

ISOTOPIC EXCHANGE REACTIONS IN
LIQUID HYDROGEN SULFIDE

by

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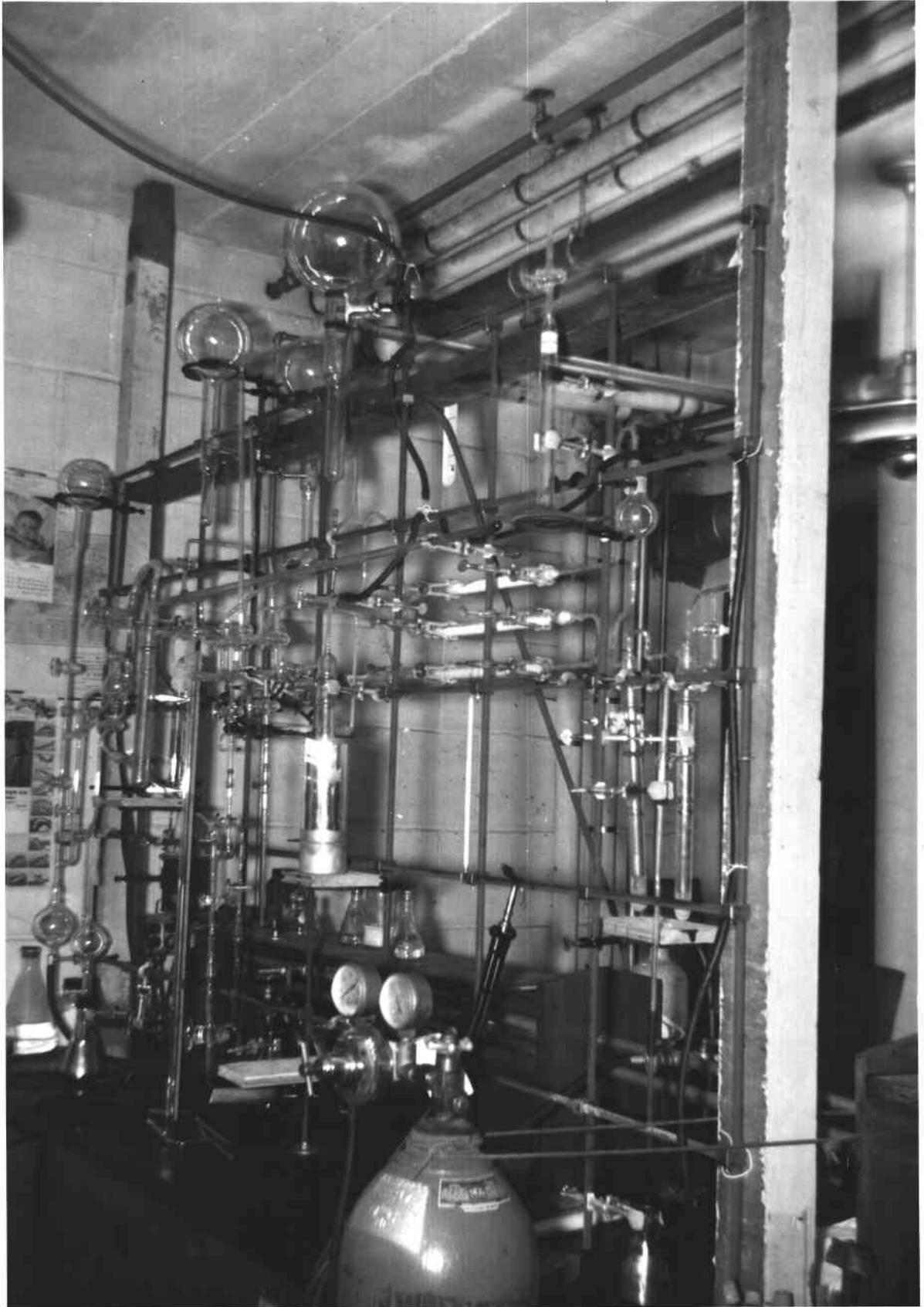
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Dean of Graduate School

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Typed by Edith R. Smith

FIGURE I



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ISOTOPIC EXCHANGE REACTIONS IN LIQUID HYDROGEN SULFIDE

I. INTRODUCTION

A. GENERAL. Largely because of its unique position on the Earth, water is by far the most important solvent in inorganic chemistry: so much so that one is normally accustomed to think of inorganic "solution" chemistry as implying water solution. It is for this reason, for example, that acids have long been regarded as substances yielding hydrogen ion in solution, and bases, substances yielding hydroxyl ions: respectively the cations and anions of the solvent water. And it is for this reason that studies of ionizing solvent systems other than water are of especial interest to the inorganic chemist.

Anhydrous liquid ammonia represents the best known and most studied non-aqueous ionizing solvent (3, p.339). This substance is presumed to undergo self-ionization to yield ammonium and amide ions, and in it ammonium salts (e.g. ammonium chloride) exhibit the properties of acids and amides exhibit those of bases. A considerable number of other non-aqueous, supposedly ionizing, solvents have been similarly investigated or discussed in greater or less detail, including sulfur dioxide, acetic acid, acetic anhydride, hydrogen sulfide, hydrogen cyanide, iodine,

iodine monochloride, phosgene and several more (all anhydrous and in the liquid state, of course). Experimentally, these investigations have used conventional physical and inorganic chemical methods: solubility, conductivity and reaction product studies, conductimetric titrations, cryoscopic measurements, etc. The availability of radioactive tracers makes possible a new avenue of approach to the investigation of these systems, and permits a direct testing of various ionization equilibrium schemes, some of them rather far-fetched, that have been proposed by different workers.

There is in progress at Oregon State College at the present time, an integrated research program in which radioactive tracers are being employed in a systematic investigation of a number of these solvents. Considerable information has already been obtained in regard to the solvents sulfur dioxide (6, pp.3049-3051; 8, pp.3052-3055), acetic acid and acetic anhydride (2, pp.1-100). The present work was undertaken as a preliminary study of the liquid hydrogen sulfide solvent system. Before proceeding to a discussion of the specific nature of the work, it seems well to review briefly some of the background material relative to this solvent.

B. LIQUID HYDROGEN SULFIDE AS A SOLVENT. The concept of liquid hydrogen sulfide as a non-aqueous ionizing

solvent has been largely developed by Wilkinson, Jander and their respective co-workers. The solvent, like water amphoteric in nature, is assumed to undergo self-ionization according to the equilibrium:



In this system, then, a base would be a substance yielding bisulfide ion, such as the compound $(\text{Et}_3\text{NH})\text{HS}$ thought by Jander (7, pp.115) to be formed when triethylamine is dissolved in hydrogen sulfide. The ordinary hydrogen acids are, of course, the typical acids of the system. Experimentation in this solvent is ordinarily conducted either at the temperature of a Dry Ice-acetone bath at ca. -80°C (at which the vapor pressure is about one-third of an atmosphere), or alternatively in sealed tubes at room temperature, (the vapor pressure being about 18 atmospheres).

Because of its low dielectric constant, 9.05 at -78.5°C , one might expect hydrogen sulfide to be a considerably less effective "inorganic type" solvent than water. That such is the case is demonstrated not only by the relatively small self-conductivity of 3×10^{-10} ohms $^{-1}$ cm. $^{-1}$ at -78.5°C , but also by the fact that investigation has in general shown the liquid in its solvent properties to be primarily organic in character. Only a few inorganic

substances have been found soluble. G.N. Quam (13, p.105) qualitatively tested the solubility at room temperature of approximately two hundred elements and compounds. He has divided them into four groups according to their solubility or insolubility and their reactivity or lack of reactivity. This list vividly shows the marked resemblance of liquid hydrogen sulfide to the usual organic solvents. Unfortunately Quam's results are of limited usefulness, since he gives no indication of their quantitative significance. For example the sulfides of arsenic, antimony and phosphorus used in the present research were described by Quam as soluble, whereas we have found their solubility to be at best extremely limited. However, a general picture of the situation is obtained by selected spot quotations from Quam's tabulations. Classed as soluble and unreactive are such substances as sulfur, iodine, hydrogen chloride, benzene, chloroform, zinc chloride, n-butyl mercaptan and pyrogallol; insoluble and unreactive examples are ammonium chloride, zinc sulfate, lead sulfide, and red phosphorus. Soluble and reactive materials include chlorine, sulfur dioxide, stannic chloride, bismuth trichloride and pyridine; apparently insoluble but reactive: sodium, silver, ammonium nitrate, potassium dichromate and calcium carbide.

"Soluble and reactive" compounds are believed to be so either because of the presence of an amino group, because thiohydrolysis takes place, or because of their oxidizing power.

Further insight into the nature of this solvent is provided by conductance studies of Quam and Wilkinson (14, pp.989-994) and, much more recently, of Lineken and Wilkinson (10, pp.251-256) in which comparisons are made among organo-substituted ammonium chlorides. Not only is it found that increase in the number of substituents greatly increases the solubility, but it also greatly increases the equivalent conductance. Thus, while ammonium chloride is practically insoluble and monomethylammonium chloride shows but little solubility and little conductivity, dimethylammonium chloride displays a molecular conductance of 0.0142 ohms^{-1} at 0.2 M and tetramethylammonium chloride 3.14 ohms^{-1} at 0.08 M. Incidentally, the conductivity curves show a minimum at a certain concentration, increasing both in more concentrated and in more dilute solutions, as is characteristic of solutions of electrolytes in solvents of low dielectric constant.

Extending and somewhat modifying Quam's results, Ralston and Wilkinson (15, pp.258-264) have shown that generally the chlorides of metallic elements are insoluble

in liquid hydrogen sulfide, exceptions being the chlorides of zinc, mercury, aluminum and iron. The chlorides of non-metallic elements which are easily hydrolyzed in water forming hydroxides, are usually soluble in this solvent, but show no thiohydrolysis. In other cases they form thiohydrates, addition products and sulfides.

Guest (5, pp.197-203) has studied the reactions of a number of inorganic compounds with liquid hydrogen sulfide. Calcium oxide and calcium carbide, in particular, give reactions similar to their reactions in water.

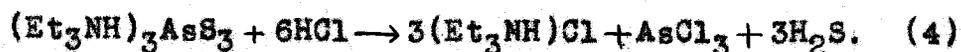
Jander, who has been quite active in the investigation of a variety of non-aqueous ionizing solvents, has done a considerable amount of work with liquid hydrogen sulfide. In addition to investigations of the type described in the foregoing paragraphs, potentiometric and conductimetric titration studies, such as of the neutralization of the base triethylammonium hydrosulfide by hydrogen chloride, form an important part of this work. Of particular interest to this thesis, however, is his study of the amphoteric qualities of arsenic trisulfide in hydrogen sulfide.

Triethylamine is considered by Jander (7, pp.114-116) to form the base $(Et_3NH)HS$, in liquid hydrogen sulfide. If, to such a solution, one adds arsenic trichloride,

precipitation, at least partially, of arsenic trisulfide occurs at first. However, this precipitate dissolves completely after a comparatively short time, the process presumably consisting of the reaction



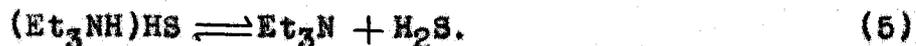
If one now passes the acid hydrogen chloride into this thioarsenite solution, the arsenic trisulfide again precipitates. Upon the addition of a large excess of hydrogen chloride the precipitate redissolves, "leaving at most a faint turbidity". The processes are represented by the equations



If the process is reversed and one adds arsenic trichloride to a hydrogen sulfide solution of hydrogen chloride, no precipitation of arsenic trisulfide results due to repression of thiohydrolysis by hydrogen ion. If one now adds triethylammonium hydrogen sulfide to this last solution, the arsenic trisulfide will again precipitate and then again dissolve on addition of excess base. Jander concludes that arsenic trisulfide conducts itself toward hydrogen sulfide acids and bases in a manner

analogous to the conduct of aluminum hydroxide toward aqueous acids and bases.

C. THE SCOPE OF THE PRESENT INVESTIGATION. The primary aim of this research was to exploit the potentialities of radioactive tracers for an investigation of the validity of some of the implications of the views outlined in the preceding section. Particularly interesting, we felt, would be a study of the rate of exchange between the solvent and a solute base such as $(Et_3NH)HS$, either the solvent or the solute being labeled with radioactive sulfur. Rapidly reversible equilibria involving the solvent self-ionization (Equation 1) and the ionization of the base, would be evidenced by a rapid and complete exchange. Unfortunately, soluble bases appear to be limited to organo-substituted sulfides or bisulfides such as the example mentioned above, and in such cases an alternative exchange path exists in the dissociation equilibrium



A possible candidate for exchange study is the base tetramethylammonium bisulfide, but since this material does not appear to have been studied in hydrogen sulfide solutions, it seemed more potentially fruitful to make a

tracer investigation of the interaction of arsenic trisulfide and similar compounds with hydrogen sulfide solutions of triethylamine. Thus we hoped to obtain some evidence as to the validity of Jander's picture of amphoterism with these materials. We had hoped, also, at first, to be able to do exchange studies with the sulfides dissolved in the pure solvent (a hope encouraged by Quam's report of their solubility), but their extremely limited solubility, which we found, prevented this. We have, therefore, investigated the rates of the exchange reactions only in basic hydrogen sulfide solution (triethylamine added), the solutes studied being arsenic trisulfide and phosphorus pentasulfide.

In view of the possibility of the formation of some type of polysulfide, it seemed of interest to investigate the exchange, with the solvent, of dissolved sulfur. In this case the solubility was found to be just sufficient to permit using the pure "neutral" solvent. In analogy with the arsenic trisulfide case, we suspected that the addition of triethylamine would enhance the solubility of the sulfur and this was found to be so. We have, therefore, studied the sulfur-hydrogen sulfide exchange both in the "neutral" solution and in the presence of added base. An interesting difference in rate of exchange is observed in the two cases.

In addition to recording the results of the foregoing exchange studies, which were the principal objects of this research, we have also set down in the following pages a number of qualitative and semi-quantitative observations made on these various solutions. Although no exchange work was done with it, we have found, for example, that the behavior of antimony trisulfide toward "neutral" and basic hydrogen sulfide solutions closely parallels that of arsenic trisulfide.

In the course of this work it has been necessary to prepare various labeled compounds. New, efficient and convenient methods, representing improvements over those hitherto used, have been developed for preparing S^{35} -labeled hydrogen sulfide, elementary sulfur and arsenic trisulfide.

D. SUMMATION. This thesis concerns itself with some introductory explorations of liquid hydrogen sulfide as a solvent, utilizing radioactive sulfur (S^{35}) as a tracer element. We have made semi-quantitative determinations of the solubilities of a few substances in the solvent; we have noted the rates of exchange of sulfur, arsenic trisulfide and phosphorus pentasulfide with the solvent and the effect of the presence or absence of the base triethylamine upon these solubilities and (where possible)

exchange rates. We have also worked out new preparation methods for obtaining labeled elemental sulfur and labeled hydrogen sulfide. No literature search was made to ascertain whether or not the labeled arsenic trisulfide had been prepared previously by the method herein used.

II. EXPERIMENTAL SECTION

A. GENERAL PROCEDURES. Standard high vacuum techniques were used for all operations throughout this work. Vacua of 10^{-5} mm. of mercury or better were obtained using a mercury diffusion pump; Apiezon grease "N" was used for lubrication of stopcocks. Either liquid nitrogen or Dry Ice-acetone baths were employed for the gas transfers. It is to be emphasized that completely anhydrous conditions were observed at all times, solid materials, for example, after initial drying, always being subjected to a final drying within the vacuum system. The necessity for the scrupulous avoidance of water arose not only from the possible effect its presence might have upon our experimental results, but also from the fact that contact of hydrogen sulfide gas with mercury (in the manometer and the diffusion pump) without reaction is possible only under strictly anhydrous conditions. In handling amines in a system such as this, it has been found necessary to avoid venting them through the oil of the forepump as they appear to form with it a sludge-like material. This was accomplished in the present instance by providing an eighteen-inch horizontal tube, three-quarters filled with concentrated sulfuric acid, which could, as occasion required, be interpolated between the pump and the vacuum

system and which served to absorb triethylamine from gases being exhausted from the system. Figure I is a photograph of the main vacuum line built by us for the following experimentation.

All exchange reactions were conducted in sealed glass tubes, provided with break-off tips for opening at the ends of runs. The technique used in filling these is described below under "Run Procedure"; it may be noted here that in this process, triethylamine was always handled with all glass technique, contact with stopcock grease being completely avoided. Inasmuch as hydrogen sulfide has a vapor pressure of eighteen atmospheres at room temperature, it was necessary to exercise caution in handling a bomb (all our experiments were done at room temperature). If a run was to be of any duration, the glass bomb was wrapped in cotton and placed in a protective iron pipe for the time of the experiment.

B. COUNTING PROCEDURES. The isotope S^{35} , used for all tracer experiments done in this research, decays with a half-life of 87.1 days, emitting soft beta particles with an energy of 0.169 Mev.

Activity determinations were made, in almost all cases, according to the technique described by Norris (12, p.1221), using an end window counter, the Tracerlab

model TGC-2 (< 2.0 milligrams per square centimeter mica window). Samples were mounted as thin layers of barium sulfate on cupped planchets. The counter had below it a shelf-like arrangement, with a number of steps, so that samples could be measured at various standardized distances from the counter, according to their activity. All counts directly connected with the exchange runs were made on the topmost shelf, a lower one being used only in connection with the initial preparation of extremely active labeled materials. Self-absorption corrections were applied as necessary. All samples connected with a given run were counted together, so that the necessity for the application of decay corrections was avoided.

The only exceptions to the foregoing general counting procedure were: (1) where very rough counts were made of crystals of radioactive substances to obtain a general idea of their activity, and (2) where sulfur dissolved in carbon disulfide was pipetted onto planchets, evaporated to dryness under a heat lamp and counted.

C. INACTIVE MATERIALS. All chemical materials used were of standard commercial origin and were, where necessary, carefully purified before use.

Hydrogen sulfide. The hydrogen sulfide used was obtained from a commercial cylinder (Ohio Chemical and Surgical Equipment Co.). It was dried and purified by running it through a purification train into storage bulbs previously evacuated to approximately 10^{-5} mm. of mercury. The first unit of the train consisted of two traps about eighteen inches long fitted with sintered glass bubblers and constructed with 34/45 ground glass joints to facilitate easy cleaning and changing of solutions. The traps were filled to a depth of approximately twelve inches with saturated solutions of barium hydroxide; the vapor pressure of water over these solutions was kept to a minimum by immersing the traps in ice-salt cooling baths. Above the second trap was a splash bulb and from this the train went, first, through a calcium chloride drying tube; next, through a phosphorus pentoxide tube; and, finally, through a tube filled with Pyrex glass wool. These tubes were all approximately eighteen inches long and thirty millimeters in diameter. From the glass wool tube the train led to a three-way stopcock: one vent from this stopcock led to the outside for disposal of surplus hydrogen sulfide and the other to a cold trap which, when the hydrogen sulfide was being passed in, was immersed in a Dry Ice-acetone bath.

A mercury pressure regulator-blow-off tube was placed at the head of the train before the first barium hydroxide bubbler and equipped with a stopcock which allowed an excellent control of the hydrogen sulfide flow. It was necessary that a positive pressure be maintained throughout the purification train at all times.

To assure pure dry hydrogen sulfide the entire vacuum line and purification train were evacuated, all glass except bubblers and drying tubes flamed, and tested for leaks. Then the train was isolated from the rest of the vacuum system by closing the three-way stopcock and the barium hydroxide solution added to the bubblers. Hydrogen sulfide was then passed through the train for at least twenty minutes to assure the complete sweeping out of all air, being vented meanwhile to the outdoors via the three-way stopcock and discarded. The stopcock was then turned to pass the hydrogen sulfide into the cold trap (which was immersed in a Dry Ice-acetone bath) and the purified gas was gradually collected by condensation over a period of time. After somewhat more than a two-fold excess of the liquid had been collected, the train was shut off and a final purification was achieved by fractionally distilling the liquid in the trap. The first twenty-five percent was evaporated off and discarded; the middle fifty percent

was used to fill the storage bulbs; the twenty-five percent residue was also discarded.

Sulfur dioxide. The sulfur dioxide used in these experiments was handled in the same manner as the hydrogen sulfide. It was taken from a commercial cylinder (Ohio Chemical and Surgical Equipment Co.) and purified by passing it through the same train, modified, that was used for the hydrogen sulfide. The only difference in the train was that the two traps with the sintered glass bubblers were filled with concentrated sulfuric acid rather than barium hydroxide solution. Exactly the same condensation and final fractional distillation procedure of the liquid was used as in the previous case.

Sulfur. Stock room roll sulfur was used in the preliminary experiment. This was purified by recrystallization from carbon disulfide. The sulfur was dissolved in hot carbon disulfide (only a small portion of the crude material was found to be soluble), and was recrystallized in an ice-salt bath and washed twice with cold carbon disulfide. It was then dried overnight at 55°C.

All the sulfur exchange experiments were made with radioactive sulfur which was prepared by the method given below.

Phosphorus pentasulfide. Baker and Adamson phosphorus pentasulfide was purified by recrystallization from carbon

disulfide. Phosphorus pentasulfide is soluble in carbon disulfide to the extent of 1 g. per 450 g. at 25°C and 1 g. per 1200 g. at -20°C. The method of purification was to saturate hot carbon disulfide with phosphorus pentasulfide, decant the hot saturated solution and place it in an ice-salt bath. The crystals formed were then washed twice with cold carbon disulfide and dried in an oven at 110°C for one hour.

Antimony trisulfide and arsenic trisulfide. Commercial laboratory chemicals (Baker and Powers-Weightman-Rosengarden Company, respectively) were used in most of the work without further purification, apart from drying. In a few cases, as noted hereafter, material was used which we had attempted to purify. This procedure, involving dissolution in fresh, colorless ammonium sulfide and reprecipitation by adding acetic acid, did not appear to be entirely satisfactory as carried out by us. Since, however, two out of three of the actual exchange experiments were made using labeled material prepared by us as described below and since for most other purposes the unpurified trisulfides were satisfactory, no attempt was made to perfect the purification procedure.

Triethylamine. Eastman White Label material was dried with sodium. In each experimental run a portion

was fractionally distilled within the vacuum system, a middle cut (ca. one-third of the total) being condensed either directly into the reaction bomb or else into an ampoule in the requisite amount for later transfer to a reaction bomb. The use of stopcock grease was avoided in these operations, all glass techniques, break-off tips, and so forth, being employed.

D. PREPARATION OF LABELED MATERIALS. It was necessary to prepare for use in these experiments the following substances labeled with S^{35} : sulfur dioxide, elementary sulfur, hydrogen sulfide and arsenic trisulfide. The S^{35} was obtained from the Oak Ridge National Laboratory of the United States Atomic Energy Commission in the form of twenty-five grams of neutron-irradiated potassium chloride¹ (Item No. 17, AEC Catalog No. 3), containing at the time of shipment one hundred millicuries of S^{35} . When used, this material was approximately three months old (i.e. ca. one half-life), so the total activity had decayed to about one-half of this figure.

Sulfur dioxide. Labeled sulfur dioxide was prepared by the method of Masters and Norris (11, pp.1-4) which involves an exchange reaction between the gas and concentrated sulfuric acid of very high specific activity.

1. The S^{35} is formed by the reaction $Cl^{35}(n,p)S^{35}$.

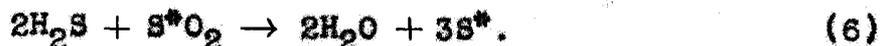
Approximately one gram of the neutron-irradiated potassium chloride was weighed into a centrifuge tube and was dissolved in six ml. of water containing 0.018 millimoles of sulfuric acid carrier². This solution was then heated and the activity was precipitated as barium sulfate by the addition of 0.2 ml. of 0.2 M barium chloride; the precipitate was digested for an hour on the steam bath and centrifuged. As a test for completeness of precipitation of activity a 0.0130 ml. aliquot of the supernatant was taken at this point and evaporated directly onto a planchet for a very rough activity determination. A similar sample had been taken from the solution before precipitation. The initial and final samples (counted some distance below the counter window) showed activities, respectively, of 2,394 and 453 counts per minute, demonstrating something like eighty percent precipitation of activity, which is about the expected amount. After centrifugation the supernatant was decanted and the precipitate was washed in the centrifuge tube with four successive 3 ml. portions of water, followed by two acetone washes, centrifugation after each wash being used. Next, the precipitate was placed in an oven and dried for fifty

2. It has been shown (9, p.4042) that the S^{35} in the potassium chloride is in the +6 oxidation state.

minutes at 130°C; then, still in the centrifuge tube, was dissolved in 1.22 millimoles of 96% sulfuric acid (approximately 0.6 ml.) and the entire tube was sealed in an exchange "reaction bomb" made from a 250 ml. distilling flask. The "reaction bomb" was evacuated on the vacuum line, then filled to a pressure of 20 mm. of mercury with sulfur dioxide (3.13 millimoles). The bomb was sealed and placed in a furnace where the temperature was kept at 310°C for eight days, a sufficient time to yield complete exchange. At the end of this time the labeled sulfur dioxide was ready for use.

Sulfur. Previous methods of preparing radioactive sulfur have required several hours' work and a considerable amount of chemical manipulation. The method developed herein is very simple, gives a good yield, and the sulfur may be made with a high specific activity. The material prepared for use in the ensuing experiments had a specific activity of over 200,000 counts per minute per milligram of sulfur (counted as barium sulfate).

The preparation was made by the gas phase interaction of hydrogen sulfide with the labeled sulfur dioxide whose preparation is described in the preceding section, the reaction proceeding, with a little added water, at room temperature, according to the equation



Although the reaction is not entirely clean-cut, various polythionic acids being formed in side reactions, a good yield was obtained; precautions were, of course, taken to purify the sulfur produced.

The bomb of radioactive sulfur dioxide was found to have a volume of 280 ml. This bomb had a break-off tip which was attached via a stopcock and ground glass joint to a secondary manifold, which was used in order to avoid contaminating the main vacuum system. The other half of the secondary manifold led through a ground joint and stopcock to a 130 ml. doser bulb. The secondary manifold was then attached via a stopcock and ground joint to the main vacuum line and the entire system evacuated to 10^{-5} mm. of mercury, after which the stopcock connecting the secondary manifold to the main line was closed, isolating the system containing the radioactive material. The break-off tip on the sulfur dioxide bomb was broken, allowing the radioactive sulfur dioxide to reach an equilibrium pressure with the doser bulb. As the bomb held initially 3.13 millimoles of active sulfur dioxide, at equilibrium approximately one millimole of sulfur dioxide was in the doser bulb.

When equilibrium was reached, the stopcock on the "reaction bomb" was closed, all of the sulfur dioxide in

the isolated secondary manifold frozen into the doser bulb with liquid nitrogen and the stopcock to the doser bulb closed. The original bomb, still containing approximately two millimoles of radioactive sulfur dioxide was removed and stored. A reaction chamber made of glass tubing to a volume of 25 ml. and containing 0.2 ml. of water, was now placed on the secondary manifold in the position the original bomb had previously occupied. After the water had been frozen by immersing the reaction chamber in a Dry Ice-acetone bath, the secondary manifold was again opened to the main vacuum line, evacuated and two millimoles of inactive hydrogen sulfide were dosed in. The secondary manifold was again closed, isolating the active material from the main vacuum line and the active sulfur dioxide was distilled over into the reaction chamber, using liquid nitrogen. This reaction vessel, now containing all the reactants, was finally sealed, removed to a hood and allowed to come to room temperature for the reaction to take place.

Reaction occurred essentially instantaneously at room temperature but to assure completeness, a half-hour's delay was allowed, after which the tube was cooled in a Dry Ice-acetone bath and broken open. It was allowed to come to room temperature in the hood and heated gently

to vaporize most of the water of reaction, then resealed and placed in an oven at 110°- 115°C for two hours. With this treatment most of the sulfur was found in the carbon disulfide-soluble, rhombic form. When cool, the reaction chamber was opened, the sides of the chamber washed down with a minimum of carbon disulfide, and the resulting solution heated, centrifuged, and pipetted into a fifteen ml. graduated centrifuge tube. The residue remaining in the reaction bomb was washed twice with approximately one-half ml. portions of hot carbon disulfide and the clear solution from the washings pipetted into the centrifuge tube. The solution was then evaporated in a water bath to a volume of approximately one-half ml. The warm carbon disulfide solution was then placed in an ice-salt bath for the slow crystallization of the radioactive sulfur. When most of the sulfur appeared to have crystallized, the tube was transferred into a Dry Ice bath to obtain more complete crystallization. Finally, the supernatant was pipetted off and the sulfur washed twice with approximately 0.06 ml. portions of cold carbon disulfide. The radioactive sulfur was allowed to dry for several days at room temperature. A yield of approximately 40 mg. was obtained (theoretical yield ca.96 mg.).

Hydrogen sulfide. Labeled hydrogen sulfide was prepared via the exchange found to occur with dissolved, labeled sulfur, addition of triethylamine being needed both to promote solubility and to catalyze the exchange rate (see the Experimental Results section). In a typical preparation ca. 0.5 mg. of active sulfur crystals, as prepared above, was placed in a thin-walled capillary tube and into this were dosed successively 0.02 millimoles of triethylamine and 0.1 millimoles of hydrogen sulfide, the reactants being frozen down with liquid nitrogen. After being sealed, the capillary was allowed to warm to room temperature which led to the formation of a clear solution. A minimum of two hours reaction time was always allowed, a check in one case having shown this sufficient to yield substantially complete exchange. At the end of this time the capillary was placed in a tube with a large stopcock, one tip of the capillary extending up into the open stopcock. Thus, when the system had been evacuated, the capillary was cracked open (the whole apparatus first having been cooled to Dry Ice temperature to inhibit spattering) by turning the stopcock and the labeled hydrogen sulfide distilled off. No particular effort was made to insure perfect fractionation from the triethylamine since the product was used only for activation

(the very high specific activity of the preparation permitted a considerable dilution) of hydrogen sulfide solutions to which the amine was also to be added, or alternatively for the synthesis of labeled arsenic trisulfide described in the section below.

Arsenic trisulfide. The arsenic trisulfide was prepared from labeled hydrogen sulfide, the product of a preparation such as that described in the foregoing section being transferred through a secondary manifold (to avoid contamination of the main vacuum system) and frozen into a reaction tube already containing excess frozen arsenic trichloride solution (0.1 M). This tube was then shut off and its contents allowed to thaw, whereupon the active hydrogen sulfide was absorbed and arsenic trisulfide precipitated out. The active precipitate was separated from the solution by centrifuging and was then washed, in the same centrifuge tube, with several successive portions, first of dilute hydrochloric acid, then water and last, acetone. It was finally dried in the oven at 110°C for one hour.

E. RUN PROCEDURE. All runs were performed in sealed bombs provided with break-off tips. The bomb filling procedure consisted of putting in the solid material (sulfur, arsenic trisulfide or phosphorus pentasulfide),

evacuating the bomb and dosing in the solvent (the bomb being in a Dry Ice-acetone or liquid nitrogen bath). The possibility that the relative order of addition of triethylamine (where used) and hydrogen sulfide may have an influence on the exchange rate is discussed in the Experimental Results section. Evidence on this point is conflicting. Finally the Dry Ice-acetone bath was replaced with liquid nitrogen, if necessary, and the bomb was sealed off. It was then carefully brought to room temperature (one or two bombs did explode) and shaken to homogenize the solution.

Dissolution was always complete to yield a clear solution in every case but one (the fourteen-minute arsenic trisulfide run, in which the attempted preliminary purification of the solute already referred to, apparently ineptly performed, had unfortunate consequences; the experimental results in this run, however, are consistent with the other arsenic trisulfide data). With sulfur, in the absence of triethylamine, solution, although eventually complete, was quite slow and was facilitated by a mechanical rocking of the bombs for the duration of the runs. At the end of a run, the bomb was cooled in a Dry Ice-acetone bath, sealed to the vacuum system, and opened by breaking its break-off tip with a magnetically

controlled, glass-enclosed, iron breaker. Separation was then effected by distilling off all volatile material into a liquid nitrogen trap, ample time being allowed for completing the process. A crystalline residue remained in every case, the nature of which is referred to hereafter. A blank experiment, following this procedure, and using labeled hydrogen sulfide and triethylamine, with no solute present, showed that no residual activity remained behind. In two of the phosphorus pentasulfide runs, the distillation was "assisted" by a final slight flaming of the residue in the reaction bomb.

All runs were done at room temperature. In the case of those lasting only a few minutes, the quoted duration represents the time from when the bomb was removed from the cold bath after filling to when it was again immersed in a cooling bath preparatory to being opened, and should probably not be taken too seriously.

After separation of reactants, part or all of the hydrogen sulfide was absorbed in copper nitrate solution. The resulting copper sulfide was dissolved in hot fuming nitric acid and from this solution, after appropriate treatment, barium sulfate was finally precipitated. The solid residue from each run was also taken up in hot

fuming nitric acid and eventually precipitated as barium sulfate, sulfate carrier sufficient to yield 100 mg. of precipitate being first added in those cases where only a small amount of solid reactant had been used; to wit, all the sulfur exchanges and the $3\frac{1}{2}$ hour arsenic trisulfide exchange.

All activity determinations were made from barium sulfate specimens mounted on planchets as already described, with the single exception of the 10-hour sulfur exchange where the sulfur was counted in elementary form evaporated onto a planchet from carbon disulfide solution.

Solubility tests. Some semi-quantitative solubility observations were made on the various solutions. Bomb tubes containing typically about one mg. of the solid under investigation together with various increasing amounts of the solvent were shaken or rocked for periods up to forty hours or more; the tubes were further allowed to stand without shaking for about 22 days before any particular trial was abandoned. A complete disappearance of the crystals was taken as the criterion for "solubility".

F. CALCULATIONS AND FORMULAS. The fraction exchange was computed with the following two formulas. The first

formula was used when the solid material was initially inactive and the hydrogen sulfide initially active.

$$F = \frac{\text{final specific activity of solid}}{\text{final specific activity of H}_2\text{S}} \quad (1)$$

The second formula was used when the solid material was initially active and the hydrogen sulfide initially inactive.

$$F = 1 - \frac{\text{final (specific) activity of solid}}{\text{initial (specific) activity of solid}} \quad (2)$$

The parentheses in Equation 2 imply that in this case, either specific activities or total activities may be used in computing F.

These formulas are approximately valid when the solvent millimoles are in large excess over the solute millimoles, which is the case for all the present experiments. For any finite number of millimoles of solute, however, the equations would not, of course, indicate unity for F, even though experimentally the exchange were actually complete. Hence, for the case of approximately 100% exchange, precise calculation would require more exact equations. This, however, represents a refinement which did not appear necessary in the present work.

Formula for standard deviation of a counting rate used in the $3\frac{1}{2}$ hour arsenic trisulfide experiment

$$\sigma = \sqrt{\frac{R}{t}} \quad (3)$$

Standard deviation of the difference of two rates (e.g. rate for sample plus background minus rate for background alone)

$$\sigma_{\text{diff.}} = \sqrt{\frac{R_e}{t_e} + \frac{R_b}{t_b}} \quad (4)$$

Where:

- R -- rate (average counts per minute)
- R_e -- average counts per minute for sample plus background
- R_b -- average counts per minute for the background
- t -- time in minutes
- t_e -- total counting time in minutes for sample plus background
- t_b -- total counting time in minutes for background.

Figures II and III present, for two sets of exchange experiments, plots of $\log(1-F)$ versus time. These graphs are based on the fact that exchange reactions are known to follow, in a given set of runs under constant conditions, a first order rate law (4, p.287). In such a case the rate is related to the fraction exchange by the following

equation which shows the slope of the straight lines of the Figures to be directly related to the rate of exchange.

$$R = - \frac{2.3(ab)}{(a+b)} \frac{d \log (1-F)}{dt} \quad (5)$$

R -- exchange rate in moles per unit time
F -- fraction exchange
a -- moles of solute present
b -- moles of solvent present

Alternatively, the rate can be described in terms of a "half-time", derived from the foregoing equation by conventional methods.

III. EXPERIMENTAL RESULTS

A. SOLUBILITY AND OTHER QUALITATIVE OBSERVATIONS.

Before undertaking the exchange experiments, we carried out a number of semi-quantitative solubility determinations (all at room temperature) which, together with a number of miscellaneous qualitative observations, are worth recording. Quam (13, p.105) has listed as soluble, along with sulfur, arsenic trisulfide, antimony trisulfide and phosphorus pentasulfide. However, our tests show the solubility of the substances other than sulfur to be extremely low. Addition of triethylamine, on the other hand, was found as has been reported at least for the case of arsenic trisulfide and as was suspected would be the case for all the substances, greatly to enhance the solubility of all four solutes.

Using one mg. samples of the solid material and distilling varying amounts of hydrogen sulfide into glass bombs which were sealed and allowed to come to room temperature, then placed upon a shaker and continuously agitated for various lengths of time, the results given below were obtained. In the solubility tests with added triethylamine, the base was added as previously described, usually in the ratio of one part amine to five parts by weight of hydrogen sulfide. Varying amounts of solid solutes were used.

Sulfur in liquid hydrogen sulfide. Tests were made with one mg. samples of sulfur which had been purified by being twice crystallized from carbon disulfide and dried first in air and then under high vacuum. The solubility was found to lie between 10 and 20 mg. of sulfur per 1000 mg. of liquid hydrogen sulfide.

Arsenic trisulfide in liquid hydrogen sulfide. The solubility of arsenic trisulfide was found to be less than 0.5 mg. per 1000 mg. solvent, perhaps as little as one-tenth or less of this figure. There was, however, a slight yellow color imparted to the solution; upon distilling off the hydrogen sulfide from the bomb, very definite rings were left on the sides of the glass, indicating some solution of the arsenic trisulfide. It should be pointed out that the arsenic trisulfide used in these tests, and also the antimony trisulfide used in the tests described in the following section, were "purified" by the procedure described in the experimental section which yielded questionable results; we feel, nevertheless, that the present observations have validity.

Antimony trisulfide in liquid hydrogen sulfide. We found the solubility of antimony trisulfide to be less than 0.7 mg. per 1000 mg. of solvent after twenty-two hours of continuous shaking. Upon distilling off the

hydrogen sulfide twenty-two days later (no agitation during this time) only faint rings were noted on the sides of the bomb, indicating, at the most, an extremely slight solubility. No coloration of the "solution" was to be observed.

Phosphorus pentasulfide in liquid hydrogen sulfide.

The solubility of phosphorus pentasulfide was found to be less than 0.5 mg. per 1000 mg. of solvent after thirty-two hours of continuous agitation at room temperature. Upon distilling off the hydrogen sulfide twenty-two days later only a few very faint rings were noted, indicating a possible slight solubility. No coloration appeared in the solvent.

Sulfur in liquid hydrogen sulfide, triethylamine

added. The sulfur was found to be soluble at least to the extent of ca. 200 mg. per 1000 mg. of hydrogen sulfide, containing 200 mg. of triethylamine. A clear solution was obtained within a few minutes of the time the bomb was taken from the cold bath.

The solution passed through several color changes worthy of note. Sulfur was placed in a bomb, the amine condensed in on top of the sulfur, then hydrogen sulfide condensed in upon the amine by means of a liquid nitrogen bath. Immediate reaction was noted between the amine

and the hydrogen sulfide producing a frozen white substance. The bomb was sealed off and subsequently brought to room temperature. As the mixture liquified the sulfur was observed to enter into the reaction and to color the solution. Some heat of reaction is liberated and the bomb was alternately dipped into a Dry Ice-acetone bath and shaken in air so that it would reach room temperature slowly. The white material first dissolved, then as the sulfur dissolved, the solution turned a yellow-orange. As more and more of the sulfur dissolved the orange color deepened and, as the bomb attained room temperature, the color darkened to a very deep red. When the solution was again placed in a Dry Ice-acetone bath, its color faded to a light orange, but the solution remained clear.

Further observations of the system were made by cooling the bomb to -78°C , breaking it open in air, and allowing the hydrogen sulfide to distill off. As the solution warmed and the hydrogen sulfide distilled away, the deep red color returned and a red crystalline material precipitated on the sides of the tube. The substance is apparently somewhat unstable at room temperature for, upon standing, the precipitate turned an orange color. The orange residue was then placed in an oven and heated to 90°C . As the temperature rose, once more the color

darkened until at 90°C only a deep blood red liquid remained. Upon raising the temperature still further to 110°C a portion of the liquid distilled off leaving only a slight yellow deposit. This deposit, however, did not appear to be pure sulfur. After cooling it gave a yellow-orange solution in carbon disulfide but was not completely soluble. Sulfur in carbon disulfide gives a colorless solution. It may also be noted that ammonium polysulfide, placed in the oven and treated in a like manner, gives a residue, presumably sulfur, soluble in carbon disulfide.

Melting points were taken of some of the original reaction residue and it was found to melt at 87°- 88°C. The color of the resulting melt was a deep red and upon cooling maintained a red plastic form to below 70°C after which the color slowly lightened but did not change completely back to the orange for some time after it reached room temperature.

The nature of this interesting crystalline material has not been further investigated at this time. It would be of value to study it further as occasion offers.

Arsenic trisulfide in liquid hydrogen sulfide, triethylamine added. The solubility in this case was shown to be at least 20 mg. (the maximum is probably much greater than this) of arsenic trisulfide in 1000 mg. of

hydrogen sulfide containing 200 mg. of triethylamine. At this ratio the arsenic trisulfide dissolved rapidly at room temperature -- within a few minutes after being removed from the Dry Ice-acetone bath. The solution was clear and pale yellow in color; it did not change color upon cooling to -78°C . When the hydrogen sulfide was distilled off in vacuo, a white residue first appeared, which then slowly seemed to decompose (at room temperature, still in vacuo) yielding a yellow residue. This yellow residue turned darker upon heating but did not give a homogeneous melting point. It was soluble in ammonium sulfide, but insoluble in water.

In the early solubility tests with the arsenic trisulfide purified by the method previously discussed, a white precipitate appeared after the arsenic trisulfide had dissolved. This white precipitate was not obtained with the radioactive arsenic trisulfide subsequently prepared nor was it found with solubility tests made later (upon which the above quoted solubility figure is based) using the unpurified arsenic trisulfide. This indicates the purification procedure to be of doubtful value. However, the use of the "purified" compound is shown later to have no effect upon the exchange reaction; it was, in any case, used in only one exchange run.

Antimony trisulfide in liquid hydrogen sulfide, triethylamine added. Although we did not do exchange experiments with antimony trisulfide, we did make some semi-qualitative observations on its solutions. A solubility test was made using 10 mg. of antimony trisulfide in 1000 mg. of hydrogen sulfide plus 200 mg. of triethylamine. The trisulfide dissolved completely to give a clear yellow-green solution, within about twelve minutes of the time the bomb was removed from the Dry Ice-acetone bath. When the hydrogen sulfide-amine mixture was distilled off (in air), the residue, left on the sides of the bomb, was red. "Unpurified" antimony trisulfide was used in this work.

Phosphorus pentasulfide in hydrogen sulfide, triethylamine added. A solubility check showed this material to be soluble at the very least to the extent of 12 mg. phosphorus pentasulfide per 1000 mg. of hydrogen sulfide, with 200 mg. triethylamine added. The phosphorus pentasulfide dissolved upon reaching room temperature to give a clear yellow solution which showed no color change upon recooling to -78°C nor did a precipitate form with recooling.

As a rough color check to determine possible sulfur contamination of the phosphorus pentasulfide, one mg. of

sulfur was dissolved in a mixture of 200 mg. of triethylamine and 1000 mg. of hydrogen sulfide. The yellow color of the resulting solution was much deeper than the color obtained with 10 mg. of phosphorus pentasulfide. If this latter color was due to sulfur contamination, the contamination was, then, less than one part in ten (ten percent). Judging roughly by a color comparison of the two solutions, we estimate that the contamination could not have exceeded one percent.

Summary of solubility observations. The foregoing observations may be summarized as follows:

Solubilities in pure liquid hydrogen sulfide at room temperature in mg. per 1000 mg. of solvent:

Sulfur: < 10-20 mg.

Arsenic trisulfide: < 0.5 mg.

Antimony trisulfide: < 0.7 mg.

Phosphorus pentasulfide: < 0.5 mg.

Solubilities in liquid hydrogen sulfide with triethylamine added in a weight ratio of five to one, in mg. per 1000 mg. of hydrogen sulfide:

Sulfur: > 200 mg; gives colors ranging from yellow to deep red depending upon temperature and concentration.

Arsenic trisulfide: >20 mg.; gives a pale yellow solution.

Antimony trisulfide: >10 mg.; gives a yellow-green solution.

Phosphorus pentasulfide: >12 mg.; gives a pale yellow solution.

B. EXCHANGE EXPERIMENTS. Exchange experiments were done with phosphorus pentasulfide, arsenic trisulfide and sulfur as solutes in liquid hydrogen sulfide, the first two with triethylamine added, the last both with and without added amine.

Sulfur and hydrogen sulfide. Two exchange experiments were done between sulfur and pure liquid hydrogen sulfide, the sulfur being labeled in both cases. There were a few deviations in these first experiments from the general procedure described in the Experimental Section. In the first experiment the sulfur residue in the bomb (after fractionation at the end of the run) was dissolved out by means of carbon disulfide rather than by being oxidized out with fuming nitric acid (the latter procedure was followed in the second of these experiments as well as in all subsequent work). In this first case the carbon disulfide solution was evaporated on a planchet, dried and counted as a thin layer of solid sulfur rather than

as barium sulfate. This was the only instance in all the exchange experiments where a count as barium sulfate was not made of a quantity to be used in computing percent exchange. It may be noted that this deviation from normal procedure leads to no difficulty since a highly accurate knowledge of the activity of the sulfur fraction is not necessary in order to compute a reasonably satisfactory percent exchange figure. The hydrogen sulfide fraction was carried to completion as described under "Run Procedure".

In the first experiment somewhat less than 0.3 mg. of labeled sulfur (visually estimated by comparison with a known weight of sulfur), containing a total of 5573 c./m., was dissolved in 100 mg. of hydrogen sulfide to give a clear solution. The run time was ten hours (at room temperature).

In the second experiment the deviation from the regular procedure included the radioactive sulfur's being initially dissolved in carbon disulfide (freshly distilled); five aliquot portions of this solution were taken, one of them being pipetted into the bomb tube and evaporated to dryness in vacuo. Thus ca. 0.3 mg. of sulfur was deposited in the bomb tube for use in the run.

As before 100 mg. of solvent was used; the run time was sixty hours and the two fractions obtained from the bomb tube carried to completion as described in "Run Procedure" by conversion to barium sulfate.

It may be mentioned, parenthetically, that in the case of the first run an effort was made to obtain an estimate of the total activity going into the experiment by counting directly, under the counter, the sulfur crystal which was to be used in the experiment. This procedure is, of course, because of excessive and unpredictable self-absorption, highly inaccurate. It was in an effort to improve the accuracy of this initial estimate that the carbon disulfide solution and five aliquot procedure described was used for the second run. The four aliquots other than the one used for the exchange itself were evaporated onto planchets, depositing thin films of sulfur, and were then counted. These presumably "duplicate" planchets gave counts ranging from 5500 to 8000 counts per minute. Thereupon the material on each of two of the planchets, after being washed out, was taken up in fuming nitric acid, a carrier added, and precipitated as barium sulfate. After being mounted and counted, these samples gave results that checked very well at a figure close to 8000 counts per minute, a value

somewhat higher than the average of the counts of the material as sulfur. This figure also checks moderately well the total sulfur activity recovered at the end of the run.

The results are given in Table I. It may easily be seen that exchange does occur but at a rather low rate. In Figure II (page 46) we give the results in the form of a plot of $\log (1-F)$ versus time. Since, as indicated under "Calculations and Formulas", an exchange reaction must follow a first order rate law, one expects to obtain a straight line plot on a graph such as this. It is evident that the points conform satisfactorily to this requirement. The half-time of the exchange, estimated from the graph, is about 123 hours.

It may be mentioned that we had hoped initially to be able to prepare labeled hydrogen sulfide by this exchange reaction. It is evident that, both because of low solubility and the slowness of the reaction, the method is not very attractive.

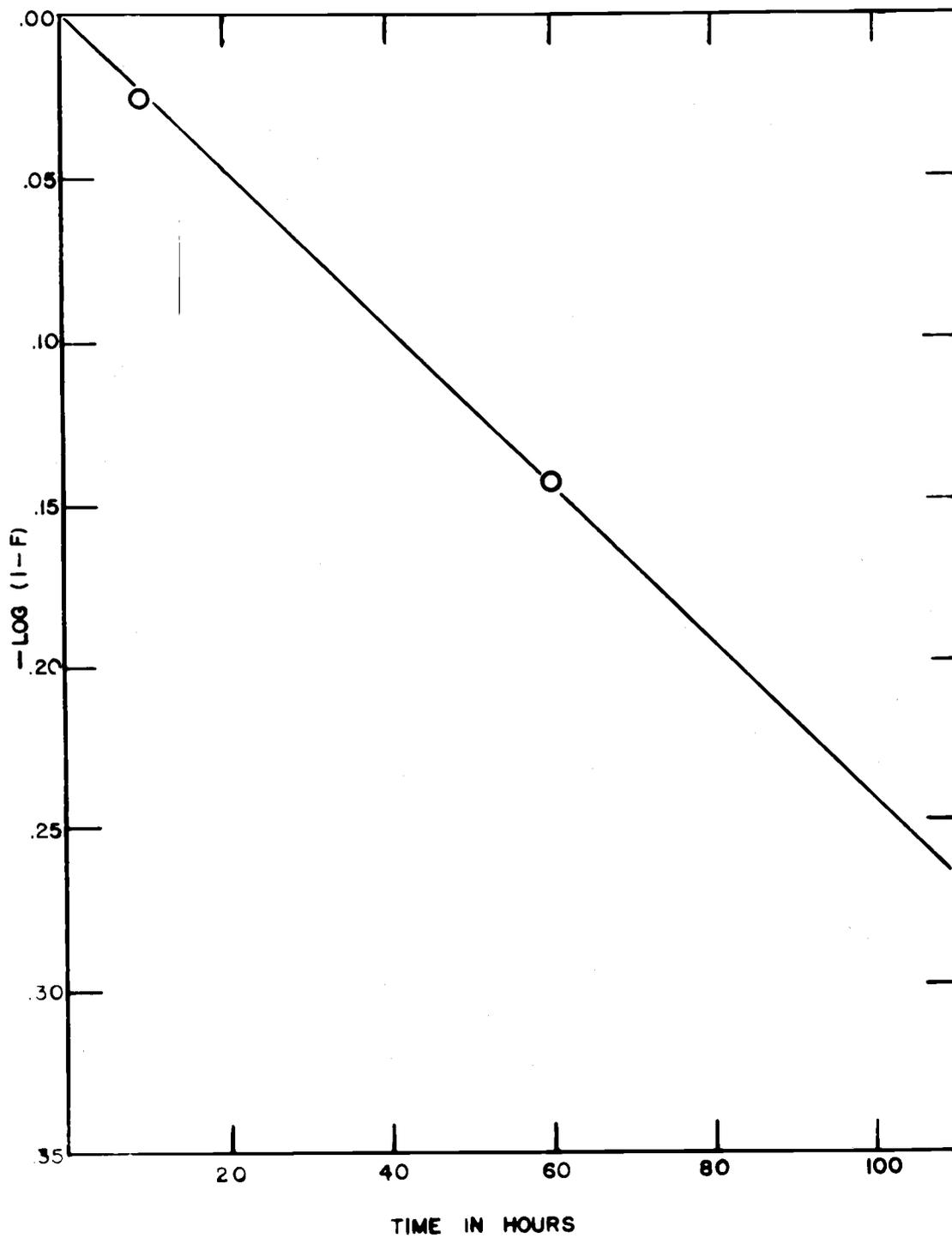
TABLE I

Exchange of Sulfur with Hydrogen Sulfide

<u>Run</u>	<u>Time in Hours</u>	<u>Fraction</u>	<u>Amounts^a (mg)</u>	<u>Spec. Activities^b (c./m./mg.)</u>	<u>Total Activities (c./m.)</u>	<u>Percent Exchange</u>
1	10	H ₂ S	100	0.50	343	6
		S	ca.0.3		5,230	
2	60	H ₂ S	100	3.88	2,710	28
		S	ca.0.3	(68.5) ^c	6,850	

- a. Amounts shown represent milligrams of solute or solvent used in a run.
- b. Specific activities are given in counts per minute per milligram of a fraction weighed (and counted) as barium sulfate.
- c. Specific activities shown in parenthesis in Tables 1, 2 and 3 represent values for a fraction to which a substantial excess amount of carrier, in every case enough to give a total of 100 mg. of barium sulfate precipitate, had been added. The figures do not, therefore, give any indication of the true specific activity of the fraction involved, but are used only in computing the total activity in a given fraction.

FIGURE II
SULFUR-HYDROGEN SULFIDE EXCHANGE



Sulfur and hydrogen sulfide, triethylamine added.

Jander's concept of the amphoterism of arsenic trisulfide in liquid hydrogen sulfide containing added triethylamine and also the tremendous increase in solubility of sulfur in hydrogen sulfide when amine was added encouraged us to attempt some exchange experiments with sulfur in such a solution. We may imagine that something of the nature of a polysulfide is formed in the solution and that its formation might be conducive to a more rapid exchange than in the case of sulfur in the pure "neutral" solvent. It was evident from the solubility tests that a somewhat unstable complex of some kind was formed.

Two experiments were performed, as in the previous case the sulfur being labeled both times. In the first experiment we used approximately 0.2 mg. of labeled sulfur and only half as much hydrogen sulfide as in the previous experiments. This was to obtain a higher specific activity in the solvent fraction even if the exchange rate was not enhanced by the amine addition. The quantities were, then: 0.2 mg. of labeled sulfur, 10 mg. of triethylamine, and 50 mg. of hydrogen sulfide, added in the sequence given.

The procedure for carrying out the experiment has been discussed; both fractions, the hydrogen sulfide and

the sulfur, were converted to barium sulfate for counting. The time (at room temperature) for the first exchange was twenty minutes. The second experiment repeated all procedure followed in the first except that the time at room temperature was two hours. For an illustration of the procedure used in computing the percent exchange, the calculations for the second experiment are given below.

Fifty mg. of hydrogen sulfide were used in the experiment which, converted to barium sulfate, gives a theoretical 343 mg. The measured specific activity of the barium sulfate was 90 c./m./mg. (corrected to zero thickness); therefore, the total activity in the hydrogen sulfide fraction was $90 \times 343 = 30,870$ c./m. Carrier was added to the sulfur fraction sufficient to give 100 mg. of barium sulfate and the specific activity of this barium sulfate was 18.4 c./m./mg. (zero thickness). The total activity in the sulfur fraction was, then: $100 \times 18.4 = 1840$ c./m. Thus the grand total activity originally in the sulfur or the total combined activity was finally: $30,870 + 1840 = 32,710$ c./m.

In this experiment the solid material was initially active; therefore, Formula No. 2 was used to calculate the fraction of exchange. The percent exchange is then

obtained by multiplying the fraction exchange by one hundred (100 F).

$$F = 1 - \frac{1840}{32,710} = \frac{30,870}{32,710} = 0.948$$

$$0.948 \times 100 = 94.8\% \text{ exchange.}$$

The results are shown in Table II (page 50). It is apparent that the exchange rate is indeed much faster with the amine added, which is in line with the concepts discussed above.

TABLE II

Exchange of Sulfur with Hydrogen Sulfide, Triethylamine Added

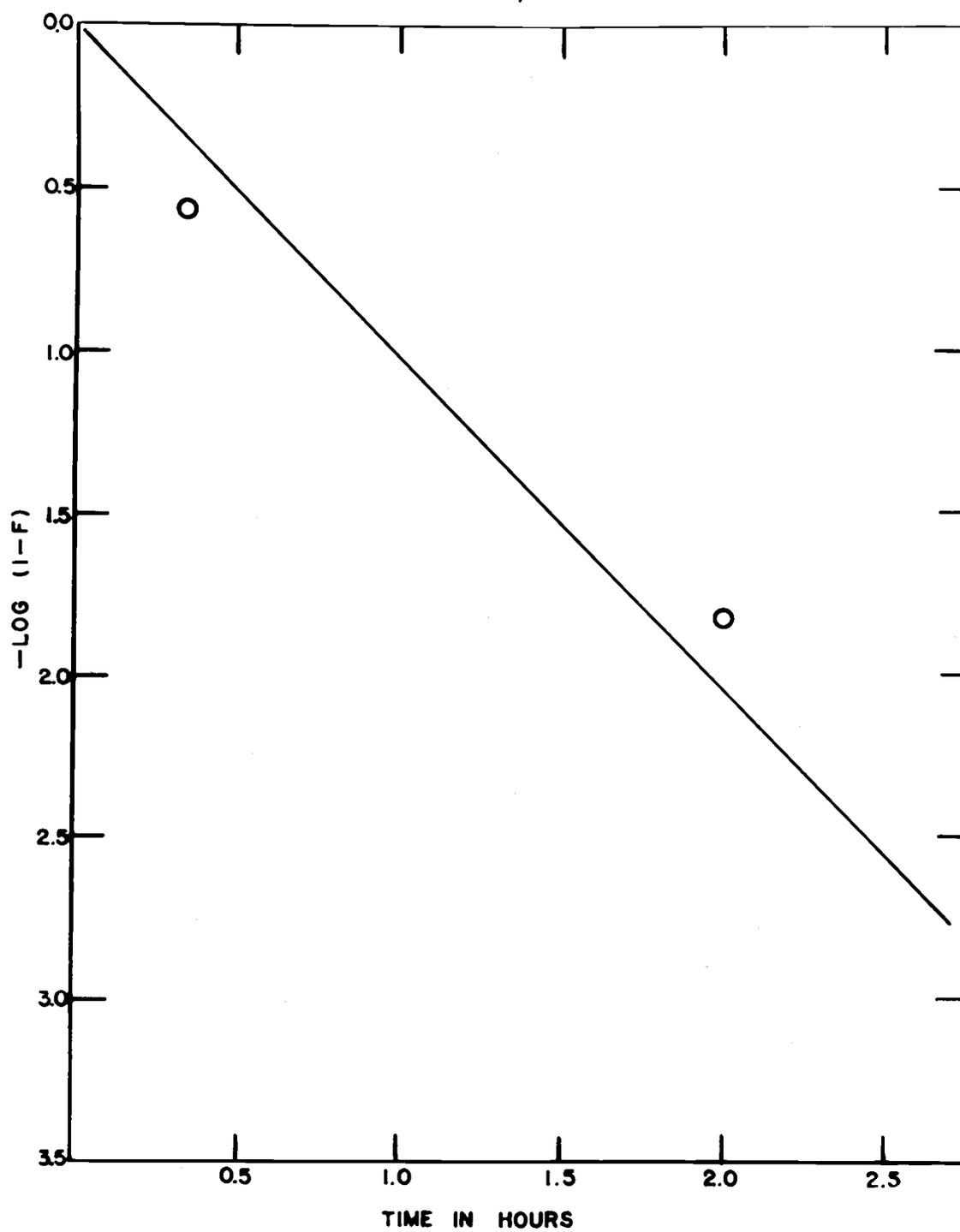
<u>Run</u>	<u>Time in Minutes</u>	<u>Fraction</u>	<u>Amounts^a (mg)</u>	<u>Spec. Activities^a (c./m./mg.)</u>	<u>Total Activities (c./m.)</u>	<u>Percent Exchange</u>
1	20	H ₂ S	50	23.7	8,100	72
		S	ca.0.2	(31.4) ^a	3,140	
		Et ₃ N	10			
2	120	H ₂ S	50	90.0	30,870	95
		S	ca.0.2	(18.4) ^a	1,840	

a. Table I footnotes apply also to Table II.

A log (1-F) versus time plot of the data is given in Figure III (page 52). The indicated half-time appears to be about thirty minutes, although the fit of the points leaves much to be desired.

The apparent lack of harmony between the two points on Figure III is probably not to be attributed to experimental inaccuracy in the quoted percent exchanges. These figures are probably good to about $\pm 3\%$ in the first case and $\pm 1\%$ (both absolute) in the second. Rather the discrepancy is more probably to be attributed to a sensitivity of exchange rate to triethylamine concentration. No great effort was made to duplicate this with precision in the two runs. Further, the amine was added to the sulfur before the hydrogen sulfide in these runs and we suspect that the resulting high base concentration prevailing prior to mixing of the solution may produce a poorly reproducible initial acceleration of the rate. Experiments described below add some weight to this hypothesis. The two experiments do indicate a fairly rapid exchange, which was all we had set out to ascertain; further fruitful investigation of the system would appear to require a more detailed study than appeared warranted in this preliminary work.

FIGURE III
SULFUR-HYDROGEN SULFIDE, TRIETHYLAMINE ADDED



In view of the foregoing it did not appear justified to do further experiments in order to obtain more points for Figure III.

A question may be raised in regard to these and the remaining experiments to be described in this research as to the significance of the fact that the residues remaining on evaporating off hydrogen sulfide were of uncertain composition. The answer is, of course, that irrespective of their composition, complete exchange is defined as that condition where the residue sulfur has the same specific activity as the sulfur in the volatile material. Incomplete exchange is indicated by any discrepancy between these quantities.

These results led to the method for preparing labeled hydrogen sulfide used throughout further exchange experiments. Using this technique, it is very simple to prepare the compound with an extremely high specific activity. The procedure is described in the Experimental Section.

Arsenic trisulfide and hydrogen sulfide, triethyl-amine added. Three experiments were done with arsenic trisulfide, the first two with the solute labeled, the last with the solvent labeled. In the first two runs the amine was added before the hydrogen sulfide; however,

the following phosphorus pentasulfide experiments appeared to indicate that the sequence of adding the amine and the hydrogen sulfide probably affected the speed of exchange so it was thought necessary to set up a further sequence of experiments. Three more runs were initiated using the method worked out in the phosphorus pentasulfide experiments, the significant feature of which is that it has the effect of adding most of the amine after the hydrogen sulfide; only one run was actually finished, however, as results in all cases showed a rapid exchange, despite the alteration in the third case of the sequence of the triethylamine-hydrogen sulfide addition.

For the first exchange the labeled arsenic trisulfide was prepared by the method previously outlined in the Experimental Section. Approximately 0.5 mg. (weighed) of radioactive sulfur was used as starting material and a yield of about 14 mg. (estimated) of $As_2S_3^*$ having a specific activity of 8080 c./m./mg. (as As_2S_3) was obtained. In this first exchange experiment 1.0 mg. (weighed) of the active arsenic trisulfide, 300 mg. of triethylamine, and 1054 mg. of hydrogen sulfide were used. The bomb was left at room temperature for three and one-half hours.

The fractionation process was carried out as usual, carrier sufficient to yield 100 mg. of barium sulfate upon precipitation being added to the arsenic trisulfide fraction (previously taken up in fuming nitric acid). The activity of this fraction when measured was too low to have quantitative significance, essentially 100% exchange being thus indicated. In order to obtain an estimate of how much less than 100% the true exchange might actually be, the standard deviation of the counting rate was computed and the highest reasonable activity so indicated for the arsenic trisulfide fraction was used in calculating the percent exchange.

In the second experiment it was decided to use enough arsenic trisulfide to make the barium sulfide precipitation carrier-free. The quantities used were: 14.0 mg. of As_2S_3^* , 933 mg. of H_2S , and 300 mg. of Et_3N . A new preparation of arsenic trisulfide was made this time using approximately 1.5 mg. of active sulfur and the arsenic trisulfide obtained had a specific activity of over 23,000 c./m./mg. as As_2S_3 , a yield roughly comparable in quantity with the previous case being obtained. The time at room temperature for the second experiment was eleven minutes and it also showed a complete, rapid exchange.

As previously mentioned, the phosphorus pentasulfide experiments appeared to indicate that the order of addition of the amine had an influence upon the time of exchange, so a third experiment was made. This time the hydrogen sulfide was added first followed by the addition of the amine. Ten mg. of arsenic trisulfide were used, only 200 mg. of amine, and 1000 mg. of hydrogen sulfide. In this case the arsenic trisulfide was initially inactive and the hydrogen sulfide active. The arsenic trisulfide used was the "purified" material described in the Experimental Section, which was found to dissolve and then lead to precipitation of a white substance. It is found here that the presence of this white precipitate in no way slows down the exchange, for with the bomb in this third experiment at room temperature for only fourteen minutes, complete exchange was observed. This finding also demonstrates, of course, for the arsenic trisulfide solutions, the irrelevance to the exchange rate of the sequence of triethylamine-hydrogen sulfide addition.

Thus complete and rapid exchange was observed in all three runs. The results are summarized in Table III. The figure of 114% shown for the third run represents an experimental error and has no real meaning other than indicating complete exchange.

These experiments appear to lend weight to Jander's concepts of amphoteric equilibria in this system as exemplified in Equations 2, 3, and 4 on page 7.

TABLE III

Exchange of Arsenic Trisulfide with Hydrogen Sulfide, Triethylamine Added

<u>Run</u>	<u>Time in Minutes</u>	<u>Fraction</u>	<u>Amounts^a (mg.)</u>	<u>Spec. Activities^a (c./m./mg.)</u>	<u>Total Activities (c./m.)</u>	<u>Percent Exchange</u>
1	210	H ₂ S	1054	1.7	12,500	100 ^b
		As ₂ S ₃	1.0		2.7 7.7 ^b	
		Et ₃ N	300			
2	11	H ₂ S	933	49.7	318,000	100
		As ₂ S ₃	14	32.8	1,300	
		Et ₃ N	300			
3	14	H ₂ S	1000	26.8	184,000	114
		As ₂ S ₃	10	30.6	870	
		Et ₃ N	200			

a. Table I footnotes apply also to Table III.

b. Standard deviation shown and used to calculate the indicated exchange percent.

Phosphorus pentasulfide and hydrogen sulfide, triethylamine added. Four exchange experiments were done with phosphorus pentasulfide. In these experiments radioactive hydrogen sulfide was prepared as previously discussed and diluted with inactive hydrogen sulfide to give approximately 1000 mg. of labeled solvent. This was homogeneously mixed, then used in the exchanges with inactive phosphorus pentasulfide.

In the first experiment 11 mg. of phosphorus pentasulfide was used, 835 mg. of labeled hydrogen sulfide and 200 mg. of triethylamine. In this experiment the amine was added before the hydrogen sulfide, as had been done in the preceding experiments. The solution was shaken for twenty minutes at room temperature and the run completed in the usual fashion. No carrier was added in the conversion of the phosphorus pentasulfide to barium sulfate. When the hydrogen sulfide-amine mixture was distilled from the phosphorus pentasulfide it was found necessary to flame the bomb gently to hasten the decomposition of the residual white complex. The complex formed with the phosphorus pentasulfide seemed a little more stable than those of the previous experiments and apparently required a higher temperature for its decomposition.

This experiment showed almost complete exchange, a result which, in view of the results of the next two experiments, we are inclined to attribute to the amine's being dosed in first. However, an experimental difficulty was unfortunately encountered in this first experiment which introduces an element of uncertainty in the interpretation of the result. In the course of filling the bomb the hydrogen sulfide pressure was accidentally permitted to become sufficiently great to blow one of the ground joints open momentarily. This ground joint was ordinarily held in place by the vacuum inside the system and further supported by rubber bands; the latter in this instance immediately pulled the joint back in place, once the excess pressure had been released. Thus, although, because of the constant existence of a positive pressure inside the apparatus, it is not probable, it is possible that some air may have entered the system when the joint blew open. Any moisture thus admitted could quite possibly have had a catalytic effect upon the exchange.

A second experiment was set up and it was decided to change the sequence of amine-hydrogen sulfide addition. This time the labeled hydrogen sulfide was added to the bomb before the amine. The time of reaction at room

temperature for the second experiment was sixteen minutes. The results indicated, surprisingly, only a 33% exchange. It did not seem probable that moisture could have entered the first experiment; we therefore concluded that the order of adding the amine must have influenced the rate of exchange. In all previous experiments the amine had been added first to the bomb containing the solid material and then the hydrogen sulfide condensed in on top of the amine. In this latest exchange the procedure was reversed -- condensing the hydrogen sulfide in upon the solid material and then adding the amine.

In view of the results of the first two runs, a new set of experiments was outlined. The third experiment was set up to repeat the second and a fourth experiment arranged to run for a longer period of time if the exchange turned out to be slow. A further modification was made in the mixing of the amine and hydrogen sulfide in these new experiments. The amine and hydrogen sulfide were distilled together into a separate bomb which was brought to room temperature allowing the amine and hydrogen sulfide to mix thoroughly. The bomb was then cooled down again and the amine-hydrogen sulfide mixture distilled over into the regular phosphorus pentasulfide bomb. When the amine-hydrogen sulfide mixture was

distilled across, it tended to leave a white residue behind. The bomb was heated slightly to hasten the decomposition of this white residue and finally no visible residue remained. It may be noted that because of the relative volatility of hydrogen sulfide and triethylamine this procedure had the effect of dosing in the amine last as had been done in the second run.

As a check on our general procedure to determine whether any activity remained in the absence of some solute, the glass of the bomb from which the hydrogen sulfide-triethylamine solution had just been distilled was crushed and carried through in a manner similar to that in which the fractions from an actual exchange were handled, finally being checked for activity. None at all was detectible.

The time of the third exchange was twelve minutes at room temperature. The result checked the second experiment quite closely, so another experiment was carried through.

The fourth experiment was done using the same hydrogen sulfide-triethylamine solvent that had been used for the third run. This was distilled off into the first trap of a long train and the third run bomb was sealed off from this train. Then, for the sake of purification,

the amine-hydrogen sulfide mixture was distilled from trap to trap along the train until it distilled across without the application of a flame and left no residue. A jar of tepid water was placed around the successive traps to hasten the distillation but this was merely a method of saving time. This mixture was finally distilled into the phosphorus pentasulfide bomb and the bomb sealed off in the usual manner. The time of reaction at room temperature was ten hours; there was no agitation. Essentially complete exchange was observed.

Table IV summarizes the results of the phosphorus pentasulfide exchanges; this indicates a rapid though measurably slow exchange -- slower than in the arsenic trisulfide runs. It appears likely that the order of addition of hydrogen sulfide and triethylamine influences the exchange rate, though this point is not definitely established.

The occurrence of this exchange presumably indicates the existence in liquid hydrogen sulfide of equilibria involving thiophosphate ions, conceivably some such equilibria as the following:

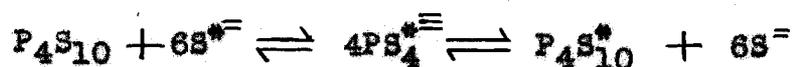
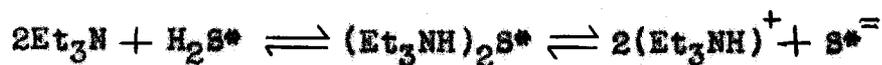


TABLE IV

Exchange of Phosphorus Pentasulfide with Hydrogen Sulfide, Triethylamine Added

<u>Run</u>	<u>Time in Minutes</u>	<u>Fraction</u>	<u>Amounts^a (mg.)</u>	<u>Spec. Activities^a (c./m./mg.)</u>	<u>Total Activities (c./m.)</u>	<u>Percent Exchange</u>
1	20	H ₂ S	835	12.4	70,680	86
		P ₄ S ₁₀	11	10.7	615	
		Et ₃ N	200			
2	16	H ₂ S	1000	30.0	206,000	33
		P ₄ S ₁₀	10	9.8	515	
		Et ₃ N	200			
3	12	H ₂ S	1000	37.3	253,000	30
		P ₄ S ₁₀	12	11.1	700	
		Et ₃ N	200			
4	600	H ₂ S	1000	37.3	253,000	97
		P ₄ S ₁₀	11.2	36.1	2,120	
		Et ₃ N	200			

a. Table I footnotes apply also to Table IV.

IV. SUMMARY AND CONCLUSIONS

The experiments performed in this thesis indicate, as other workers in the field have shown, the small likeness of liquid hydrogen sulfide to the common inorganic solvent water. Our tests indicate arsenic trisulfide, antimony trisulfide and phosphorus pentasulfide are relatively insoluble in pure liquid hydrogen sulfide. The only material tested that was soluble to any measurable extent was sulfur. It is evident, therefore, that exchanges with these inorganic substances, other than sulfur, are impractical without the addition of a base such as triethylamine. The tremendous increase in solubility with the addition of the amine makes all the above-mentioned substances excellent subjects for exchange reactions. A summary of the solubility tests is given on pages 40 and 41.

Concerning the exchange reactions, arsenic trisulfide exchanges immeasurably fast in a hydrogen sulfide-triethylamine solution, while the sulfur and phosphorus pentasulfide exchange at an easily-measurable rate. Sulfur, the only material used in an exchange made in pure hydrogen sulfide, exchanges slowly with a half-time of approximately 123 hours. The order of addition of the amine appears possibly to have a critical effect on the exchange rate in those experiments in which it

is used and in which the rate is measurable, i.e. the sulfur and the phosphorus pentasulfide experiments.

These experiments have been somewhat of an exploratory nature. They appear to indicate that, while the behavior of liquid hydrogen sulfide in its role as a non-aqueous ionizing solvent is not striking (cf. the low solubilities in the pure solvent), there do definitely appear to be rapid, reversible acid-base equilibria involving the solutes studied. Jander's (7, p.114-116) view of the solubility of arsenic trisulfide in hydrogen sulfide and triethylamine as being an exhibition of amphoterism, leading to the formation of a thiocarsenite, is probably correct. Furthermore, the rapid completeness of the exchange bespeaks the importance of some type of ionic equilibrium in the system, presumably involving a ready mobility of sulfide or hydrosulfide ion. In the case of phosphorus pentasulfide, one presumes that solution yields a thiophosphate and that exchange proceeds via such a species. The explanation of the fact that, in contrast to the arsenic trisulfide case, this exchange is not immeasurably rapid, can only be speculated upon at the present stage. Perhaps it is to be attributed to a less ready dissociability of thiophosphate than thiocarsenite, due to the greater acidity of

phosphorus pentasulfide than of arsenic trisulfide. Alternatively, the formation of some more complex thiophosphate ion, other than the simple, obvious orthothio-phosphate might tend to inhibit the exchange.

The behavior of sulfur is especially interesting. The slowness of the exchange in the pure solvent is perhaps to be attributed to a slow dissociation of S_8 molecules as the rate-determining step; Cooley & Yost (1, pp. 2474-2477) proposed such a situation as explanation for the slowness of the sulfur-sulfur monochloride exchange, which they observed. When triethylamine, however, is added, the sulfur presumably assumes the form of polysulfide ions, which then exchange much faster. It is curious, though, that in this case the exchange remains measurably slow.¹ It may or may not be significant that the rate of this exchange process seems to be roughly of the same order of magnitude as that of the phosphorus pentasulfide exchange.

It would be interesting to investigate in more detail some of the questions raised in this work, such, for example, as the effect of triethylamine concentration

¹ In this connection it might be mentioned that in the case of the aqueous system, although complete exchange among the sulfurs of polysulfide ion has been found (16, pp. 1032-1035) the actual rate of this exchange in a solution containing excess sulfide ion has not been investigated.

on the exchange rates particularly in the sulfur and phosphorus pentasulfide systems. Of especial interest might be a detailed study of the nature of the red crystalline material left on evaporation of the sulfur-triethylamine-hydrogen sulfide solution.

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