APPLICATIONS OF ISOTOPES
TO
CHEMICAL PROBLEMS

Thesis by

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SUMMARY

In the first part of this thesis is described research in nuclear physics on radioactive isotopes of barium, cesium, and bismuth. Isotopes of barium and cesium were chemically identified and their properties were determined.

The second part consists of studies of exchange reactions involving the following radioactive elements: sulfur, phosphor~~o~~us, bromine, iodine, and vanadium. Rate of reaction measurements were made. The kinetics of the exchanges were considered, and interpretation of the exchanges in terms of the structure and nature of the reactants was made where possible.

The solution of a problem for the National Defense Research Committee, which is of a confidential nature, is submitted as the third part of this thesis.

The fourth part contains miscellaneous studies. The structural parameters of thionyl bromide were determined by electron diffraction experiments. Experience was gained in rare earth inorganic chemistry by preparative work and observations on the very interesting bivalent state of europium.

PART I

NUCLEAR REACTIONS OF CESIUM AND BARIUM*

Introduction

Nuclear reactions of cesium were chosen for study because early work had not chemically identified possible cesium isotopes critically enough and because deuteron and gamma-ray bombardment of cesium had never been reported. Beta decay of cesium yields barium. Therefore, some radioactive barium isotopes were examined and chemically identified to establish possible relationships between barium and cesium isotopes.

It was the purpose of this research to investigate, with the aid of chemistry, nuclear reactions caused by the irradiation of cesium with deuterons, fast neutrons, slow neutrons, and gamma-rays and by the irradiation of barium with deuterons and neutrons.

State of Knowledge Concerning Cesium in May, 1938

Aston[1,2] has shown that cesium is one of the twenty-one elements consisting of a single stable isotope. The

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*This research was carried out in cooperation with Dr. D. C. Kalbfell at the University of California Radiation Laboratory during the summer of 1938.

fact that the mass number was 133 led Latimer, Hull and Libby[3] to think that cesium might be an exception to the rule, (1935) "all cases of radioactivity induced by neutron bombardment show beta-ray activity". Their reasoning was based on the fact that at that time* Ba^{134} was not known to exist as a stable isotope while Xe^{134}, the product nucleus if Cs^{134} should emit a positron, was known to exist. They bombarded cesium nitrate encased in paraffin with a 150 millicurie radon source. The activity produced was chemically that of cesium, beta particles were emitted, and the half-life was about 100 minutes. However, the activity produced was not intense enough to afford accurate determination of the half-life.

Amaldi, D'Agostino, Fermi, Pontecorvo, Rasetti and Segre[4] had earlier found that cesium tartrate showed a weak activity on neutron bombardment but the half-life was not measured with accuracy. McLennan, Grimmett, and Read[5] exposed cesium nitrate to neutrons and estimated the half-life to be in the neighborhood of 75 minutes. Dopel[6] reported the rather surprising observation that alpha particles from cesium chloride that had been irradiated with neutrons could be detected by a scintillation screen. He observed a half-life period of about two

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*Ba^{134} has since been shown to constitute 2.42% of ordinary barium.

minutes for the alpha particles, whose range he found to be about two centimeters in air. This nuclear reaction would scarcely be predicted and is doubtless a spurious observation since neither our work nor that of Funfer[7] was confirmatory.

The principal factor that kept the radioactivity of cesium in an unsatisfactory state was the lack of a sufficiently strong neutron source to obtain reasonably active samples.

Experimental Part

For deuteron bombardment, samples of cesium nitrate were glazed onto a knurled copper target which was placed in the 37 inch Berkeley cyclotron. Barium in the form of the metal was mounted on the target for deuteron bombardment.

Slow neutron bombardment was obtained by exposing the target element encased in paraffin to the neutrons from the cyclotron when lithium or berylium was bombarded with deuterons. For fast neutron bombardment the target element was placed in metallic cadmium boxes or in boxes of borax and exposed to neutrons from the cyclotron.

The source of gamma rays was proton bombardment of lithium in the cyclotron.

Measurements of radioactivity were made either with a Lauritsen electroscope or a freon-filled ionization chamber connected to a FP54 circuit.

Bombardment of Cesium. After a copper target supporting about ½ gram of $CsNO_3$ had been irradiated with about 40 microampere hours of 8 Mev deuterons, it was removed from the cyclotron. The $CsNO_3$ was washed off the copper target into a carrier solution containing about one millimole of each of the following elements: Li, Na, K, Rb, Cu, Ag, Hg, Fe, Zn, Zr, Ca, Ba, Sr, Ce, Yt. These elements were selected as carriers after consideration of all possible contaminants that might have initially been present in the c.p. cesium nitrate or introduced in the target chamber or formed by nuclear reactions. In accordance with the Noyes and Bray system of analysis[8], all elements were removed from solution until there remained only the alkalies. Potassium, rubidium and cesium perchlorates were collected by the Noyes and Bray procedure and converted to chlorides by ignition. Addition of silicotungstic acid according to the method worked out by O'Leary and Papish[9] yielded a precipitate of cesium, free of rubidium and potassium.

Deuteron bombarded cesium thus chemically purified was found to emit beta-rays of 1 Mev (upper limit) by absorption measurements and decayed with a 3 hour half-life as shown in Fig. 1 and Fig. 4.

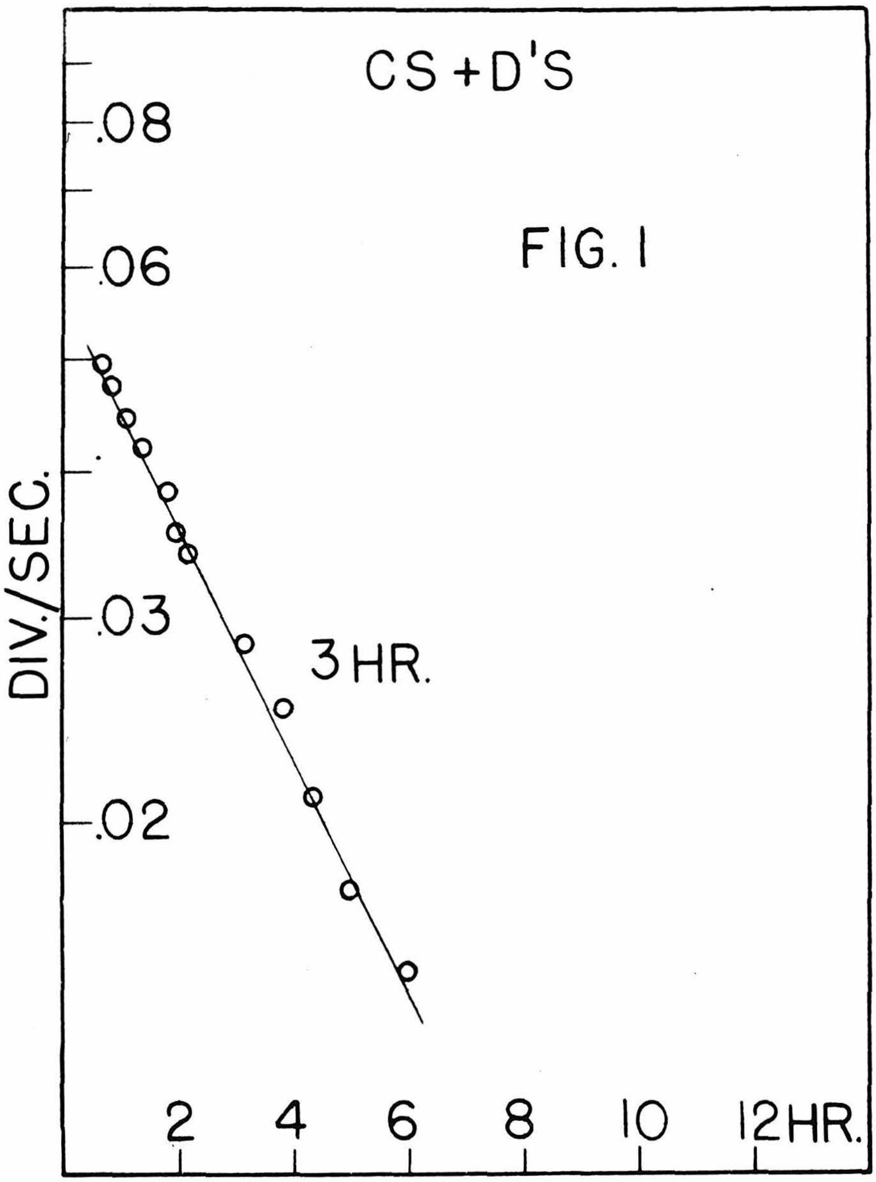


FIG. 1

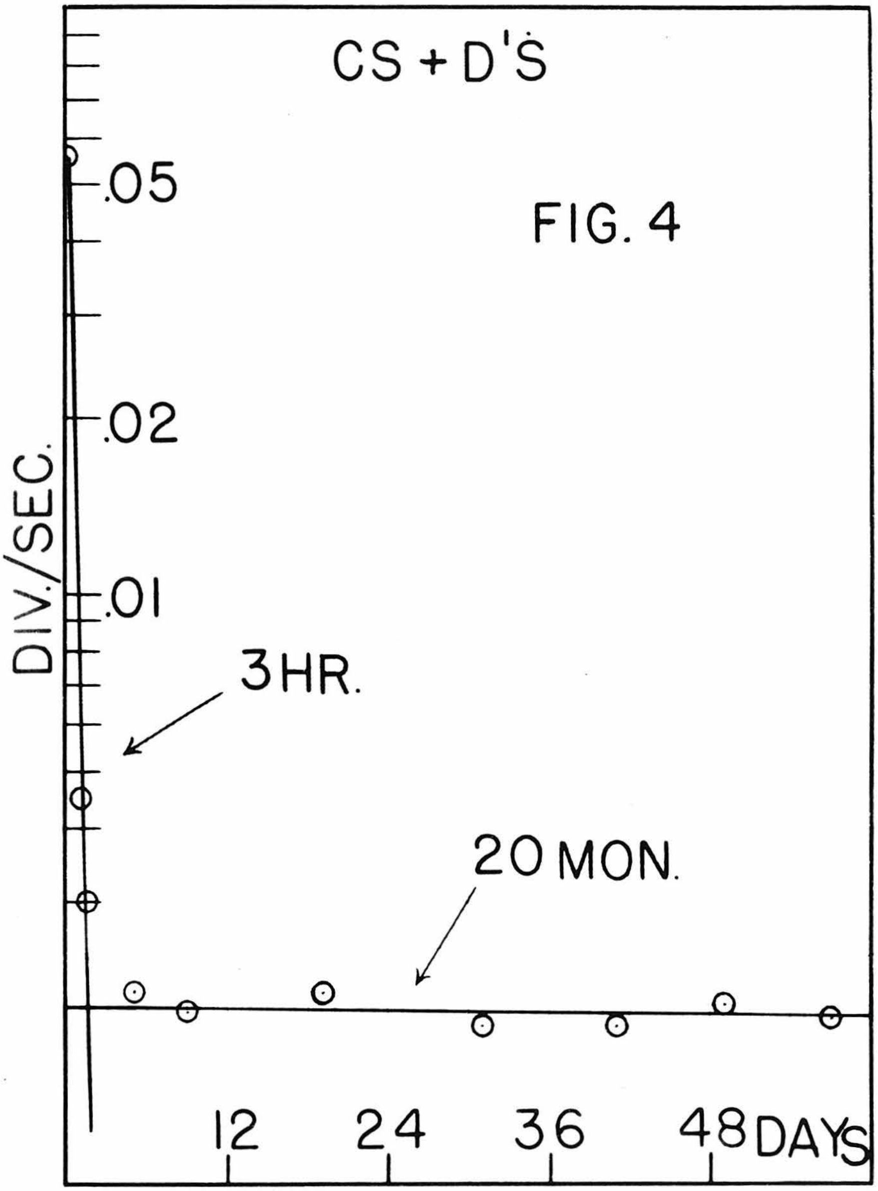


FIG. 4

Fig. 4 shows how the long period (20 months) isotope appears after the short period dies out. The long period activity was identified as cesium by chemical treatment as above of a deuteron bombarded sample after the short period had become negligible.

The long period cesium isotope has a normal beta-ray spectrum with an upper limit of .9 Mev. Careful search by absorption experiments did not reveal any soft monochromatic electron groups. An x-ray of about the correct ($\sim$ 32KV) energy to be a Cs or Xe $K\alpha$ x-ray was found by absorption experiments. The x-ray was not definitely identified with critical absorbers.

Since there is only one stable isotope of cesium known, it must be concluded that this long period isotope is isomeric with the 3 hour period (Cs^{134}) because both are found to be chemically cesium and are formed with slow neutrons and with deuterons.

Fig. 3 shows the decay with time of two cesium nitrate samples after exposure to slow neutrons. The half-life indicated is 3 hours.

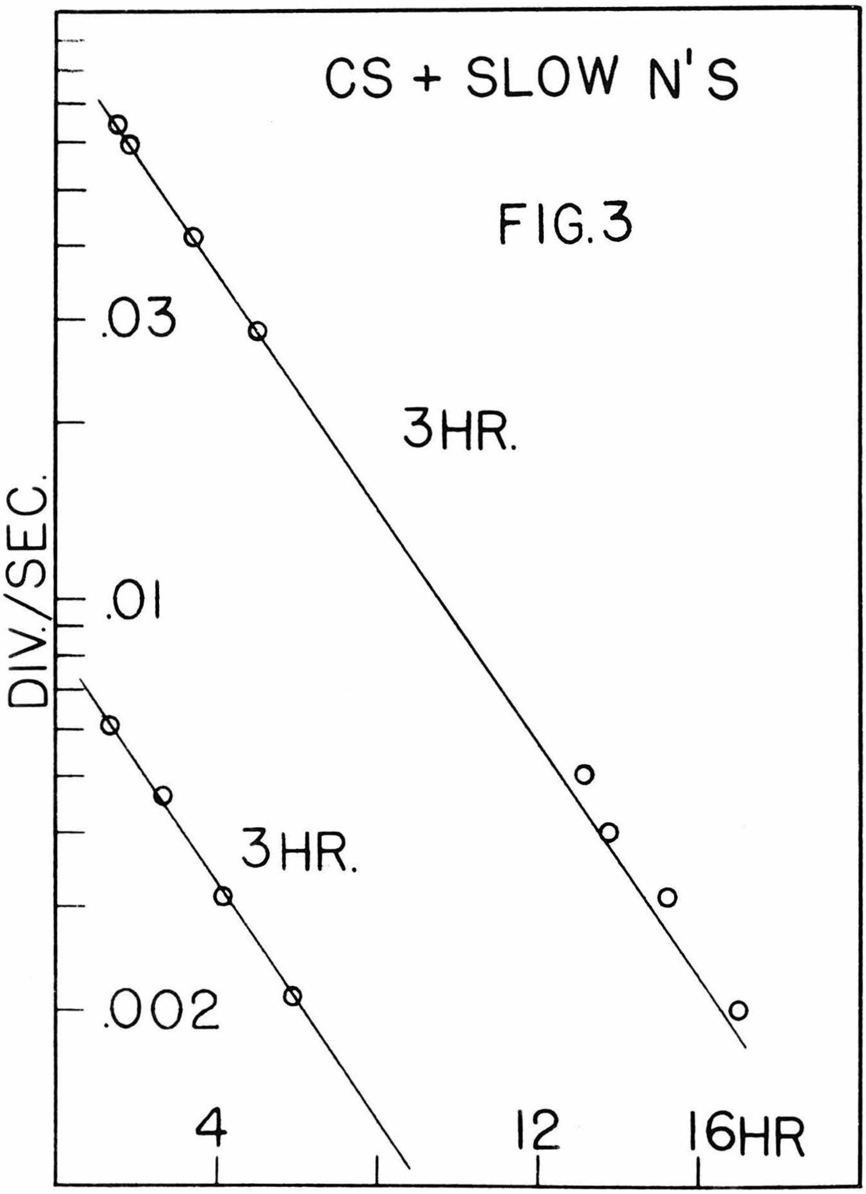


FIG.3

Fig. 2 shows a decay curve of $CsNO_3$ bombarded with fast neutrons. The period indicated is 3 hours.

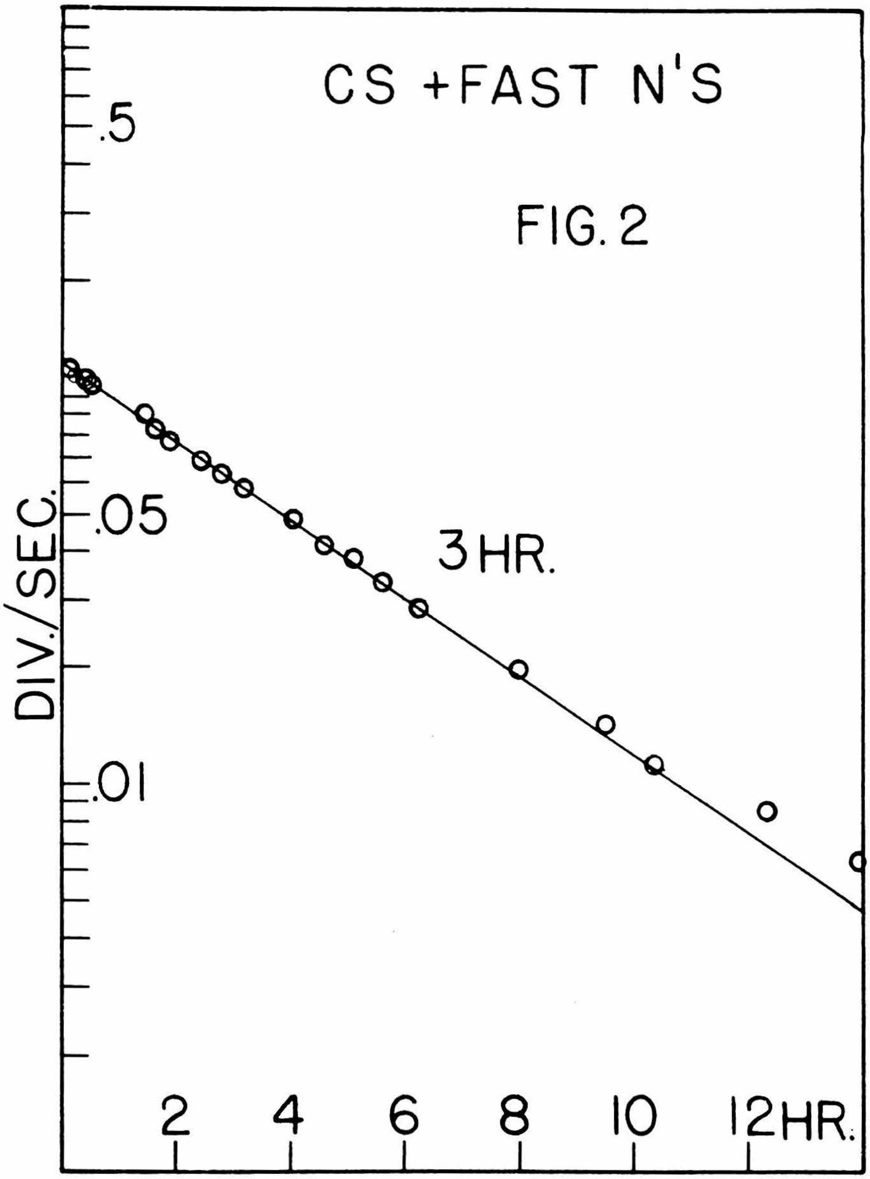


FIG. 2

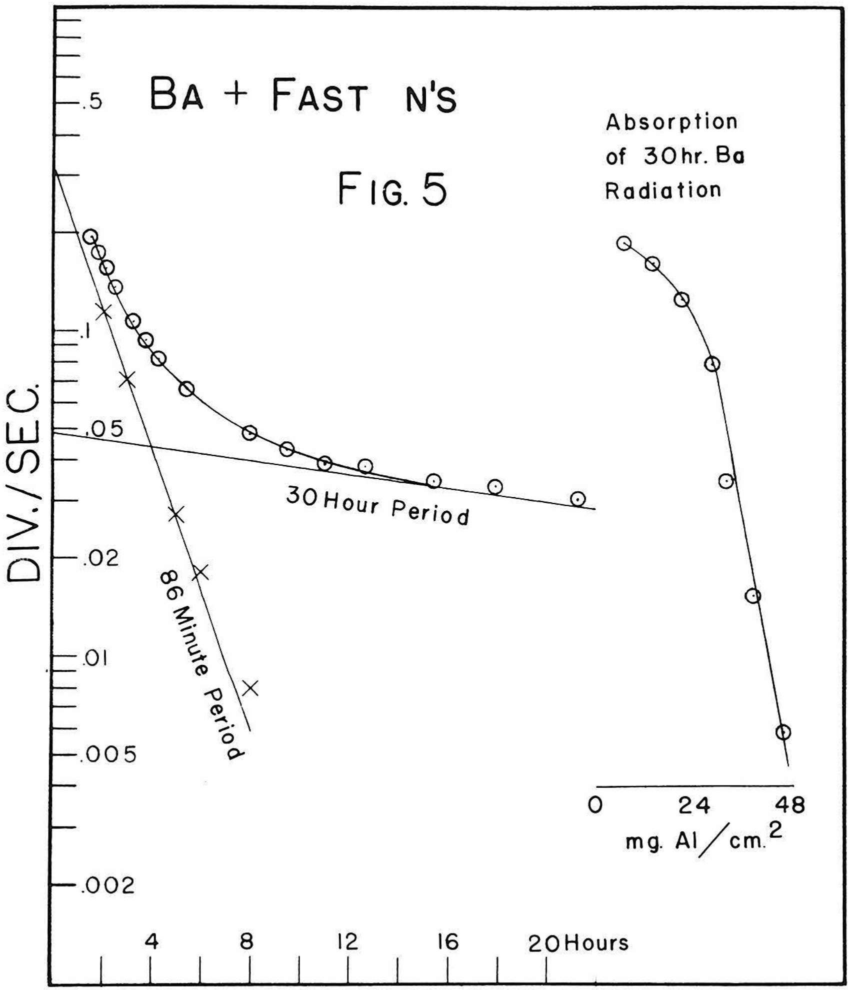
Irradiation of cesium with gamma-rays gave no radioactivity. However, the intensity of gamma-rays was not very great, since the source of gamma-rays was the bombardment of lithium with protons. The protons used were of high energy and low intensity. Due to competing reactions between lithium and protons, the yield of high energy gamma-rays from the reaction is least with high energy protons.

Bombardment of Barium. Barium irradiated with neutrons gave an isotope, separated chemically according to the Noyes and Bray system of analysis[8], of half-life 30 ± 1 hour. This isotope was found to emit a monochromatic group of electrons at 250 KV as shown by absorption measurements on a thin sample. Also, x-rays of approximately the characteristic energy for Ba $K\alpha$ x-rays, and strong gamma-rays of about 250 KV, as well as a soft complex spectrum of gamma-rays were emitted. Due to the soft spectrum of gamma-rays an attempt to identify the x-rays was unsuccessful. That this isotope was due to a (n, 2n) reaction was indicated by the fact that paraffin shielding decreased the yield of this activity.

The maximum energy of neutrons obtainable from lithium plus deuterons ($\sim$25 Mev) exceeds the maximum energy of neutrons obtainable from berylium plus deuterons, but the yield of these high energy lithium neutrons is small compared to the yield of beryllium neutrons. Our observation that beryllium plus deuterons was a more effective source of neutrons than lithium plus deuterons in the preparation of the 30 hour barium isotope indicates that the threshold neutron energy for the reaction is less than 8 Mev.

Deuteron bombardment of barium gave an 86 minute barium period having a beta-ray upper limit of about 1 Mev and a gamma-ray of about 0.6 Mev. This is in agreement with an earlier report[11]. A search for soft monochromatic electrons by absorption experiments on thin samples was unsuccessful.

Fig. 5 is a plot of the activity of a sample of barium hydroxide wrapped in metallic cadmium and placed in borax for fast neutron irradiation. The sample was left in front of the cyclotron lithium target during a 200 microamp~~h~~ere hour bombardment of deuterons. A decay curve was obtained which may be resolved into an 86 minute period and a 30 hour period. The inset curve in Fig. 5 represents the absorption of the radiation from a thin sample of the 30 hour barium isotope which had been chemically purified. The curve indicates the presence of monochromatic beta-rays due to high internal conversion of gamma-rays.



Barium irradiated with gamma-rays from proton bombardment of lithium in the cyclotron gave practically no activity.

Discussion

Due to the present state of the theory of nuclear reactions, little of new significance may be said regarding the above observations. Nuclear isomerism found in Cs^{134} was one of the early artificially activated cases reported. Many such cases have now been found, and recently Collar, Cork and Smith[12] investigated further the nuclear reactions of cesium and barium and report nuclear isomerism in the case of Ba^{134}.

Summary

See following reprint.

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Radio-Isotopes of Ba and Cs

With the 37-inch Berkeley cyclotron as a neutron source for irradiating Ba, a chemically identified Ba isotope of half-life 30±1 hour was found.[1] The emitted radiations consisted of a "monochromatic" group of electrons at 250 KV, x-rays of approximately the characteristic energy for Ba *K* x-rays, and strong gamma-rays of about 250 KV, in addition to a soft complex spectrum of gamma-rays. This soft spectrum made it impossible to identify the x-rays definitely by using critical absorbers. Paraffin shielding decreased the yield of this activity, and Li was found to be a less effective source of neutrons than Be. This would seem to indicate that it is a neutron loss reaction, but that extremely high energy neutrons are not required. Deuteron bombardment of Ba metal did not give this period at all.

The 2.5-minute Ba period[2] was prepared by irradiating Ba with $Li+H^2$ neutrons and was proved to be chemically Ba.

The 87±1-minute Ba period[3] was strongly activated by deuteron bombardment of Ba and gave a β-ray upper limit of about 1 MV and a gamma-ray of about 0.6 MV according to absorption coefficients in lead and copper. There are no very strong soft "monochromatic" electrons with this period.

Cs bombarded with deuterons or neutrons consistently gave a 3-hour±10-minute period rather than the previously reported period[4,5,6] of 1.5 hours. The normal β-ray absorption spectrum indicates an upper limit of about 1 MV. Little if any gamma-radiation is associated with this period. It is more strongly activated with slow than with fast neutrons, and was proved to be chemically Cs.

A long period (20±1 month) isotope,[7] chemically identified as Cs and apparently isomeric with the 3-hour Cs^{134}, was prepared by neutron or deuteron bombardment of Cs. Its normal β-ray spectrum has an upper limit of 0.9 MV, and there is fairly strong gamma-radiation.

Cs^{132} evidently has a very short period, a very long period, or one close to three hours, as nothing new appeared with fast neutron bombardment.

We are grateful to Professor E. O. Lawrence for his cooperation in these experiments, and to the Research Corporation and the Rockefeller Foundation for financial assistance.

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June 3, 1940.

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[1] D. C. Kalbfell, Phys. Rev. **54**, 543 (1938).
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[3] M. L. Pool and J. M. Cork, Phys. Rev. **51**, 1010 (1937).
[4] E. Amaldi *et al.*, Proc. Roy. Soc. **A149**, 522 (1935).
[5] McLennan, Grimmet, and Read, Nature **135**, 505 (1935).
[6] Latimer, Hull and Libby, J. Am. Chem. Soc. **57**, 781 (1935).
[7] Alexeeva, Comptes rendus USSR **18**, 553 (1938).

AN ATTEMPT TO PRODUCE ELEMENT 85 BY ALPHA PARTICLE BOMBARDMENT OF BISMUTH*

An attempt to prepare ekaiodine by irradiating metallic bismuth with 16 Mev alpha particles was made. Induced radioactivity was found in the irradiated sample. However, this activity was attributed to impurities, since on taking the bismuth into solution and precipitating silver iodide from the solution, no activity was found in the precipitate.

Subsequently element 85 was prepared[13] and it was then shown that alpha particles of at least 20 Mev were required. This accounts for our failure using 16 Mev alpha particles. It is encouraging to note that on the completion of the new cyclotron, which can supply alpha particles of 200 Mev, the potential barriers of all nuclei may be penetrated.

It is surprising that the chemical behavior of element 85 appears to be more similar to polonium than to the halogens as shown by the inability of silver iodide to precipitate element 85 quantitatively.

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*Carried out in cooperation with Dr. D. C. Kalbfell.

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(3) Latimer, Hull and Libby, J. Am. Chem. Soc., 57, 781 (1935).

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PART II

EXCHANGE REACTIONS

[Reprinted from the Journal of the American Chemical Society, **61**, 2970 (1939).]

The Non-interchange of Elementary Radiosulfur with Carbon Disulfide

BY ROBERT A. COOLEY, DON M. YOST AND EDWIN McMILLAN

Radioactive sulfur (half life eighty to ninety days) finds important application as a tracer in chemical and biochemical investigations,[1] and at some stages in these studies it proves convenient to use carbon disulfide as a solvent for elementary sulfur. In order to be certain that this solvent can be used without danger of loss of the radioactive sulfur, it is necessary to show that there is no interchange between elementary sulfur and carbon disulfide. Judging from the nature and structure of carbon disulfide,[2] any appreciable interchange seems unlikely, but the great solubility of sulfur in carbon disulfide (50.49 g./100 g. carbon disulfide at 25°) suggests the possible rapid reversible formation of complex compounds that might make interchange possible.

The radiosulfur used was formed by bombarding a metal sulfide with 4 Mev. deuterons in the cyclotron at the University of California radiation laboratory. Elementary sulfur was obtained from the metal sulfide by dissolving it in hydrochloric acid and passing the hydrogen sulfide formed into a 1 *N* solution of potassium iodide saturated with iodine. After warming the resulting solution to volatilize the excess iodine, and to coagulate the very fine precipitate, the sulfur was collected as small globules on a sintered glass filter. An appreciable proportion of the sulfur obtained in this manner is in the amorphous (μ) form and is slow to dissolve in carbon disulfide. It has been found by Mr. J. B. Hatcher at this Institute that heating the sulfur precipitate in an autoclave is not attended with losses and that it is thereby converted into a readily soluble form.

The exchange experiments were carried out in sealed U-tubes one leg of each containing a solution of about 3 mg. of radiosulfur in 300 mg. of C. P. carbon disulfide. The filled tubes were heated in a thermostat at 100° for forty-two to sixty-eight hours, and after the heating period about one-half of the carbon disulfide was caused to distil into the empty leg of the tube by cooling it with liquid air. The contents of the two legs were subjected to a Carius combustion, and the resulting sulfuric acid was then converted into dry lithium sulfate. Thin layers of the lithium sulfate, all of equal area, about 20 sq. cm., were prepared on metal plates for the measurement of the activity. Lithium rather than the more easily prepared barium sulfate was used in the radioactivity measurements because the barium absorbs the weak (107 Kev. maximum) beta radiation[3] of sulfur more extensively than does lithium. The thickness of the mounted lithium sulfate samples was >0.015 g./sq. cm. and was such that the beta particles from the bottom of a sample could not penetrate to the top and from there reach the electroscope chamber. This arrangement greatly simplifies the quantitative treatment of the results.

In our current experiments with radiosulfur it has been found possible to make the mounted samples of elementary sulfur by reducing barium sulfate to the sulfide with hydrogen at about 900°. Barium sulfide is then treated in the manner described above for the recovery of the sulfur. The reduction procedure was suggested to us by Professor J. E. Bell of this Institute, and the technique for its use was developed by Mr. J. B. Hatcher. Complete reduction of barium sulfate is not attained if the salt melts.

The activity of the lithium sulfate samples was measured with a lead shielded quartz fiber Lauritsen electroscope. A thin aluminum foil, 0.15 mg./sq. cm., served as the window on the ionization chamber. The background was about 0.001 div./~~min.~~sec and varied no more than 30% in a two-week period. By taking background readings immediately before and after readings with the samples, the activities of the latter were determined to ±0.0002 div./sec. The results, corrected for background, are shown in Table I. The same range of the electroscope scale was used throughout in determining the effect due to the background and to the samples, and therefore no correction for linearity of scale was required.

TABLE I

RADIOACTIVITY OF DISTILLATES AND RESIDUES FROM HEATED SOLUTIONS OF RADIOSULFUR IN CARBON DISULFIDE

Expt.		Activity in div./sec.	Time soln. heated at 100°, hours
1	Distillate	0.000014	42
	Residue	.0095	
2	Distillate	− .00017	48
	Residue	.0028	
3	Distillate	.00009	68
	Residue	.0102	

It is evident from the results that there is practically no interchange between sulfur and carbon disulfide even at 100°. The extent of any interchange must be less than 2%, that is, it must be less than the experimental error of the activity measurements. It is also clear that carbon disulfide may be used as a solvent for radiosulfur without fear of loss by interchange.

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RECEIVED AUGUST 4, 1939

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(2) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 182.

(3) W. F. Libby and D. D. Lee, *Phys. Rev.*, **55**, 245 (1939).

In regard to the method of converting amorphous sulfur into a form completely soluble in carbon disulfide described in the above note, an alternative and perhaps simpler method may be mentioned. The alternative method utilizes the finding of Sommer[1] that pyridine is an excellent solvent for sulfur even of the amorphous modification and that on cooling all the dissolved sulfur is deposited in a form entirely soluble in carbon disulfide.

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[1] H. Sommer, Ind. and Eng. Chem., p. 368, June 1940.

[Reprinted from the Journal of the American Chemical Society, **62**, 2474 (1940).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 776]

The Rate of Exchange of Elementary Radiosulfur with Sulfur Monochloride

BY ROBERT A. COOLEY AND DON M. YOST

Introduction

The reactions between sulfur or sulfur monochloride and chlorine have been the subject of investigation since 1782. The mechanisms that have been suggested for the reactions usually involve intermediates having the general formula S_mCl_n, or even ions,[1] but of these compounds only S_2Cl_2, SCl_2, and SCl_4 have been isolated, the evidence for the existence of such substances as S_3Cl_4, S_4Cl_2, S_2Cl, S_3Cl_2, and chloride or sulfur chloride ions being of an indirect nature. In the interpretations of the results of both equilibrium and kinetic studies of the sulfur chlorides, the existence of one or more of the compounds not capable of isolation, in slow or rapid equilibrium with sulfur, frequently is assumed, but has never been proved directly. The use of radiosulfur makes it possible for the first time to establish the existence of such equilibria.

In this paper are described the results of experiments made on the slow rate of interchange of radiosulfur in solutions of sulfur dissolved in sulfur monochloride. The experiments show that exchange of dissolved sulfur with the combined sulfur does take place at a measurable rate, and some light is thrown on the mechanism of the reaction, but further investigation will be necessary to establish the steps in other reactions of the sulfur–chlorine system.

Preparation of Materials and Experimental Procedures

Materials.—The radiosulfur was obtained from iron sulfide which had been bombarded with 8 MEV deuterons in the cyclotron at the University of California Radiation Laboratory. To remove radioactive contaminants completely, the irradiated sulfide was treated with acid, the resulting hydrogen sulfide was passed into an acid solution of cupric ion, and the precipitate of cupric sulfide was filtered and washed. Continued digestion of the cupric sulfide with concentrated nitric acid converted it into sulfate and this was precipitated as barium sulfate. The barium sulfate was completely reduced at 900° to barium sulfide with hydrogen. Addition of hydrochloric acid to the barium sulfide produced hydrogen sulfide which was oxidized to elementary sulfur by passing through a solution of triiodide ion. Finally, the elementary sulfur was converted into a form completely soluble in carbon disulfide by heating in an autoclave.[2]

The sulfur monochloride was prepared by causing accurately weighed, equivalent amounts of pure dry liquid chlorine and purified sulfur to react at 100° for one hour in the sealed evacuated tube B of Fig. 1. The sulfur monochloride was completely distilled, after breaking the tip at C with the glass-enclosed magnetic hammer M, at room temperature into the evacuated tube F which contained a weighed amount (usually 6 mg.) of radiosulfur. The operations of preparation and distillation without losses were facilitated by using liquid air-baths. After sealing the reaction vessel at D and E, it was brought to the temperature at which the exchange was to be measured.

Rate Measurements.—The first experiments made showed the rate of exchange of the dissolved radiosulfur with the sulfur in the monochloride to be extremely slow at

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[1] See, for example, Spong, *J. Chem. Soc.*, 1283 (1934).

[2] Cooley, Yost and McMillan, THIS JOURNAL, **61**, 2970 (1939).

25°. In subsequent runs the reaction vessel was completely submerged in a bath of boiling water for a measured time (usually ten minutes), and immediately after removal the side arm G was immersed in liquid air until about one-third of the liquid had distilled over. Only the monochloride and not the uncombined sulfur is sufficiently volatile to distil over in this operation. F, G, and H were then cooled in liquid air and G was sealed off at its constriction. The reaction vessel was again placed in the boiling water-bath for a measured time and the distillation procedure repeated. This distillation procedure effected the separation of the solvent sulfur monochloride from the dissolved sulfur; a simpler method of separating the two substances is desirable, but no satisfactory one was hit upon.

In order to measure quantitatively the radioactivity of the sulfur monochloride removed from the reaction mixture, the former was converted to lithium sulfate. This was accomplished by breaking the removed side arm G, after weighing and cooling in liquid air, in a glass stoppered flask containing a known amount of silver nitrate dissolved in concentrated nitric acid, and then boiling the resulting mixture until oxidation to sulfate was complete.[3] After removing and weighing the glass fragments, the calculated amount of hydrochloric acid was added to the sulfate solution to precipitate all of the silver as the chloride, and the precipitate was then filtered off and washed. To the filtrate was added the exact amount of lithium carbonate necessary to convert the sulfuric acid to lithium sulfate, and the resulting solution was then evaporated to dryness. The dry lithium sulfate prepared in this way was ground to a fine powder in an agate mortar, and with the aid of absolute alcohol a thin, uniform layer of the dry powder was placed in a definite area on a metal sample holder. Although the layer was thin, it was of such a thickness, 15 mg./sq. cm. or greater, that the beta particles of maximum energy, 0.107 MEV, originating on the lower side could not penetrate to the top of the layer. The activity of the samples was measured in a lead-shielded Lauritsen quartz fiber electroscope whose ionization chamber was covered with a 0.15 mg./sq. cm. aluminum foil.

The activities of the samples and of the background were determined in terms of the time necessary for the quartz fiber to pass between two fixed scale positions; in this way the necessity for a calibration of the scale for linearity was eliminated. The background, about 0.0016 div./sec., was determined before and after each measurement on a sample.

The time intervals found for the samples of lithium sulfate are, after correcting for background and rate of radioactive decay, directly related to the concentration of radiosulfur in the samples. Since the weights of the sulfur monochloride used to make up the lithium sulfate were known, it is clear that the measurements will yield quantities proportional to the concentration of radiosulfur in the sulfur monochloride.

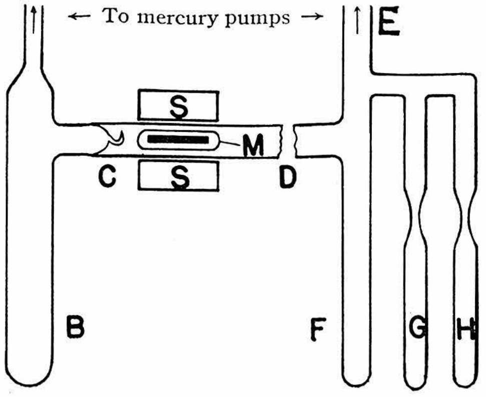

Fig. 1.—Reaction vessel.

Treatment of the Experimental Results

G. Bruni[4] has shown that sulfur dissolved in sulfur monochloride exists mainly in the form of S_8 molecules. If (S_2Cl_2) and (S_8) are the concentrations, respectively, of sulfur monochloride and sulfur in atomic weights of sulfur per liter of solution, and if α and β are the fractions of the sulfur atoms in the monochloride and the dissolved sulfur, respectively, that are radioactive, then the conservation of radiosulfur, S^{35}, is expressed by the relation

$$\Sigma(S^{35}) = \alpha_0(S_2Cl_2) + \beta_0(S_8) = \alpha(S_2Cl_2) + \beta(S_8) \qquad (1)$$

where the subscript zero refers to the initial time. Without reference to the order of the exchange reaction, let R be the constant rate at which sulfur atoms pass from S_8 to S_2Cl_2 or the reverse. Since the concentration of radiosulfur atoms, S^{35}, is extremely small, practically no S_8 molecules will contain more than one S^{35} atom; consequently in the reaction

$$\text{ClSCl} + S^{35}S_7 \underset{R}{\overset{R}{\rightleftarrows}} \text{ClS}^{35}\text{SCl} + S_8 \qquad (2)$$

one-eighth of the reactions going to the right and one-half of those going to the left will involve an S^{35} atom. It is assumed here, in accordance with the results of crystal structure and electron diffraction investigations,[5,6] that the sulfur atoms in both S_2Cl_2 and S_8 are equivalent.

Inasmuch as the probability that an S^{35} will be transferred from $S^{35}S_7$ to S_2Cl_2 is $\beta/8$, and the probability of transfer from $S^{35}SCl_2$ to S_8 is $\alpha/2$, we may write for the net rate of transfer of S^{35} atoms

$$d(\alpha(S_2Cl_2))/dt = (\beta/8 - \alpha/2)R \qquad (3)$$

On using (1) to eliminate β and then integrating, there results the relation

$$R = \frac{8(S_8)/(S_2Cl_2)}{t\{(S_2Cl_2) + 4(S_8)\}} \ln \frac{(\beta_0 - 4\alpha_0)(S_8)}{(S_2Cl_2)(\alpha_0 - \alpha) + \beta_0 - 4\alpha} \qquad (4)$$

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[5] Ackermann and Mayer, *J. Chem. Phys.*, **4**, 377 (1936).

[6] K. J. Palmer, THIS JOURNAL, **60**, 2360 (1938).

which can be evaluated from the experimental data.[7] Both α and β may be evaluated to within the same multiplicative constant from the electroscope measurements and the known weights of sulfur and sulfur monochloride in the samples. The principal errors in the results are believed to arise from uncertainties in the time required for the reaction mixtures to come to the temperature of the bath. The background of the electroscope averaged about 0.0016 div./sec., and the activities of the lithium sulfate samples varied from 0.0380 to 0.0030 div./sec. Repeated measurements on a sample of the time interval required for the electroscope fiber to move nine divisions showed the error in the interval to be from 1 to 2%. The error in the rate constants k_1 of Table I that result from the errors in the electroscope measurements amounts to about 10%. When account is taken of the fact that the energies of the beta particles from radiosulfur are low and that the amount of radioactive material available is small, the stated error is about as small as can be attained with an electroscope.

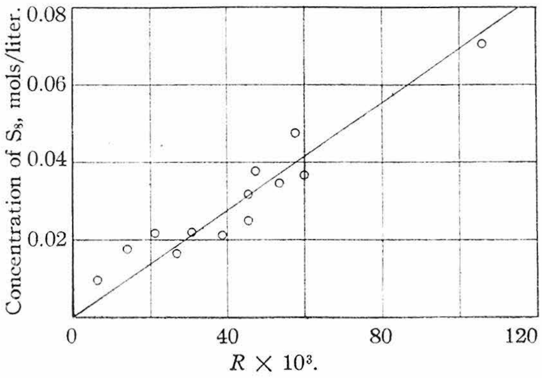

Fig. 2.—Curve showing dependence of R on $[S_8]$.

Discussion of the Results

It will be assumed that equilibrium between the molecular species present in the solutions is effectively established at all times. R, which is the constant rate at which sulfur atoms pass from S_8 to S_2Cl_2 or from S_2Cl_2 to S_8, will be some function of the concentrations of these two compounds. A study of the experimental results showed that they were in best accord with the relations

$$R = k_1[S_8] \text{ or } R = k_2[S_8][S_2Cl_2]^n \qquad (5)$$

where $[S_8]$ and $[S_2Cl_2]$ are the concentrations of the species indicated in moles per liter of solution. The second expression reduces to the first in the present case, since the concentration of the sulfur monochloride solvent was effectively constant in all experiments.

The results of the experiments together with the values of k_1 are presented in Table I. The constants k_1 show appreciable variation, but this variation is not correlated with changes in concentration, and it is believed to be due to the errors mentioned above. In Fig. 2 the values of R are shown plotted against $[S_8]$; it is clear that a linear relationship is indicated, and that therefore the rate R is first order with respect to $[S_8]$.

From the results at the two temperatures an approximate value of the energy of activation was calculated to be 33 kcal.

Experiment 7, the results of which are not plotted in Fig. 2, differed greatly from the other experiments in the concentration of S_8, and in that initially there was no elementary radiosulfur present, all the radiosulfur being introduced in the form of S_2Cl_2.

TABLE I

THE RATE OF EXCHANGE OF SULFUR BETWEEN S_8 AND S_2Cl_2

	Moles S_8 per liter of soln. $[S_8]$	Time for exchange, in reciprocal min., $1/t$	Temp. at which exchange occurred, ° C.	$R \times 10^3$	$k_1 = R/[S_8]$
	0.0316	0.00114	25.0	0.023	2.3×10^{-5}
1	.0378	.20	98.5	47.2	1.3
	.0477	.0667	98.5	57.7	1.2
	.0704	.0667	98.5	106	1.5
4	.0212	.20	98.3	38.6	1.8
	.0319	.10	98.3	45.3	1.4
2	.0097	.20	98.5	6.36	0.7
	.0165	.10	98.5	26.7	1.6
3	.0177	.10	98.5	14.0	0.8
	.0250	.05	98.5	45.4	1.8
5	.0218	.20	98.5	21.1	1.0
	.0345	.05	98.5	53.6	1.6
6	.0220	.20	98.5	30.8	1.4
	.0364	.10	98.5	60.0	1.7
7	.4606	.0677	98.5	188	0.4
	.6921	.0677	98.5	181	0.3

In arriving at a mechanism for the exchange reaction only the first form of the rate equation will be considered. It will be assumed, in accord with the fact that the rate is first order with respect to the concentration of S_8, that the rate determining step consists in the slow reversible dissociation of S_8 into S_6 and S_2, $S_8 = S_2 + S_6$. The exchange is assumed to be accomplished by the rapid reversible step, $2S_2Cl_2 = S_2Cl_4 + S_2$, a reaction postulated

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[7] For the analysis for a somewhat similar case see J. N. Wilson and R. G. Dickinson, THIS JOURNAL, **59**, 1358 (1937).

by Patrick and Hackerman[8] to explain their results on the boiling points of solutions of sulfur monochloride in various solvents. The first step recalls the slow reactions that have been postulated to explain the well-known equilibria between S_λ and S_μ in liquid sulfur.

Since the dependence of R on $[S_2Cl_2]$ in the second form of the rate equation is not known, it is not possible to give an unambiguous mechanism for the case that the monochloride is involved in the slow step of the exchange. A different kind of investigation will be required to settle this point, namely, one in which both the sulfur and the sulfur monochloride are present in small concentrations in a common solvent.

We wish to express our gratitude to Professor Edwin McMillan and Dr. Martin Kamen of the Radiation Laboratory of the University of California for furnishing us with radiosulfur, and to Dr. J. Norton Wilson for helpful suggestions.

Summary

In solutions of radiosulfur in liquid sulfur monochloride the rate of exchange of sulfur between solute and solvent is very slow at room temperature but is measurably rapid at 100°. From quantitative measurements it was found that the rate at which sulfur atoms pass from S_8 to S_2Cl_2 is directly proportional to the concentration of S_8. If the rate is not dependent on the concentration of sulfur monochloride, a satisfactory mechanism for the reaction consists in the slow dissociation $S_8 = S_6 + S_2$ followed by the rapid reversible reaction $S_2 + S_2Cl_4 = 2S_2Cl_2$.

PASADENA, CALIF. RECEIVED MAY 20, 1940

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[8] Patrick and Hackerman, *J. Phys. Chem.*, **40**, 679 (1930).

THE NON-EXCHANGE OF RADIOPHOSPHOR~~O~~US BETWEEN PHOSPHATE AND HYPOPHOSPHOROUS IONS

The possibility of exchange of phosphor~~o~~us between phosphate and hypophosphite was investigated in acidic and alkaline solutions at 25°C. to determine if the reaction

$$H_3PO_4 + H_3PO_2 = H_4P_2O_5 + H_2O$$

took place to an extent great enough to be detected by the tracer technique. Although the reverse reaction occurs, the forward reaction cannot be detected by ordinary chemical methods. Exchange would take place if the following two conditions obtained: (1) the above reaction took place to only a very slight extent, but was rapid and reversible; (2) the phosphor~~o~~us atoms in pyrophosphorous[1] acid were equivalent, as they would be in the proposed structure[2,3] $(HO)_2P\text{-}O\text{-}P(OH)_2$. Since experimentally it was found that no appreciable exchange occurred even after 107 hours at 25° C., we may conclude that at least one of the conditions is not satisfied.

Exchange might also have occurred thru the rapid reversibility of the following reaction which thermodynamically should take place, but is actually immeasurably slow:

$$H_3PO_4 + H_3PO_2 = 2H_3PO_3 \qquad \Delta F^\circ = -18 \text{ Kcal.}$$

Experimental Part

Radio phosphor~~o~~us was obtained from carbon tetrachloride which had been irradiated with neutrons. After steps were taken to remove radiosulfur contamination, a standard stock solution of $Na_3P^*O_4$ was prepared. A standard solution of KH_2PO_2 was also prepared. From the combination of measured volumes of these two solutions, solutions of known concentrations of radiophosphate ion and hypophosphite ion were made up and placed in a thermostat for measured times. Separation of the ions was effected by making the solution alkaline and adding barium chloride which precipitated barium phosphate but left hypophosphite ion in solution. To insure complete removal of radio phosphate ion from hypophosphite ion, a second precipitation of barium phosphate was carried out after the addition of inactive phosphate ion. The solution containing hypophosphite was boiled with concentrated alkali to oxidize hypophosphite which was finally precipitated as barium phosphate. Equal amounts of these two barium phosphate precipitates were examined for radioactivity in an electroscope as previously described.

Results. The results of seven experiments are recorded in Table I. In no case was the extent of the exchange

TABLE I

The Non-Exchange of Radiophosphorous between Phosphate and Hypophosphorous Ions at 25.0° C.

Time allowed for exchange	Concentration in moles/liter		pH of solution	Specific activity in div./sec.		Per cent exchange
	Phosphate	Hypophosphite		Phosphate	Hypophosphite	
1 hr.	.183	.183	13	.0197	.0001	0.5
1 hr.	.183	.183	13	.0204	.0000	0.0
48 hrs.	.183	.183	13	.0213	.0000	0.0
48 hrs.	.183	.183	13	.0208	.0001	0.5
44 hrs.	.0735	.0735	3.1	.0185	.0004	2.1
44 hrs.	.0735	.0735	3.1	.0180	.0002	1.1
107 hrs.	.0735	.0735	3.1	.0115	.0001	.9

appreciably greater than the experimental uncertainty. This is in agreement with Perrier and Segre[4] whose work, published in an Italian journal, was overlooked until these experiments were completed. Wilson[5] found no exchange of phosphor~~o~~us between phosphate and phosphite ions and Hull[6] found no exchange of phosphor~~o~~us between ortho-, pyro-, and metaphosphoric acids.

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THE NON-EXCHANGE OF SULFUR BETWEEN CARBON DISULFIDE AND HYDROGEN SULFIDE DISSOLVED IN BENZENE*

Mills and Urey[1] have shown that the exchange of oxygen between carbon dioxide and water is due only to the reversible hydration,

$$CO_2 + H_2O = H_2CO_3 .$$

A very similar kind of exchange reaction in which the exchange of sulfur between carbon disulfide and hydrogen sulfide might occur thru the reversible reaction,

$$CS_2 + H_2S = H_2CS_3,$$

is considered in this article. Since trithiocarbonic acid is more stable[2] than carbonic acid, it might be thought that exchange of sulfur atoms between carbon disulfide and hydrogen sulfide would occur as certainly as oxygen atoms exchange between carbon dioxide and water. However, experimentally it was found that no exchange greater than the experimental uncertainty ($\sim 1\%$) occurs between carbon disulfide and hydrogen sulfide dissolved in benzene even after 95 hours at 120° C.

Professor W. L. Libby[7] first pointed out the interest in this problem and later found no exchange in the gas phase (14 mm. of H_2S and 7 mm. of CS_2) after 21 hours at 25° C.

*The assistance of Mr. D. L. Douglas in the experimental work of this paper is gratefully acknowledged.

Biltz and Brautigam[3] from a study of freezing point data for the system hydrogen sulfide plus carbon disulfide, found evidence for a compound of formula H_2CS_3, but suggested that the compound they obtained was an isomer of the H_2CS_3 of Yeoman[2] and of von Halbon, Merkert and Ott[4] Although Biltz and Brautigam's isomer may have been rapidly and reversibly formed in our experiment, exchange would not necessarily have occurred since the sulfur atoms in their isomer may not be equivalent. The observations of Biltz and Brautigam on hydrogen sulfide and carbon disulfide may have simply been evidence of hydrogen bonding.

Experimental Part

Procedure. A solution of carbon disulfide in benzene and one of radioactive hydrogen sulfide in benzene were prepared and standardized. After about a ml. of each of the solutions was introduced into a 5 ml. glass bulb, the bulb was sealed off and set in a thermostat for a measured period.

Hydrogen sulfide was extracted from the benzene carbon disulfide mixture with aqueous sodium hydroxide. The sulfide ion in the aqueous solution was tested for radioactivity as a measured amount of silver sulfide. The carbon disulfide remaining in the benzene fraction was converted to potassium xanthate[5,6] and extracted with water before being converted to copper xanthate for radioactivity measurements.

Results. Table I contains the results of these experiments.

TABLE I

The Non-Exchange of Sulfur between Carbon Disulfide and Hydrogen Sulfide Dissolved in Benzene

Temperature	Time allowed for exchange	Concentration in moles/liter		Observed activity in counts/minute		Per cent exchange
		H_2S	CS_2	Ag_2S from H_2S	CuXn from CS_2	
97° C.	1 hr.	0.0042	0.108	411±3	0±1	0.3
120° C.	95 hrs.	0.0042	0.108	178±1	0±2	0.8
120° C.	95 hrs.	0.0042	0.108	181±1	0±1	0.3

References

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THE NON-EXCHANGE OF BROMINE AND CARBON TETRABROMIDE

Radiobromine and carbon tetrabromide dissolved in carbon tetrachloride at 25° C. in ordinary daylight were found not to exchange beyond the limits of experimental uncertainty. This result may be contrasted with the very rapid exchange between bromine and the metallic bromides (cf. page 37).

Rollefson and Libby[1] have shown that exchange does not occur between chlorine and carbon tetrachloride even under irradiation with light of the proper wave-length to dissociate carbon tetrachloride. Wilson[2] found no exchange between bromine and ethylene bromide or trichlorobromomethane in the dark at 100° C., but that a rapid exchange with trichlorobromomethane is induced by green light at 76° C.

It was observed that carbon tetrabromide dissolved in carbon tetrachloride decomposes under ordinary light, and it may be that the amount of exchange observed, which is of the order of magnitude of the experimental error, may be due to slight decomposition.

Experimental Part

Solutions of radiobromine and carbon tetrabromide were prepared and mixed. Separation was achieved by shaking the solution with aqueous sulfite solution, which brought the bromine into the aqueous layer as bromide ion. The undissolved carbon tetrabromide was separated by filtration and tested for radioactivity in the solid form.

Results. The results of one experiment are recorded below.

TABLE I

The Non-Exchange of Bromine and Carbon Tetrabromide Dissolved in Carbon Tetrachloride after 13 hours at 25°C.

Concentration in moles/liter		Observed activity in counts/minute		Per cent exchange
Br_2	CBr_4	Br_2 as AgBr	CBr_4 as CBr_4	
.075	.294	752±25	23±1	3.3

References

1. Rollefson and Libby: J. Chem. Phys., 5, 569 (1937)

2. Wilson and Dickinson: J. Am. Chem. Soc., 61, 3519 (1939)

HALOGEN-INORGANIC HALIDE EXCHANGE REACTIONS IN NON-AQUEOUS SOLVENTS*

Introduction

Rapid exchange[1,2,3,4] of bromine atoms between bromine and inorganic bromides occurs in non-aqueous solvents, although organic bromides do not undergo this type of exchange. It was the purpose of this investigation to learn if the exchange between bromine and titanium tetrabromide dissolved in carbon tetrachloride was rapid at 25° C. and to determine if the rate of exchange between bromine and mercuric bromide dissolved in carbon disulfide could be measured at 0° C. The rate of exchange in the latter case is surprisingly rapid and may occur thru the formation of an unstable addition complex. A mechanism involving an addition complex is attractive since metallic elements generally form coordination complex molecules containing equivalent halide atoms, and in the case of bromine and mercuric bromide in aqueous solution Herz and Paul[5] found evidence for the existence of $HgBr_4$.

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*The assistance of Mr. D. L. Douglas in the experimental part of this work is gratefully acknowledged.

Experimental Part

<u>The Exchange of Bromine and Mercuric Bromide in Carbon Disulfide.</u> Standardized solutions of radiobromine in carbon disulfide were prepared from radiobromine obtained from neutron bombardment of butyl bromide. Radiobromide was extracted from the irradiated butyl bromide with water containing sodium bromide carrier and converted to bromine through oxidation by a solution of sodium bromate and perchloric acid. The bromine formed was extracted from the aqueous phase with carbon disulfide. The bromine carbon disulfide solution was dried by addition of phosphorous pentoxide, followed by filteration. Before the solution was used, twenty-four to thirty hours were allowed for short-lived bromine isotopes to decay. A solution of mercuric bromide in carbon disulfide was prepared and analyzed.

In a typical experiment 5 ml. of radiobromine solution were introduced into a 250 ml. distilling flask containing 5 ml. of the mercuric bromide solution at 0° C. The side arm of the distilling flask passed into a trap (cooled to about -75° C.) which was connected to a Cenco vacuum pump. After the solutions had mixed, the distilling flask was closed with a ground glass stopper and the vacuum pump was turned on. This caused bromine and carbon disulfide to distil from the flask to the trap where both condensed. The time allowed for the exchange to occur, as recorded in Table I, is the time from the introduction of the first drop of bromine solution until the distilling flask appeared to be entirely dry. It was estimated that the distillation of the last 15% of the solution required as long as the first 85%.

The bromine collected in the trap was reduced and precipitated as silver bromide, in which form its specific activity was determined with a Geiger-Mueller counting tube coupled to a scale-of-sixteen counting circuit.

The mercuric bromide left in the distilling flask was converted to silver bromide whose specific activity was determined. The weight of each silver bromide sample was determined after its activity had been measured.

Due to the rapid rate of evaporation in the separation procedure the temperature of the mixture was somewhat less than 0° C.

<u>Results.</u> The results of four experiments are recorded in Table I.

TABLE I

Exchange of Bromine and Mercuric Bromide in Carbon Disulfide at $< 0^\circ$ C.

Time allowed for exchange in seconds	Concentration in moles/liter		Observed activity* in counts/minute		Fraction of AgBr from Br_2 measured	Per cent exchange
	Br_2 $\times 10^3$	$HgBr_2$ $\times 10^3$	AgBr from Br_2	AgBr from $HgBr_2$		
324	1.34	1.67	82±1	252±6	.406	100±3
290	1.34	1.67	130±4	250±5	.650	100±3
245	6.26	1.67	3066±18	1160±7	.670	96±1
157	6.26	1.67	2863±16	1318±9	.596	102±1

*All activities with their statistical errors recorded in this thesis have been corrected for time and background effects.

The Exchange of Bromine and Titanium Tetrabromide in Carbon Tetrachloride. Titanium tetrabromide was prepared[6] by the action of reagent bromine on pure metallic titanium. The product was thrice distilled under reduced pressure and first and last fractions, each about one third of the total, were discarded. The final product, a lemon-yellow solid, was sealed off in glass.

Dry radiobromine was obtained from radio sodium bromide which had been prepared by neutron irradiation of butyl bromide. The sodium bromide as a dry solid was mixed with dry potassium permanganate and introduced into a glass apparatus. The whole glass apparatus was evacuated and concentrated sulfuric acid was introduced to cause the production of bromine which was passed through a tube containing phosphorous pentoxide and then condensed in a cooled tube. Sealed glass ampoules containing dry radio bromine were broken under carbon tetrachloride to form the solutions of bromine in carbon tetrachloride. Similarly, glass ampoules of titanium tetrabromide were broken under carbon tetrachloride. These solutions were analyzed, and measured equal volumes were transferred to one arm of an inverted U-tube. The liquid in the tube was quickly frozen and the tube then evacuated to 10^{-4} mm. mercury and sealed off. After the tube had remained in a thermostat for a measured time, the bromine in the solution in one side arm was distilled into the other side arm of the U-tube by cooling the empty side arm while the side arm containing the solution remained in the thermostat. The side arm containing the condensed bromine was sealed off and the specific activity of the bromine therein was determined in the form of silver bromide. The specific activity of the radiobromine after conversion to silver bromide had also been determined before the exchange occurred.

Results:

TABLE II

Exchange of Bromine and Titanium Tetrabromide in Carbon Tetrachloride at 25.0°C.

Time in minutes	Concentration in moles/liter		Specific activity of Br_2 in cts./min.		Per cent exchange
	Br_2	$TiBr_4$	before exchange	after exchange	
40	0.024	0.100	148±5	16.5±1.5	100±10
11.5	0.0297	0.0363	605±21	192.0±7	100±10

Discussion

At least three mechanisms for the above exchanges must be considered:

(1) Halogen and inorganic halide may ionize.

(2) A chain reaction may be initiated by atomic bromine formed thermally or by ionization

processes associated with radioactive bromine radiations.

(3) An unstable addition complex containing equivalent halogen atoms may be formed between halogen and inorganic halide.

There is little probability of mechanism (1) occurring to any marked extent in view of the very low conductance of halogens and metallic halides in non-polar solvents.

Mechanism (2) is considered because Liberatore and Wiig[3] claim that it "appears to be the only possible mechanism" for the rapid gas phase exchange between radiobromine and hydrogen bromide at 25° C. Because mechanism (3) appeals to us, for reasons to follow, as the most likely in the case of a number of halogen-inorganic halide exchanges in non-aqueous solution, we feel that it may also take place in the case of the gas phase bromine-hydrogen bromide exchange. It is generally not wise to attempt to draw conclusions about gas phase reactions from information on liquid phase reactions. However, even indirect evidence should be presented against Liberatore and Wiig's explanation since, until it is clearly proved or disproved, grave doubt is cast on the value of the radiotracer method.

The rapid exchanges summarized in Table III would scarcely be predicted to be due to an atom chain mechanism since the solvent would tend to break chains formed and minimize production of primary bromine atoms by disintegration radiation. Ten examples recorded in Table III occur so rapidly that the rate can not be conveniently measured.

TABLE III

Rapid* Halogen-Inorganic Halide Exchange Reactions

Halogen	Halide	Solvent	Temperature	Authority
Br_2	HBr	Gas Phase	25° C.	3,4,7
Br_2	HBr	CCl_4	25° C.	1
Br_2	$HgBr_2$	CS_2	0° C.	10
Br_2	$AsBr_3$	CCl_4	25° C.	2
Br_2	$SnBr_4$	CCl_4	25° C.	2
Br_2	$TiBr_4$	CCl_4	25° C.	11
Br_2	Al_2Br_6	None	25° C.	7
Br_2	AgBr**	EtBr	25° C.	8
Br_2	$CuBr_2$***	None	100° C.	9
I_2	HI	C_5H_{12}	25° C.	4
I_2	HgI_2	CS_2	100° C.	12
I_2	SbI_3	C_5H_{12}	37° C.	13

*Complete exchange in less than 30 minutes is considered rapid.

**The rate of exchange depends on the freshness of the AgBr precipitate, and is slower than the other cases recorded.

***Surprisingly, the authors state that the bromine atoms in $CuBr_2$ are not equivalent.

In the case of mercuric bromide an attempt was made to measure the rate by carrying out the reaction somewhat below 0° C. and with very low (0.00167 moles/liter) concentration of mercuric bromide, but the reaction was complete in not more than three minutes. Furthermore, to minimize effects of nuclear processes on the chemical exchange only the isotope Br^{82} was used. An estimate of the number of unstable atoms of Br^{82} in our reaction mixture at the time of the exchange is 10^5, which is smaller by a factor of about 10^4 than the number of unstable atoms used in the experiments of Liberatore and Wiig on the exchange of bromine and hydrogen bromide.

Libby[4], in order to disprove the atom chain mechanism in the gas phase bromine-hydrogen bromide exchange, carried out experiments under conditions nearly identical with those of Liberatore and Wiig except that the intensity of the radioactive radiations was about 20,000-fold smaller. In answer to Libby's results, Liberatore and Wiig suggested that a chain atom mechanism, initiated by bromine atoms produced thermally instead of by radiation effects, accounts for his results. However, it was admitted that a reliable calculation, within a factor of 100, of the number of bromine atoms produced thermally could not be made from the data available. Furthermore, they discounted the addition complex mechanism. They argued that if it obtained, then exchange should also occur between ethylbromide and bromine, since the strength of the C-Br bond (ca. 65 kcal.) is less than that of the H-Br bond (ca. 86 kcal.). Experimentally they had found that the bromine-ethylbromide exchange did not occur.

Mechanism (3) is an acceptable and likely general mechanism for all of the exchanges recorded in Table III. The inability of carbon to form coordination complexes* with bromine as metals do, or the lack of ability of bromine bonded to carbon to form addition complexes analogous to HBr_3 may be substituted for the explanation of the non-interchange of bromine and ethylbromide given by Liberatore and Wiig who considered only the relative bond energies of C-Br and H-Br.

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*It would be interesting to test the exchange between bromine and silicon tetrabromide since silicon is too small to form coordination complexes with bromide readily.

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EXCHANGE REACTIONS OF SOME SULFUR-CONTAINING ANIONS

Introduction

Exchange of sulfur atoms between the following pairs of anions was studied: sulfide and thioantimonate, sulfide and thiocyanate, sulfate and peroxydisulfate, sulfate and dithionate. The purpose of this investigation was to extend earlier observations[1,2] and to make comparisons with oxygen exchange reactions.

Experimental Part

Exchange of Sulfur between Sulfide and Thioantimonate Ions. Recrystallized sodium thioantimonate was prepared according to the directions of Vanino[3]. Alkaline solutions of the salt were prepared and the concentrations determined by analyzing for antimony according to Swift's[4] procedure. No quantitative method of separating sulfide ion from thioantimonate could be found in the literature, so the following one was devised and tested for the conditions under which it was to be applied. After an alkaline solution 0.00158 molal in thioantimonate ion and 0.197 molal in sulfide ion had stood at about 23° C. for two days, 2 ml. of 0.1n $BaCl_2$ and 20ml. of absolute ethyl alcohol were added and the precipitate was collected. Blank experiments performed under identical conditions showed that 60±5% of the thioantimonate was recovered in the precipitate for radioactive measurement and that 22±2% of the sulfide ion in solution was occluded by the precipitated $Ba_3(SbS_4)_2$. The specific radioactivity of the sulfide ion solution was determined separately. The results of the two experiments are recorded in Table I. Account was taken of errors due to absorption of radiosulfur beta rays. The per cent exchange was calculated on the assumption that all the sulfur atoms in thioantimonate are equivalent. A relatively slow exchange is indicated.

TABLE I

The Exchange of Sulfide and Thioantimonate Ions at 23°C. in One Molal Sodium Hydroxide Solution after 48 Hours

Concentration in moles/liter		Observed activity of $SbS_4^=$ in counts/min.	Fraction of total $SbS_4^=$ measured	Percent exchange
$S^=$	$SbS_4^=$			
0.00197	0.00158	43.1	.58	51±10%
0.00197	0.00158	44.2	.63	47±10%

Non-Exchange of Sulfide and Thiocyanate Ions. Radiosulfide ion was mixed with a solution of thiocyanate ion. After a measured time, sulfide was separated by acidifying the mixture and collecting silver sulfide according to the details given by Swift[5]. The results, which indicate no appreciable exchange are recorded in Table II.

TABLE II

The Non-Exchange of Sulfur between Sulfide and Thiocyanate Ions

Temperature	Time allowed for exchange	Concentration in moles/liter			Observed activity in div./sec.		Per cent exchange
		CNS^-	$S^=$	OH^-	$S^=$	CNS^-	
98.0° C.	3 hrs.	0.37	0.21	1.30	0.0015 ±0.0002	0.0002 ±0.0002	13±13
25.0° C.	53 hrs.	0.30	0.50	.2	0.6654 ±0.0002	0.0200 ±0.0002	3±2
25.0° C.	83 min.	0.067	0.11	0.67	0.6654 ±0.0002	0.0021 ±0.0002	0.3±2
95.0° C.	79 min.	0.067	0.11	0.67	0.5868 ±0.0002	0.0068 ±0.0002	1.1±2
95.0° C.	37 min.	0.067	0.11	0.67	0.5542 ±0.0002	0.0021 ±0.0002	0.4±2

Non-Exchange of Sulfate and Peroxydisulfate Ions. Radio sulfur in the form of sodium sulfate, after remaining in solution with ammonium peroxydisulfate, was separated by addition of barium chloride to the slightly acidic solution. After the barium sulfate was filtered off for radioactivity measurement, the peroxydisulfate in the filtrate was reduced to sulfate and precipitated as barium sulfate for activity measurement. The results are shown in Table III. No appreciable exchange occurred even in the presence of silver ion.

TABLE III

The Non-Exchange of Sulfur between Sulfate and Peroxydisulfate Ions at 25 C.

Time	Concentration in moles/liter		pH	Observed activity in div./sec.		Percent exchange
	$SO_4^=$	$S_2O_8^=$		$SO_4^=$	$S_2O_8^=$	
17 hr.,56 min.	.0430	.0215	7	.2506	.0005	0.2
78 hr.,05 min.	.0860	.0430	7	.2449	.0007	0.3
60 hr.,35 min.	.0688	.0344	13	.2100	.0006	0.3
57 hr.,15 min.	.0688	.0344	1	.1985	.0001	0.1
*232 hr.	.033	.0166	7	.2365	.0001	0.0

*In this experiment the silver ion concentration was about 0.004 normal.

Non-Exchange of Sulfur between Sulfate and Dithionate Ions. A procedure similar to the one above was used. Sulfate was precipitated and measured as barium sulfate and the filtrate was evaporated to dryness so that dithionate could be tested for radioactivity in the form of the sodium salt. No exchange was observed, as shown in Table IV.

TABLE IV

The Non-Exchange of Sulfur between Sulfate and Dithionate Ions at 18° C. after 21 Hours

Concentration in moles/liter		pH	Observed activity in counts/minute		Per cent exchange
$SO_4^=$	$S_2O_6^=$		$SO_4^=$	$S_2O_6^=$	
.19	.24	6	118	2.4	2±2

Discussion

Before the exchange reactions recorded above are discussed, a summary of existing data on sulfur and oxygen exchange reactions is presented in the following two tables. Table VI contains results of studies using O^{18} in different laboratories. Perfect unanimity of the various authors is not indicated, but the disagreements are now fairly satisfactorily settled.[11]

TABLE VI

Exchange Reactions of Oxygen between Water and Various Soluble Oxygen-Containing Salts

Oxygen-containing salt	Time allowed for exchange	Temp.	Observed exchange	Authority
K_2SO_3	24 hrs.	100° C.	*None	10
K_2SO_3	8 hrs.	100° C.	Complete	11
K_2SO_3-NaOH	5 hrs.	100° C.	None	11
$Na_2S_2O_5$	1 to 24 hrs.	19.3° C.	Partial	10
$K_2S_2O_3$	2 hrs.	19.3° C.	None	10
$K_2S_2O_3$	2 hrs.	100° C.	Partial	10
$K_2S_2O_3$	24 hrs.	100° C.	Complete	10
$Na_2S_2O_3$	5 hrs.	100° C.	Complete	11
$K_2S_2O_3$-NaOH	4 hrs.	100° C.	None	10
$Na_2S_2O_3$-NaOH	3 hrs.	100° C.	None	11
$KHSO_4$	25 hrs.	100° C.	Partial	10,7,8
$KHSO_4$	38 hrs.	100° C.	None	9
Na_2SO_4	24 hrs.	100° C.	None	11,6,7,8
Na_2SO_4-HCl	12 hrs.	100° C.	23%	11,8,9
Na_2SO_4-NaOH	18 to 26 hrs.	100° C.	Partial	6,7,8
Na_2SO_4-NaOH	15 hrs.	100° C.	None	11,9
Na_2SeO_3	5 hrs.	100° C.	Complete	11
Na_2SeO_3-NaOH	1 hr.	100° C.	Complete	11
Na_2SeO_4	24 hrs.	100° C.	None	11
Na_2SeO_4-NaOH	12 hrs.	100° C.	None	11

*Observation considered likely to be in error.

The principal generalization that may be drawn from the data in Table VI is that in a series of oxy-anions with the same central atom, the anions with the smallest number of oxygen atoms exchange most readily. This generalization is obeyed in the cases of the following pairs of anions: sulfate and sulfite, sulfate and thiosulfate, selenate and selenite. Sulfate ion, in agreement with its interatomic distances and resonance,[12] might have been predicted not to exchange any of its oxygen atoms, regardless of hydration effects, and is actually found not to exchange.

TABLE VII

Exchange Reactions of Sulfur-Containing Anions

Exchanging anions		Time allowed for exchange	Temp.	Observed exchange	Authority
$S^{=}$	$SO_4^{=}$	36 hrs.	100° C.	None	1,2
$S^{=}$	$S_2O_3^{=}$	23 hrs.	100° C.	Appreciable	1,2
$S^{=}$	SCN^{-}	79 min.	95° C.	None	13
$S^{=}$	$SbS_4^{\equiv}$	48 hrs.	25° C.	Appreciable	14
$S^{=}$	S°	1 hr.	100° C.	*Appreciable	1,2
CS_2	S°	68 hrs.	98° C.	None	15
#$S_2O_3^{=}$				None	16
$SO_4^{=}$	$SO_3^{=}$	36 hrs.	100° C.	None	1,2
$SO_4^{=}$	$S_2O_6^{=}$	21 hrs.	18° C.	None	17
$SO_4^{=}$	$S_2O_8^{=}$	232 hrs.	25° C.	None	17
$SO_3^{=}$	$S_2O_3^{=}$	1 hr.	100° C.	Appreciable	1,2
SO_3	SO_2	17 hrs.	280° C.	None	1,2

*Predicted by the authors to be rapid at 25 C.
#Exchange between peripheral and central sulfur atom in $S\overset{O}{\underset{O}{S}}O$ is meant here.

For the purpose of comparing the exchange reactions of oxygen and sulfur which are in the same periodic group, hydrogen sulfide is taken as the sulfur-containing compound which is the analog of the oxygen-containing compound, water. Possible reasons why hydrogen sulfide and carbon disulfide do not exchange, although water and carbon dioxide do,[10] have been considered on page 32 of this thesis.

In agreement with the non-exchange of oxygen between sulfate ion and water in alkaline solution, sulfide ion does not exchange with sulfate.

Although water does not exchange with molecular oxygen, sulfide ion does exchange with elementary sulfur. This difference is not surprising in view of the stability of polysulfide ion compared to the non-existence of an analogous oxygen compound. Elementary sulfur does not exchange with carbon disulfide, so it may be predicted that oxygen will not exchange with carbon dioxide under similar conditions.

The exchange of sulfide ion with the peripheral sulfur atom of thiosulfate suggests very strongly the possibility of exchange of oxygen between water and thiosulfate. This latter exchange does take place. Since sulfide ion does not exchange with thiocyanate ion, we predict that water will not exchange with cyanate ion. However, water does exchange with sulfite ion, although sulfide ion does not exchange with sulfite ion.

In view of the non-exchange of the oxygen in water between alkaline phosphate and alkaline sulfate, the exchange of sulfur between sulfide ion and thioantimonate[20,21] was somewhat unexpected. However, the exchange of sulfide and thiosulfate had suggested that it might occur.

The non-exchange of sulfur between sulfite and sulfate is to be expected because of the nature of sulfate ion. The exchange of sulfur between sulfite and thiosulfate is in agreement with the ready exchange of both of these ions with water.

There is no exchange of sulfur between sulfur dioxide and sulfur trioxide at 280° C. in the presence of platinum or water although a very simple mechanism, ${}^{*}\underset{O}{\overset{O}{S}} + O\underset{O}{\overset{O}{S}} = {}^{*}\underset{O}{\overset{O}{S}}O + \underset{O}{\overset{O}{S}}$, might have allowed exchange. Surely under the above conditions in the presence of water oxygen atoms would exchange since sulfite exchanges readily with water and the sulfur trioxide could exchange its oxygen atoms with water by reversible hydration.

The exchange of sulfur between sulfate ion and peroxydisulfate ion, which did not occur was studied to determine if the sulfate group as a unit would exchange, possibly by simultaneous rupture and formation of a peroxide bond. The previous results on the exchange of sulfate ion suggested that individual sulfur atoms would not exchange.

The non-exchange of sulfur between sulfate and dithionate might have been predicted from the above exchange but was shown not to occur.

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THE EXCHANGE OF VANADIUM BETWEEN VANADYL AND VANADATE IONS

Introduction

Speculations[1,2] based on electromotive force measurements of cells containing pentavalent vanadium have not definitely proven the exact constitution of the vanadium in acidic aqueous solution. It was hoped that a thorough study of the exchange of vanadium between the pentavalent and tetravalent forms as a function of hydrogen ion concentration might indicate something of interest regarding the postulated forms of pentavalent and tetravalent vanadium. The investigation of the exchange was not completed, but the preliminary results are given.

Experimental Part

Radiovanadium[3] of mass number forty-eight, and of half life sixteen days was prepared by bombarding titanium dioxide with deuterons from the Berkeley cyclotron.* To dispose of radioactive contaminants the following carrier elements were added to the deuteron irradiated titanium dioxide: V, Yt, P, S, Si, Fe, C, N, Na, K. The mixture

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*We wish to thank Professor E.O. Lawrence and Dr. M. Kamen for the gift of this sample.

was fused with six parts of sodium carbonate and one part of potassium nitrate. The melt was treated with water and the aqueous phase filtered. The filtrate was made neutral and mercurous vanadate was quantitatively precipitated.[4] The mercurous vanadate was ignited to vanadium pentoxide. The vanadium pentoxide was again mixed with the carrier elements and the procedure described above was repeated twice. Finally the vanadium pentoxide was dissolved in nitric acid and precipitated as lead vanadate. A stock solution of radiovanadium sulfate was prepared by treating the lead vanadate with sulfuric acid and filtering off the lead sulfate.

Two methods of separating vanadyl and vanadate ions were used. In the first method the addition of concentrated ammonium hydroxide to a solution containing vanadyl and vanadate ions yielded a precipitate of tetravalent vanadium which was collected by centrifuging. The precipitate was washed with water and again centrifuged before being examined for radioactivity. The results obtained using the first method of separation indicated that solutions 0.05 molal in vanadate and vanadyl ion and 0.23 normal in sulfuric acid exchanged to the extent of 60% in 50 minutes at 25° C.

Because of the possibility that pentavalent vanadium might be occluded by the precipitate of tetravalent vanadium, thus vitiating activity measurements, and because the precipitation was not quantitative, a second method, considered more reliable, was used. The second method of separation involved the extraction of pentavalent vanadium from a mixture of vanadyl and vanadate ions 7.75 normal in hydrochloric acid by means of isopropyl ether.[5]

The stock solution of radiovanadate was converted quantitatively into a vanadyl solution by reduction[6] with sulfur dioxide. After a solution of vanadate and radiovanadyl at a known concentration of acid had stood for a measured time, enough concentrated hydrochloric acid was added to make the solution 7.75 normal in hydrochloric acid. A volume of isopropyl ether equal to the volume of the solution was shaken with the solution and the ether phase withdrawn. Evaporation of the ether phase yielded a sample whose radioactivity was measured. The vanadium in the aqueous phase was also collected by evaporation and examined for radioactivity. After activity measurements were made, the amounts of vanadium in the measured samples were determined volumetrically.[6]

Results and Discussion

The results using the second method of separation, recorded in Table I, indicate that at high concentrations (7.75 normal) of hydrochloric acid no appreciable **exchange** occurs within an hour, whereas at concentrations of hydrochloric acid of the order of 0.1 normal appreciable exchange occurs within an hour. The fact that the rate of exchange appears to increase with decrease in acid concentration might be explained by the slowness of the first step in the following possible mechanism of exchange:

$$\overset{*}{V}O^{++} + H_2O = \overset{*}{V}O_2 + 2H^{+} \quad \text{slow}$$

$$\overset{*}{V}O_2 + VO_2^{+} = \overset{*}{V}O_2^{+} + VO_2 \quad \text{fast}$$

TABLE I

The Exchange of Vanadium between Vanadyl and Vanadate Ions at 25° C.

Time allowed for exchange	Concentration in moles/liter			Observed activity in div./sec.		Per cent exchange
	V^{+4}	V^{+5}	Acid	V^{+4}	V^{+5}	
5 min.	0.032	0.029	7.75	0.2205	0.0004	2±5
60 min.	0.032	0.029	7.75	0.2760	0.0005	2±5
60 min.	0.011	0.026	0.07	0.0167	0.0006	26±5
105 min.	0.076	0.043	0.16	0.1464	0.0108	95±5

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6. Treadwell, op. cit., p. 575

PART III

THE SOLUTION OF A PROBLEM
FOR THE
NATIONAL DEFENSE RESEARCH COMMITTEE

PART IV

MISCELLANEOUS RESEARCHES

[Reprinted from the Journal of the American Chemical Society, **62**, 2477 (1940).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 778]

The Structure of Thionyl Bromide

BY D. P. STEVENSON AND ROBERT A. COOLEY

In this communication we report the results of an electron diffraction investigation of the structure of thionyl bromide. The structure of this molecule is of particular interest since it is, as far as we are able to ascertain, the only molecule possessing a sulfur–bromine bond which is sufficiently stable to permit the preparation of electron diffraction photographs of the vapor.

Experimental

The electron diffraction apparatus used in this investigation has been described by Brockway.[1] The camera distance was 10.85 cm. and the wave length of the electrons, determined in the usual way[1] from transmission photographs of gold foil (a_0 = 4.070 Å.), was 0.0618 Å.

The thionyl bromide was prepared by the reaction of thionyl chloride with dry hydrogen bromide at 0° as described in "Inorganic Syntheses."[2] The product was twice distilled *in vacuo*, generous first and last portions being discarded. Analysis of the final material by the precipitation and weighing of silver bromide gave 76.88% bromine (theoretical 76.88%). After standing for thirteen weeks the sample showed 76.90% bromine, indicating that no appreciable decomposition had taken place.

The high temperature nozzle was used to form the gas jet in order to avoid the long gas path and resultant condensation difficulties which accompany the use of the low temperature nozzle. It was found that a temperature of from 40 to 60° sufficed to give the vapor pressure necessary for the preparation of the electron diffraction photographs.

The photographs showed eight measurable rings whose s $\left(s = \frac{4\pi}{\lambda} \sin \frac{\Theta}{2}\right)$ values are given in Table I. The appearance of the photographs is very satisfactorily reproduced by curve C of Fig. 1.

TABLE I

Max.	Min.	C_n	s_0	s_c[a]	s_c/s_0
	1	−7	1.69	1.64	(0.970)[b]
1		6	2.54	2.63	(1.035)
	2	−5	3.23	3.25	1.006
2		13	4.16	4.10	0.986
	3	−17	5.10	5.11	1.002
3		20	6.20	6.18	0.997
	4	−15	7.53	7.38	0.980
4		18	9.10	9.08	0.998
	5	−22	10.28	10.48	1.019
5		19	11.57	11.61	1.003
	6	−12	12.89	12.77	0.991
6		14	14.58	14.92	1.023
	7	−15	15.86	16.10	1.015
7		12	17.33	17.24	0.995
	8	−10	18.52	18.32	0.989
8		8	19.95	19.30	(0.967)
		Average of 13 features			1.000 ± 0.009

[a] Model of curve C of Fig. 1. [b] Values in parentheses omitted from average because of unreliability of the measurements.

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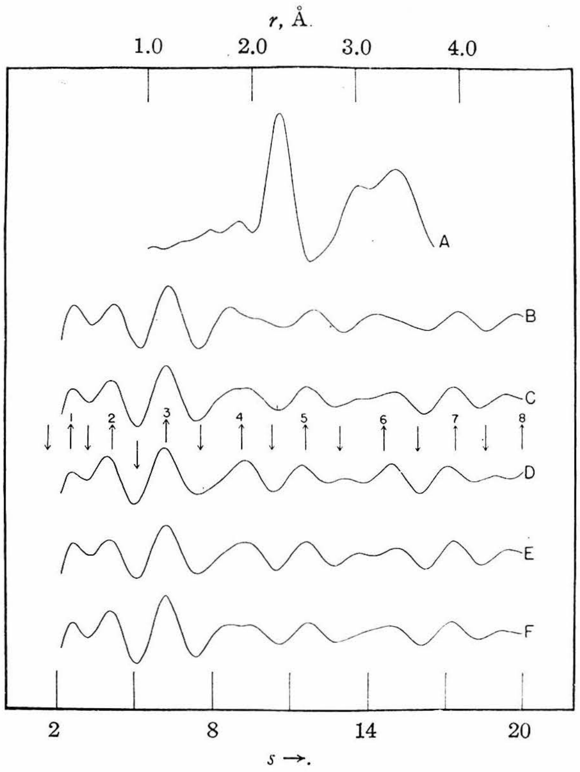

Fig. 1.—Curve A, radial distribution function. Curves B through F, theoretical intensity curves. S–Br = 2.27 Å., S–O = 1.45 Å.

Curve	Br–S–Br	Br–S–O
B	93°	108°
C	96°	108°
D	99°	108°
E	96°	105°
F	96°	111°

Interpretation

The radial distribution function[3a,b] shown as curve A of Fig. 1 was calculated with the coefficients C_n given in column 3 of the table. The three maxima at 2.27, 3.04 and 3.37 Å. correspond to the sulfur–bromine, bromine–oxygen and bromine–bromine distances, respectively. Using the first and last of these distances one obtains 96° for the bromine–sulfur–bromine angle, and if one assumes 1.45 Å. for the sulfur–oxygen distance (as found in thionyl chloride[4]) the bromine–oxygen distance of 3.04 Å. corresponds to 108° for the bromine–sulfur–oxygen angle.

Theoretical intensity curves were calculated for a number of molecular models closely related to the one suggested by the radial distribution function and the known structure of thionyl chloride.[4] The formula

$$I(s) = \sum_{i,j} \frac{(Z_i - f_i)(Z_j - f_j)}{(Z - f)^2_{\mathrm{Br}}} \frac{\sin l_{ij}s}{l_{ij}s}$$

was used for the theoretical intensity. The various symbols have their usual significance,[4] and the atomic scattering factors for x-rays, f, were taken from the table of Pauling and Sherman.[5] The curves for models with either of the bond angles more than two degrees different from those suggested by the radial distribution function do not satisfactorily reproduce the appearance of the fourth and sixth maxima while the curve for the model suggested by the radial distribution function reproduces the entire appearance of the photographs very well (see curve C of the figure).

Quantitative comparison of the photographs with curve C given in the table leads to the following values for the structural parameters.

S–Br = 2.27 ± 0.02 Å.
Br–O = 3.05 ± 0.03 Å.
Br–S–Br = 96 ± 2°

Due to the fact that the sulfur–oxygen term contributes but 5% to the total molecular scattering, it was not feasible to determine either the sulfur–oxygen distance or the ratio of the sulfur–bromine distance to the sulfur–oxygen distance.

Discussion

The sulfur–bromine distance found in thionyl bromide (2.27 ± 0.02 Å.) is considerably greater than the sum of the covalent radii of sulfur and bromine (2.18 Å.). The reason for this discrepancy is not known but it should be noted that the sulfur–chlorine distance in thionyl chloride[4] (2.06 ± 0.02 Å.) is also greater than the covalent radius sum (2.03 Å.) and the bond distance observed for sulfur dichloride[4] (2.00 Å.).

The bromine–sulfur–bromine angle (96 ± 2°) agrees well with the value found for the chlorine–sulfur–chlorine angle in thionyl chloride (97.5 ± 3°).[4b] The assumption of 1.45 Å. for the sulfur–oxygen distance seems quite safe since this distance has been found to be 1.45 ± 0.02 Å. in thionyl chloride and 1.46 ± 0.02 Å. in methyl sulfoxide.[6] The value of the bromine–sulfur–oxygen angle which results from this assumption (108 ± 3°) is in good agreement with the values found for the similar angle in thionyl chloride (107.5 ± 3°)[4b] and methyl sulfoxide (106 ± 3°).[6]

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(4) (a) K. J. Palmer, This Journal, **60**, 2361 (1938). (b) D. P. Stevenson and J. Y. Beach, unpublished observations.

(5) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(6) R. E. Rundle and D. P. Stevenson, unpublished observation.

Summary

The interpretation of electron diffraction photographs of thionyl bromide yields the following values for the structural parameters in the gas phase.

S–Br = 2.27 ± 0.02 Å.
Br–S–Br = 96 ± 2°
Br–O = 3.05 ± 0.03 Å.
S–O = 1.45 Å. (assumed)

PASADENA, CALIFORNIA

RECEIVED JUNE 19, 1940

PREPARATION OF BIVALENT EUROPIUM SALTS[1]

By

Robert A. Cooley and Don M. Yost

As more and more interest is being shown in non-trivalent rare earth salts, a convenient method of obtaining them is desirable. The reduction of trivalent europium to the bivalent state may be accomplished simply with a Jones reductor[2] or more elaborately by the reduction of europium trichloride with hydrogen[3] at 700°C. The importance of europous carbonate is to be emphasized here since, by the addition of the proper acid to it, practically any europous salt may be secured. In the following there are described three procedures, the first for the preparation of europous sulfate, the second for europous carbonate, and the third for europous chloride. Fortunately, these europium salts when dry are not appreciably oxidized by dry air and hence may be conveniently handled and stored. The first procedure given is based on the preparation of insoluble europous sulfate with a Jones reductor. The washed europous sulfate is converted to europous carbonate according to the revers-

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1. This method of preparation was submitted for publication in Inorganic Syntheses, Vol. II, W. C. Fernelius, Editor.
2. McCoy, J.A.C.S., 57, 1756 (1935).
3. Baxter and Truemmler, J.A.C.S., 59, 1131 (1937); 60, 602 (1938).

ible metathetic reaction.-

$$EuSO_4 + Na_2CO_3 \rightarrow EuCO_3 + Na_2SO_4$$

(Procedure 2). The third procedure involves treating dry europium trichloride in a quartz boat at about 700°C with an approximately equimolal mixture of dry hydrogen and hydrochloric acid to prepare europous chloride.

Procedure 1.- Preparation of $EuSO_4$.

About 3.5 grams of Eu_2O_3 are dissolved in sufficient hydrochloric acid to give, on dilution, about 200 ml. of solution 0.05 molal each in trivalent europium and hydrochloric acid. A Jones reductor containing 20 to 30 mesh amalgamated zinc in a column 40 cm. high and 2 cm. in diameter is flushed out with 200 ml. of 0.05 molal hydrochloric acid, just enough acid being finally left in the column to cover the zinc. The nozzle of the reductor is then dipped into 50 ml. of 8 molal sulfuric acid in a 500 ml. beaker covered with a paper disc; a stream of carbon dioxide is passed into the beaker to insure the exclusion of air. The europium trichloride solution is slowly passed through the reductor and is followed by a wash solution of 150 ml. of .05 molal hydrochloric acid. A feathery or tuft-like white precipitate, the α modification of europous sulfate is formed at first. The mixture is heated to 80°C. whereupon the α form changes to the more stable

β form which is dense and crystalline and settles to a compact mass. The β form, unlike the α form, is only slightly soluble in sulfuric acid solution. The mixture containing the dense white europous sulfate is filtered, and the precipitate is washed with dilute hydrochloric acid and methyl alcohol. The final product is dried in air at 75°C.; the yield is about ninety-nine percent.

Procedure 2.- Preparation of $EuCO_3$.

To 300 ml. of a vigorously boiling[1] solution, 1 normal in sodium carbonate and 0.4 normal in sodium hydroxide, there are added about 5 grams of dry europous sulfate as prepared above. Shortly after the addition, the mixture becomes dark in color, but on continued boiling the dark color disappears, and a lemon yellow, dense, crystalline precipitate of europous carbonate[2] forms. The europous carbonate is filtered and dried in air at 75°C.

Procedure 3.- Preparation of $EuCl_2$.

About 3 grams of dry europic chloride[3] in a quartz

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[1] Boiling rids the solution of dissolved oxygen which rapidly oxidizes europous ion.

[2] Treatment of larger quantities requires removal of the first amount of sulfate ion formed, and renewal of the carbonate ion used up.

[3] See Anhydrous Rare Earth Chlorides, Procedure II, Vol. I, Inorganic Syntheses.

4.

boat[1] are introduced into a vitrified quartz tube[2], and the tube is placed in an electric furnace. A stream of a one to one mixture of hydrogen gas and hydrochloric acid gas is passed through the tube, and the temperature is raised first to 120°C. The heating is continued for two hours at 700°C. The furnace is then turned off, and when it is cool the hydrogen-hydrochloric acid atmosphere is replaced by one of dry nitrogen[3]. Dry air does not oxidize dry europous chloride.

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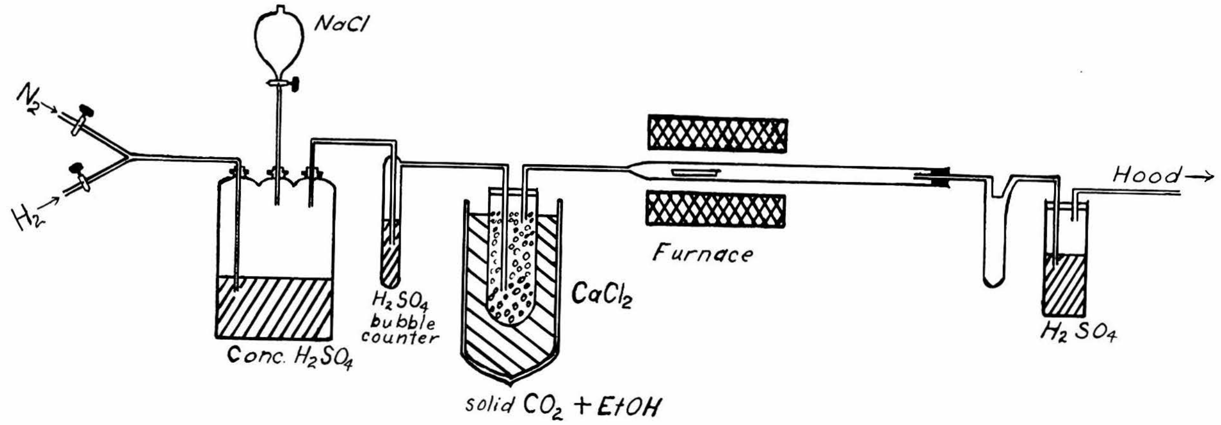
[1] Platinum is slightly attacked by the molten salt but quartz is affected but little.

[2] Vitrified quartz tubing is much cheaper than transparent quartz. The former may be purchased from the Thermal Syndicate, Limited, Schenectady and Atlantic Avenues, Brooklyn, New York.

[3] To avoid any possibility of a hydrogen-oxygen explosion, the introduction of the hydrogen gas mixture should precede turning on the furnace, and the hydrogen gas mixture should be replaced by nitrogen before removing the quartz boat.



Preparation of $EuCl_2$

The diagram depicts a convenient apparatus for carrying out the above procedure. The introduction of tank hydrogen or nitrogen may be controlled by stopcocks as indicated at the left of the diagram. Hydrochloric acid gas is formed by dropping a saturated solution of NaCl into concentrated sulfuric acid. The bubble counter filled with concentrated sulfuric acid is used as follows. Hydrogen gas is introduced through the counter at the rate of one bubble per second, and then the rate of formation of hydrogen chloride gas is regulated so that the rate of flow of the gas mixture through the counter is two bubbles per second. Water in the gas mixture is removed when it reaches the trap, T, containing freshly fused calcium chloride immersed in a solid carbon dioxide-alcohol bath. A thermocouple wrapped in asbestos paper and placed between the furnace and quartz tube indicates the temperature.

OBSERVATIONS ON THE OXIDATION OF EUROPOUS ION BY PERCHLORATE ION AND HYDROGEN ION

Introduction

Perchlorate ion is reduced at a measurable rate by few reducing agents. The rate of reduction of perchlorate ion by many moderately strong reducing agents is negligibly slow, whereas the reduction of perchlorate ion by strong reducing agents at elevated temperatures frequently proceeds with explosive velocity. The only ions so far reported[1] to reduce perchlorate ion at a measurable rate are trivalent titanium, trivalent molybdium (olive green and orange forms) and bivalent chromium. Ruthenium catalyzes the reduction of perchlorate ion by hydrobromic acid.

Of all the rare earths, europium is the only one sufficiently stable in the bivalent state in aqueous solution to allow very extensive investigation. Preliminary experiments carried out by Mr. Phillip Grieger indicated that 0.003 normal europous chloride in 0.02 normal perchloric acid was ninety per cent oxidized to trivalent europium in seven hours at 25° C.

Experimental Part

Professor H. N. McCoy kindly made available to us several grams of europium oxide containing not more than one per cent of other rare earths. In the first experiments a solution of europous chloride was prepared by passing a solution of europic chloride through a Jones reductor such as the one described on page 70. The solution was protected from atmospheric oxidation by having the nozzle of the reductor dip into a covered beaker through which a stream of carbon dioxide was flowing. This europous solution, about 0.001 normal, was pipetted into a solution of perchloric acid from 3 to 0.001 normal. After measured intervals of time samples from the reacting solution, thermostated at 25° C., were pipetted out and analyzed for divalent europium by adding to each sample a known excess of standard potassium permanganate and then an excess of solid potassium iodide. The amount of iodine formed was determined by titration with thiosulfate solution and was a measure of the amount of divalent europium present, since permanganate rapidly oxidizes divalent europium to the trivalent state. The results of these experiments at 25° C. indicated that complete oxidation occurred in about five minutes when the europous ion concentration was 0.003 normal and the perchloric acid was 0.010 normal. However, there was not any significant trend in the time required for complete oxidation when the concentration of europous ion was increased two-fold and the concentration of perchloric acid was increased one thousand-fold. It was thought that the rapid oxidation of the europous ion might have been caused by oxygen[2] in the solution or atmosphere in spite of the effort that had been made to avoid the introduction of oxygen by using carbon dioxide.

After the above experience, more elaborate precautions were taken to prevent oxidation of europous ion by oxygen. The water used in making solutions was freed of oxygen by boiling and cooling under an atmosphere of tank nitrogen which had passed through alkaline pyrogallol. Solid europous carbonate (prepared as described on page 71) was weighed into vessels filled with carbon dioxide, and oxygen-free perchloric acid solution at 0° C. was introduced. Using this new method 0.1 normal europous ion and 0.1 normal perchloric acid required about two hours for complete oxidation of the europous ion. However, reproducible results were not obtained, possibly because of the oxygen error.

Initially it was thought that the reaction under study was simply

$$8Eu^{++} + ClO_4^- + 8H^+ = Eu^{+++} + Cl^- + 4H_2O. \quad (1)$$

Qualitative tests with very small amounts of divalent europium and perchloric acid indicated that the reaction was not (1) above because little or no silver chloride appeared on addition of silver nitrate to the product solution.

Quantitative experiments using larger amounts of europium were carried out as follows. Weighed amounts of europous carbonate were introduced into test tubes containing carbon dioxide gas. Two milliliters of 9 normal perchloric acid were then pipetted into the test tubes and the test tubes were stoppered tightly with rubber. A black precipitate, which may have been $Eu(ClO_4)_2$, formed on the addition of the acid. The black precipitate, which formed only when the acid concentration was high, disappeared very slowly with time. The tubes were left stoppered at room temperature until it was estimated that 99% of the black precipitate had disappeared. Oxygen was then introduced into the solution, the solution made slightly acid with nitric acid, and silver nitrate added. The precipitate was collected and weighed in a small sintered glass funnel. The results of these experiments are recorded in Table I.

TABLE I

The Formation of Chloride Ion in the Reaction between Europous Carbonate and Perchloric Acid at 25° C.

Wt. of $EuCO_3$ in grams	Vol. of 9n $HClO_4$ in ml.	Time allowed for reaction	Per cent of theoretical yield of chloride ion according to (1)
.310	2	45 days	30
.456	2	47 days	5.6
.460	2	210 days	26
.66	1	1 day	27
.20	2	13 hours	2.9

It is difficult to explain the large variation in the per cent of the theoretical yield of chloride ion under the apparently identical experimental conditions. However, it is clear that the reduction of perchlorate ion does not take place according to (1) without side reactions. Hydrogen ion, which is thermodynamically capable, must oxidize europous ion under the above conditions.

A qualitative experiment on the stability of insoluble europous sulfate in perchloric acid solution showed that 0.1 gram of europous sulfate placed in 10 ml. of a solution 2 normal in sulfuric acid and 0.3 normal in perchloric acid, and sealed off from air was about 95% dissolved after eight months at room temperature.

The difficulty of excluding oxygen in the manipulation of europous solutions led to the search for a more convenient and certain method of analysis than the one so far employed. The fact that the magnetic susceptibility[3] of divalent europium is much greater than that of trivalent europium suggested that it would be possible to determine the bivalent europium concentration of a reacting solution by magnetic susceptibility measurements. An important advantage of this method is that after the reacting solution is prepared, it may be sealed up with no possibility of oxygen from the atmosphere interfering, and practically continuous readings may be taken.

The rate of oxidation of europous ion by hydrochloric acid was investigated at 25°C. using the Gouy method of measuring magnetic susceptibility. After the constants of a Gouy tube had been measured, the part of the tube used to hold the europium solution was filled with carbon dioxide. A weighed amount of solid europous carbonate was placed in the tube and the tube was closed with a thin rubber stopper. A stainless steel hypodermic needle was then passed through the rubber stopper, and a pipette fitted with a hypodermic needle and containing oxygen-free hydrochloric acid solution was made to pierce the rubber stopper. The solution in the pipette was forced into the tube by applying a pressure of carbon dioxide gas to the pipette. The hypodermic needles were then removed,and after the solution was stirred susceptibility measurements were commenced.

The results of two runs, shown in Fig. 1 and Fig. 2, indicate that the reaction is too slow to follow conveniently. The initial concentrations of europous chloride and hydrochloric acid used in the runs are indicated on the figures.

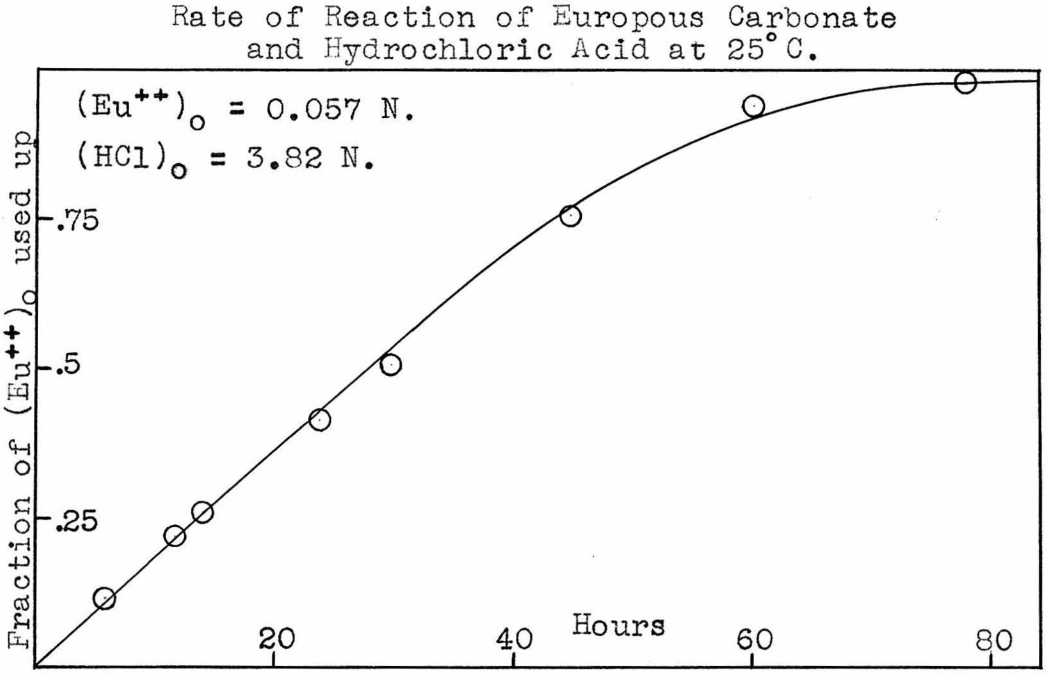

Rate of Reaction of Europous Carbonate and Hydrochloric Acid at 25° C.

Fig. 1

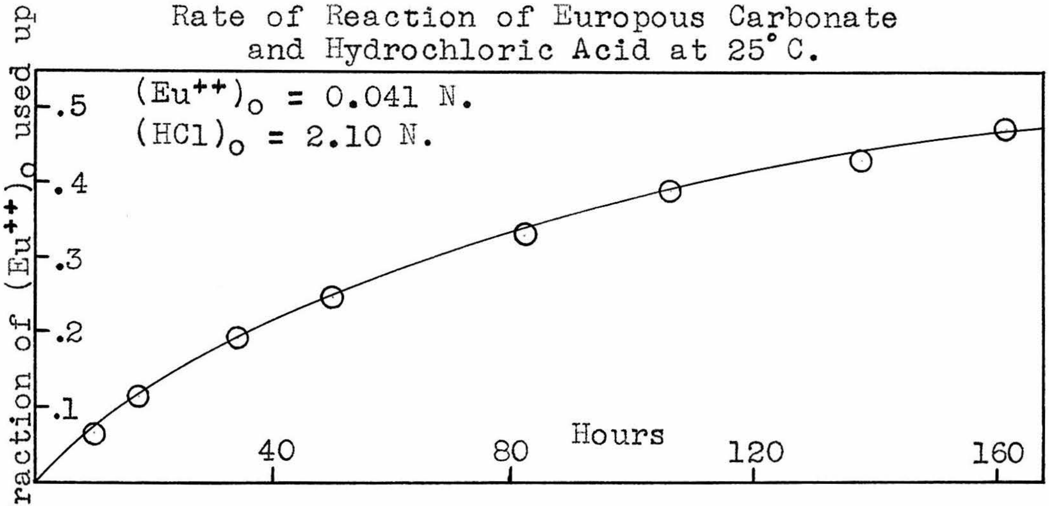

Rate of Reaction of Europous Carbonate and Hydrochloric Acid at 25° C.

Fig. 2

References

1. Bredig and Michel: Zeit. phys. Chem., <u>100</u>, 124 (1922)
2. McCoy: J. Am. Chem. Soc., <u>58</u>, 1577 (1936)
3. Selwood: J. Am. Chem. Soc., <u>55</u>, 4869 (1933)

NOTE ON THE ELECTROSCOPE

The electroscope, in its simplest form, developed largely through the pioneer work of C. T. R. Wilson[1] and extensively applied to radioactive measurements by Rutherford[2], consists of an insulated leaf system enclosed in an ionization chamber. The leaf system is charged electrostatically and the rate of movement of the leaf due to decrease in potential is observed. The movement of the leaf may be viewed with a telemicroscope having a scale engraved on the eyepiece, or an image of the leaf may be projected on a screen for magnification.

Bastings[3] has conclusively shown that an electroscope may be designed to give an accuracy of at least 0.1% in measuring radiations from unstable bodies. The influence of the nature and pressure of the gas in the ionization chamber on the performance of the electroscope in measuring penetrating radiation has been experimentally investigated[3]. The following gases are listed in the order of their ability to increase the sensitivity of the electroscope: SO_2, CO_2, A, O_2, air, N_2, H_2. SO_2 is about ten times as effective as H_2. The specific sensitivity of the electroscope for penetrating radiation is approximately proportional to the pressure of the gas in the ionization chamber, within reasonable limits.

The volume and shape of the ionization chamber is significant because the rate of movement of the leaf or fiber depends on the arrival at the positively charged leaf or fiber of anions formed in the gas by the radiation. The larger the volume of the chamber the more radiation enters the chamber. However, increasing the volume increases the chance of anions formed in the gas far from the leaf being neutralized by cations before reaching the leaf. It has been shown experimentally[3] that when the leaf system is centrally located in a chamber, a cylindrical chamber with hemispherical ends is superior to a spherical or cubical chamber.

Professor C. C. Lauritsen[4] has perfected an electroscope consisting of a light cantilever quartz fiber system mounted on an amber insulator contained in a 200 ml. aluminum ionization chamber. The movement of the metallized quartz fiber 3μ in diameter and 1 mm. long is viewed by means of a microscope with a graduated eyepiece. The characteristics of the electroscope are:

(1) A high sensitivity of 4 division/minute/millicurie at one meter.

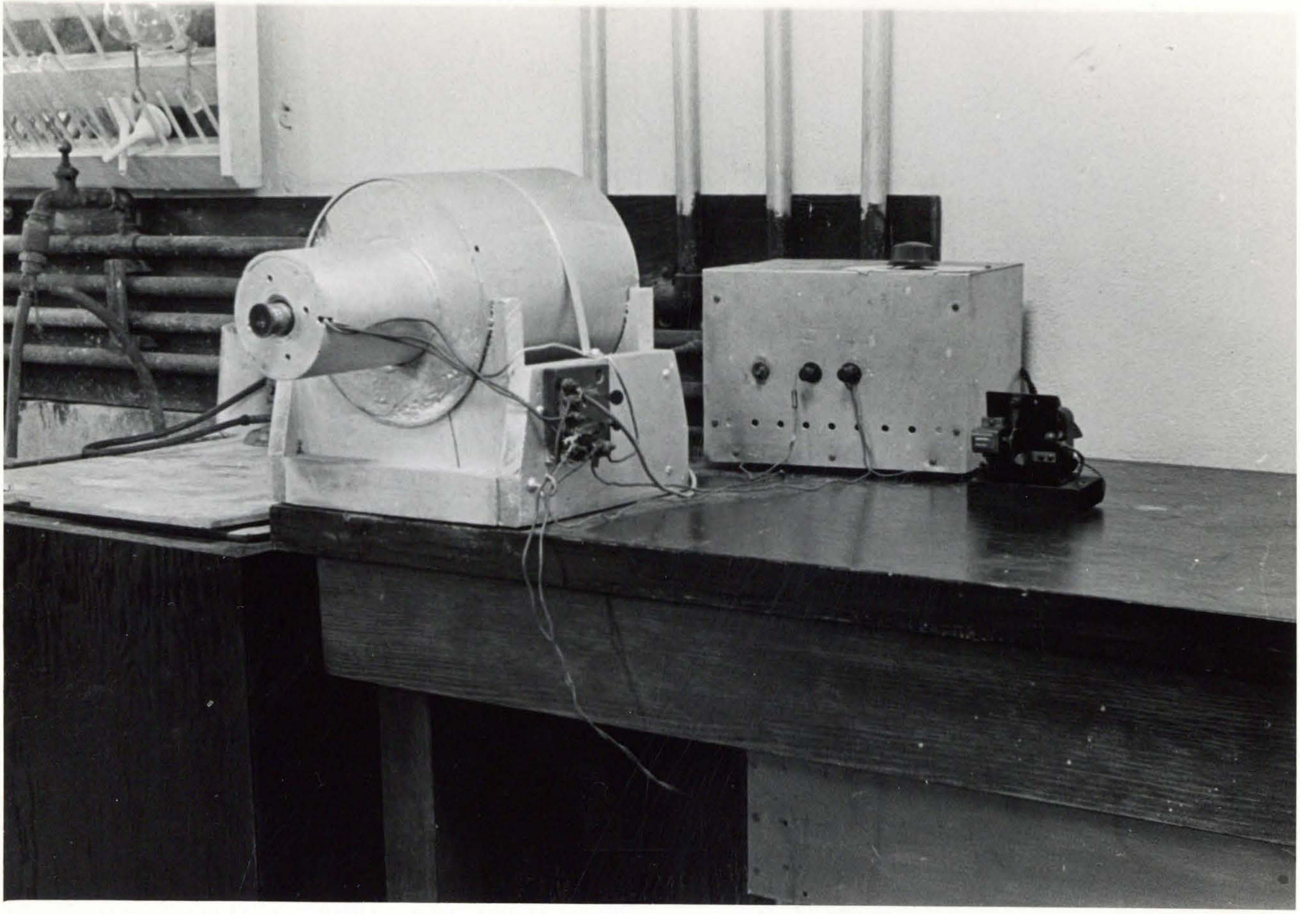
(2) A background of 1.3 divisions/hour.

(3) A low capacity of about $1/3$ centimeter.

(4) Small insulator surface (1 mm. diameter x 3 mm. long) to minimize dielectric absorption and effect of stray charge.

(5) An approximately linear scale.

A Lauritsen electroscope, enclosed in a lead cylinder (O.D. 21 cm., I.D. 9 cm., Length 20 cm.) to reduce ionization due to natural penetrating radiation and to prevent disturbing convection currents in the chamber was used to measure quantitatively the specific radioactivity of samples as described in part of this thesis. The original aluminum can of the electroscope was replaced by a brass can having a screen window 5 cm. x 7 cm. covered with .00025 inch thick aluminum foil. In this apparatus it was possible to introduce a sample in a sample holder reproducibly, close the end of the lead cylinder with a lead plug 5 cm. thick and charge the electroscope by means of a solenoid-operated device inside the lead shield. About 200 volts was used to charge the electroscope and a flashlight bulb mounted on the lead plug illuminated the quartz fiber.



The picture above shows, from left to right, the electroscope, the voltage source, and a second counting synchronous motor clock.

Fig. 1 shows a plot of the natural leak of the lead shielded electroscope for a twelve day period. The variation in the natural background of the electroscope from day to day was taken care of in a sample measurement by measuring the background just before and just after the sample was measured.

Variation of Lead Shielded Electroscope Background
April 1, 1939 to April 12, 1939

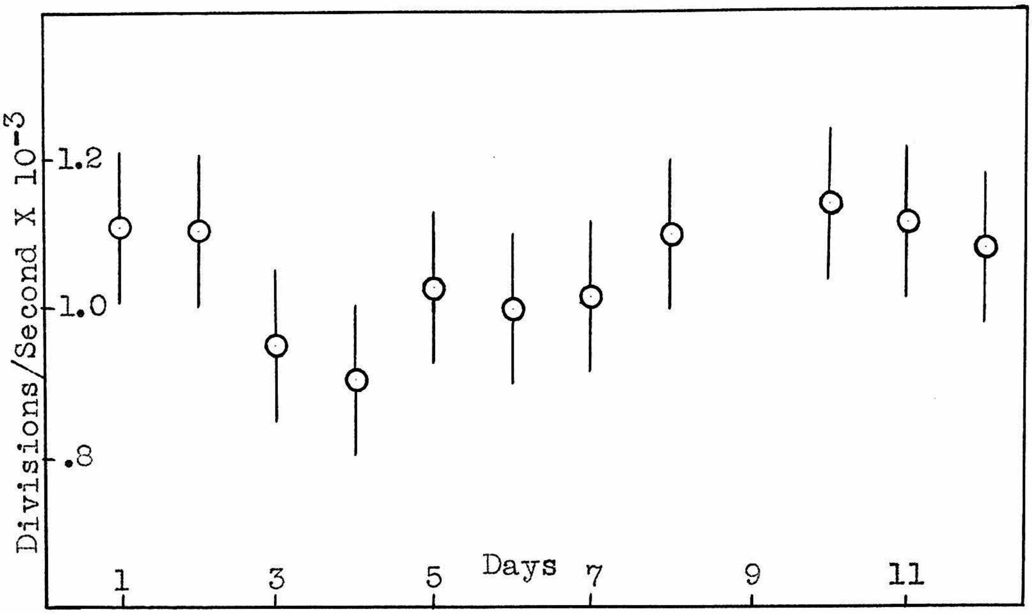


Fig. 1

Fig. 2 shows the linearity of scale of the electroscope with a sample whose activity was about ten times the natural leak. When measuring the activity of a sample, the time for the indicating fiber to pass between two positions on the scale was always measured to avoid errors due to the non-linearity of scale.

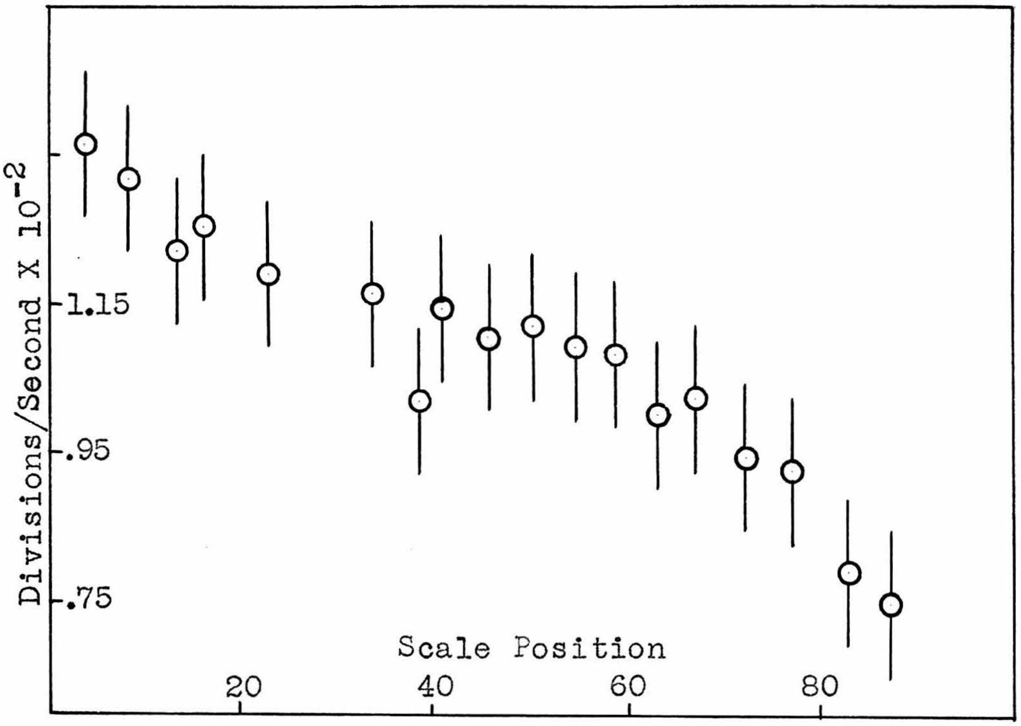

Linearity Test of Electroscope

Fig. 2

References

1. Wilson: Proc. Roy. Soc., 68, 151, 69, 277, (1901)
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2. Rutherford: Phil. Mag., 5, 177, (1903)

3. Bastings: J. Sci. Instru., 5, 113, (1928)

4. Lauritsen: Rev. Sci. Instru., Nov. 1937, p.438.