THE RADIOSULFUR EXCHANGE REACTION BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE

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THE RADIOSULFUR EXCHANGE REACTION BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE

I. INTRODUCTION

Acid-base phenomena have presented an intriguing puzzle to chemists since the time of Robert Boyle. The curious chemist wonders about the fundamental nature of materials he has chosen to call "acids" or "bases," and he wonders about exactly which substances should be included in these catagories. He further would like to understand the role of solvents in acid-base behavior and the relationship, if any, to these phenomena of other chemical processes such as oxidation-reduction phenomena. Thus, for example, he would be pleased to fit into the framework of such understanding an interpretation of the role of a solvent such as water, which may be viewed as an acid in its behavior towards ammonia, as a base towards sulfur dioxide, and which acts as an oxidant toward sodium, and a reductant towards fluorine.

At least five theories have been advanced in efforts to clarify these phenomena: (1) The Water-ion Theory (Arrhenius Theory); (2) The Proton Theory (Brönsted-Lowry Theory); (3) The Solvent Systems Theory (Franklin-Germann Theory); (4) The Electronic Theory (Lewis Theory); and (5) The Positive-negative Theory (Usanovich Theory). While each of these theories has its advantages and disadvantages, a detailed discussion of their relative merits exceeds the scope of this thesis. Rather, brief looks at the Solvent Systems and the Electronic Theories will be appropriate to provide a background for the results to be here presented.

The Solvent Systems Theory was evolved as investigators came to realize the importance of acid-base phenomena in solvents other than water. That such an evolution would have been delayed in its appearance is, of course, a natural consequence of the overriding familiarity of chemists with the solvent water as a medium for ionic reactions. According to this theory, the various solvents in which acid-base reactions occur all exhibit, in varying degrees, self-ionization equilibria to yield some finite concentrations of "characteristic" cations and anions. Then an acid is defined, in analogy with the behavior of hydrogen acids in water, as a solute that enhances the characteristic cation concentration in a particular solvent over that in the pure solvent; a base enhances the characteristic anion concentration. Thus the self-ionization process in a number of solvents, showing the characteristic cations and anions, are assumed to occur as follows:

$$\begin{array}{llll}
2\,H_2O & \rightleftarrows & H_3O^+ & +\ OH^- \\
2\,NH_3 & \rightleftarrows & NH_4^+ & +\ NH_2^- \\
2\,SO_2 & \rightleftarrows & SO^{+2} & +\ SO_3^{-2} \\
2\,HF & \rightleftarrows & H_2F^+ & +\ F^- \\
2\,H_2S & \rightleftarrows & H_3S^+ & +\ SH^- \\
2\,CO\,Cl_2 & \rightleftarrows & CO\,Cl.CO\,Cl_2^+ & +\ Cl^-
\end{array}$$

Among these solvents and many others, liquid ammonia has been, apart from water, the most fully investigated (20, p. 1-104) and (4, p. 15-75). The water-like character of this solvent is reflected in its general physical and chemical properties. According to the Solvent Systems Theory, and in line with the above auto-ionization scheme, a solute such as ammonium chloride is not a salt, as in the water system, but an acid, since it increases the concentration of the ammonium ion; also a solute such as sodium amide is a base in liquid ammonia solution, owing to the increase in concentration of the amide ion already present in the solvent.

The Solvent Systems Theory suffers a severe limitation in the restriction of its conception of acid-base phenomena to processes occurring in solution, and furthermore in solution in solvents which are themselves, through their self-ionization equilibria, significantly involved in the acid-base processes. The Electronic Theory, formulated by G. N. Lewis (13, p.293-313) avoids any such limitations. Lewis advanced, as the basis for his ideas, four so-called phenomenological criteria for acids and bases. Thus, for a substance to be properly considered an acid or a base it must, according to Lewis, do a minimum of four things. (1) It must undergo relatively rapid neutralization by its opposite number, base or acid, as the case might be. (2) It must show displacement reactions, a stronger acid (or base) displacing a weaker one. (3) It must give characteristic colors with acid-base indicators, making acid-base titrations possible. (4) Finally it must display an ability to catalyze reactions normally subject to acid or base catalysis. Apart from these criteria, no other test need apply. Thus, for example, the restriction of acid-base phenomena to reactions in solution and to ionic processes is eliminated.

With the foregoing criteria as a basis, Lewis defined acids and bases in terms of their electron structures and properties towards coordinate covalent bond formation. Specifically, an acid was defined as an electron pair acceptor in such a process and a base as an electron pair donor. Thus the acid boron trifluoride "neutralizes" the base ammonia to form a 1:1 addition compound:

$$F_3B + :NH_3 = F_3B:NH_3$$

Such a process might or might not occur in a solvent, and it might or might not involve charged species. The Solvent System neutralization between ammonium ion (acid) and amide ion (base) would involve a hydrogen-bonded intermediate

$$H_3N{:}H^+ \ + \ {:}NH_2^- \ = \ H_3N{:}H\cdots{:}NH_2 \ = 2\ H_3N{:}$$

It is to be noted however, that, while the Solvent Systems Theory visualizes this latter neutralization as occurring only in liquid ammonia, no such solvent restriction applies for the Lewis Theory. This example illustrates the much greater scope of the latter theory. It embraces every acid-base process covered by the Solvent Systems Theory, but is much broader and more general, and covers other processes clearly acid-base in character which the former theory fails to include.

Since about 1950, there has been in process at Oregon State University a continuing study of the nature of acid-base equilibria postulated by the Solvent Systems Theory. Solvents Studied have included, in particular, liquid sulfur dioxide, liquid hydrogen sulfide and sulfuric acid. This work was made possible by the fact that, somewhat over a decade ago, an invaluable aid for such research, in the form of radioactive isotope tracers, became much more readily available than had previously been the case. With isotopic tracers, for example, it has been possible to check postulated ionization and self-ionization schemes. Thus, in a solvent such as sulfur dioxide where both the solvent and solute acids are assumed to yield the common characteristic cation, thionyl ion, SO^{++}, in presumably rapid reversible equilibria, the labeling of either the solvent or the solute with radiosulfur or oxygen-18 should show a rapid exchange (i.e. radomization) of the tracer between solvent and solute. It is of interest to note that, in the case of the particular example cited, no such rapid exchange was found, a result showing, at least for this case, the inadequacy of the Solvent Systems Theory (11, p. 3052-3056). Thus, in this instance the exchange results imply that thionyl halide acids in solvent sulfur dioxide do not, in fact, undergo the type of ionic dissociation process postulated by the Solvent Systems Theory.

The present research is concerned specifically with an extension of previous studies dealing with the solvent liquid hydrogen sulfide. The concept of this material as a water-like solvent was developed early by Wilkinson and coworkers (24, p. 237-250) and Jander and coworkers (10, p. 77-119). This solvent, like water, is assumed to be amphoteric in nature and to undergo the following self-ionization:

$$2\ H_2S \rightleftarrows H_3S^+ + SH^-$$

In accordance with the Solvent Systems Theory, Jander indicated that triethylamine is a base when dissolved in liquid hydrogen sulfide owing to the equilibria

$$Et_3N + H_2S \rightleftarrows (Et_3NH)(SH)$$

$$(Et_3NH)(SH) \rightleftarrows Et_3NH^+ + SH^-$$

Jander further emphasized the occurrence in this solvent of amphoterism with such materials as arsenic trisulfide, insoluble in the pure solvent, but dissolving in basic, triethylamine-containing solutions, to form thioarsenite

$$As_2S_3 + 6\ (Et_3NH)(SH) \longrightarrow 2\ (Et_3NH)_3(AsS_3) + 3H_2S$$

Because of the solvent's low dielectric constant, 9.05 at -78.5° C, one finds that there is a limit to the water-like character of hydrogen sulfide. Thus it shows but a small self-conductivity (3×10^{-10} ohm^{-1} cm^{-1} at -78.5° C) and a solvent nature towards potential solutes more like an organic solvent than water. The latter aspect of the solvent's character was shown particularly in a study of Quam (16, p. 105) of the solubilities of some two hundred different materials. Although only qualitative in nature, Quam's results do indicate that hydrogen sulfide is closer in characters to organic than to inorganic solvents.

In 1952 Smith (19, p. 1-70) reported the results of an exploratory study of this solvent which included both some semi-quantitative solubility measurements and some radiotracer studies with sulfur-35. He found that arsenic trisulfide, antimony trisulfide and phosphorus pentasulfide are quite insoluble in pure liquid hydrogen sulfide, while elemental sulfur dissolves to a measurable extent. (These results are consistent with Jander's work, but conflict somewhat with those of Quam, who had reported arsenic and antimony trisulfides to be soluble.) In line with the type of amphoterism reported by Jander, Smith found that the addition of triethylamine to the solutions renders the arsenic, antimony and phosphorus sulfides quite soluble, presumably due to thio-anion formation. Likewise elemental sulfur was found to be much more soluble in triethylamine-containing solutions, giving yellow to deep red colors, depending on concentration, polysulfide formation presumably being involved. Smith carried out radiosulfur exchange experiments between solute and solvent in four cases where solutions of finite concentration were obtained. In the case of arsenic trisulfide in triethylamine-containing solutions, the exchange between solute and solvent was too fast to measure, a result presumably consistent with the postulated thioarsenite formation. In the analogous case involving phosphorus pentasulfide an observed exchange half-time of about thirty minutes suggested a greater complexity in the system than for the arsenic sulfide, possibly slow equilibria between various thiophosphate species being involved. With elemental sulfur, Smith found an apparently slow exchange of solute with solvent in the absence of triethylamine, the half-time being approximately 123 hours. Addition of triethylamine served not only to increase the solubility of sulfur but also greatly to increase the exchange rate, a half-time of about thirty minutes being found. In each case, these conclusions were drawn from a quite limited number of experiments and so can be taken as only semi-quantitative in nature.

In 1956 J. R. Mickelsen (14, p. 1-138) extended and verified Smith's introductory work. Using radioactive sulfur as a tracer, Mickelsen studied the exchange between liquid hydrogen sulfide and dissolved sulur, with and without added triethylamine. In addition, he conducted experiments between the solvent liquid hydrogen sulfide, containing triethylamine, and five sulfur-bearing solutes: arsenic trisulfide, arsenic pentasulfide, antimony trisulfide, antimony pentasulfide and phosphorus pentasulfide, finding immeasurable fast exchange in all cases except the last, where a moderate rate in what appears to be a complex system was observed. He also studied the system carbon disulfide-hydrogen sulfide (solvent), with and without triethylamine, at different temperatures, and drew some conclusions about the exchange which was found to occur in the presence of the amine.

To check Smith's results for the exchange between dissolved elemental sulfur and pure liquid hydrogen sulfide (reported by Smith to have a half-time of 123 hours), Mickelsen conducted a careful and extensive study and found that, in fact, there is almost a complete lack of exchange. If there is any significant exchange rate at all, it will correspond to a half-time of the order of years, rather than the 123 hours reported by Smith.

On addition of triethylamine to the foregoing system, Mickelsen found an exactly opposite effect. Where Smith had found a fast, but apparently measurable half-time, Mickelsen, after extensive investigation, found the exchange immeasurably fast no matter what the conditions (except for some very low temperature runs of questionable validity). In attempting to obtain a measurable rate he reduced the triethylamine concentration to the merest trace, but still the exchange was complete within the time of experiments.

On the basis of his exchange results, Mickelsen concluded that elemental sulfur dissolves in liquid hydrogen sulfide, as in other solvents, as an inert solute, presumably S_8 rings, no reversible equilibrium to form any such species as, for example, H_2S_2 occurring. In contrast, in the presence of triethylamine, Mickelsen concluded, on the basis of his observations, radiochemical and otherwise, that sulfur dissolves to form some polysulfide of uncertain composition, the S_8 rings evidently being opened up in the basic solution. The observed fast exchange (in Mickelsen's own words) "indicates that the polysulfide formed in the solution is in rapid reversible equilibrium with the solvent--a reversible equilibrium promoted by the presence of very small amounts of amine, indeed." In this same context it may be noted that Voge (21, p. 1032-1035), studying the exchange between radioactive sulfur and polysulfide ion in aqueous solution, found a very rapid exchange at 90° and 100°.

One of the difficulties in studying the kinetic's of an exchange reaction involving the solvent itself as one of the exchanging species is the impossibility of varying the solvent concentration. Furthermore, the high concentration of the solvent makes difficult the slowing down of a fast reaction to an experimentally convenient rate. A potential resolution of these difficulties is offered by the possibility of employing some inert solvent for studying the same exchange observed in a "solvent system" (and involving the solvent directly). Such experiments are further attractive in offering the possibility of a test of just how specific the particular observed reaction is in terms of the particular solvent system. The observation of the same general kinetics in an inert solvent as in a "solvent system" would appear to suggest a much lower degree of such specificity than is inherent in the general philosophy of the Solvent Systems Theory. On the basis of such ideas, T. M. Beasley (1, p. 1-70) extended Mickelsen's research on the exchange between liquid hydrogen sulfide and carbon disulfide, both with and without added triethylamine, using benzene as the inert solvent. Although a complete quantitative comparison of the systems as yet awaits further study, to all appearances the reactions in the new media appear to be probably almost the same as in liquid hydrogen sulfide.

Beasley's results were particularly encouraging and on this basis it seemed of interest to attempt a further extension of Mickelsen's research using an inert solvent. Such an investigation forms the subject of the present thesis. First, the radiosulfur exchange reaction between arsenic trisulfide and hydrogen sulfide, with added triethylamine, was examined in the inert solvent chloroform, the hope being to obtain a measurably slow exchange rate in the amine-containing solutions. When this hope was not realized, study of a second exchange was initiated, and the latter study forms the greater part of the research here reported. This work consists of a study of the kinetics of the radiosulfur exchange reaction between elementary sulfur and hydrogen sulfide, with and without added triethylamine, in chloroform solution. In the case of the amine-containing solutions it has been possible to obtain measurable rates for a reaction that, in liquid hydrogen sulfide as solvent, was invariably complete within the time of the experiments. On the basis of these measurements, it has further been possible to evolve a reasonable rate law, suggesting a plausible mechanism for the exchange reaction.

II. EXPERIMENTAL

A. COUNTING PROCEDURE AND FRACTION EXCHANGE CALCULATION

The isotope sulfur-35, with a half-life of 87.1 days, was used as the tracer throughout this research. This isotope decays by emission of a beta particle of 0.168 Mev maximum energy. The counting methods used were essentially those given by Norris (15, p. 1220-1223). An end window counter (Tracerlab, Inc., Model TGC-2, with a 1.8 mg. per square centimeter window) was employed together with a scaler, at first a Berkeley Model 1000B, later a Nuclear-Chicago Model 182X. The same counter tube (Serial No. 2DJ24) was used throughout the work. All necessary corrections for background and self-absorption were applied, the latter from an empirically determined curve. The counter used was equipped with a series of shelves below it, so that samples of high activity could be counted at a greater distance from the window. In most cases the samples were counted on the second shelf (the closest useable). When lower shelves were employed, empirically determined correction factors were applied. In addition to this procedure, small coincidence loss corrections were applied in those cases where the activity as measured required it. Decay corrections were also made whenever needed. The total number of counts accumulated for each sample were, except for the very lowest activities (where the errors are recorded in the tables), always such as to correspond to an expected standard deviation of less than 5 per cent, a figure roughly within the overall accuracy of the counting procedure.

The radiosulfur samples from the hydrogen sulfide, the arsenic trisulfide or the elementary sulfur were all counted as barium sulfate, isolated by precipitation from dilute hydrochloric acid solutions. Analytical techniques were used in the preparation of the barium sulfate, namely, precipitation, digestion on a steam bath or low temperature hot plate, filteration on a sintered glass filter, washing with acid, and finally washing with water. After drying, a portion of the solid material was slurried with acetone in weighed, nickel-plated cupped planchets and allowed to dry under an infrared heat lamp. Then a thin mat of barium sulfate was deposited on the planchet. The amount deposited ranged from 10 to 100 milligram of barium sulfate (cpm/mg) and are so tabulated throughout this thesis.

At the end of each experiment, both of the exchanging reactants were recovered and radioassayed, making possible a check comparison with the original specific activity. The exchange was followed in every case by employing the specific activity of the initially inactive component, namely hydrogen sulfide. The fraction exchange, F, was obtained by dividing the observed specific activity of the hydrogen sulfide fraction by the specific activity one would expect in this fraction at infinite exchange. This "infinite exchange specific activity" was calculated from a knowledge of the concentration (gram-atoms per liter) of sulfur in each of the two exchanging species, together with the initial specific activity of the elementary sulfur or arsenic trisulfide used to prepare the reaction mixture. In some cases a particular run was allowed to go to completion so that a check on the infinite time activity of the hydrogen sulfide could be obtained experimentally.

A sample data sheet, that for Experiment 50, shown in Table I, should help to clarify the procedure. The counting data are shown in column form and were accumulated normally in the order shown (down each column and then to the next, etc.), beginning at the indicated time on the indicated date. As shown in this run, duplicate planchets were normally prepared and counted for each fraction. The weights of barium sulfate on each planchet are given at the top of the sheet, representing the difference between the weights of clean and loaded planchets. As in this case, the background activity was always counted twice, once before and once after the counting of the samples. The average background was then subtracted from the average counting rate for each planchet, the latter figure having previously been arrived at on the basis of three successive counts, each lasting three minutes. Before subtracting background, any necessary coincidence correction was applied. This correction (indicated in Table I as f_{τ}) was applied whenever the counting rate exceeded 2000 cpm. Hence none was necessary in the present experiment. In this experiment the samples were all counted on the second shelf, so that no "shelf correction" (^{f}shelf) was necessary. Had it been necessary, an appropriate correction factor would have been shown on the indicated line. Samples showing more than about 3000 cpm on the second shelf were generally counted on a lower shelf. On the line marked "$f_{shelf-abs.}$", figures taken from an empirically prepared correction table are recorded. These figures represent the product of the self-absorption correction factor multiplied by the number of milligrams on the planchet, and are such that division of the observed activity by them serves simultaneously to correct the sample activities for self-absorption and to lead to a specific activity value (counts per minute per milligram as barium sulfate). This last figure, then, is the one recorded on the next to the last line in Table I. On the last line of the table the average specific activities derived from the duplicate planchets are given.

The specific activity of the original starting material (either arsenic trisulfide or elementary sulfur) was counted as a check every week or so, and then multiplied by whatever decay factor was appropriate before being used in calculations. Thus, in Run 50, the initial specific activity of the elementary sulfur was 146.8 cpm/mg (as barium sulfate) at 5 P.M. on November 21, 1961. Hence, for use in connection with the data recorded in Table I, counted November 28, a decay correction factor of 94.58 per cent was applied. In this experiment, 3.00 milligram-atoms of labeled elementary sulfur were dissolved along with 5.10 millimoles of hydrogen sulfide and one lambda (10^{-3} milliliters) of triethylamine in 100 milliliters of chloroform. Hence the calculated infinite time specific activity is

$$S_\infty = 146.8 \times 0.9458 \times \frac{3.00}{5.10 + 3.00} = 51.4 \text{ cpm/mg}$$

On the basis of this figure the fraction exchange, F, becomes

$$\frac{32.6}{51.4} = 0.634 = 63.4\%$$

These calculations are shown at the bottom of Table I.

TABLE I
SAMPLE DATA SHEET AND EXCHANGE CALCULATION

Experiment No. 50
Volume I Page 13

Counter No. 2DJ24
Scaler No. N.C. 182

Hi Voltage 1450

Sample No.	5H	6H	7H	8H
gross (g)	2.5263	2.5601	2.4043	2.4138
tare (g)	2.5000	2.5264	2.3807	2.3888
sample (mg)	26.3	33.7	23.6	25.0

DATE of counting 11 P.M. 11/28/61

		(-----H_2S------)		(---Residual S---)		
Sample No./Shelf	Bkg.	5H/2	6H/2	7H/2	8H/2	Bkg.
Counts/min 1	89/3	1581/3	1730/3	3540/3	3640/3	92/3
2	104/3	1620/3	1677/3	3409/3	3607/3	99/3
3	93/3	1563/3	1708/3	3592/3	3731/3	98/3
Total	286/9	4764/9	5115/9	10541/9	10978/9	289/9
Avg. CPM	31.8	529	568	1171	1219	32.1
(Avg CPM)f_r-Bkg.		497	536	1139	1187	
f_{shelf}		1	1	1	1	
$f_{self\text{-}abs.}$		15.06	16.59	14.34	14.73	
Sp.Act.(c/m/mg)		33.0	32.2	79.6	80.6	
Avg. S.A.(c/m/mg)			32.6		80.1	

$S_\infty = 146.8 \text{ X } 94.58\% \text{ X } \frac{3.00}{5.10 + 3.00} = 51.4$ cpm/mg

TIME: 7.00 hours

$F = \frac{32.6}{51.4} = 0.634 = 63.4\%$

1-F = 0.366

It may also be noted that the observed specific activity of the "residual sulfur" fraction may be combined with that observed for the recovered hydrogen sulfide to provide an alternative calculation of the infinite time specific activity and thus be used to give a check on the overall procedure. Thus, in Run 50 the the alternative calculation is given by

$$\frac{(32.6)(5.10) + (80.1)(3.00)}{5.10 + 3.00} = 50.2 \text{ cpm/mg}$$

The check is seen to be within about 2.5 per cent, which is entirely satisfactory.

B. PREPARATION OF MATERIALS

1. Hydrogen sulfide used for these experiments was obtained from a commercial cylinder (Matheson, 99.5% purity). Although no special effort was made to purify this gas to a greater extent, the first one-tenth of the cylinder was used up in the preliminary exploratory work before any of the experiments recorded here were commenced. Since the cylinder contained the hydrogen sulfide as a liquid, this procedure was equivalent to a discarding of the first portion of a distillate. In addition, in preparing the solutions of hydrogen sulfide in chloroform for each experiment, the gas was first allowed to flow into the hood for about two minutes before being

passed into the chloroform contained in the experimental Erlenmeyer flask.

2. Chloroform (Baker's Analyzed Reagent) was used without any further purification. The degree of purity of this solvent was checked by use of a Beckman GC-A2 vapor fractometer as well as with a Bausch and Lomb refractometer. Figure I shows a recording of the vapor fractometer analysis of a sample of the chloroform. Only a small attenuation factor was used with the vapor fractometer in order to show any possible peak other than chloroform. The curve obtained, except for the chloroform peak itself, is almost completely smooth, a fact which may be considered as a good criterion for the purity of the chloroform. The refractive index of the chloroform was measured at 20° C and was found to be 1.4468. The value listed in the International Critical Tables for pure chloroform is 1.4467 (23, p. 176,277).

3. Triethylamine (Eastman White Label) was shaken for about five minutes with freshly cut sodium and then was allowed to stand over the sodium for approximately one hour to remove any primary or secondary amines that might have been present. The triethylamine was then distilled from the sodium and about the middle third was retained. This distillate was then subjected to a second distillation, again only the middle one-third of the second distillation being retained for subsequent use.

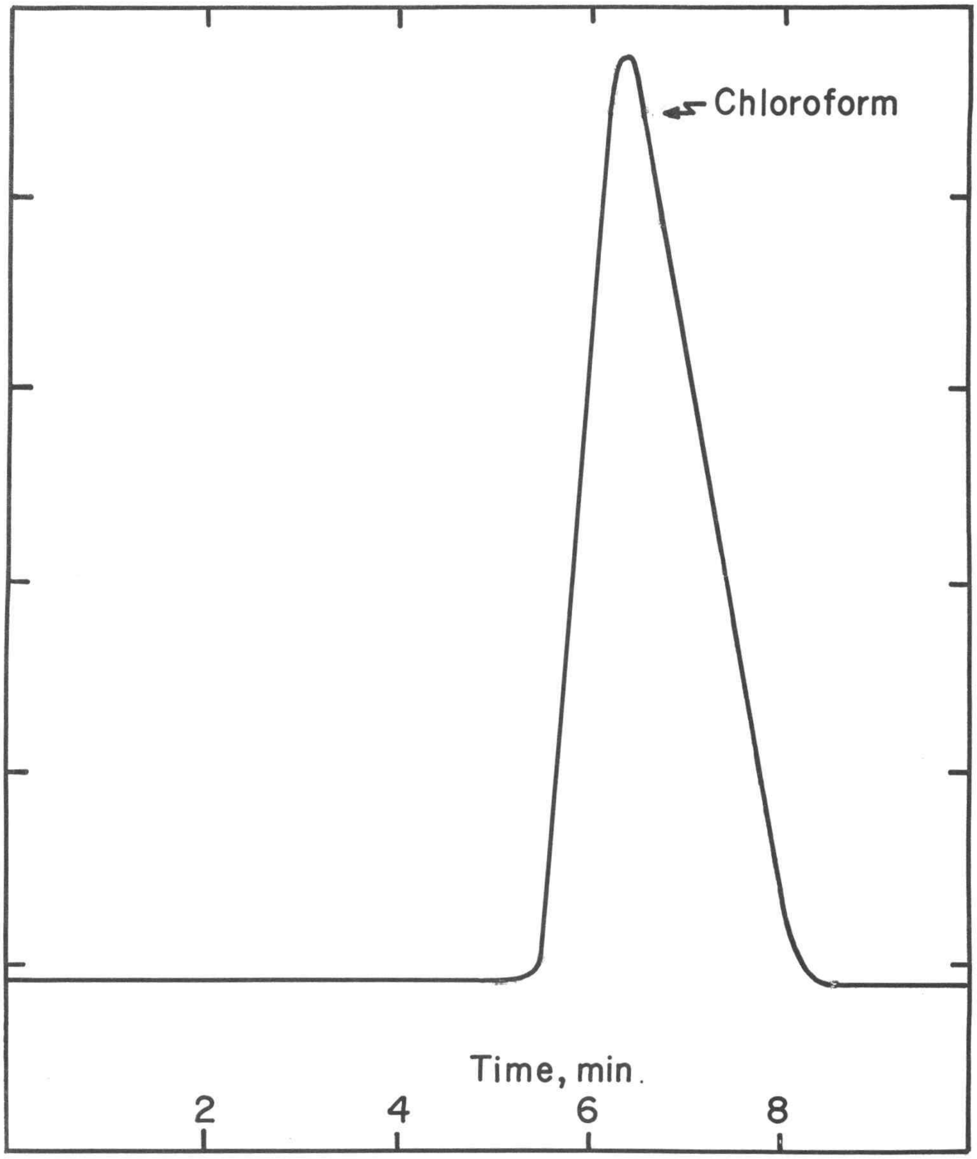

Figure I. Vapor Fractometer Recording of Chloroform

4. Labeled elementary sulfur was prepared from material obtained from the Oak Ridge National Laboratory. This was furnished as 0.4 ml. of solution in a small glass ampoule containing high specific activity labeled barium sulfide in 0.01 N barium hydroxide solution. The specific activity and concentration at time of shipment were, respectively; 41734 mc/g of sulfur and 39.23 ± 10% mc/ml of solution. (The work reported in this thesis was carried out over a period of two half lives after receiving this material.) The sulfide solution also contained about 5 per cent of non-sulfide sulfur. The contents of this ampoule were diluted very carefully in a dry nitrogen atmosphere in a dry box with 10 ml of a solution of 0.0725 M Na_2S in 0.05 M NaOH. A 0.5 milliliter portion of this solution was then further diluted with 5 milliliters of the same basic sodium sulfide solution. This final "stock" radioactive sulfide solution ("Solution A") was then used for all subsequent preparations. In a typical elementary sulfur preparation, 100λ of Solution A were added to 50 ml of one molar Na_2S in one molar NaOH ("Solution B"). After shaking, the resulting solution was oxidized by 0.1 N iodine solution prepared from an "Acculute" concentrate[a], using starch as an indicator. Hydrochloric acid (1N)

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[a] These solutions are available from Anachemia, Ltd., Montreal, Canada.

was added gradually during the oxidation so that the final solution was acidic. The residual iodine was driven away by boiling, a procedure which at the same time helped to coagulate the milky sulfur. The foregoing procedure is essentially that described in *Scott's Standard Methods of Chemical Analysis* (6, p. 924). After precipitation and thorough washing, the sulfur was dried in the oven at 60°C for at least ten hours, then it was dissolved in reagent grade carbon disulfide and recrystallized twice. The resulting crystals were finally dried in the oven at 60°C for twenty-four hours. The fresh one molar Na_2S in one molar NaOH solution (Solution B) used in the procedure just described was prepared by passing hydrogen sulfide into one liter of one molar NaOH for a long enough time to insure the formation of one molar NaHS in the solution. After this, two moles of sodium hydroxide were added to convert the sodium bisulfide solution into one of one molar Na_2S in one molar NaOH.

5. *Labeled arsenic trisulfide.* A *fresh* one molar Na_2S in one molar NaOH (Solution B) was prepared as described above in connection with the preparation of labeled sulfur. Exposure of the solution to the air was minimized as much as possible to prevent the formation of any polysulfides which would, in the preparation, lead to the production of arsenic pentasulfide instead of arsenic

trisulfide. One hundred lambdas of the stock basic radioactive solution (Solution A) were added to 50 ml of the basic sodium sulfide solution (Solution B). Ten millimoles of initially non-radioactive arsenic trisulfide (Amend Drug & Chemical Co., Purified), were dissolved in this solution (it dissolves quickly), the solution was diluted with 100 milliliters of distilled water and the container was shaken for about ten minutes. Then arsenic trisulfide was reprecipitated from the thioarsenite solution by the addition of dilute hydrochloric acid (approximately 2N), and the hydrogen sulfide formed was driven away by bubbling nitrogen through the solution for about half an hour. The arsenic trisulfide was then filtered, washed, and dried in the oven at 100° C for twenty-four hours. To demonstrate the non-formation of arsenic trisulfide, a precisely known amount of the prepared material was oxidized by the method that will be described in the next section, and then the barium sulfate was precipitated, washed, dried and weighed following standard analytical procedure. The percentage sulfur found was 40.3 per cent, to be compared to 39.1 per cent expected for As_2S_3 or 51.5 per cent for As_2S_5. This check was repeated a second time with substantially the same result. The deviation of the result from that expected for As_2S_3 is within the overall accuracy of the barium sulfate sulfur determination method.

III. RUN PROCEDURE AND RATE CALCULATION METHODS

A. GENERAL

As indicated before, this research consists of two main parts. (1) A series of measurements were made of the rate of radiosulfur exchange between hydrogen sulfide and arsenic trisulfide in the presence of triethylamine, all three compounds being dissolved together in chloroform solution. No exchange experiments were done without the presence of triethylamine because arsenic trisulfide does not dissolve sufficiently under such circumstances. (2) Another series of measurements were made of the rate of radiosulfur exchange between hydrogen sulfide and elementary sulfur in the presence of triethylamine, all three compounds being dissolved together in chloroform solution. In addition, some experiments were done without triethylamine present.

In both parts of the research, experiments were run at various concentrations of the reactants and at different temperatures ranging from -35.7 to 24.5°C. These temperatures, except as otherwise indicated, were maintained to ±0.1°C, generally by the use of a large, well-stirred, refrigerated thermostat containing a fifty-fifty mixture of a commercial ethylene glycol antifreeze and water. The temperature was measured by thermometers calibrated by the National Bureau of

Standards. The constancy of the bath temperature within the indicated range ($\pm 0.1^{\circ}C$) was checked by the use of a five junction iron-constantan thermocouple, most of whose output voltage was "bucked" by a Leeds and Northrup potentiometer. The resulting voltage difference was applied to a Varian Model G-11A strip chart recorder (10 millivolts, full scale).

B. HYDROGEN SULFIDE-ARSENIC TRISULFIDE EXCHANGE EXPERIMENTS

Sets of experiments were run under varying conditions of temperature and concentration in an effort to establish the effect of such factors on the exchange rate. Within each set, the individual experiments, under identical or closely similar conditions of temperature and concentration, were run for various lengths of time with the object of obtaining data from which one might calculate the exchange rate by means of a plot of log (1-F) versus time. (See "Exchange Rate Calculation Methods," below.)

Each individual experiment in a particular set was run in a separate 500 ml., glass-stoppered Erlenmeyer flask. The solution in the flask was first prepared by bubbling hydrogen sulfide, using a sintered glass bubbler, through 100 milliliters of chloroform in the flask, at room temperature, for about five minutes. At the end of this time, 10 milliliters of the solution were withdrawn with a volumetric pipette and diluted to 100 milliliters with additional chloroform in a separate glass-stoppered Erlenmeyer flask, giving a solution to be used to determine the concentration of the hydrogen sulfide in the original solution by iodometric titration as will be described below. To the remaining 90 milliliters of the experimental hydrogen sulfide solution a known weighed amount (±0.1 mg) of triethylamine was added, and then a calculated volume of fresh chloroform was also added to bring the concentrations of reactants to the desired values. It should be noted here that all volumes were assumed additive, no correction for any volume change on mixing being applied. A weighed amount (±0.1 mg) of labeled arsenic trisulfide was finally added and the glass-stoppered flask (the stopper greased with Apiezon M to inhibit loss of hydrogen sulfide) was shaken until all the arsenic trisulfide had completely dissolved, a process requiring from about two to six minutes. The "beginning" time of the experiment (zero time) was considered as the middle time between the addition of the arsenic trisulfide and the time corresponding to complete dilution. The experiment was terminated by the addition of concentrated hydrochloric acid through a dropping funnel and then bubbling nitrogen through the solution for about ten minutes, using a sintered glass bubbler. The evolved hydrogen sulfide, carried in the nitrogen stream, was absorbed by passage of the gas, using a sintered glass bubbler, through aqueous sodium hydroxide solution (about 2M). In this separation procedure the arsenic trisulfide, precipitated by acidification, remained behind with the chloroform solution. The two fractions so obtained, following further treatment as described below and final radioassay, led to the specific activity values labeled respectively "hydrogen sulfide" and "arsenic trisulfide" which are subsequently presented in this thesis.

As was indicated before, hydrogen sulfide concentration was determined by iodometric titration. Typically, a ten milliliter aliquot of the diluted hydrogen sulfide solution mentioned before (obtained by the dilution of 10 milliliters of the original hydrogen sulfide solution to 100 milliliters) was pipetted into 50 milliliters of a slightly acid (HCl) water solution containing a known excess of 0.1000 N iodine. All titrations were carried out in glass-stoppered Erlenmeyer flasks. The solution was stirred for approximately ten minutes by means of a magnetic stirrer and teflon-covered stirring bar, and then back titrated for excess iodine with 0.1000 N sodium thiosulfate solution, using starch as the indicator. The standard solutions used were prepared from "Acculute" concentrates, the thiosulfate being checked for normality by titration against potassium iodate using standard methods (25, p. 266). Despite the hetrogeneous character of the titration, its reliability was attested by the reproducibility of the results and by the weight of the barium sulfate obtained from the oxidation and precipitation of the separated hydrogen sulfide fraction. Thus, for example, in Experiment 13, the iodometrically-determined hydrogen sulfide concentration was 0.205 M, contained in a total volume of 274 milliliters, correction of this value for the loss of hydrogen sulfide consequent to opening of the flask after the titration but before the actual start of the experiment (see below) led to a "corrected" hydrogen sulfide concentration of 0.200 M, a quantity which should have led to the eventual recovery from the "hydrogen sulfide" fraction of 0.0548 moles or 12.77 grams of barium sulfate. The amount actually recovered was 13.06 grams, a figure within the accuracy of the barium sulfate method. This same barium sulfate precipitation procedure check was repeated in two other cases. The average deviation of the recovered weight of barium sulfate from that expected for all such trials (including the above) was only 2.6 per cent.

The magnitude of the correction for loss of hydrogen sulfide on opening of the reaction flasks above referred to was established experimentally. To this end the above described analysis was carried out on five samples taken consecutively from a single hydrogen sulfide solution (the flask being closed about long enough for a titration between each such sampling). Thus, the average decrease in hydrogen sulfide concentration per flask opening was found to be about 1 per cent of the total concentration. This correction was applied as necessary to establish the hydrogen sulfide concentrations recorded in the data tables to follow in this thesis. In general the total correction amounted to only 1 per cent or 2 per cent.

After the separation of the exchange reaction ingredients, the resultant sodium sulfide solution (i.e. the "hydrogen sulfide" fraction) was oxidized by adding about two grams of sodium peroxide ("Baker's Analyzed Reagent"). The solution was then boiled to insure the complete conversion of the sulfide ion into sulfate ion, and to destroy excess sodium peroxide or any persulfate that might be present. The solution was then acidified with hydrochloric acid (to a pH of two as measured with indicator paper) and the precipitation of the sulfate was accomplished with 0.5 N barium chloride solution in the usual manner.

The chloroform solution remaining after the separation and containing the precipitated arsenic trisulfide was filtered on a Buchner funnel. The arsenic sulfide obtained was dissolved in basic solution (about 2M sodium hydroxide), and finally about two grams of sodium peroxide were added to oxidize the sulfur-containing compound and convert it to sulfate. After boiling and acidification, barium sulfate was precipitated in the same manner as was done with the hydrogen sulfide fraction.

The two sintered glass crucibles containing the barium sulfate obtained from both fractions were dried in the oven at 120° C for about four hours. Two planchets were prepared from each in the way described before, followed by the radioassay measurements of the specific activity of each fraction.

C. HYDROGEN SULFIDE-SULFUR EXHCANGE EXPERIMENTS

The run procedure of the hydrogen sulfide-elementary sulfur exchange experiments was generally similar to the procedure just described for arsenic trisulfide with certain modifications. In these experiments hydrogen sulfide concentration usually exceeded sulfur concentration by a significant amount, and both of these concentrations always definitely exceeded triethylamine concentration. As before, a solution of hydrogen sulfide in chloroform was first prepared in the reaction flask by passing the gas for about five minutes through the chloroform. A total of 110 milliliters of solution was prepared, ten milliliters being then withdrawn for hydrogen sulfide concentration determination. No further dilution of the reaction solution with chloroform was done in these experiments, 100 milliliters total volume being used in every case. After determination of the hydrogen sulfide concentration by the previously described iodometric method, a small known weighed amount (±0.1 mg) of elementary labeled sulfur was added to the solution. Siedell (18, p. 1446) reported that at 24°C, 100 milliliters of chloroform dissolve 1.216 grams of sulfur.

Although we did not need to dissolve such large amounts, it took about one minute to dissolve 96.2±0.1 mg of sulfur (the amount most often used) in 100 ml chloroform solution. Complete dissolution of the sulfur was insured before the addition of the small amount of triethylamine to the reaction flask. The latter was then finally added as a dilute solution in chloroform, using a micro-pipette.

The zero time of the run was taken as the time when the last drop of the triethylamine had just drained into the flask. It might seem wiser to have taken the zero time as the time of half emptying of the triethylamine micro-pipette, especially for the shorter time runs; however, the time of emptying the micro-pipette was essentially negligible (about 10 seconds) compared to the duration of almost all the runs. It should be noted here that whenever a run had to be done at 0°C or less, the addition of the triethylamine was accomplished after the reaction flask had been placed in the thermostat at the desired temperature.

As indicated, the small amounts of triethylamine employed were measured by micro-pipettes, the dosage amounts being taken from a dilute solution of triethylamine in chloroform. This was prepared for most of the runs by diluting one milliliter of triethylamine with 99 milliliters of chloroform. Consequently a micro-pipette dosage of 100 λ ($1\lambda = 10^{-3}$ milliliter) of this solution (the dosage amount used in almost all cases) contained 1λ of pure triethylamine. In some experiments only one-tenth lambda of pure triethylamine was needed. This was obtained by dilution of 100λ of pure triethylamine with 100 ml. of chloroform. Again the dosage amount taken from the diluted solution was 100λ.

In this work it was essential that reaction flasks had to be scrupulously clean, since even a very small contamination might interfere with the micro amounts of triethylamine used. This was particularly important in those experiments involving the very lowest triethylamine concentrations. In fact, in these cases, erratic exchange results were obtained until this fact was appreciated. In all cases the flasks, after thorough washing with soap and thorough rinsing, were rinsed carefully with concentrated hydrochloric acid, followed, at the higher triethylamine concentrations, by a thorough distilled water rinse and drying in the oven. At the lower concentration of triethylamine, a rinse with concentrated nitric acid followed the hydrochloric acid rinse, and then the flasks were rinsed with flowing distilled water for about ten minutes, after which they were dried in the oven for at least two hours. Finally the low triethylamine concentration flasks were rinsed with chloroform before the actual reaction mixtures were prepared.

After an exchange experiment was done, the run was terminated by purging the hydrogen sulfide (present in excess) from the solution by bubbling nitrogen through the reaction flask for about ten minutes. The "end" time of the run was taken as the time of the first bubbles. The hydrogen sulfide was absorbed by sodium hydroxide solution and then oxidized and treated in the same way described before. The dissolved sulfur was recovered by completely evaporating the chloroform on a low temperature hot plate. To oxidize this sulfur and convert it into sulfate, 5 milliliters of ($\sim$5N) sodium hydroxide plus two grams of sodium peroxide were added to the same reaction flask (after the evaporation process) and the mixture was heated on the hot plate until boiling. Then ten milliliters of distilled water were added, followed by a small additional amount of sodium peroxide to oxidize any remaining sulfur. After dilution with more distilled water, the solution was transfered to a beaker and boiled to destroy any remaining sodium peroxide or any persulfates formed. Acidification with hydrochloric acid, followed by precipitation with barium chloride, finally yielded barium sulfate ready for radioassay measurements.

D. EXCHANGE RATE CALCULATION METHODS

All isotopic exchange reactions of the type

$$AX + BX^{*} \rightleftarrows AX^{*} + BX$$

are known to follow, for a homogeneous system at chemical equilibrium, a first order rate law (5, p. 192). The rate of exchange of the atoms X between the two species AX and BX has been shown to be:

$$R = - \frac{2.303\,ab}{(a + b)} \frac{d \log (1-F)}{dt}$$

R = The gross rate of exchange of X in gram-atoms/ liter minute.

a = Concentration of X in the first exchange reactant in gram-atoms per liter.

b = Concentration of X in the second exchange reactant in gram-atoms per liter.

F = Fraction of equilibrium exchange that has occurred in time t.

We notice here that the rate, R, does not correspond to the rate of transfer of the radioactive species only, but to the total rate of exchange of all atoms of the elemental species being traced, whether radioactive or not. Consequently, in our experiments, while we follow the exchange by observing the growth of radiosulfur activity in the hydrogen sulfide fraction, the calculated rate, R, will correspond to the total rate of exchange of all the sulfur atoms between hydrogen sulfide and sulfur (or arsenic trisulfide), irrespective of isotopic composition. This rate, under fixed conditions of concentration and temperature, is constant and does not depend on the presence of the isotopic tracer. The concentration units quoted in the previous expression arise from the fact that for the general exchange reaction

$$AX_n + n\ BX^* \rightleftarrows AX_n^* + n\ BX$$

the rate expression (with a and b given in moles per liter of $AX_n + AX_n^*$ and $BX + BX^*$, respectively) would be

$$R = -\frac{2.303\ nab}{na + b}\ \frac{d \log (1-F)}{dt}$$

The fraction exchange "F" has been determined by dividing the observed specific activity of the hydrogen sulfide fraction at the end of each run (time = t) by the specific activity one would expect the hydrogen sulfide to have at complete exchange. This "infinite time" specific activity has been calculated from the initial specific activity of the labeled material used (elementary sulfur or arsenic trisulfide) together with the known concentrations of sulfur in the exchange ingredients. Then, according to the rate expression, it may be seen that a plot of log (1-F) versus time should give a straight line, from the slope of which the exchange rate might be calculated. In the present work every particular set of experiments (at the same concentration and the same temperature) has been used to make such a graph. In general, the data obtained fit the expected straight line nicely. Fraction exchange calculations have previously been illustrated for Experiment 50, Set (C). With the aid of the other experiments in this set (49, 51, 52) a plot of log (1-F) versus time was made. Figure 2 shows such a plot illustrating the adherence of the data to the first order exchange law.

By the introduction of the concept of "half-time of the exchange reaction," which is the time necessary to achieve 50 per cent of exchange equilibrium (i.e. an F

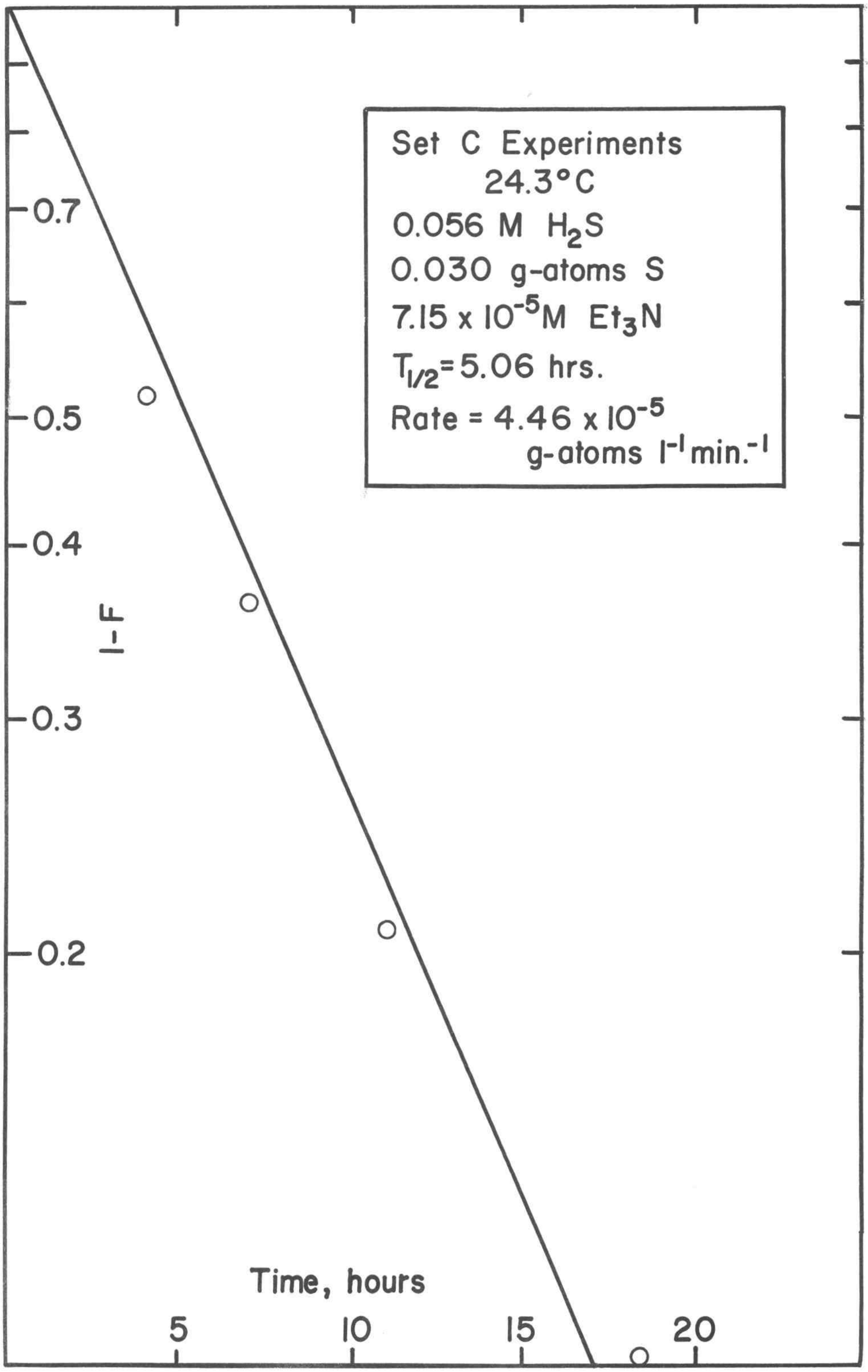

Figure 2. Log (1-F) vs Time

value of 0.5), computations become easier. Calling this half-time $T_{\frac{1}{2}}$, the rate expression reduces to

$$R = \frac{(ab)}{(a + b)} \cdot \frac{0.693}{T_{\frac{1}{2}}}$$

Thus, for the data displayed in Figure 2, with sulfur concentration = 0.03 g-atoms l^{-1} $\left[(S_8) = 0.00375M\right]$, $(H_2S) = 0.056M$ and $T_{\frac{1}{2}} = 303.6$ minutes, the exchange rate calculation becomes

$$R = \frac{(0.056)(0.030)}{(0.086)} \quad \frac{0.693}{303.6}$$

$$R = 4.46 \times 10^{-5} \text{ gram-atoms liter}^{-1} \text{ minute}^{-1}.$$

IV. EXPERIMENTAL DATA

In the early stages of this work a radiosulfur preparation thought to be a basic solution of radioactive sulfide was employed in an effort to prepare labeled arsenic trisulfide. When difficulty with this preparation was experienced, several different experiments were done to check the chemical identity of the preparation, which had been in the laboratory for some time. The material was found to be essentially all oxidized to a higher oxidation state, a result which emphasized the necessity for precautions against unnecessary exposure of sulfide solutions to air. Consequently a fresh preparation was obtained from the Oak Ridge National Laboratory and used thereafter with appropriate precautions.

In the following pages, experiments done are listed into four tables. Table II (IIa and IIb) corresponds to the experiments dealing with the radioisotopic exchange between arsenic trisulfide and hydrogen sulfide in chloroform solutions containing triethylamine. Table III contains the experiments corresponding to the sulfur-hydrogen sulfide exchange in chloroform solutions without any triethylamine added. Table IV corresponds to this same exchange but with triethylamine added. In this table, the experiments are grouped into sets, each of which is designed to study the effect of one reactant on the rate of the exchange. Table V, finally, contains experiments of the same last type of exchange but at different temperatures.

TABLE IIa

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ARSENIC TRISULFIDE IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE

Run	Time a) (min)	Vol (ml)	(Et_3N) (mols/l)	(H_2S) (mols/l)	(As_2S_3) (mols/l)	Temperature b) C°
8	20	98	0.800	0.735	0.0100	24.5
9	7	98	0.800	0.605	0.0050	24.5
10	6	98	0.800	0.580	0.0050	24.5
11	2	98	0.800	0.690	0.0050	24.5
12	7	213	0.800	0.200	0.0050	0
13	4	274	0.800	0.200	0.0050	0
15	10	270	0.080	0.020	0.0005	-21.3
16	9	400	0.080	0.020	0.000125	-35.7

---

a) This time is obtained by considering the zero time of the run as the middle time of dissolution of arsenic trisulfide; hence there is an estimated error of ±0.5 min.

b) The first four experiments from this set were done in the atmosphere; the rest were done in the thermostat. In all of them the temperature was good within ±0.1°C.

TABLE IIb

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ARSENIC TRISULFIDE IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE

Run	Specific Activities (CPm/mg)				% Exchange d)
	$(As_2S_3)_o$ c)	$(H_2S)_t$	$(As_2S_3)_t$	$(As_2S_3)_\infty$	
8	110.3	4.44	5.36	4.43	99.0
9	123.6	2.80	3.05	3.10	100.0
10	122.4	2.50	3.50	3.20	99.8
11	120.8	2.51	3.00	2.62	99.7
12	118.9	8.26	8.92	8.28	99.5
13	117.0	8.49	7.75	8.17	100.3
15	332.1	20.18	39.51	22.93	94.6
16	328.0	5.84	11.12	6.08	98.9

c) Three separate labeled arsenic trisulfide preparations were used in these runs as follows: (1) in Run 8; (2) in Runs 9-13; and (3) in Runs 15 and 16. Whenever the same labeled material was used in consecutive runs, the specific activity of arsenic trisulfide in one run was calculated from the previous run's value by applying a suitable decay factor.

d) The per cent exchange values were calculated from the final specific activity of the arsenic trisulfide fraction as compared to the infinite time specific activity of the arsenic trisulfide, which in turn, was calculated from the initial specific activity of the arsenic trisulfide and the concentrations of the exchange ingredients. The formula used was $\frac{S_o - S_t}{S_o - S_\infty}$ where all the symbols refer to arsenic trisulfide specific activites.

TABLE III

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS WITHOUT TRIETHYLAMINE

Vol = 100 ml   Temp.[d] = 24 ± 3°C

Run	Time (min)	(H_2S) (mols/l)	(S) (g-atoms/l)	Specific Activities[a] cpm/mg)			% Exchange[b]
				$(S)_o$	$(H_2S)_t$	$(S)_t$	
18	115	0.390	0.0300	190.2	0.084±0.08[c]	190.3	0.62±0.59[c]
21	9600	0.510	0.1125	195.9	1.485±0.12	192.9	3.95±0.32
36	1535	0.500	0.1000	183.1	0.080±0.09	180.9	0.26±0.30
37	38880	0.420	0.1000	160.3	0.870±0.20	158.5	3.00±0.67
38	270	0.420	0.0300	176.0	0.242±0.09	172.6	2.07±0.73

a)The infinite time specific activity of the hydrogen sulfide $(H_2S)_\infty$, used to calculate the per cent exchange, was itself calculated from the measured initial specific activity of the elementary sulfur used in preparing the reaction mixture, together with the recorded concentrations of H_2S and S.

b)Calculated from the ratio $(H_2S)_t/(H_2S)_\infty$.

c)The indicated errors represent standard deviations computed from the calculated standard deviations of the actual counting data.

d)This set of experiments was done at room temperature, which was checked at periodic intervals.

TABLE IV

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE, AT 24.3 ± 0.1°C.

Vol = 100 ml

Run[a]	Time (min)	$(Et_3N)\times10^5$ (mols/l)	(H_2S) (mols/l)	(S) (g-atoms/l)	Specific Activities[b] (cpm/mg)			% Exchange[c]
					$(S)_o$	$(H_2S)_t$	$(S)_t$	
19	60	2.86	0.600	0.0300	190.2	8.98	9.98	99.1
20	6	7.15	0.653	0.0300	185.5	0.756	179.8	9.26
22	61	7.15	0.730	0.0300	183.8	4.91	77.25	67.6
A23	6	7.15	0.421	0.0300	200.7	0.685	185.4	5.11
A24	12	7.15	0.420	0.0300	200.7	1.59	157.1	11.7
A25	34	7.15	0.423	0.0300	200.7	4.18	134.3	31.3

---

a) Experiments used in drawing log (1-F) vs. time plots to obtain exchange rates are shown as members of a "set" by prefixing the run number with a capital letter characteristic of each set.

b) Activities for a given number experiment are given for the time of counting or, for the original sulfur, converted to that time.

c) The percentage exchange was in every case calculated from comparison of the activity of the recovered hydrogen sulfide (Column, 7) with that expected for complete exchange on the basis of the activity in the original sulfur (column, 6).

TABLE IV (cont'd.)

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE, AT 24.3 ± 0.1°C.

Vol = 100 ml

Run	Time (min)	$(Et_3N) \times 10^5$ (mols/l)	(H_2S) (mols/l)	(S) (g-atom/l)	Specific Activities (cpm/mg)			% Exchange
					$(S)_o$	$(H_2S)_t$	$(S)_t$	
A26	62	7.15	0.420	0.0300	200.7	6.53	101.3	48.5
28	113	7.15	0.512	0.0300	195.9	8.45	22.4	77.6
29	96	7.15	0.520	0.0300	144.0	6.83	55.1	64.6
30	140	7.15	0.512	0.0300	192.6	8.20	42.0	76.6
A31	73	7.15	0.420	0.0300	192.1	6.99	96.7	54.6
A32	130	7.15	0.422	0.0300	192.1	10.50	56.8	82.0
A33	190	7.15	0.425	0.0300	192.1	11.13	33.9	87.8
A34	240	7.15	0.420	0.0300	192.1	11.84	30.0	94.6
39[d)]	1020	0.715	0.425	0.0300	176.1	2.35	126.1	20.1

---

d) The "B set" experiments were designed to check the effect of Et_3N concentration on the rate of the exchange reaction. Runs 39, 40, 41, 42 were done for the same purpose, but the results were not meaningful, presumably because the flasks were not adequately clean to stand so small amount as 0.1λ of Et_3N (which corresponds to only 0.715×10^{-5} mole/l).

TABLE IV (cont'd.)

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE, AT 24.3 ± 0.1°C.

Vol = 100 ml

Run	Time (min)	$(Et_3N) \times 10^5$ (mols/l)	(H_2S) (mols/l)	(S) (g-atom/l)	Specific Activities (cpm/mg)			% Exchange
					$(S)_o$	$(H_2S)_t$	$(S)_t$	
40	1830	0.715	0.420	0.0300	179.5	1.64	149.5	14.0
41	2910	0.715	0.421	0.0300	174.7	3.69	120.5	31.7
42	4470	0.715	0.428	0.0300	173.0	1.05	147.5	9.26
B43 d)	1005	0.715	0.440	0.0300	146.8	6.36	47.2	67.0
B44	2100	0.715	0.451	0.0300	146.8	8.02	28.5	87.5
45	3720	0.715	0.450	0.0300	146.8	8.28	15.5	90.6
B47	410	0.715	0.422	0.0300	141.1	3.52	84.0	37.3
B48	540	0.715	0.420	0.0300	141.1	4.49	79.4	47.6
C49 e)	240	7.15	0.041	0.0300	138.8	28.1	95.8	47.9
C50	420	7.15	0.051	0.0300	138.8	32.6	80.1	63.4

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e) The "C Set" experiments were designed to check the effect of H_2S concentration on the rate of the exchange reaction. which is also the purpose of "C′ Set" experiments which had, however, a different H_2S concentration from that of the C experiments.

TABLE IV (cont'd.)

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE, AT 24.3 ± 0.1°C.

Vol = 100 ml

Run	Time (min)	$(Et_3N)x10^5$ (mols/l)	(H_2S) (mols/l)	(S) (g-atom/l)	Specific Activities (cpm/mg)			% Exchange
					$(S)_o$	$(H_2S)_t$	$(S)_t$	
C51	1100	7.15	0.060	0.0300	137.8	41.3	51.4	89.8
C52	665	7.15	0.070	0.0300	131.2	31.6	49.0	80.2
C'54	510	7.15	0.0125	0.0300	107.0	31.9	82.0	42.2
C'55	625	7.15	0.0125	0.0300	106.1	37.6	89.9	50.2
C'56	875	7.15	0.0125	0.0300	107.0	42.8	81.7	56.7
C'57	1772	7.15	0.0125	0.0300	107.0	66.0	80.9	87.4
58	660	7.15	0.420	0.0050	104.9	1.25	1.52	105.5
59	373	7.15	0.441	0.0050	373	4.00	6.35	95.5
60	228	7.15	0.450	0.0050	376.8	3.71	6.27	89.4
D62[f)]	41	7.15	0.421	0.0050	349.2	2.78	139.1	67.5

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f) The "D set" experiments were designed to check the effect of sulfur concentration on the exchange rate, which is also the purpose of the D' experiments, which had, however, a different sulfur concentration from that of the D experiments.

TABLE IV (cont'd.)

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE, AT 24.3 ± 0.1°C.

Vol = 100 ml

Run	Time	$(Et_3N)x10^5$	(H_2S)	(S)	Specific Activities			% Exchange
	(min)	(mols/l)	(mols/l)	(g-atom/l)	(cpm/mg)			
					$(S)_o$	$(H_2S)_t$	$(S)_t$	
D63	32	7.15	0.430	0.0050	350.0	2.15	209.5	53.2
D64	33	7.15	0.412	0.0050	350.0	2.41	119.5	57.2
D65	58	7.15	0.440	0.0050	350.0	2.89	80.5	73.1
D67	65	7.15	0.420	0.0050	338.0	3.23	5.99	81.2
D68	15	7.15	0.400	0.0050	338.0	1.56	98.7	37.2
D69	20	7.15	0.423	0.0050	338.0	1.71	151.0	43.3
D'70	268	7.15	0.427	0.1800	113.8	29.0	35.3	84.5
D'71	62	7.15	0.400	0.1800	112.2	12.4	72.2	35.7
D'72	124	7.15	0.421	0.1800	111.2	20.3	46.3	60.7
D'73	35	7.15	0.426	0.1800	109.7	7.22	79.2	21.9

TABLE V

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE, AT -20.8 ± 0.1°C AND AT 0.2 ± 0.1°C

Vol = 100 ml $(Et_3N) = 7.15 \times 10^{-5}$ mols/l

Run[a)]	Time	(H_2S)	S	Temperature	Specific Activities[b)]			% Exchange[c)]
	(min)	(mols/l)	(g-atoms/l)	± 0.1°C	(cpm/mg)			
					$(S)_o$	$(H_2S)_t$	$(S)_t$	
E74	80	0.420	0.0300	-20.8	98.9	1.07	79.9	16.4
E75	137	0.421	0.0300	-20.8	98.9	1.64	73.9	24.9
E76	260	0.450	0.0300	-20.8	98.1	2.77	55.6	45.2
E77	508	0.425	0.0300	-20.8	98.1	4.37	24.7	67.4
E78	876	0.420	0.0300	-20.8	98.1	5.78	14.12	88.3
F79	246	0.420	0.0300	+ 0.2	95.0	3.95	36.9	62.5
F80	367	0.420	0.0300	+ 0.2	95.0	4.76	22.4	75.3
F81	450	0.421	0.0300	+ 0.2	95.0	5.35	9.77	84.5
F82	81	0.400	0.0300	+ 0.2	93.8	2.08	64.5	31.7
F83	176	0.420	0.0300	+ 0.2	93.8	3.46	44.8	55.2

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a) See footnote a), Table IV

b) See footnote b), Table IV

c) See footnote c), Table IV

V. RESULTS

A. ARSENIC TRISULFIDE EXCHANGE EXPERIMENTS

Arsenic trisulfide gave no evidence of dissolving in chloroform solutions containing hydrogen sulfide; even trace amounts of the arsenic trisulfide did not dissolve. The addition of triethylamine enhances the solubility greatly, although it was found that the mixture had to be shaken for a time before all the arsenic trisulfide present was completely dissolved. In a typical experiment (Run No. 8 in Table IIa) it took 5.5 minutes to dissolve one millimole of arsenic trisulfide in 98 milliliters of chloroform containing 0.072 moles of hydrogen sulfide and 0.078 moles of triethylamine. The colorless chloroform solution which becomes a faint yellow when saturated with hydrogen sulfide, changes to a somewhat less faint yellow when the triethylamine is added, and becomes deeper when the arsenic trisulfide is dissolved.

Table II (IIa and IIb) indicates clearly the occurrence of a rapid and complete exchange between arsenic trisulfide and hydrogen sulfide solutions containing triethylamine even at a very low temperature (-21.3°C in Run 15 and -35.7°C in Run 16). An estimated half-time at 24.3°C would certainly be less than one minute (cf. Run 11).

B. ELEMENTAL SULFUR EXCHANGE EXPERIMENTS WITHOUT TRIETHYLAMINE ADDED

The results of the exchange experiments listed in Table III, involving elementary sulfur dissolved in chloroform solutions containing hydrogen sulfide without any triethylamine, indicate very clearly an almost complete lack of exchange even after 27 days at room temperature. This result presents an exact parallel to the complete lack of exchange observed by Mickelsen in his study of the system liquid hydrogen sulfide-elementary sulfur (14, p.87).

C. ELEMENTARY SULFUR EXCHANGE EXPERIMENTS WITH TRIETHYLAMINE ADDED

1. General. The addition of triethylamine to the exchange mixture described in the previous section produces a completely changed situation. The first preliminary experiment (No. 19, Table IV) indicated that with 40 λ of triethylamine added to the exchange mixture (equivalent to 28.6 x 10^{-5} mole), the exchange is complete. The next experiments done, (Experiments 20 and 22, Table IV) showed that the rate was measurable if the quantity of triethylamine was cut to 1λ (equivalent to 0.715 x 10^{-5} mole). In Table IV detailed results have been presented for forty-five experiments, all done at 24.3°C. These

experiments were grouped into sets to find how the exchange rate varies with reactant concentrations. On the basis of these data, plots of log (1-F) versus time were drawn, from the slopes of which (or from the thereby indicated half-times of the exchange reactions) the exchange rates were calculated as described in Section III. Figure 3 shows a typical plot, obtained in the case of the Set A experiments. The log (1-F) versus time plots for the other sets of experiments had generally similar appearances.

Table VI gives a summary of the sets of experiments with the rates observed in each case. Set A served as a basis of comparison for all the other sets. In Set B, for example, the effect of varying the triethylamine concentration was examined by decreasing this factor ten-fold, other concentrations being maintained constant. The value of Rate/(Et_3N) in Set A is $3.23 \times 10^{-4}/7.15 \times 10^{-5} = 4.52$ min.$^{-1}$, whereas for Set B the corresponding quantity is $2.95 \times 10^{-5}/7.15 \times 10^{-6} = 4.12$ min^{-1}. This suggests a first order relationship between the exchange rate and the triethylamine concentration. To study the effect of the hydrogen sulfide concentration on the rate, Sets C and C' were performed, involving the reduction of this concentration by factors of about 7.5 and 34, respectively. For Set A, Rate/(H_2S) $= 3.23 \times 10^{-4}/0.421 = 7.68 \times 10^{-4}$ min.$^{-1}$, whereas for Set C, Rate/(H_2S) $= 4.46 \times 10^{-5}/0.056 =$

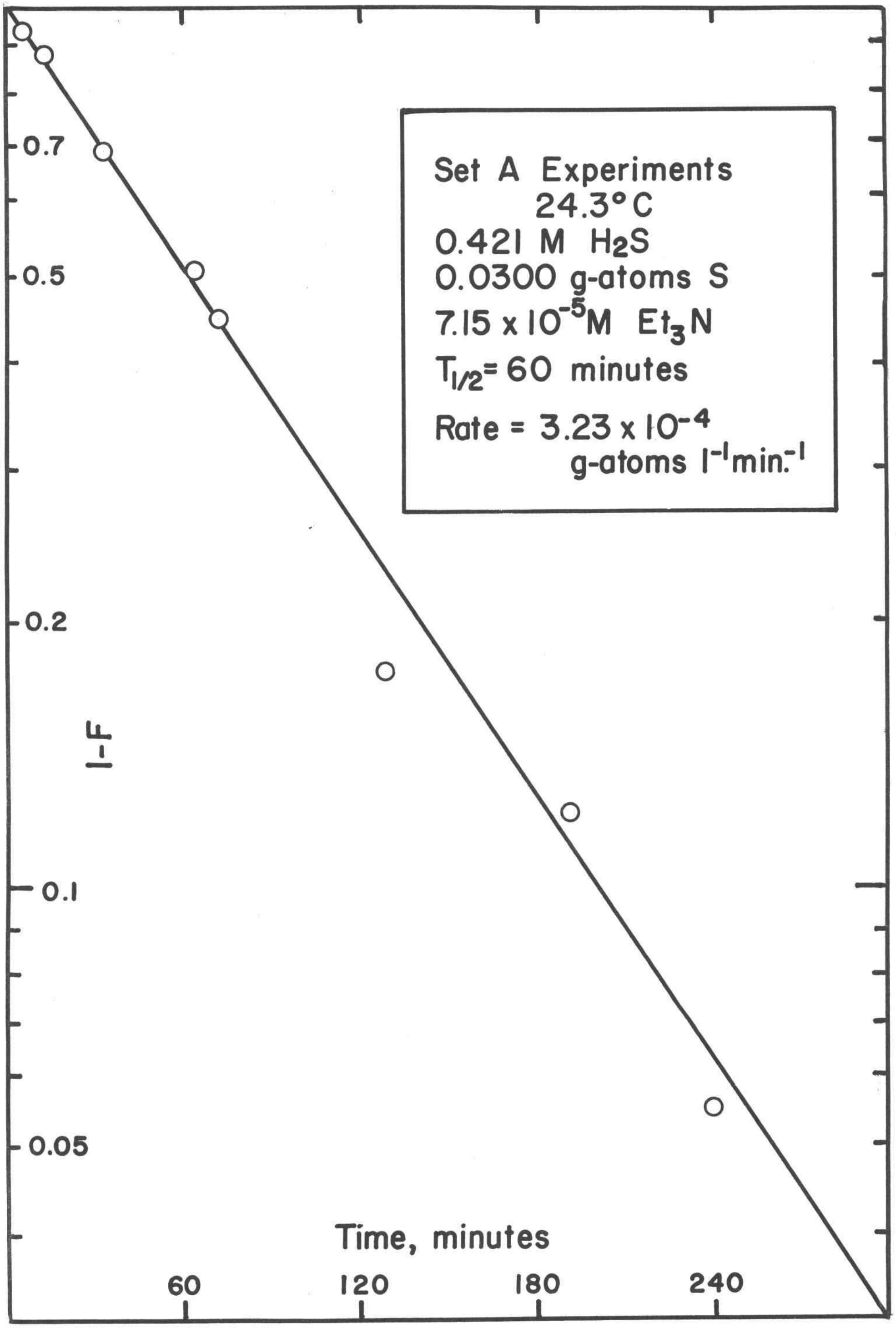

Figure 3. Log(I-F) vs Time

TABLE VI

RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND ELEMENTARY SULFUR IN CHLOROFORM SOLUTIONS CONTAINING TRIETHYLAMINE

Rates and Rate Constants

Set	$(Et_3N) \times 10^5$	(H_2S) a)	(S) b)	Temp.	Half-Time c)	Rate x 10^4 d)	k x 10^{-2} e)
	(mols/l)	(mols/l)	(g-atoms/l)	C°	(min)	g-atoms $l^{-1} min^{-1}$	$mole^{-3/2}\ l^{3/2}\ min^{-1}$
A	7.15	0.421	0.0300	24.3	60	3.23	1.75
B	0.715	0.433	0.0300	24.3	660	0.295	1.67
C	7.15	0.0560	0.0300	24.3	303.6	0.446	1.79
C'	7.15	0.0125	0.0300	24.3	667	0.092	1.70
D	7.15	0.421	0.0050	24.3	26.6	1.29	1.71
D'	7.15	0.420	0.1800	24.3	99.5	8.78	1.94
E	7.15	0.427	0.0300	-20.8	309	0.628	0.336
F	7.15	0.416	0.0300	+ 0.2	167	1.16	0.629

---

a) Each of these concentration values is the average of the concentrations of the individual runs in one set.

b) Note that sulfur concentrations are given in gram-atoms/liter. (S_8) concentrations, in moles/l would be numerically one-eighth of the values recorded.

c) These half-times are obtained from the log(1-F) vs. time plot for every set.

d) Calculated from the formula

$$R = \frac{(H_2S)(S)}{[(H_2S)+(S)]} \, \frac{0.693}{T_{\frac{1}{2}}}$$

e) Calculated on the basis of the rate law: $R = k\,[H_2S]\,[Et_3N]\,[S_8]^{\frac{1}{2}}$

7.96×10^{-4} min.$^{-1}$, and for C! Rate/(H_2S) = 9.20×10^{-6}/ $0.0125 = 7.35 \times 10^{-4}$min.$^{-1}$. Clearly, these values suggest also a first order relationship between the rate and the hydrogen sulfide concentration. Finally, the D and D' sets were done to check the effect of sulfur concentration on the rate, involving respectively a six-fold reduction and a six-fold enhancement of this factor. A log-log plot of rate versus sulfur concentration (Figure 4) gives a good straight line with a slope of 0.522. Consequently, a one-half order relationship is suggested.

On the basis of the results presented in the previous paragraph, the rate law for the exchange appears to be given by the expression

$$\text{Rate} = k(H_2S)(Et_3N)(S_8)^{\frac{1}{2}} \qquad (1)$$

values for the specific rate constant, k, according to Equation (1) have been calculated for each of the sets of runs shown in Table VI, and are recorded in the last column of this table. It is apparent that all of the sets at 24.3°C present a gratifying degree of constancy, lending good support to the validity of Equation (1).

2. Rate Variation With Temperature.-In addition to the experiments at 24.3°C runs were made at 0.2°C and -20.8°C, the observed corresponding rates being recorded in Table VI. A plot of the data obtained from these two sets and from Set A in Figure 5, as log (Rate) versus the

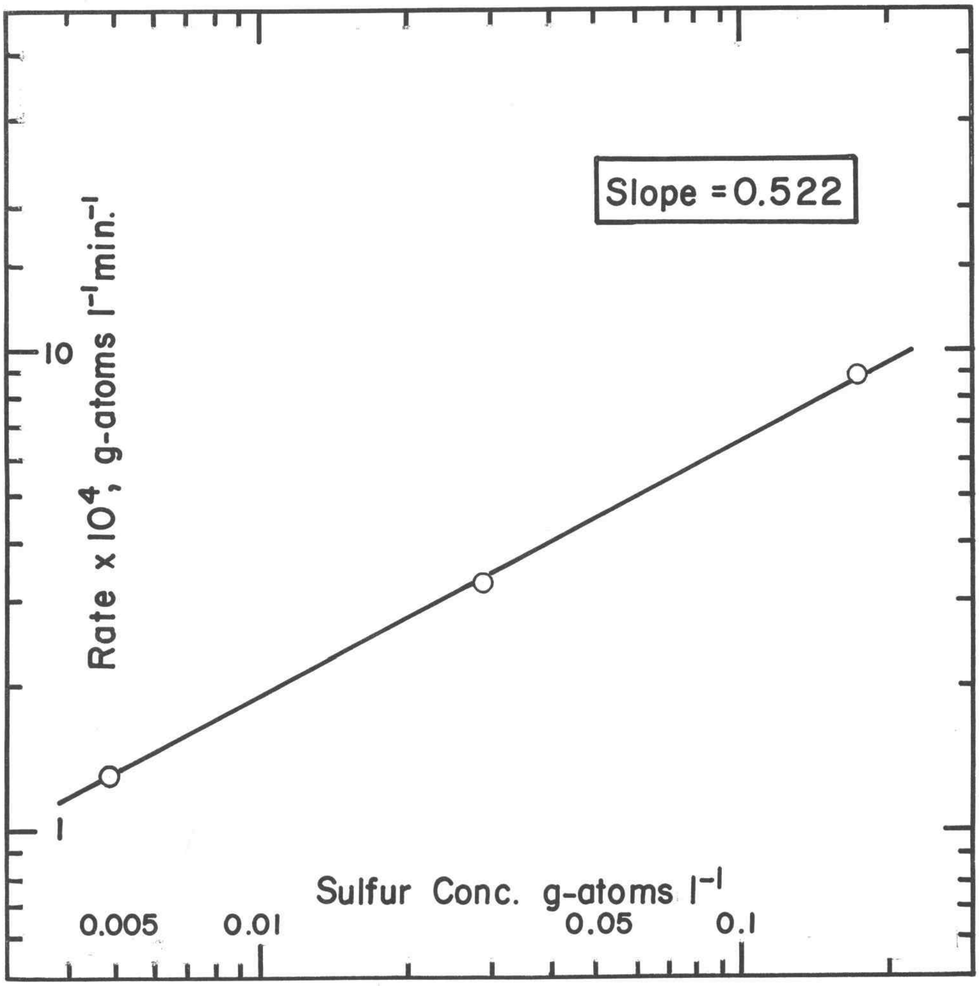

Figure 4. Log Rate vs Log S Concentration

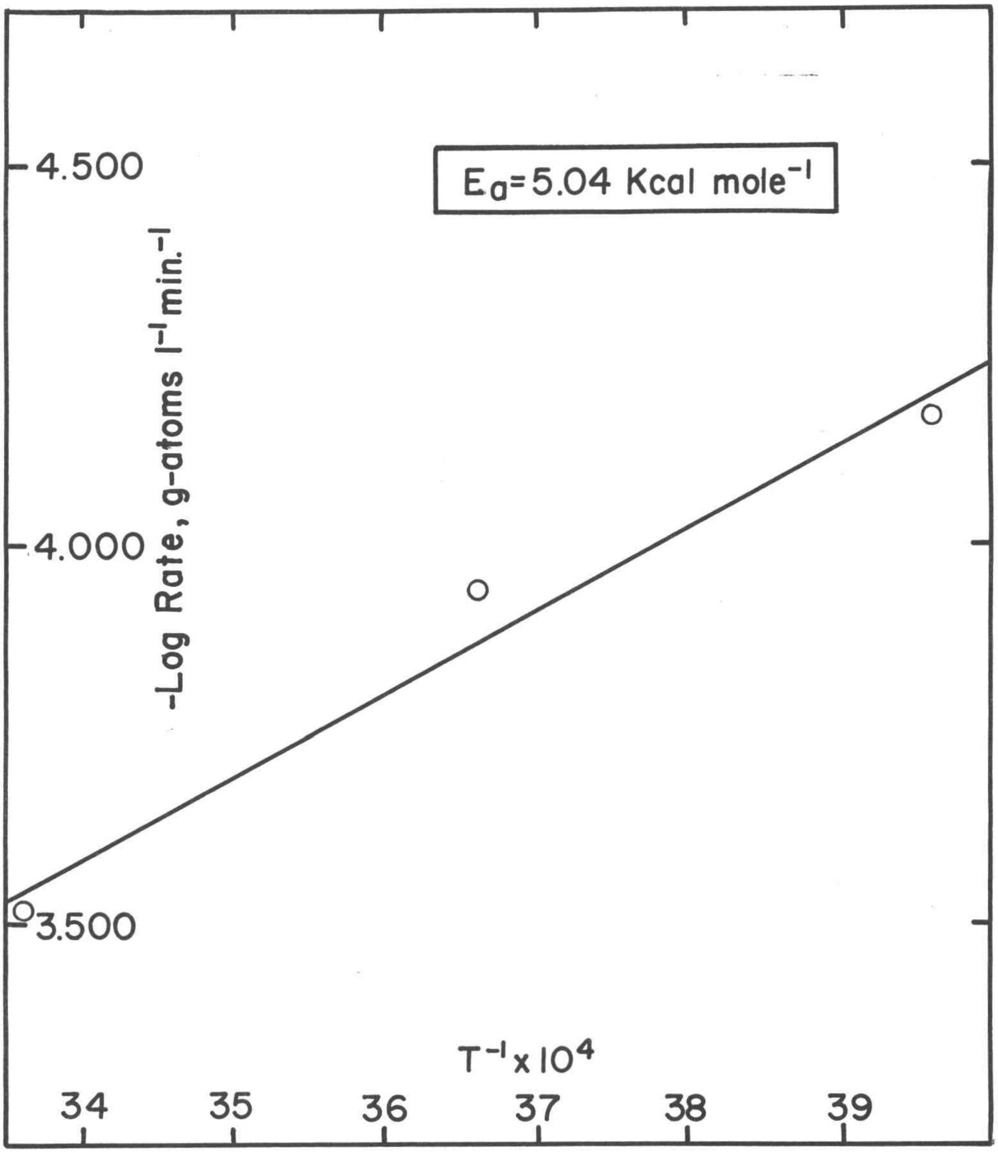

Figure 5. Rate-Temperature Dependence of S-H_2S (Et_3N) Exchange

reciprocal of the absolute temperature, yields an apparent activation energy of 5.04 kilocalories per mole according to the Arrhenius equation

$$-\frac{d\ \log\ (\text{Rate})}{d\ {}^{1}/T} = \frac{Ea}{2.3R} \qquad (2)$$

This activation energy, together with all eight sets of runs (Table VI) may be used to calculate an average value of the pre-exponential term in the intigrated form of the Arrhenius equation

$$k = A\ e^{-Ea/RT} \qquad (3)$$

The value of A so obtained is 1.48×10^{4} mole $^{-3/2}$ $l^{3/2}$ sec^{-1}.

The foregoing data may also be used to obtain a value of the apparent entropy of activation based on the equation (7, p. 199):

$$k = e\ \frac{k\ T}{h}\ e^{-Ea/RT}\ e^{\Delta S^{\ddagger}/R} \qquad (4)$$

Where

k is the rate constant (see below) =

2.842 mole $^{-3/2}$ $l^{3/2}$ sec^{-1}

e is the logarithm base = 2.718

k' is the Boltzmann constant = 1.380×10^{-16} erg deg^{-1}

h is Planck's constant = 6.624×10^{-27} erg sec^{-1}

T is the absolute temperature = 297.5°A

Ea is the apparent activation energy = 5040 cal mole^{-1}

R is the gas constant = 1.987 cal deg^{-1} $mole^{-1}$

In the application of Equation (4), we have substituted as the value of k, the specific rate constant, a value calculated from the integrated form of the Arrhenius equation (Equ. 3), together with the average value of A given in the preceeding paragraph. For the temperature we have used that corresponding to the majority of the experiments, 24.3°C. The value obtained for $\Delta S^{\ddagger}$ is -41.2 cal $deg^{-1}mole^{-1}$.

VI. DISCUSSION

A. ARSENIC TRISULFIDE EXCHANGE EXPERIMENTS

As mentioned in Section I, Jander was the first to study the behavior of arsenic trisulfide in liquid hydrogen sulfide solutions containing triethylamine, and developed the concept that this material is amphoteric in this solvent. According to Jander, the dissolution of arsenic trisulfide in liquid hydrogen sulfide solution containing triethylamine is due to the reaction:

$$As_2S_3 + 6(Et_3NH)\,SH \longrightarrow 2(Et_3NH)_3\,AsS_3 + 3\,H_2S$$

Then, when hydrogen chloride is next passed into the solution, the arsenic trisulfide again precipitates, and upon the addition of excess hydrogen chloride, the precipitate redissolves. These two steps were represented by Jander by the equations:

$$2(Et_3NH)_3\,AsS_3 + 6\,HCl \longrightarrow 6(Et_3NH)Cl + As_2S_3 + 3H_2S$$

$$As_2S_3 + 6\,HCl \longrightarrow 2\,AsCl_3 + 3\,H_2S$$

Jander's ideas were verified in a general way by the use of the tracer sulfur-35 in the form of arsenic trisulfide. This is what Mickelsen had done in 1956, when he found that in all the cases he investigated, the sulfur exchange between arsenic trisulfide and the solvent was rapid and complete indicating that the thioarsenite, $(Et_3NH)_3AsS_3$, proposed by Jander is, in fact, quite possibly formed in the solution, and that once formed, it maintains a reversible dissociation equilibrium with its decomposition products:

$$2(Et_3NH)_3AsS_3 \rightleftarrows 6\ Et_3N + 3H_2S + As_2S_3$$

In Mickelsen's research the exchange rate was immeasurably fast, so that no kinetics study was possible. In his work, the solvent itself was one of the exchanging species. The present research was undertaken in the hope that, in the solvent chloroform, sufficiently low exchange reactant concentrations might be used so that a measurable exchange rate might be found. Thus, it was hoped that a kinetics study could be possible.

Since Mickelsen's experiments were done in liquid hydrogen sulfide as a solvent, the hydrogen sulfide concentration was much higher than either the triethylamine or the arsenic trisulfide. (In a typical run, he used 14.7 millimoles of hydrogen sulfide, 0.303 millimoles of triethylamine and 0.0406 millimoles of arsenic trisulfide.) It was for this reason that he assumed that the basic solution formed, upon the addition of the triethylamine to the liquid hydrogen sulfide, contained the acid sulfide, $(Et_3NH)(SH)$. In this work, however, the concentration of the triethylamine was always higher than that of the hydrogen sulfide. Thus one might assume that the species triethylammonium sulfide would be found in the solution in place of the acid sulfide. According to this point of view, the following equilibria may then be assumed possibly to take place

$$2\ Et_3N + H_2S \rightleftarrows (Et_3NH)_2S$$

$$As_2S_3 + 3(Et_3NH)_2S \rightleftarrows 2(Et_3NH)_3AsS_3$$

In all cases investigated in this work, the exchange was found to be rapid and complete in less than two minutes. Efforts were made in vain to render the exchange slow, so that the rate could be determined. As steps towards this end, reactions were run both at low temperature, (down to -35.7°C) and at low reactant concentrations (see Runs 15 and 16), but in no case was a measurable rate obtained. It might seem possible that by drastically cutting down the triethylamine concentration (i.e. to a volume much below those of the two sulfur-containing species) one might hope to achieve a measurable rate. This avenue was blocked, however, by the fact that under such circumstances the dissolution of the arsenic trisulfide could not be accomplished.

While it was disappointing not to be able to find a measurable rate and so to study the kinetics in this exchange system, it is clear that the results observed are in a general way consistent with those observed by Mickelsen. Thus, as in liquid hydrogen sulfide, it seems probable that thioarsenite formation occurs in chloroform solution and that the rapid exchange between hydrogen sulfide and arsenic trisulfide is to be accounted for by a ready reversibility of equilibria such as those indicated by the last two equations on page 64.

B. ELEMENTAL SULFUR EXCHANGE EXPERIMENTS

Mickelsen, in his study of the exchange of elementary sulfur with liquid hydrogen sulfide, found that, in the absence of triethylamine, the exchange was too slow to measure. The addition of the merest trace of triethylamine to the exchange mixture, however, led to an immeasurably rapid exchange. Again, as in the hydrogen sulfide-arsenic trisulfide system, it seemed that the best hope of obtaining a measurable exchange rate in the elemental sulfur-hydrogen sulfide systems containing triethylamine was to carry out experiments in an inert solvent rather than in the liquid hydrogen sulfide itself as solvent. There seemed a possibility that the much lower hydrogen sulfide concentrations thereby attainable might yield an observably slow rate. Experiments in the solvent chloroform were therefore undertaken to this end.

As in the case of Mickelsen's work, the first experiments in this research involved an investigation of the possibility of exchange between sulfur and hydrogen sulfide in chloroform with no triethylamine present. Thus one might test for the possible occurrence between these two sulfur-containing species of some type of interaction related to polysulfide formation. The experiments listed in Table III indicate claearly the lack of any significant exchange at room temperature. Although the apparent percentage exchanges found in the five experiments listed in Table III show a certain amount of scatter among themselves, they seem to display no tendency to increase with time, so that one is led to attribute the scatter largely or entirely to experimental error. The apparent half-time shown by the longest time experiment (Run No. 37) amounts to 616 days. It seems reasonable, therefore, to accept this figure as an approximate lower limit for the half-time of the exchange. This result rules out the possibility of any significant sulfur-hydrogen sulfide interaction of the nature of polysulfide formation in these solutions. Thus chloroform represents an inert solvent for the two sulfur-containing solutes, the elementary sulfur presumably existing here unperturbed, in the form of S_8 molecules (17, p. 876). It is of interest to note that this result is in accordance with that found by Mickelsen (14, p. 87) for sulfur dissolved in liquid hydrogen sulfide, where the results also indicated the lack of any apparent sulfur-hydrogen sulfide interaction suggestive of polysulfide formation.

The addition of triethylamine to the exchange mixtures was found to lead to a complete change in the picture. While the amount of triethylamine added relative to the other exchange ingredients was too small to have any material effect on the sulfur solubility, it did suffice, even in very small amounts, to render the exchange rapid, just as Mickelsen had observed in his research. On the other hand, the hope with which this work was started was realized in that, unlike the situation with the liquid hydrogen sulfide solutions, it was here possible to obtain measurable rates, the results of which have been presented in the previous section.

Thus, in contrast to the solutions lacking triethylamine, it seems probable that polysulfide-formation equilibria do operate in these solutions. The fact that it has been possible to study the kinetics of the exchange has further made it feasible to arrive, at least tentatively, at certain conclusions as to the possible nature of such equilibria. The results presented in the last section show that the rate law for the exchange reaction studied is

$$\text{Rate} = k\,[H_2S]\,[Et_3N]\,[S_8]^{\frac{1}{2}} \qquad (1)$$

A reasonably plausible (although certainly not a unique) interpretation of this rate expression and the data it represents would appear to be offered by the following equilibria:

$$Et_3N + H_2S \rightleftarrows (Et_3NH^+)(HS^-) \text{ fast} \qquad (2)$$

$$S_8^* \rightleftarrows S_6^* + S_2^* \text{ fast} \qquad (3)$$

$$(Et_3NH^+)(HS^-) + S_2^* \rightleftarrows (Et_3NH^+)(HS_3^{*-}) \text{ slow} \qquad (4)$$

It is readily seen that these equilibria lead to the rate law represented by Equation (1). On the assumption, as indicated, that Equilibria (2) and (3) are rapid compared to Equilibrium (4), the latter may be considered as the rate-determining step, and hence the rate formula may be expressed as

$$\text{Rate} = k_1(1)(2) \left[(Et_3NH^+)(HS^-)\right] \left[S_2\right] \qquad (5)$$

The factors of one and two in this equation represent, respectively, the number of gram-atoms per mole of sulfur in $(Et_3NH^+)(HS^-)$ and in S_2. They are introduced so that the reactant concentrations in (5) may be expressed in molar units, while the exchange rate and the specific rate constant will be in gram-atms of sulfur per liter per unit time. If it is further assumed that both Equilibria (2) and (3) lie well to the left and have equilibrium constants designated respectively K_1 and K_2, one may write for the molar concentrations of the reactants in (5) the expressions

$$\left[(Et_3NH^+)(HS^-)\right] = K_1 \left[Et_3N\right] \left[H_2S\right]$$

$$\left[S_2\right] = K_2^{\frac{1}{2}} \left[S_8\right]^{\frac{1}{2}}$$

The latter expression is based on the assumption that no interfering sulfur dissociation equilibrium other than (3) operates in the solution, so that the concentration equality $[S_2] = [S_6]$ would apply. Substitution of these reactant concentration expressions in (5) leads to a rate expression in terms of the original measured reactants

$$\text{Rate} = 2k_1\, K_1K_2^{\frac{1}{2}}\, [Et_3N]\, [H_2S]\, [S_8]^{\frac{1}{2}} \qquad (6)$$

It is evident that this equation is identical in form with the experimentally observed rate law, (1), and thus the validity of Equilibria (2), (3) and (4) as an interpretation of Equation (1) is established. Comparison of Equations (6) and (1) shows that the specific rate constant of (1) represents a composite of the other constants as given by the relation

$$k = 2k_1\, K_1K_2^{\frac{1}{2}} \qquad (7)$$

In commenting on the plausibility of the above postulated reaction mechanism, it is appropriate to consider the value of the apparent activation energy for the reaction, namely 5.04 kcal. mole^{-1}. While this figure may appear relatively small, it must be recognized that it represents a composite of the true activation energy associated with Equation (4) and the ΔH values associated with (2) and (3). Thus from (7) one might write

$$-\frac{d \ln k}{d\, 1/T} = -\frac{d \ln k_1}{d\, 1/T} - \frac{d \ln K_1}{d\, 1/T} - \frac{1}{2}\frac{d \ln K_2}{d\, 1/T} \qquad (8)$$

Using the Van't Hoff and Arrhenius equations

$$-\frac{d \ln K}{d\ 1/T} = \frac{\Delta H}{R}$$

$$-\frac{d \ln k}{d\ 1/T} = \frac{Ea}{R}$$

One obtains from (8) the relation

$$(Ea)_{apparent} = (Ea)_{true} + \Delta H_1 + \tfrac{1}{2}\Delta H_2$$

or

$$(Ea)_{true} = (Ea)_{apparent} - \Delta H_1 - \tfrac{1}{2}\Delta H_2 \qquad (9)$$

where ΔH_1, and ΔH_2 refer respectively to Equilibria (2) and (3), $(Ea)_{apparent}$ is the observed value and $(Ea)_{true}$ is the activation energy associated with the rate expression (5).

While neither of the ΔH values on the right in (9) are known, it seems quite possible that they are of opposite sign and very roughly of the right magnitudes approximately to cancel each other. Thus, from data given by Bichowsky and Rossini (2, p. 27), one may calculate for the gas phase reaction

$$S_8\ (g) \rightleftarrows S_6\ (g) + S_2\ (g) \qquad (10)$$

ΔH (at 18°) = 31.8 kcal. $mole^{-1}$. If we assume approximately the same value to apply in chloroform solution, it is evident that $\frac{1}{2}\Delta H_2 \approx 16$ kcal. $mole^{-1}$. Hence if the suggested approximate cancellation is to occur, ΔH_1 would have to have roughly the same negative value, viz. $\Delta H_1 \approx -16$ kcal. $mole^{-1}$. While the value of

ΔH_1 is not independently known, a figure of the indicated magnitude would not seem unreasonable. Thus an acid-base neutralization such as indicated by equation (2) would certainly be exothermic (i.e. negative ΔH). More specifically one may refer to the related gas phase reaction

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(g)} \qquad (11)$$

For this reaction the measured ΔH is -9.4 kcal. mole^{-1}. (2, p. 208), a value not too far from the required figure.

On the basis of the foregoing points it would seem quite possible that the two ΔH terms in Equation (9) do in fact, approximately cancel each other. This leads to the conclusion that $(Ea)_{true} \approx (Ea)_{apparent} = 5$ kcal. mole^{-1}. The approximate nature of this equality would appear to allow ample latitude to cover any reasonable value that $(Ea)_{true}$ might be expected to have. However, it would seem worth noting that the chemical nature of the species involved in Equation (4) would appear not to be inconsistent with a relatively low activation energy of the general order of magnitude of that suggested by this approximation.

Relative to the postulated mechanism, it is of some interest to consider the numerical magnitudes of the specific rate constant observed in this work, and the probable value of the pre-exponential Arrhenius A factor which may be inferred from this figure. Thus at 24.3°C the observed average value of k (Equation (1)) was 176 $l^{3/2}$ $mole^{-3/2}$ min^{-1} or 2.93 $l^{3/2}$ $mole^{-3/2}$ sec^{-1}. This figure is related to the rate constant, k_1 of the rate-determining step (Equation (4)) by the relation (see Equation (7))

$$k_1 = \frac{k}{2K_1 \; K_2^{\frac{1}{2}}} \qquad (12)$$

While it is not easy to arrive at any precise quantitative estimates of K_1 and K_2, it seems certain that they must both be relatively small, i.e. Equilibria (2) and (3) must lie well to the left. This follows for (2) from the fact that the reaction rate increases linearly with increase in concentration of either of the species shown on the left, even though one (H_2S) is already present in much higher concentration than the other (S_8). For (3) it follows from the observation of the square root relationship. Thus, at least qualitatively, it is clear that k_1 will be numerically much larger than k.

Despite the inherent approximations necessary, it is desirable to attempt a more qualitative estimate of k_1. As a first step towards this end, one may arrive at some idea of the possible magnitude of K_2 on the basis of data given by Lewis and Randall (12, p. 536-539) for the gas phase dissociation of sulfur (Equation 10). For this reaction one obtains (at 25°C) $\Delta F^{o} = 20.18$ k cal. mole^{-1}. Hence, on the basis of the relationship

$$\Delta F^{o} = -RT \ln K$$

one calculates $K = 1.7 \times 10^{-15}$. Thus, for the same dissociation equilibrium in chloroform solution (Equation (3)) one may perhpas roughly estimate $K_2 \approx 1 \times 10^{-15}$. With regard to K_1, while no information is at hand, the nature of the equilibrium involved would suggest that the constant should not be nearly so small, and yet, as indicated above, the observed kinetics of the reaction shows it to be clearly less than unity. Perhaps, strictly as a trial guess, one might tentatively estimate $K_1 \approx 10^{-4}$. Substitution of these two equilibrium constant estimates in (12), together with the observed rate constant at 24.3°, leads to the estimated value for the rate constant of the rate-determining step (Equation 4), $k_1 = 5 \times 10^{11}$ l g-atom^{-1} sec^{-1}.

Substitution of this estimated value of k_1 in the Arrhenius equation

$$k = Ae^{-Ea/RT}$$

together with the previously estimated value for Ea of ~ 5 kcal. mole^{-1} leads now to a calculated value for A of $\sim 2 \times 10^{15}$ l g-atom^{-1} sec^{-1}. This figure, then, constitutes the apparent frequency factor for the bimolecular process represented by Equation (4). It is helpful to compare this figure with the "typical" value of about 10^{11} - 10^{12} (5, p. 148) expected for such a bimolecular process. (Since this is an order of magnitude consideration only, any apparent discrepancy between units of l g-atom^{-1} and l mole^{-1} may be safely ignored.) It is evident that the estimated A value is somewhat higher than might have been expected, but certainly not unreasonably so. On the other hand, it must be recognized that the calculation involves estimates that could easily be off by several orders of magnitude. Thus a certain amount of increase in the estimated K_1 and K_2 values, plus, perhaps, a slightly smaller activation energy, would significantly reduce any apparent conflict between the estimated and "expected" A values. On any case it is evident that these considerations based on the observed rate constant indicate no basic inconsistency with the postulated reaction mechanism. They would appear to suggest, however, that the true activation energy associated with the rate-determining step cannot be much larger than the estimated 5 kcal. mole^{-1}, and if anything, would be smaller.

A comment on the fact that the sulfur (-II) exchanging species is shown as the ion pair (Et_3NH^+) (HS^-) rather than the free ion HS^- would appear called for. This situation arises since a free ion participation would require a square root dependence of rate on hydrogen sulfide and triethylamine concentrations rather than the linear dependence actually observed. A ready explanation for this state of affairs, however, is at hand in the fact that the concentration of free ions relative to ion pairs will be extremely small in a solvent of polarity as low as that of chloroform, with its dielectric constant of 4.806 at 20°C, as compared to 80.37 for water at the same temperature. It is well established (9, p. 44) that in such solvents, salts exist mainly as ion pairs (and also as triplets and higher aggregates) even at fairly low concentrations. This phenomenon occurs also even in water at higher solute concentrations. It may be noted that Herber, Norris and Huston (8, p. 2015) observed the same ion pair dependence in liquid sulfur dioxide during their study of chloride ion catalysis of isotopic exchange reactions in that system.

In connection with the present results, reference should be made to the work of Cooley and Yost (3, p. 2474). These investigators studied the radiosulfur exchange between elementary sulfur and the solvent sulfur monochloride, and found the exchange rate to be very slow at room temperature, but measurably rapid at about 100°C. From quantitative measurements they 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. They were, of course, unable to observe the dependence of the rate on the solvent, sulfur monochloride. On the basis of their observations they postulated that a satisfactory mechanism for the reaction consists in the slow dissociation of sulfur

$$S_8^* \rightleftarrows S_6^* + S_2^* \text{ (slow)} \qquad (13)$$

followed by a rapid exchange between S_2 and S_2Cl_2

$$S_2^* + S_2Cl_2 \rightleftarrows S_2^*Cl_2 + S_2 \text{ (fast)} \qquad (14)$$

The rate constant calculated on the basis of the rate law

$$\text{Rate} = k\,[S_8] \qquad (15)$$

was found to be ~ 0.023 min^{-1} (22, p. 21) at 98.3°C, with an activation energy of 33 kcal./g-atom.

Now it is significant to observe that Cooley and Yost presented as the rate-determining step at a relatively high temperature a process which has been assumed in the present work to be fast and not rate-limiting at a much lower temperature. This apparent inconsistency is further emphasized by a further consideration of Cooley and Yost's quantitative data. Thus, from their figures, one may calculate a value of k (Equation (15)) which one might expect at 24.3°C, the temperature of the majority of the present experiments. The value so found is 3.5×10^{-7} min^{-1}. If, now, one employs this constant to calculate the S_8 dissociation rate that one might expect (on the basis of Equation (15)) at the sulfur concentration prevailing, for example, in Set A of the present experiments (see Table VI) one obtains a rate of 1.05 x 10^{-8} g-atoms $l^{-1}$$min^{-1}$. Yet the rate actually observed for this set was 3.23 x 10^{-4} g-atoms l^{-1} min^{-1}. The latter figure in the present interpretation is assumed to represent the rate of the slow step, Equation (4), with the sulfur dissociation process (Equation (3)) being definitely faster. Clearly an inconsistency exists between the present research and that of Cooley and Yost.

The basis of the inconsistency between the interpretation here presented and that of Cooley and Yost is not entirely clear at the present time. In comparing the two sets of data the tacit assumption has been made that the change in solvent from chloroform to sulfur monochloride would not have a great effect on the rate constants. This might or might not be valid, although it is difficult to believe, as would be necessary to effect a reconcilation between the results, that the sulfur dissociation rate would be slower in sulfur monochloride by a factor of about 10^5 or more. Another point to bear in mind, however, is that Cooley and Yost were unable to observe any possible kinetic dependence on sulfur monochloride, with this material as solvent.

If thier interpretation is correct, the exchange should be zero order in this species. One would feel more confidence in making comparison between the two sets of data had it been possible specifically to establish this dependency.

This last point suggests a worthwhile extension of the present experiments which one might hope would bring about a reconciliation between Cooley and Yost's results and the present ones and, in the process, either eliminate or lend further support to either or both of the two reaction mechanisms offered. Thus if one were to study the radiosulfur exchange between elementary sulfur and sulfur monochloride in the solvent chloroform, one could both ascertain the kinetic dependence of the exchange rate on the sulfur monochloride and at the same time determine whether the change in solvent does, in fact, lead to an important change in the rate constants. Alternatively, it may be noted in this same connection that it would be of interest to study the possible exchange between H_2S and S_8 in S_2Cl_2 solutions containing triethylamine. It should be most helpful to ascertain whether the S(-II) would exchange at room temperature only with S_8, the S_2Cl_2 acting simply as an inert solvent, or, on the other hand, whether the exchange, at whatever temperature it was found to occur, would involve the solvent S_2Cl_2 as well as either or both S_8 and the S(-II) species. The interpretation of the results so obtained would provide an important supplement to the work so far done and help materially in resolving the apparent conflict between the present interpretation and that given by Cooley and Yost.

In summary it may be noted that study of the radiosulfur exchange between elementary sulfur and hydrogen sulfide in chloroform solutions containing triethylamine has made possible the deduction of a plausible rate law for a process which was too fast to follow in the solvent liquid hydrogen sulfide. Whether the exact reaction mechanism offered is correct is, of course, subject to further investigation, as indicated above (and such work would certainly be desirable), but whatever the mechanism, it seems certain that some process of the general sort suggested must be involved, and it seems quite likely that the process is of the same general nature as the fast one occurring in liquid hydrogen sulfide. The results thus present an analogy to the situation observed by Beasley (1, p. 1-70), who, as described in the Introduction, found what appeared to be the same exchange process between carbon disulfide and hydrogen sulfide (in solutions containing triethylamine) occurring in the inert solvent benzene as in the "solvent system" solvent liquid hydrogen sulfide. Such results as Beasley's and the present ones are of importance in their indication of the limitations of the "Solvent Systems" interpretation of acid-base phenomena.

VII. SUMMARY

A series of radiosulfur exchange experiments have been carried out with arsenic trisulfide and hydrogen sulfide dissolved in the inert, non-aqueous solvent chloroform, in the presence of triethylamine. Earlier studies showed that the exchange is immeasurably rapid when carried out in liquid hydrogen sulfide. By the use of chloroform as a solvent it had been hoped to slow down the exchange reaction to a measurable rate, so that the kinetics might be investigated. All efforts, however, failed to accomplish this purpose; the reaction was found to be rapid and complete, even at the low temperature of $-35.7^{\circ}C$, owing presumably to some such rapid reversible equilibrium as

$$3(Et_3NH)_2S + As_2S_3 \rightleftarrows 2(Et_3NH)_3\,AsS_3$$

A more rewarding series of radiosulfur exchange experiments were carried out with elemental sulfur and hydrogen sulfide dissolved in the same inert solvent chloroform, with and without triethylamine added to the exchange mixture. Earlier studies in liquid hydrogen sulfide as a solvent had indicated the lack of any significant exchange between the two materials in the absence of triethylamine. The present investigation has demonstrated this same result in chloroform solution. On the other hand, however, the presence of triethylamine leads to a rapid but measurable exchange rate, whereas the earlier studies in liquid hydrogen sulfide had shown this exchange reaction to be immeasurably rapid. The concentrations of the reactants were varied in a series of sets of experiments, to develop a suitable rate law, which turned out to be

$$\text{Rate} = k(H_2S)(Et_3N)(S_8)^{\frac{1}{2}}$$

This rate expression has been interpreted reasonably adequately in terms of the following equilibria

$Et_3N + H_2S \rightleftarrows (Et_3NH^+)(HS^-)$ Rapid (1)

$S_8^* \rightleftarrows S_6^* + S_2^*$ Rapid (2)

$(Et_3NH^+)(HS^-) + S_2^* \rightleftarrows (Et_3NH^+)(HS_3^{*-})$ Slow (3)

The rate constant k has been shown to include other constants

$$k = 2k_1 K_1 K_2^{\frac{1}{2}}$$

where k_1 is the rate constant of (3) and K_1, K_2 are the equilibrium constants for (1) and (2), respectively. From runs at different temperatures the apparent activation energy was found to be 5.04 kcal. mole^{-1} and the apparent entropy of activation, -41.2 cal deg^{-1} mole^{-1}. Both of these values represent composite effects involving both the true rate constant, k_1, and the equilibrium constants K_1 and K_2. Thus it has been shown that the ΔH

terms associated with the latter two constants may well be of opposite sign and of such magnitude as approximately to offset each other's effect, so that the true activation energy associated with the rate-determining step, Equation (3), may well have a magnitude not greatly different from that of the apparent activation energy.

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