experimental studies[8] have shown that potassium, thallium and the halogens can be incorporated in alkali halide crystals. From such work it appears reasonable that the crystals in question can contain appreciable amounts of a gaseous substance such as air. The oxygen in a potassium chloride crystal may be present there as a result of two processes (1) diffusion and (2) incorporation in the crystal during the formation of the crystal from a solution. The latter is probably the most effective mechanism since diffusion of gases into solids is slow at ordinary temperatures; consequently only the surface layers would contain atmospheric oxygen which arrived through diffusion and absorption, whereas the body of the crystal would have oxygen which was probably introduced during crystal growth.

S^{35} from Outgassed Potassium Chloride.—In a number of experiments on a certain sample of outgassed and irradiated potassium chloride it was found that about 64% of the total sulfur activity present was in the hexavalent state and the remainder in a lower state. Essentially the same value was obtained even if the amounts of carriers were varied, indicating that there was no exchange between sulfide and sulfate or between sulfite and sulfate complicating the picture. This observation on the exchange is in agreement with the prior work of Voge and Libby.[9] It might be mentioned that different samples of potassium chloride varied widely as to per cent. activity present as sulfate. Some irradiated crystals have been obtained with as low as 15% of total activity present as sulfate. There are also indications that not even all of the individual crystals that have been irradiated simultaneously in the same container have the same per cent. total activity as sulfate. Only a few experiments have been done in this connection, but an indication has been obtained that the larger crystals have a much greater percentage of activity present as sulfate than the smaller crystals. This may not be too unexpected since a larger crystal would require more prolonged pumping and more severe outgassing conditions to remove its occluded oxygen.

Behavior of Trace Amounts of Sulfur Compounds in Solution.—It may be appropriate to comment at this point on the behavior of sulfur compounds in solution. If some potassium chloride crystals containing 63% of the activity as sulfate are put into ordinary distilled water from which no pains were taken to remove air and then carriers of sulfide and sulfate are added and separated, it is found that all of the activity appears as sulfate ion. If, on the other hand, the crystals are dissolved in a solution of sulfite and sulfate carriers and then some sulfide carrier is added, analysis shows that the activity is now 63% sulfate and 37% sulfite with the sulfide ions carrying no activity. Apparently the activity that was present as sulfide ions in trace amounts is rapidly oxidized to sulfite ion, and further rapid oxidation is prevented by the presence of macro amounts of sulfite carrier. As a result of a number of such experiments it was concluded that in general if the irradiated potassium chloride crystals were dissolved in distilled water from which air had not been removed the trace amount of radiosulfur is oxidized to the chemical form of the carrier having the lowest oxidation state. If no carrier or if only sulfate ion is present as a carrier the radiosulfur goes up to the hexavalent state. Water solutions of radiosulfur could be kept for hours without appreciable oxidation if care was taken to exclude atmospheric oxygen. This observation leads us to conclude that the free chlorine present in the crystal as a result of irradiation is not producing oxidation of the sulfur on solution of the crystal. It was found that if a potassium chloride crystal was dissolved in alcohol there was no oxidation even if the solution was kept for weeks. If a portion of the alcohol solution was put into distilled water containing dissolved air the sulfur compounds did oxidize with a half-time of about thirty minutes for 50% of the sulfide to be oxidized to sulfate. On the other hand, if the crystal was dissolved directly in a portion of the same water, the oxidation was complete in less than three minutes, indicating that in the presence of solid potassium chloride the oxidation is much faster and may be well a heterogeneous process on the surface of the crystal.

State of Oxidation of the Non-Sulfate Sulfur.—The results obtained for three samples of outgassed and neutron-irradiated potassium chloride crystals are summarized in Table I. These samples are not strictly comparable since sample number 2 was outgassed at a somewhat higher temperature than number 1 and sample number 3 was composed of very small crystals selected from sample number 2 after irradiation.

TABLE I

ACTIVITY IN CARRIERS

Carriers	Sample no.	Sulfide	Sulfite	Sulfate	Total activity	% activity as sulfate
Sulfide, sulfate	1	396	...	750	1160	64.6
Sulfite, sulfate	1	...	403	776	1194	64.9
Sulfide, sulfite, sulfate	1	430	36	755	1200	63
Sulfide, sulfate	2	780	...	465	1270	36.6
Sulfite, sulfate	2	...	630	430	1080	39.8
Sulfide, sulfate	3	602	...	121	758	16
Sulfite, sulfate	3	...	673	105	802	13

It is clear from these results which are representative of a number of such experiments that very little of the activity is present in the form of sulfite ion. It is felt that a safe upper limit is

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[8] R. M. Barrer, "Diffusion in and through Solids," Cambridge University Press, 1941, p. 110.

[9] H. H. Voge and W. F. Libby, This Journal, **59**, 2474 (1937).

5% and very probably the figure is lower than this. The small amount of activity present in the sulfite may actually be due to a slight solution of the copper sulfide in the acid that was present or there may be a small amount of reaction between sulfide and sulfite ions. In the case of precipitation of the sulfide in strongly alkaline solution, no reaction between sulfide and sulfite is to be expected but here also a small residual activity seemed to be present in the sulfite carrier, although there was some indication that it might be less than that found in the former case. Normally one would expect the oxidation of sulfur to stop at sulfur dioxide, but as has been already pointed out, the conditions under which the sulfur finds itself in the crystal are far from normal and apparently when oxidation does occur it goes up to the hexavalent state.

The small amount of activity present as sulfite has an additional significance. It means that no appreciable portion of the recoiling sulfur fragments formed in the nuclear reaction Cl^{35} (*n.p.*) S^{35} react chemically with chlorine to form such compounds as SCl_2, S_2Cl_2, etc., for such compounds on hydrolysis give sulfur dioxide. Likewise the absence of sulfite activity indicates the absence of thionates and polythionates.

These various results indicate that the nonsulfate sulfur is either in the form of elementary sulfur or sulfide ions. Attempts to distinguish between sulfur and sulfide ions were unsuccessful because of the rapid exchange that exists between these two states of sulfur in solution.

Heating irradiated potassium chloride crystals above the melting point in an atmosphere of carbon monoxide failed to produce any carbonyl sulfide. This observation would indicate that little or no free sulfur was present, but admittedly this evidence is not too good since under such drastic treatment and in such an unusual habitat free sulfur if present may well undergo some chemical transformation.

Acknowledgment.—The author wishes to express his appreciation to Professor R. D. Fowler for many illuminating discussions which were extremely helpful during the course of this investigation. It is also desired to acknowledge the coöperation of various members of the staff of the Brookhaven National Laboratory where the initial phase of this work was carried out.

Summary

The state of oxidation of S^{35} formed by neutron irradiation of potassium chloride depends on the pre-irradiation treatment of the crystals. If the crystals were carefully outgassed by heating and pumping the radioactive sulfur appeared in part either as sulfur or more probably as sulfide ion. If no precaution was taken to remove air from the crystals all of the S^{35} appeared in the hexavalent state. In all cases tested there was always some activity present as hexavalent sulfur and in the most favorable situation as little as 15% of the total sulfur activity was present in the highest oxidation state. It is concluded that atmospheric oxygen which is occluded in the crystal is responsible for the hexavalent state of the radio sulfur.

BALTIMORE, MARYLAND RECEIVED MAY 5, 1949

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, AND BROOKHAVEN NATIONAL LABORATORY]

Infrared Spectra of Ortho-, Meta-, Para- and Omega-Monodeuterotoluenes in the 2–16 Micron Region[1a]

BY JOHN TURKEVICH,[1] HUGH A. MCKENZIE,[2] LEWIS FRIEDMAN AND ROBERT SPURR[3]

In connection with studies being carried out on the mechanism of exchange reaction between deuterium and aromatic compounds, it was found necessary to investigate the infrared spectrum of the monodeuterotoluenes. The present paper contains information on the preparation of these compounds and the infrared spectrum in the 2–16 micron region.

Preparation of the Compounds

The various monodeuterotoluenes were prepared by deuterolysis of the appropriate Grignard reagent. The latter was made using the procedure and apparatus of Weldon and Wilson.[4] After the formation of the ether solution of the Grignard reagent, it was connected to a vacuum system and most of the ether was distilled off. It was found preferable not to remove the ether completely since complete removal would make it extremely difficult to effect the reaction between the Grignard compound and the heavy water. The reaction flask was cooled in a Dry Ice–acetone-bath and the heavy water was added dropwise. The system was then allowed to warm up slowly overnight. The reaction mixture was shaken vigorously and then allowed to stand for at least twenty-four hours. The hydrocarbon and remaining ether were removed from the flask

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[1] Consultant, Brookhaven National Laboratory.

[1a] Research carried out, in part, under the auspices of the Atomic Energy Commission.

[2] Visiting Fellow at Princeton University of the Australian Council for Scientific and Industrial Research.

[3] Visiting Assistant Professor, Princeton University.

[4] L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, 235 (1946).