

As shown already by the pioneer theoretical work of Bernal and Fowler,⁶ these studies seem to indicate that independently of the temperature the water molecules tend to bond themselves tetrahedrally to four neighboring molecules although according to Morgan and Warren the intensity distribution curves cannot be interpreted uniquely in terms of an exact number of neighbors at definite distances.

Summary

The density of aqueous solutions of sodium hydroxide has been measured over a concentration range of from 1 to 26 molal in the temperature range 0 to 70°. The partial molal volume of the hydroxide as calculated from these measurements gives when plotted against the square root of the concentration a straight line up to a definite

(6) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

point at which a break occurs which shifts toward higher concentrations with increasing temperature. The values of the apparent partial molal volume of the hydroxide and the slope of the curves on either side may be calculated from the following equations:

(A) For sodium hydroxide concentrations below the break

$$\varphi_1^0 = -10.580 + 0.2863t - 0.00470t^2 + 0.0000266t^3$$

$$k_1 = 5.3342 - 0.08788t + 0.001603t^2 - 0.00000994t^3$$

(B) For sodium hydroxide concentrations above the break

$$\varphi_2^0 = -3.798 + 0.1030t - 0.001312t^2 + 0.000008563t^3$$

$$k_2 = 3.181 - 0.0155t + 0.000201t^2 - 0.00000145t^3$$

where t is the temperature in °C. A density table similar to the one in "I. C. T." was computed using these equations.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

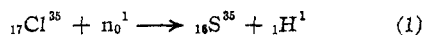
Exchange Reactions with Radiosulfur

BY HERVEY H. VOGÉ¹

Radioactive isotopes are peculiarly suitable for indicators or "labels" in chemical reactions, and the technique of their use is usually simpler than that for concentrated, stable, mass isotopes, because an electroscope or Geiger counter can be used for analysis instead of a mass spectrograph or elaborate density measurements. Furthermore, radioactive specimens of common elements are now quite easy to obtain. Radiosulfur, though it emits beta rays of low penetrating power, is attractive because of the long half-life, eighty days. Experiments with radiosulfur were made for the purpose of investigating certain phases of the chemistry of sulfur. A number of exchange reactions of inorganic sulfur compounds were studied; a few of these already have been reported briefly.²

Production of Radiosulfur

Radiosulfur was first reported by Andersen,³ who produced it by neutron bombardment of carbon tetrachloride. The supposed reaction is



(1) Now at Shell Development Co., Emeryville, Calif.

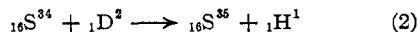
(2) H. H. Vogé and W. F. Libby, *THIS JOURNAL*, **59**, 2474 (193).

(3) E. B. Andersen, *Z. physik. Chem.*, **B32**, 237 (1936).

A small amount of inactive sulfur was added as a carrier, and after evaporation of the carbon tetrachloride the active sulfur remained concentrated in the residue. Much stronger samples of radiosulfur than those used by Andersen were obtained by leaving a liter bottle of carbon tetrachloride near the California cyclotron when it was producing fast neutrons. It may be questioned whether all the radiosulfur produced in reaction (1) exists as free sulfur and remains in the residue. When first formed, the sulfur atom has a large recoil energy, amounting to about one hundred volts, and is undoubtedly removed from the original carbon tetrachloride molecule, but its further history is uncertain. Probable end-products are S, SCl₂, SCl₂, CScCl₄, and SCl₄. Of these only sulfur would remain in the residue upon distillation. The others are for the most part hydrolyzable in alkali to sulfide or sulfite, and to test for their presence a carbon tetrachloride distillate was shaken with concentrated sodium hydroxide solution and sodium hypobromite for about twenty-four hours. To the acidified aqueous phase was added a small amount of sodium sulfate, and then barium sulfate was precipitated. The sulfur activity of the barium sulfate from the

extract of the distillate was over twice that of the barium sulfate from the non-distillable sulfur, which shows that much of the radiosulfur produced in the carbon tetrachloride exists as volatile, hydrolyzable compounds.

Another preparation of radiosulfur used was the bombardment of sulfur with deuterons.



Purification and Transformation.—In either mode of production of radiosulfur, radiophosphorus of half-life 14.5 days is formed. This may be removed by precipitation of added phosphate from an oxidized solution, or by burning the sulfur in air and filtering out the non-volatile phosphorus compounds by passing the gases over glass wool.

The products of reactions usually were transformed to barium sulfate and the activities measured in that form. The sulfur was then reconverted to a useful form by reduction to sulfide with carbon at 1000°, according to the experiments of Wells.⁴ Hydrogen sulfide could be generated readily from the sulfide, and sulfur was made by passing hydrogen sulfide into aqueous iodine solution.

Measurement of Activity.—Radiosulfur emits beta particles with a maximum energy of 107,000 volts.⁵ Since such particles will penetrate only about 0.015 g./cm.,² special care has to be taken in measuring activities. Most samples were measured in a screen-walled Geiger counter of the type described by Libby,⁶ which permitted background activities to be determined without removing the sample. Backgrounds with the counter employed averaged 160 counts/min.

Activities of the stronger samples could be estimated readily with an electroscope with a screened or aluminum foil-covered window. Samples with activities up to 70 times background (as observed with the electroscope) were used.

The biggest obstacle to quantitative work with radiosulfur is the low penetrating power of the radiation. No attempt was made in the experiments reported to determine activities precisely, but it is thought that quantitative experiments could be made with strongly active samples, using "infinitely thick" layers.

Exchange Reactions

Polysulfide.—An apparent exchange was expected for the sulfur atoms in polysulfide ion,

(4) A. E. Wells, *J. Ind. Eng. Chem.*, **8**, 770 (1916).

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

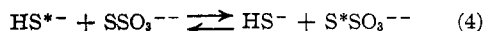
(6) W. F. Libby, *ibid.*, **46**, 196 (1934).

since the reaction involves merely a transfer of valence electrons and a proton



In an experiment performed to test this exchange, radiosulfur was added to an oxygen-free solution of ammonium sulfide, and the solution was shaken and heated at 90 to 100° until the sulfur had dissolved, which took nearly an hour. The solution was then acidified and the resulting hydrogen sulfide was passed into lead acetate solution. The counts from the experiment, in which 0.01 mole of radiosulfur and 0.01 mole of ammonium sulfide were used, were $582 \pm 50/\text{min.}$ for the lead sulfide from the sulfide and 332 ± 40 for the barium sulfate from the sulfur, indicating complete exchange. It is probable that this exchange reaction takes place very quickly even at room temperature.

Sulfide-Thiosulfate.—A possible reaction of considerable interest is that between sulfide and thiosulfate ions



Blumenthal and Herbert⁷ found that the analogous reaction



was complete in two hours at room temperature.⁸ But reaction (4) is much slower; the results in Table I show that in one hour at 100° it was incomplete, although after twenty-four hours at 100° it was substantially complete. The experiments were performed as follows. Radioactive hydrogen sulfide was passed into a solution of sodium thiosulfate in approximately normal sodium hydroxide. The oxygen-free mixture was sealed in a Pyrex tube, heated for the required time, cooled, and treated with lead acetate to precipitate lead sulfide; the lead sulfide was

TABLE I

Temp., °C.	Time, hrs.	Counts per minute	
		PbS from S ³⁶	BaSO ₄ from S ³⁶ O ₃ ²⁻
22	28	234 ± 40	0 ± 20
57	24	154 ± 30	0 ± 20
100	1	0.03 ^a	0.003 ^a
100	2	230 ± 40	0 ± 20
100	16	400 (ca.)	250 (ca.)
100	23	228 ± 12	198 ± 16

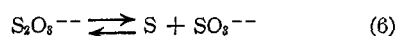
^a Division/second on an electroscope.

(7) E. Blumenthal and J. B. M. Herbert, *Trans. Faraday Soc.*, **33**, 849 (1937).

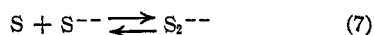
(8) Whether reactions (3), (4) and (5) actually involve hydrogen sulfide, hydrosulfide ion or sulfide ion, or water, hydroxide ion or oxide ion, etc., is not known. The equations have been written (usually) in terms of the molecular species of greatest concentration.

removed, and the thiosulfate was oxidized to sulfate, which was precipitated as barium sulfate. Tests performed before the oxidation showed that the solutions were free of sulfite and sulfate. A light yellow color developed in all solutions during heating, but this was found to be due to iron from the glass, and not to polysulfide.

The mechanism of the exchange reaction (4) is uncertain. It may involve a direct substitution such as that postulated by Blumenthal and Herbert for the phosphate-water exchange, or it may depend upon the reactions

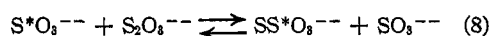


and



The speeds of reactions (6) and (7) are not known accurately, but polysulfide is decolorized by sulfite in a few minutes at 100°. The equilibrium constant for (6) at 100° is about 3×10^{-7} , and hence it appears likely that these reactions could account for the observed change. There is little difference between these two possible mechanisms as far as the general theory of reactions is concerned.

Sulfite-Thiosulfite.—Experiments on the exchange reaction



were conducted by Mr. Ronald Geballe. The procedure was to generate radioactive sulfur dioxide by burning radioactive sulfur in air and to pass it into a solution of sodium thiosulfate in approximately normal sodium hydroxide. Oxygen was removed with nitrogen, and then the tube was sealed and heated. After being heated, the solution was removed from the tube, neutralized, and treated with calcium chloride to precipitate sulfite. In order to get a good precipitation it was necessary to heat for about twenty minutes at 60°, and this put a lower limit to the reaction time. Following the removal of the sulfite, barium chloride was added to precipitate any sulfate formed by oxidation of the sulfite or from sulfur trioxide formed in burning the sulfur. Then the thiosulfate was oxidized with bromine and the sulfate precipitated. The activities of the sulfite and the second sulfate precipitates are compared in Table II. From the results it appears that the sulfite-thiosulfate exchange is much faster than the sulfide-thiosulfate exchange. The fact that (8) is so much faster

TABLE II

Temp., °C.	Time, hrs.	Counts per minute		Interpretation as to exchange
		CaSO ₃ from SO ₃ ⁻⁻	BaSO ₄ from S ₂ O ₃ ⁻⁻	
20	20	100 (ca.)	0 ± 10	None
57	1	21 ± 8	16 ± 12	Partial
57	1	0.12 ^a	0.03 ^a	Partial
57	21	0.12 ^a	0.064 ^a	Complete
100	1	150 (ca.)	112 (ca.)	Complete

^a Division/second on an electroscope.

than (4) makes rather unlikely the mechanism by way of reactions (6) and (7), especially when the high speed of the polysulfide exchange, reaction (3), is taken into account, and thus a direct exchange seems to be favored for (8).

Sulfide-Sulfate.—The reaction between sulfide and sulfate in alkaline solution was not appreciable after thirty-six hours at 100°. In the experiment, sodium sulfide was added to an oxygen-free, alkaline solution of radioactive sulfate, and the mixture was heated at 100°. After thirty-six hours it was cooled, acidified, and the hydrogen sulfide removed and oxidized. The barium sulfate from the sulfate gave a count of $680 \pm 30/\text{min.}$, while that from the sulfide gave $0 \pm 16/\text{min.}$

Sulfite-Sulfate.—No exchange took place between sulfite and sulfate in either alkaline or acidic solutions. In one trial, sodium sulfite was added to an alkaline solution of radioactive sulfate. The mixture was heated for thirty-six hours at 100°, and then the sulfite was removed from the cooled, acidified solution by passing through it a current of nitrogen. The barium sulfate from the sulfite gave a count of $5 \pm 40/\text{min.}$, and that from the sulfate gave $446 \pm 40/\text{min.}$

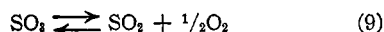
In another experiment (performed by Mr. Ronald Geballe), ordinary sodium sulfite and radioactive sodium sulfate were heated together in approximately tenth normal hydrochloric acid for thirty-five hours at 100°. The barium sulfate from the sulfite had an activity corresponding to 8 ± 10 counts/min., while that from the sulfate showed more than 250 counts/min. The lack of exchange in these cases is explained easily by the stability of the sulfate ion, but it is hard to understand the lack of exchange when sulfur dioxide is heated with concentrated sulfuric acid, as it was in the following experiments.

Sulfur Dioxide-Sulfur Trioxide.—An attempt was made to find the conditions under which sulfur dioxide and sulfur trioxide exchange an oxygen atom. The results, although incomplete, im-

TABLE III

Mixture	Temp., °C.	Time, hrs.	Counts per min.		Interpretation as to exchange
			SO ₂ part	SO ₃ part	
SO ₂ + SO ₃	280	17	0 ± 10	> 250	None
SO ₂ + SO ₃ + H ₂ O	50	3	0 ± 20	> 1000	None
SO ₂ + SO ₃ + 1/3H ₂ O	280	15	50 ± 14	> 1000	Slight
SO ₂ + SO ₃	335	24	150 ± 25	> 1000	Partial
SO ₂ + SO ₃ + Pt on asbestos	280	4	55 ± 14	> 1000	Slight

ply that the exchange occurs only by way of the reaction



The non-exchange in the presence of water is surprising in view of the oxidizing action of sulfuric acid, and the ease of oxidation of sulfur dioxide. The data are shown in Table III, and were gotten by the following experimental methods.

Radioactive sulfur trioxide was generated by burning radiosulfur in oxygen, passing the gases, enriched with more oxygen, over platinized asbestos at 360°, and condensing the sulfur trioxide at -10°. The sulfur trioxide thus prepared contained from 1 to 3% sulfur dioxide, and in all cases the results of experiments were corrected according to the activity of the sulfur dioxide in a control batch; the correction was never more than 40 counts/min. The trap containing the sulfur trioxide was sealed to a vacuum line containing several 100-cc. reaction bulbs, and was cooled with liquid air while the system was evacuated. The sulfur trioxide was then distilled to another trap, and again pumped while being cooled with liquid air. Finally it was allowed to evaporate into the reaction bulbs. At no time did the sulfur trioxide come into contact with anything but glass and dry mercury. No special precautions were taken to remove traces of water or mercury from the bulbs, but they were heated to about 150° while being pumped. After the bulbs were filled with radioactive sulfur trioxide, an equal amount of inactive sulfur dioxide was introduced and the bulb was sealed off and heated as desired. The total pressure at room temperature was usually 40 cm. of mercury.

For analysis, the bulbs were rinsed with water, and the sulfur dioxide was removed from the

acidified solution with nitrogen. Both portions were precipitated as barium sulfate and counted.

In the experiments in which water was added, a small bulb containing the water was broken in the reaction bulb after the sulfur trioxide and sulfur dioxide had been sealed in. In these experiments a small amount of decomposition of sulfurous acid to sulfur and sulfuric acid may have occurred; however, no sulfur was observed, and much sulfurous acid remained.

The platinized asbestos used was an active catalyst for the oxidation of sulfur dioxide at 360°.

Thanks are due to Professor E. O. Lawrence and his colleagues at the Radiation Laboratory of the University of California for the radiosulfur, and to Professor W. F. Libby for much assistance.

Summary

The use of radiosulfur as a reaction indicator has been illustrated with several exchange reactions.

In polysulfide ion the sulfur atoms have been found to exchange places rapidly.

One of the sulfur atoms in thiosulfate ion is rapidly transferred to a sulfite ion at 100°, but the exchange between thiosulfate and sulfide at 100° is much slower.

Sulfate ion was found to exhibit no exchange (transfer of an oxygen atom) with sulfite or sulfide in thirty-six hours at 100°.

Sulfur dioxide and sulfur trioxide did not exchange at temperatures appreciably below those at which dissociation of the trioxide might be expected, and this was found to be true also in the presence of platinum or water.

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