#### ISOTOPIC EXCHANGE REACTIONS OF HYDROGEN SULFIDE IN NONAQUEOUS SOLUTIONS

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A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

June 1961

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Date thesis is presented August 11, 1960

Typed by LeAnna Harris

#### ACKNOWLEDGEMENT

My sincere thanks to Professor T.H. Norris, whose time, energy and advice made this investigation possible.

Appreciation is also extended to my wife, Erin, whose patience and understanding have encouraged the author throughout the course of this work.

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#### ISOTOPIC EXCHANGE REACTIONS OF HYDROGEN SULFIDE IN NONAQUEOUS SOLUTIONS

#### I. INTRODUCTION

Over the years, a most fruitful field of research and investigation has been that of acid-base reactions. To the chemist of the late nineteenth century, the hydrogen and hydroxide ion acid-base concept, derived from the Arrhenius theory of electrolytic dissociation, may have appeared entirely comprehensive. This concept relates, however, specifically to acid-base behavior in aqueous solution, and with subsequent growing interest in the chemistry of, and the occurrence of acid-base processes in nonaqueous solvents, the need for more comprehensive acid-base concepts emerged. In the last fifty odd years, various further explanations of acid-base phenomena have been propounded. Among these, for example, is the socalled solvent systems interpretation, which includes the Arrhenius theory as a special case (4,p.1425-1428). The solvent systems theory has the advantage over other theories in that it is not restricted to aqueous solutions, nor to the presence of the particular entity, hydrogen ion. This theory directs attention to the cation and anion presumably formed by self-ionization of the particular solvent, and defines an acid as a solute which gives rise to an enhanced

concentration of the solvent's "characteristic" cation, and a base, one giving an enhanced concentration of the anion.

Clearly this theory should be useful in explaining a number of reactions occurring in solvents other than water, such as liquid ammonia, liquid sulfur dioxide, liquid hydrogen sulfide and a host of others. It appears, however, that, while it is often suggestive and helpful in providing a device to aid in systematizing information, the apparent interpretation of acid-base behavior offered is frequently more formal than true. A specific example is to be found in the widely accepted (7,p.510-513) interpretation of the nature of acid-base processes in liquid sulfur dioxide (due largely to the work of Jander and coworkers) in terms of this concept. This solvent was thought of as undergoing self-ionization to give small concentrations of thionyl and sulfite ions

$$2SO_2 \Longrightarrow SO^{++} + SO_3^{=}$$
 (1)

Thus, thionyl compounds and ionic sulfites would be, respectively, acids and bases in the solvent liquid sulfur dioxide. Specifically, they would undergo ionization processes such as

$$SOC1_2 \implies SO^{++} + 2C1^{--}$$
 (2)

$$(Me_{L}N)_{2}SO_{3} \rightleftharpoons 2Me_{L}N^{*} + SO_{3}^{*}$$
(3)

where thionyl chloride acts as an acid to increase the cation

concentration and tetramethylammonium sulfite acts as a base to increase the anion concentration.

Radioactive tracers have provided a novel means of testing these particular postulated solvent systems equilibria. If such dissociations do occur, the labeling of either solvent or solute (acid or base) with either radiosulfur or oxygen-18 should see a rapid exchange of these tracers between the solvent and either solute. That such an exchange does, in fact, not take place has been demonstrated, at least for thionyl halide solutes, by Johnson, Norris and Huston (10, p. 3052-3055) as well as by others (9,p.1039-1041 and 14,p.1489-1491). Thus, while research oriented largely in terms of the solvent systems theory has clearly served to create an extensive, organized body of knowledge relative to liquid sulfur dioxide solutions, it is equally clear that the detailed ionization predictions of the theory must not be taken literally. To be specific, the occurrence of the dissociation process shown in equation (2) is probably quite negligible, any significant ionic dissociation of thionyl chloride probably leading to the inherently more likely species SOC1 +.

The nature of acid-base processes in the solvent liquid hydrogen sulfide has also been interpreted (7,p.513-515) essentially in terms of the solvent systems theory (again due largely to Jander's work). In this contest, for example,

the occurrence of the phenomenon of amphoterism has been described. Thus, arsenic trisulfide dissolves in basic, triethylamine containing solutions (thought themselves to contain triethylammonium bisulfide, (EtaNH)(HS)) presumably to give thioarsenite ion in solution. Again for this type of process, the use of radiosulfur provides a means of testing the validity of the interpretations, since, if initially labeled arsenic trisulfide could be recovered from solution without any exchange with the solvent having occurred, one could certainly conclude that no thicarsenite had been formed. Mickelsen (12,p.42-61) has done a series of such radiosulfur experiments, and has shown that, with all four substances, arsenic and antimony tri- and pentasulfides, exchange is actually rapid and complete. Similarly, elementary sulfur, while not exchanging at all with "neutral" hydrogen sulfide, dissolves readily in basic solutions to give complete and rapid exchange, polysulfide formation clearly being suggested. Thus here, unlike the situation with sulfur dioxide, the radiosulfur exchange results appear to be at least consistent with an acid-base interpretation related to the solvent systems picture.

Continuing his work, Mickelsen studied the exchange between carbon disulfide and the solvent liquid hydrogen sulfide, with and without the addition of triethylamine. Without triethylamine, he found no exchange to occur, any possible

formation of thiocarbonic acid thus being shown also not to occur. When triethylamine was added, however, exchange did occur, the rates, now measurable, being dependent both on carbon disulfide and on triethylamine concentration. The occurrence of exchange in these triethylamine containing solutions, as well as the appearance of color (yellow to red depending on triethylamine or carbon disulfide concentration) clearly suggested the formation of some type of thiocarbonate in solution resulting from a reaction between the three materials, carbon disulfide, hydrogen sulfide, and triethylamine.

Mickelsen attempted to interpret his kinetics observations for this exchange reaction in terms of the chemical composition of the thiocarbonate species (one or more) formed in solution. Unfortunately it was found that at least three models would explain the results about equally well. Thus he first envisioned the formation of the acid thiocarbonate, (Et<sub>3</sub>NH)(HCS<sub>3</sub>), which, with increasing triethylamine concentrations, was assumed to react further with the amine to form a progressively increasing proportion of the normal thiocarbonate, thus

$$Et_{3N} + H_{2}S + CS_{2} \Longrightarrow (Et_{3}NH)(HCS_{3})$$
(4)

$$(Et_3NH)(HCS_3) + Et_3N \rightleftharpoons (Et_3NH)_2CS_3$$
 (5)

The rate of the exchange was assumed to be given by the rate

of dissociation of the acid thiocarbonate, any normal thiocarbonate having a negligibly slow exchange rate, thus

Rate = 
$$k_1[(Et_3NH)(HCS_3)]$$
 (6)

An appropriate choice of  $K_1$  and  $K_2$ , the equilibrium constants associated with equations (4) and (5), served to make this interpretation fit the data.

Mickelsen's second exchange model was similar to the first, except that it assumed the normal thiocarbonate also to undergo exchange via dissociation (evidently not specifically the reversal of equation (5)) but at a rate somewhat slower than that for the acid thiocarbonate, the rate law thus becoming

Rate = 
$$k_1[(Et_3NH)(HCS_3)] + k_2[(Et_3NH)_2CS_3]$$
 (7)

With an appropriate readjustment of the values of  $K_1$  and  $K_2$  this interpretation also gave a reasonably adequate fit to the experimental data.

Finally, a third model was proposed in which two carbon disulfides were incorporated into the thiocarbonate species, the proposed stoichiometry being

$$Et_{3}N + H_{2}S + 2CS_{2} \rightleftharpoons (Et_{3}NH)(HC_{2}S_{5})$$
(8)

Here the equilibrium was assumed to lie well to the right and

once again the rate was taken to depend on the rate of dissociation of the thiocarbonate, giving the rate law

$$Rate = k \left[ (Et_3NH) (HC_2S_5) \right]$$
(9)

In the case of this model, too, a reasonable fit to the data was obtained.

Since in Mickelsen's research hydrogen sulfide was the solvent, there was no possibility of observing the kinetic effect of a variation of its concentration. Furthermore, its presence in high concentration would have, of course, a significant tendency to drive such an equilibrium as that of equation (8) essentially completely to the right, so that the concentration of thiocarbonate and hence the exchange rate would, as was observed apparently to be the case, depend simply on the concentration of triethylamine or carbon disulfide, whichever was limiting. Assuming this third model correct, for example, it might be expected that, if one were able to study the exchange at significantly lower hydrogen sulfide concentrations, one might hope that equilibrium (8) would be shifted sufficiently to the left so that the complex concentration, and hence the exchange rate would approach a second power dependence on carbon disulfide concentration, as called for by the stoichiometry of equation (8). Thus, conceivably, by such experiments it might be possible to find a basis for

choice, as Mickelsen from his data was unable to do, between the three alternative exchange models.

With this end in view, it seemed of interest to see whether the radiosulfur exchange between hydrogen sulfide and carbon disulfide in the presence of triethylamine would go at a measurable rate in some exchange-inert, nonaqueous solvent, and, if such were the case, to make a study of the kinetics of the process. The present research is concerned with such an investigation in the solvent benzene. Using sulfur-35 as a radioactive tracer, exchange rates have been measured as a function of the three reactant concentrations, making possible the derivation of a reasonable rate law and mechanism for the process and a comparison of the results with those of Mickelsen.

#### II. EXPERIMENTAL

#### A. COUNTING PROCEDURES

The isotope used in all of this work was sulfur-35, with a half-life of 87.1 days. The decay occurs by emission of a 0.168 Mev beta particle. The counting procedures employed were those described by Norris (11,p.1220-1223). An end window counter (Radiation Counter Laboratories Model 10100 with a 1.0 milligram per square centimeter mica window) was used with a Berkeley Model 1000 B scaler. The necessary corrections for background, and self-absorption were applied to all measurements, the latter from an empirically determined curve. None of the counted samples were of sufficient activity to require coincidence loss corrections. Decay corrections were applied as necessary, but, except in the case of Experiment A (Table I), all the samples taken in any particular run were counted within a twelve hour period of each other, thus eliminating the need for decay corrections within any such set of figures. The total number of counts taken on each sample were, except for the very lowest activities, always such as to correspond to a statistical counting error (standard deviation) of less than about 5%, a figure roughly within the overall accuracy of the radioassay procedure.

The radiosulfur from both the hydrogen sulfide and the carbon disulfide was counted as barium sulfate, isolated by

precipitation from a dilute hydrochloric acid solution. Analytical techniques were employed in the preparation of the barium sulfate, namely, precipitation, digestion on a steam bath, filtration on a sintered glass filter, washing with acid, and finally washing with water. After drying, a portion of the solid material was slurried with 95% ethyl alcohol in weighed, nickel plated planchets and allowed to dry under an infrared heat lamp. Thus a thin film of barium sulfate was left on the planchet. The amount deposited on the planchet ranged from 20 to 80 milligrams. All specific activities, for ether the carbon disulfide or the hydrogen sulfide fraction, were computed in terms of counts per minute per milligram of barium sulfate and are so recorded in all subsequent tables in this thesis.

In all cases, activity was sought in the component which was initially inactive, 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. The activity at infinite exchange was calculated from a knowledge of the total gram atoms per liter of sulfur present in each fraction in any one run, and the initial specific activity (corrected to the time of the run samples) of the carbon disulfide used to prepare the reaction mixture. Frequently, 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. Sample calculations will be given to clarify these points as they arise. In a considerable number of the experiments, the specific activities of the carbon disulfide fractions were also determined along with those of the hydrogen sulfide fractions, for each of the successive samples, an alternative method for calculating fraction exchange values and hence exchange rates thus being provided. This method was in general far less precise than that actually used, involving as it did the determination by subtraction of a small difference between two relatively large numbers (i.e. the decrease in the carbon disulfide specific activity). Nevertheless, the data so obtained furnished in general a reasonably satisfactory check on the exchange rates obtained from the hydrogen sulfide activities.

B. PREPARATION OF MATERIALS

1. <u>Hydrogen sulfide</u> used for these experiments was obtained from a commercial cylinder (Ohio Chemical and Surgical Equipment Company, purity 99.0%). The gas was purified by the method of Bickford and Wilkinson (2,p.111-112). First the gas was bubbled through sintered glass bubblers immersed in two successive saturated solutions of barium hydroxide. The barium hydroxide solutions were contained in 500 milliliter

Erlenmeyer flasks, which were surrounded with an ice-salt mixture to reduce the vapor pressure of the water. Next, the train ran through two consecutive drying tubes, the first containing phosphorus pentoxide, and the second, calcium chloride. From the latter drying tube, the train led finally to another sintered glass bubbling tube which was immersed in purified benzene. Hydrogen sulfide was allowed to flow through the system for several minutes before the sintered glass bubbler was actually inserted in the benzene. The rate of flow of the hydrogen sulfide was made slow to insure maximum mixing and solution of the gas. The benzene solution thus obtained was used in preparing the reaction mixtures.

2. <u>Benzene</u> (Baker and Adamson, "thiophene free," reagent grade) was twice distilled from calcium chloride, the middle fraction boiling at  $80^{\circ}$ C ( $\pm$  0.5°) being retained in each case, and generous first and third fractions being discarded (roughly 25% and 15%, respectively, both times). This purification method was used rather than the more common one of extraction with sulfuric acid in order to minimize the possibility of any sulfur containing material remaining in the product. To check the purity of the benzene, samples were analyzed with a Perkin-Elmer vapor fractometer, and a Bausch and Lomb refractometer. Figure I shows a recording of the vapor fractometer analysis of the purified benzene.



The small peaks located at about three minutes on the base line of the strip chart (time following sample injection) were not identified, but in any case wore not the sulfur containing material thiophene, which might conceivably have constituted a problem relative to the radiosulfur exchange experiments which were to be carried out in this solvent. This is clearly shown in Figure 2, which presents a recording of a comparable vapor fractometer analysis of thiophene itself. As may be seen, the thiophene peak occurs at about eleven minutes, well beyond the small three minute peaks in Figure 1 and even beyond the benzene peak.

The refractive index of the benzene was measured at 20°C and was found to be 1.5006. The value listed in the International Critical Tables for pure benzene is 1.5014 (17,p.198,277).

3. <u>Carbon disulfide</u> (Baker and Adamson, reagent grade) was twice distilled from phosphorus pentoxide. After addition of the carbon disulfide to the phosphorus pentoxide, the mixture was allowed to stand each time for approximately one hour to allow the drying agent to remove any water present. The middle fraction, boiling at  $46^{\circ}$ C ( $\pm$  0.5°) was retained in each case, substantial first and third fractions being discarded (roughly 35% and 20% each time).

4. Triethylamine (Eastman White Label, reagent grade)



was allowed to stand over sodium for approximately an hour, to remove any primary and secondary amines that might be present. The triethylamine was then distilled from the sodium, only about the middle one-third being retained. This distillate was then subjected to a second distillation, again only the middle one-third of the second distillation being retained for the experiments.

5. Labeled carbon disulfide was prepared using a modification of the method of Edwards, Nesbett, and Solomon (6,p.1670). Typically, a twenty-five milliliter aqueous solution of 0.5 molar sodium sulfide solution was prepared. To this solution was added 0.5 ml of a radioactive barium sulfide solution of high specific activity (low concentration barium sulfide in 0.03 N sodium hydroxide). The latter solution was itself prepared by dilution of a higher specific activity barium sulfide preparation obtained from the Oak Ridge National Laboratory. Then, twenty-five milliliters of purified carbon disulfide were mixed with the active aqueous solution. Although some of the carbon disulfide dissolved in the aqueous sodium sulfide to form the red thiocarbonate, most of the carbon disulfide remained as a separate phase in the bottom of the glass stoppered Erlenmeyer flask. This solution was then agitated for twenty-four hours at room temperature, during which time the carbon disulfide was

rendered radioactive by exchange. Separation of the carbon disulfide and sodium sulfide was effected by means of separatory funnels, the carbon disulfide being washed four times with about equal volumes of 0.100 N aqueous sodium hydroxide to remove any sulfide. The product was finally distilled from phosphorus pentoxide (after about twenty minutes contact), the middle fraction, boiling very close to  $46^{\circ}$ C being retained, and initial and final fractions amounting each to roughly one-tenth of the total preparation being discarded.

#### III. RUN PROCEDURE AND CALCULATION METHODS

A. GENERAL

As indicated in Section I, this research consisted of a series of measurements of the rate of radiosulfur exchange between hydrogen sulfide and carbon disulfide in the presence of triethylamine, all three compounds being dissolved together in benzene solution. Experiments were run at various concentrations of the three reactants, one experiment also being done with no triethylamine present. For each experiment, about 100-150 ml (except in Experiment A where a larger volume was used) of reactant solution was prepared in a glass stoppered Erlenmeyer flask. This flask was then placed in a thermostat and samples were periodically withdrawn for analysis as the run proceeded, about four successive samples normally being taken. Separation of the exchange reactants was effected by extraction of the hydrogen sulfide from the benzene solution by aqueous sodium hydroxide, the carbon disulfide remaining in the benzene. 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 "carbon disulfide" which are subsequently presented in this thesis.

All the experiments in this research were done at

 $10.0 \pm 0.1^{\circ}$ C. Temperatures were maintained within the indicated range by the use of a large, well stirred, refrigerated thermostat, containing a 50-50 mixture of a commercial ethylene glycol antifreeze and water.

Since the purified hydrogen sulfide had been prepared as a solution in benzene, and since this "stock" solution was to be used in making up reaction mixtures of known reactant concentrations, it was necessary to determine the hydrogen sulfide concentration in the solution. This was accomplished by iodometric titration. Typically, a one milliliter aliquot of the stock hydrogen sulfide solution (in benzene) was pipetted into one hundred milliliters of a slightly acid (HCl) water solution containing an 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 "Acculate" concentrates, a) the thiosulfate being checked for normality by titration against potassium iodate, using standard methods. Despite the heterogeneous character of the titration, its reliability was attested both by the reproducibility of

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

the results obtained and by the fact that infinite time specific activities (see below), calculated on the basis of the hydrogen sulfide concentrations obtained using the method, checked satisfactorily with those observed experimentally. Since each time the stock hydrogen sulfide solution bottle was opened, some of the gas would escape, its concentration gradually decreased slightly with time. Therefore the above described analysis was carried out twice immediately prior to each run, once before and once after the taking of the sample used to prepare the mactant solution. The average of the two concentration figures so obtained (the second figure being typically  $\approx 0.4\%$  lower than the first) was then used in making concentration calculations in connection with that particular experiment.

Except for Experiments 15-18, which involved low hydrogen sulfide concentrations, 100 ml of the hydrogen sulfide stock solution was taken to prepare each reaction solution. Thus the hydrogen sulfide concentration, as above determined by analysis, itself determined the total volume that the solution must have in order to yield a desired hydrogen sulfide concentration. The necessary additional volume was made up by adding diluant purified benzene, carbon disulfide and triethylamine, in relative proportions determined by the concentrations desired for the two latter reactants. The hydrogen

sulfide solution was measured out with a 100 ml pipette; the other two reactants. (pure liquids) and the diluant benzene were in general measured out with graduated pipettes. For the extremely low triethylamine concentrations of approximately 4 X 10-4 molar, aliquots were taken from triethylamine solutions in benzene (prepared by dissolving known volumes of triethylamine and diluting to volume in a volumetric flask). In preparing these solutions, all volumes were assumed additive, no corrections for any volume change on mixing being applied. Furthermore, all the reagents were stored in the constant temperature bath at 10.0°C; hence, in calculating reactant concentrations, no corrections for change in volume with temperature were necessary. This latter fact was further, of course, of primary importance in providing that the reaction mixtures, as prepared, were very close to the reaction temperature.

To prepare a typical reaction mixture, the desired volume of the hydrogen sulfide stock solution was added to a glass stoppered Erlenmeyer flask. Next the necessary amount of diluant benzene was added, followed by labeled carbon disulfide and finally triethylamine. The pipettes used for the latter purposes were fitted with cork stoppers so as to close the opening of the reaction flask during the time needed for the pipettes to drain, this precaution serving to minimize

the loss of hydrogen sulfide from the reaction solution. In this connection it is further to be noted that the size flask used in each experiment was such as to minimize the gas volume over the solutions, a 125 ml flask being used wherever feasible, (see the recorded volumes in Table II), 250 ml flasks being used otherwise (except for Experiment A where a 500 ml flask was needed). After the last reactant had been added, the resulting solution was agitated to insure homogeneity. As already indicated, the reactants were maintained at 10.0° before mixing; the mixing of the reactants to form the solution was, furthermore, carried out with the receiving flask already in the thermostat. Zero time for most of the runs was taken as the time when the last of the triethylamine (the last reactant added) had just drained into the flask. In the shorter time runs, Numbers 13, 15, and 16, done towards the end of the research, it was felt wiser to take zero time as the time of half emptying of the triethylamine pipette. In this context, however, it is to be noted that the exact establishment of the zero time is not particularly important, since the exchange rates were calculated from the rates of increase of apparent fraction exchange (specifically, from the slopes of log(1-F) plots versus time--see below) rather - 21 than from their instantaneous absolute values.

The periodic samples taken to follow the progress of the exchange were obtained by means of a pipette, which again was fitted with a cork stopper to minimize loss of hydrogen sulfide from the reaction solutions. The required amount having been obtained (ten or twenty milliliters, depending on hydrogen sulfide concentration -- or carbon disulfide concentration, where this might be limiting), the pipette was quickly and forcibly emptied (using a rubber pipette bulb) into ten milliliters of 0.1000 N aqueous sodium hydroxide in a separatory funnel. The resulting mixture was then instantly shaken to extract the hydrogen sulfide, the carbon disulfide remaining in the benzene. The sampling time was taken as the time of emptying of the pipette into the base, extraction of the hydrogen sulfide evidently quenching the reaction. After separation of the two layers, the benzene solution was extracted twice more with ten milliliter portions of 0.1000 N base. The combined aqueous extracts were then treated with approximately ten milliliters of 30% hydrogen peroxide (Mallinckrodt, reagent grade) to oxidize the sulfide to sulfate. After evolution of bubbles stopped, the solution was boiled to remove any excess peroxide and to destroy any possible persulfate that might have been formed. The solution was then acidified with hydrochloric acid (to a pH of two as measured with indicator paper) and precipitation of the sulfate

was accomplished with saturated barium chloride solution.

The benzene solution remaining from the extraction, and containing the carbon disulfide, was treated with ten milliliters of alcoholic potassium hydroxide (10% KOH by weight), to form the potassium ethyl xanthate, which was then extracted with about an equal volume of water. After separation of the two layers, the treatment of the benzene phase with alcoholic potassium hydroxide and the water extraction was repeated twice more. Finally the combined aqueous extracts from this procedure were also treated with 30% hydrogen peroxide to oxidize the xanthate to sulfate. The resulting solution was then handled in exactly the same manner as described for the hydrogen sulfide fraction.

The efficiency of the above procedure for the separation of the exchange reactants was checked in a number of ways. In this connection it is to be noted that the progress of the exchange was followed by measuring the specific activity of the barium sulfate derived from the aqueous base extract fraction, i.e. the "hydrogen sulfide" fraction. Thus while completely quantitative recovery of the hydrogen sulfide was not essential (since specific activity rather than total activity was measured), it was desirable that a minimum amount of the carbon disulfide be extracted along with the hydrogen sulfide. A first test of this matter is to be found in the results of some actual exchange experiments involving labeled

carbon disulfide. Early in this research, an experiment was initiated to verify the previously reported absence of radiosulfur exchange (5,p.3237-3238) between hydrogen sulfide and carbon disulfide in benzene (no triethylamine). The results (Experiment A, Table I) did, in fact, verify the earlier report, and, in so doing, provided a test of the separation procedure. Thus, as may be seen in Table I, successive samples, taken over a long period of time, showed apparent percentage exchange values initially of 2.4 ± 0.9% and, after 1320 hours, of 0.71 ± 1.1%, the indicated errors representing the standard deviations of the counting data actually taken. Clearly no progressing exchange had occurred, the specific activities of the last two samples in the experiment being statistically indistinguishable from zero. The fact that the first two apparent percentage exchanges were a bit high is almost certainly to be ascribed to the fact that they were derived from separations carried out early in the research, before complete facility with the separation technique had been developed. The last two samples, taken at the same general time as most of the rest of the experiments were being done. are unquestionably more representative, and as such, demonstrate the almost complete absence of tendency for the carbon disulfide to appear in the hydrogen sulfide fraction. It may be noted that the maximum estimated apparent percentage

exchanges in Table I for the first and last fractions (i.e. 3.3% and 1.8%) would correspond, respectively, to 1.3% and 0.7% extraction of the original carbon disulfide into the aqueous layer.

An additional test was made along exactly the same lines as the above, but with higher specific activity carbon disulfide and with a much higher ratio of carbon disulfide to hydrogen sulfide concentration (0.3 M and 0.01 M instead of 0.0332 M and 0.0445 M as in Table I). These changes served to provide a far more critical test than before. Two samples taken from this solution were subjected to the standard separation procedure and once again the apparent specific activities of the hydrogen sulfide fractions were indistinguishable from zero, the specific activities observed this time actually being both less than background. On the basis of the standard deviations of these apparent zero specific activities, one may compute that less than 0.003% of the carbon disulfide had been extracted. Clearly the separation is a "clean" one.

As a second check on this matter, two inactive solutions containing known amounts of carbon disulfide in benzene were prepared, no hydrogen sulfide or triethylamine being present. These solutions were each extracted three times with ten milliliter portions of 0.100 N aqueous sodium hydroxide, just as in the separation procedure. The aqueous extracts were then

analyzed for carbon disulfide by the method of Bang and Szybalski (1,p.926-929), which consists of forming the potassium ethyl xanthate, with subsequent titration of this material with iodine solution. Thus to each of the two basic extracts (thirty milliliters each) ten milliliters of alcoholic potassium hydroxide were added to form the xanthate. The solution was allowed to stand for five minutes in the dark to insure completeness of reaction. Acetic acid was next added until phenolphthalein was colorless in the solution, this being followed by one gram of sodium carbonate to make the solution slightly basic. The resulting solution was diluted to approximately 100 milliliters and was finally titrated with 0.1000 N iodine solution. Comparison with the amount of carbon disulfide originally present in the benzene made possible a calculation of the percentage which had been extracted into the basic aqueous layer (and hence would have turned up in the hydrogen sulfide fraction, in a conventional separation). The percentages so found for the two cases amounted, respectively. to 1.5% and 1.0%, amounts clearly small enough to be of no consequence in this work.

The foregoing tests clearly demonstrate the fact that, at least in the absence of tricthylamine, carbon disulfide has no significant tendency to appear in the hydrogen sulfide fraction. What, however, if tricthylamine is present? In

this connection, it is to be remembered that the interpretation of these exchange experiments involves the assumption of the formation of thiocarbonate species in the benzene solution (see "Introduction" and "Results"). The question naturally arises, therefore, as to what effect the tying up of some or all of the carbon disulfide and of the hydrogen sulfide in such form might have on the success of the separation. Observations regarding the colors of the solutions would appear to have a certain bearing on this point. In the first place, it may be noted that a solution of hydrogen sulfide and carbon disulfide together in benzene is completely colorless. When triethylamine is added, however, a pale yellow to orange solution is obtained, depending on concentration, clearly suggesting the possible presence of thiocarbonate in the solution (13,p.2326-2332; 15,p.1812-1813; and 19,p.38). When, as in this work, this solution was extracted with base in the separation procedure, the color disappeared from the benzene layer (almost all in the first extraction), seemingly being transferred to the aqueous layer.

This last observation suggested that any thiocarbonate initially in the benzene was being extracted into the water. If such were the case, it could, naturally, seriously interfere with the success of the separation procedure and might result, for solutions where triethylamine was present, in the

transfer of an appreciable amount of the material originally present as carbon disulfide into the so-called hydrogen sulfide fraction. Thus it was particularly important to test the efficiency of the separation procedure for triethylamine containing solutions.

As an effort in this direction, experiments were done with inactive solutions which simulated in a general way the reaction solutions. Two benzene solutions were prepared in which the amounts of hydrogen sulfide, carbon disulfide, and triethylamine were accurately known. These solutions were each subjected to the separation procedure exactly as outlined above. and the yields of barium sulfate for both fractions determined by weighing. The recoveries obtained in the two cases were respectively: (1) H2S fraction, 81%; CS2 fraction, 85%; (2) H2S fraction, 99%; CS2 fraction 86%. It may further be noted that the benzene solution remaining after the base extraction had no odor of hydrogen sulfide. These figures do, of course, suggest a certain amount of loss of material. This, in itself, as already indicated, is of no particular consequence. What the figures do suggest--and this is the important thing-is that the separation has been reasonably complete, no significant portion of material which was supposed to appear in one fraction having been found in the other fraction.

Even more significant than the foregoing test, however,

is the evidence provided by the exchange experiments themselves. Now, if any great amount of carbon disulfide were transferred to the hydrogen sulfide fraction in the separation procedure, this would show up as a very significant apparent zero time exchange. This would be all right, so long as the "separation error" were always reproducible, the exchange rate then being obtained from the slope of a log(1-F) versus time plot that might miss going through the origin by a very considerable margin. Obviously, however, a minimum extraction of carbon disulfide into the water layer, corresponding to a minimum apparent zero time exchange, would represent a far more desirable situation than one involving a separation error that might or might not be reproducible.

As already mentioned, the log(1-F) versus time plots did not, in fact, always go back through the origin. The deviation from such behavior, however, was not excessive, and was found to correspond to apparent negative zero time exchanges as well as positive ones, a phenomenon not to be accounted for in terms of transfer of active carbon disulfide to the hydrogen sulfide fraction. The exact source of this occasional deviation was never isolated, but it was not, in any case, great enough to be a cause for concern, since it is easy to show that complete transfer, for example, of all the thiocarbonate complex assumed to be present at equilibrium in

the benzene solution into the aqueous extract would have led to a far greater effect. Furthermore, it is to be noted that the occurrence of this deviation was the exception rather than the rule, it being observed in more cases than not, that the log(1-F) versus time plots actually did go either close to or actually through the origin. As a further final observation in this connection, it should be pointed out that, in a reasonable number of instances, log(1-F) versus time plots derived from specific activity measurements made on the carbon disulfide fractions actually coincided with the plots derived from the hydrogen sulfide counting data, both plots going, if not through, at least close to the origin. Clearly such an observation indicates both that no great separation error has occurred, either in the form of carbon disulfide being extracted into the hydrogen sulfide fraction, or of hydrogen sulfide being left unextracted in the carbon disulfide fraction.

The foregoing tests appear to establish satisfactorily the efficiency of the separation method employed and hence the absence of any cause for concern, at least on this score, as to the reliability of the exchange rates derived from the experiments involving such separation procedures. A question does remain, however, as to why on basic extraction, the color assumed to be associated with thiocarbonate complex transferred itself from the benzene to the aqueous layer, if no great
amount of complex was, in fact, so transferred. While a complete explanation of this effect must certainly await fuller investigation, certain plausible explanations appear to present themselves. In the first place it is possible, of course, that the equilibrium amount of thiocarbonate in the benzene solution is actually much smaller than suggested by the interpretation of the present results offered in Section IV (where, for example, with triethylamine, hydrogen sulfide and carbon disulfide each in the range 0.3-0.5 M, about 30% of the material is tied up as complex). Thus it might be so small as not to be a factor relative to the efficiency of the reactant separation. Obviously one would prefer some other explanation that did not run so directly counter to the conclusions derived from the work itself, which one would like to feel are reasonably close to the way things truly are.

A more satisfactory alternative explanation would appear to be that, in the course of the separation process, the complex is very largely decomposed, only a small residue remaining to be oxidized by the peroxide. In part, such decomposition might occur at the time of water-benzene phase separation, and, in part, it might occur while the water extract is awaiting oxidation, any carbon disulfide so released possibly subsequently escaping by evaporation (all steps following the extraction being done in open beakers). Thus

both the absence of any significant carbon disulfide in the aqueous extract would be accounted for, as well as would be the apparent tendency of sulfate recovery from both fractions to be somewhat low. (It should be noted however, that any such latter indication must be interpreted with caution, all efforts in this work being aimed at cleanness of separation rather than highly quantitative recovery of material from the two fractions, a factor in itself, as previously indicated, of only minor importance).

An explanation along with the foregoing lines certainly does not run counter to the observations regarding the behavior of color in solution, since these were strictly qualitative in character. As a further point in this connection, it seems also possible that at least some of the color appearing in the basic aqueous extract may have had its origin in air oxidation of the sulfide solution to yield colored polysulfides. In any case, it is clear, from the evidence cited, that whatever thiocarbonate may possibly have existed in the aqueous solution at the time of peroxide oxidation was certainly of an amount small enough to be unimportant as far as interfering with the efficiency of separation of the two exchange reactants one from the other. Hence, by extension, it was unimportant relative to exchange rate calculations.

33

### B. EXCHANGE RATE CALCULATION METHODS

Isotopic exchange reactions are known to follow, for a homogeneous system at chemical equilibrium, a first order rate law. (8,p.317). The rate of exchange is given by the expression

$$R = -\frac{2.303 \text{ (ab)}}{(a + b)} \frac{d \log(1-F)}{dt}$$
(10)

where

- R = exchange rate in g-atoms/1-min
- a = concentration of exchange reactant 1 in
  g-atoms per liter
- b = concentration of exchange reactant 2 in
  gram atoms per liter
- F = fraction exchange

Although the use of radioactive tracers involves specifically, of course, the observation of the transfer of the radioactive species from one reactant to the other, the above equation gives the <u>total</u> rate of exchange of all the atoms of that elemental species being traced, whether radioactive or not. Thus in the present instance, while the exchange is followed by observing the growth of radiosulfur activity in the hydrogen sulfide fraction, the calculated rate, R, will correspond to the total rate of transfer of sulfur atoms between hydrogen sulfide and carbon disulfide, irrespective of isotopic composition. This rate, under fixed conditions, is a constant and depends in no way even on the presence of an isotopic tracer.

The two exchange reactants in the present instance are, naturally, hydrogen sulfide and carbon disulfide. The unusual concentration units quoted above arise from the fact that, for the present work, it is imperative to express the concentrations of carbon disulfide and hydrogen sulfide in terms of the gram atoms of sulfur present in each reactant, i.e. the "concentration" of carbon disulfide will be twice its molar concentration. The fraction exchange "F" has been determined by dividing the observed final specific activity of the hydrogen sulfide by the specific activity one would expect the hydrogen sulfide to have at complete exchange, (i.e. at "infinite time"), on the assumption of complete randomization of activity between the two sulfur containing species. This infinite time specific activity has been calculated from the known specific activity of the carbon disulfide used in preparing the reaction mixtures, together with the known concentrations (g-atoms per liter) of sulfur in each of the two reactants.

On the basis of equation (10), 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. The successive samples taken in the present work have been used to make such plots. In general the fraction exchange figures found have fallen quite well along the expected straight line, an observation of value in verifying the experimental procedure.

It may help to illustrate the foregoing with a specific example (Experiment 14). In this experiment the initial specific activity of the carbon disulfide was 193.6 cpm/mg, and the concentrations of carbon disulfide and hydrogen sulfide in the run were 0.0100 molar and 0.434 molar, respectively. Therefore, the gram atoms per liter of sulfur contributed by the carbon disulfide will be 0.0200 gram atoms per liter (one carbon disulfide contributing two sulfur atoms) and 0.434 gram atoms per liter will be contributed by the hydrogen sulfide. At infinite time exchange one would see complete randomization of the sulfur atoms, and hence the final specific activity of the carbon disulfide. This specific activity can thus be expressed as

$$S_{\infty} = 193.6 \text{ x} \frac{(0.0200)}{(0.454)} \text{ epm/mg}$$
 (11)

where

S<sub>co</sub> = specific activity of hydrogen sulfide at infinite time exchange

Since

$$F = \frac{(Sp. Act. H_2S)_t}{(Sp. Act. H_2S)}$$
(12)

it is possible to compute the fraction exchange by measuring the specific activity of the hydrogen sulfide (counted as barium sulfate). The hydrogen sulfide fraction in Experiment 14 had a specific activity of 1.36 cpm/mg after four minutes at 10.0°C. The fraction exchange at this time is, then

$$\frac{1.36}{8.52} = 0.160$$

or 16.0%.

Four such samples were taken at various times for Experiment 14, and from the specific activities of the hydrogen sulfide fraction obtained, a plot of log(1-F) versus time, was made. Figure 3 shows such a plot illustrating the adherence of the data to the first order exchange law.

To facilitate computation, it is convenient to simplify equation (10) in the following manner. When the fraction exchange in any one run is 50%, the time of exchange can be expressed as the half-time of the reaction,  $T_{\frac{1}{2}}$ . At this point, equation (10) reduces to



Figure 3. Log(I-F) vs. TIME

2.30

$$R = \frac{(ab)}{(a+b)} \cdot \frac{0.693}{T_{12}^{1}}$$
(13)

From Figure 3,  $T_{\frac{1}{2}} = 15.5$  minutes, and the rate for exchange becomes

 $R = \frac{(0.0200)(0.434)}{(0.454)} \cdot \frac{0.693}{15.5}$   $R = 8.55 \times 10^{-4} \text{ g-atoms/1-min}$ 

The activity of the hydrogen sulfide at infinite time (16.7 hours) was shown experimentally to be 8.08 cpm/mg which checks quite satisfactorily with the calculated value of 8.52 cpm/mg. The linearity of the (1-F) plot and the agreement between calculated and experimental infinite time hydrogen sulfide specific activities serve as good checks on the experimental procedure.

It must be mentioned that not all the (1-F) plots passed strictly through the origin. This, however, does not affect the calculation of the rate, for it is the slope of such plots that are used in such a calculation (16,p.17-18). For such a case, of course, it is necessary that the half-time,  $T_{\frac{1}{2}}$ , in equation (13) be defined, not as the time for 50% exchange, but as the time needed for the (1-F) value to drop to half its initial apparent value.

C. LEAST SQUARES ANALYSIS

An interpretation of the exchange rates is offered in

Section IV which involves the formation of the thiocarbonate species (Et3NH)(HCS3), (often referred to in this thesis as a "complex"), with an unknown association constant, K, the exchange being first order in this species with an again unknown specific rate constant, k. Thus

$$K = \frac{x}{(a-x)(b-x)(c-x)}$$
(14)

and

Rate = 
$$R$$
 =  $k \cdot x$  (15)

In these equations x represents the concentration of the thiocarbonate complex and a,b and c represent, respectively, the molar concentrations of Et<sub>3</sub>N, H<sub>2</sub>S and CS<sub>2</sub> actually put into the reaction mixture. Although in principle two rate measurements under different concentrations should suffice to determine the values of the two unknown constants, the practical problem in an investigation of the present type is to determine the "best" values of the unknowns on the basis of all the data (eighteen experiments in the present case). For this purpose a least squares method of analysis was employed. This method has been described in detail by Burge (3,p.76-80) and will therefore be only briefly outlined here.

If one considers that there is an error in each measurement of the rate of exchange, this assumption can be expressed symbolically as

$$R_{i} = kx_{i} + \varepsilon_{i}$$
(16)

analogous to equation (15) but containing the error term,  $\mathcal{E}_{\mathbf{i}}$ . This error term represents the deviation of the observed rate from a value predicted by any particular choice of K and k, the choice being aimed at obtaining the "best fit" of the data for all experiments performed. The purpose of the least squares analysis of the data is to choose values of K and k that will minimize the sum of the squares of these error terms, the sum being taken over all the experiments. Solving equation (16) algebraically for  $\mathcal{E}_{\mathbf{i}}$ , we obtain

$$\mathcal{E}_{i} = R_{i} - kx_{i} \tag{17}$$

Assuming the expected percentage error in the rate to be constant, (i.e. independent of the magnitude of the rate), we must weight each term by the factor  $1/R_1^2$  to make all terms in the summation of the same order of magnitude. Therefore, we obtain the expression

$$(\varepsilon_{i}/R_{i})^{2} = (1/R_{i}^{2})(R_{i} - kx_{i})^{2}$$
(18)

Since we wish to minimize the summation of this error term with respect to K and k, our final expression becomes

$$\sum (\epsilon_{i}/R_{i})^{2} = \sum (1/R_{i}^{2})(R_{i} - kx_{i})^{2}$$
(19)

Notice that equation (16) states that the observed rate,  $R_i$ , is equal to the calculated rate,  $kx_i$  plus an error term,  $\mathcal{E}_i$ . In order to obtain a calculated rate for each experiment, it was necessary, using the known measured values of the reactant concentrations, a, b, and c, to solve equation (14) algebraically for the complex concentration, x. This involved the solution of a cubic equation with three roots, only one of which, however, was acceptable from a practical point of view. The problem thus resolved itself into a matter of choosing a trial value for K, solving a cubic equation for each of the eighteen runs performed and, with the calculated complex concentration so obtained, computing expected rate values on the basis of equation (15). This last computation was performed, again for all eighteen runs, for each of a series of trial values of the rate constant, k.

Having thus obtained calculated rate values, equation (19) was employed to find the sum of the squares of the error terms, the summation being carried out over all eighteen runs, and repeated for each of the trial values of k. The value of k corresponding to a minimum value for the error term summation was then established graphically.

The foregoing having all been for one particular trial choice of K, the entire process was then repeated for a succession of further trial choices of K. The summation

term minima established at each such value were finally plotted against the selected range of chosen K figures, making possible the observation of an ultimate minimum corresponding to the "best" values of both K and k.

#### IV. RESULTS

1. The Non-Exchange of Radiosulfur between Hydrogen Sulfide and Carbon Disulfide in Benzene Solution in the Absence of Triethylamine.-- As already indicated, it has been previously shown by Douglas, Cooley and Yost on the one hand and by Mickelsen on the other that, in the absence of triethylamine, the rate of radiosulfur exchange between hydrogen sulfide and carbon disulfide is negligible, either in benzene solution or in liquid hydrogen sulfide. Before undertaking experiments in the present research involving triethylamine solutions, it seemed appropriate to verify the former finding. An experiment designed for this purpose was therefore carried out.

A solution of hydrogen sulfide and labeled carbon disulfide in benzene was prepared, and was found to be quite colorless, just as Mickelsen had observed for carbon disulfide in liquid hydrogen sulfide. The exchange results are presented in Table I. Clearly, at the indicated concentrations, these compounds had undergone no significant exchange in 1320 hours at 10.0°C. It is true that the first two samples listed in Table I suggest a slight apparent exchange. As indicated in Section III, however, such an effect is almost certainly to be related to a lack of complete facility with the separation technique at the time these two samples were taken, this being quite early in the research. The later samples quite satis-

### TABLE I

# RADIOSULFUR EX CHANGE BETWEEN HYDROGEN SULFIDE AND CARBON DISULFIDE IN BENZENE SOLUTION (NO TRIETHYLAMINE)

### Experiment A

Conc's: H<sub>2</sub>S = 0.0445 molar; CS<sup>\*</sup><sub>2</sub> = 0.0332 molar; Vol. = 500 ml.

Temp. =  $10.0 \pm 0.1^{\circ}C$ 

Spec. Act'sa): (CS2) b) = 25.0 cpm/mg; (H2S) c) = 14.97 cpm/mg

% Exchanged)	Specific Activitiesa)	Time
	(ucs)	(hours)
2.4 ± 0.9°)	$(\frac{125}{12})_{\pm}^{t}$ 0.13 <sup>e)</sup> 24.2	0.583
2.4 ± 0.8	0.36 ± 0.12 21.6	11.75
$1.8 \pm 0.9$	0.27 ± 0.14 22.5	154.25
$0.54 \pm 1.0$	0.081 0.15 22.0	623.0
0.71 ± 1.1	0.11 ± 0.16	1320.0

- a) All specific activities have been corrected for decay to the time of the beginning of the experiment.
- b) The specific activity listed is that of the carbon disulfide used in preparing the reaction mixture.
- c) The infinite time specific activity of the hydrogen sulfide, used to calculate the percent exchange, was itself calculated from the measured initial specific activity of the carbon disulfide used in preparing the reaction mixture, together with the recorded concentrations of H<sub>2</sub>S and CS<sub>2</sub>.
- d) Calculated from the ratio (H2S)t/(H2S)co
- e) The indicated errors represent standard deviations computed from the calculated standard deviations of the actual counting data.

factorily demonstrate the absence of any progressing exchange, the last two percentage exchange figures actually being calculated from measured specific activities which one should probably consider as essentially indistinguishable from background. On the basis of the indicated maximum values for, these last two figures, one may estimate an approximate lower limit for the half-time of the reaction at about five years. Clearly the earlier findings of Douglas, Cooley and Yost are amply verified.

2. <u>Rates of Radiosulfur Exchange between Hydrogen</u> <u>Sulfide and Carbon Disulfide in Benzene Solutions Containing</u> <u>Triethylamine</u>.--In contrast to the foregoing results, it has been found that, when triethylamine is added to the benzene solutions, radiosulfur exchange between hydrogen sulfide and carbon disulfide does occur at a measurable rate, a result consistent with the earlier observations of Mickelsen for liquid hydrogen sulfide solutions. Furthermore, in contrast to the complete lack of color in the absence of triethylamine, it has also been found that the solutions now take on a color, pale yellow to distinctly orange, depending on triethylamine concentration. This observation is again consistent with Mickelsen's findings with liquid hydrogen sulfide solutions, though no reddish hue, as suggested by the latter was ever here observed, presumably to be related to the fact that the present experiments

were not extended to quite as high a triethylamine concentration as were the former (see below).

Table II presents detailed results for eighteen experiments, all at  $10.0^{\circ}$ C, in which an attempt was made to find how the exchange rate varies with reactant concentrations. On the basis of these data plots of log(1-F) versus time were made ( $100 \cdot F = \%$  exchange), and, from the slopes of the resulting straight lines, exchange rates were calculated as described in detail in Section III. The rates so computed are recorded for all eighteen runs in the fifth column of Table III. These rates correspond to observed exchange half-times ranging from about five minutes to about 12,000 minutes (eight days).

In this work, the greatest effort was directed towards observing how the exchange rate varies with triethylamine concentration, twelve experiments with hydrogen sulfide and carbon disulfide held approximately constant at about 0.4 Mand 0.3 M, respectively, being done to this end. The rates observed for these runs (Experiments 1-12) are presented in Figure 4 in the form of a plot of the logarithm of the exchange rate versus the logarithm of triethylamine concentration. Figure 4 also shows the rates observed in two further experiments (Numbers 17 and 18), done at lower hydrogen sulfide and carbon disulfide concentrations.

### TABLE II

### RADIOSULFUR EXCHANGE BETWEEN HYDROGEN SULFIDE AND CARBON DISULFIDE IN BENZENE SOLUTIONS CONTAINING TRIETHYLAMINE

Temp. =  $10.0 \pm 0.1^{\circ}C$ 

Run	(Time (min.)	Vol. (ml)	(mols/l)	H2S (mols/1)	(mols/1)	Speci	fic Activities (cpm/mg)	<u>% E</u>	xchg <sup>a</sup> )
						(CS2) b)	(H2S)t	(CS2)t	
1	4 9 14 19 141c) & d)	127.3	1.41	0.430	0.300	28.0	7.65 11.49 13.93 14.95 16.90 16.31(cale)	22.26 19.41 18.49 17.62	46.9 70.5 85.4 91.7
2	3 20 30 ∞d)	112.0	0.643	0.424	0.296	28.3	4.57 8.23 13.43 14.43 16.49(calc)	25.52 21.82 18.60 17.05	27.7 49.9 81.4 87.5

a) Calculated from the ratio of (H2S)t to (H2S) (calc).

b) The values of the carbon disulfide specific activities listed are those of the carbon disulfide used in preparing a reaction mixture.

c) Infinite time experiments were performed as a method for checking the experimental procedure. In all cases, infinite time was taken as the time required for the reaction to proceed through at least twenty half-lives.

d) The infinite time specific activity of the hydrogen sulfide used to calculate the % exchange for all runs, was itself calculated from the measured initial specific activity (shown in column six) of the carbon disulfide used in preparing each reaction mixture, together with the recorded 50 concentrations of H2S and CS2.

				TABLE II	(Cont'd.	)			5 - F 2 - <sup>6</sup>
Run	Run Time (min.)	Vol. (ml)	(mols/l)	( <u>mols/</u> 1)	(mols/l)	Speci:	fic Activities (cpm/mg)		% Exchga)
3	5 10 20 30 cod)	109.3	0.441	0.442	0.304	28.3	3,90 6.77 11.04 12.54 16.39(calc)	25.18 23.73 19.84 18.56	23.8 41.3 67.3 76.5
4	5 10 25 35 675e) ∞ d)	122.7	0.147	0.436	0.297	27.4	2.32 4.20 7.31 9.55 15.37 15.81(calc)	25.49 24.18 17.86 20.68	14.7 26.6 46.2 60.4
5	2 7 17 34 ∞d)	110.2	0.102	0.388	0.301	28.3	1.83 3.42 6.15 9.64 17.21(calc)	23.17 23.33 19.19 19.86	10.6 19.9 35.7 56.0
6	3 10 30 co d)	110.0	0.0458	0.397	0.302	28.3	0.995 3.04 6.66 17.07(calc)	25.74 27.77 26.43	5.83 17.8 39.0

									7
Run	(min.)	Vol. (ml)	(mols/1)	H2S (mols/l)	(mols/1)	Speci	fic Activities cpm/mg)	<u> </u>	% Exchg.a)
						$(\underline{cs_2})_{o}^{b}$	(H2S)t	$(\underline{CS_2})_t$	2 M (M) 
7	120 270 420 630 12840 <sup>c</sup> ) <sub>∞</sub> d)	117.2	0.0092	0.432	0,311	75.1	10.20 24.46 38.38 39.89 40.00 44.32(calc)	64.70 56.32 55.33 40.57	23.0 55.2 86.6 90.0
8	120 2300 540 630 10080c) 0080c) 0080d)	117.0	0.0040	0.432	0.312	75.1	5.06 14.10 23.25 26.00 42.55 44.38(calc)	72.36 59.70 55.76	11.4 31.8 52.4 58.6
9	1440 2880 4320 5760 ∞ <sup>d</sup> )	118.0	0.000428	0.434	0.308	65.3	6.18 10.40 14.22 16.54 38.30(calc)	57.85 52.92 54.56 53.90	16.1 27.2 37.1 43.2
10	1440 2880 4320 5760 00 e)	118.0	0.000428	0.434	0.308	189.6	15.41 27.02 30.76 41.52 111.20(calc)		13.9 24.3 27.7 37.7

TABLE II (Cont'd.)

Run	Time (min.)	Vol. (ml)	EtaN (mols/l)	(mols/1)	(mols/1)	Specif	fic Activities	3	% Exchg.a)
		a				(CS2) b)	(H2S)t	(CS2)t	- 1 S
ц	60 210 420 1740 1830 ∞d)	130.0	0.000399	0.435	0,306	26.9	0.561 0.523 0.756 1.68 3.01 15.52(calc)	23.23 24.85 24.71 24.10 23.04	3.61 3.37 4.87 10.80 19.40
12	660 1380 2100 2820 3600 <sub>∞</sub> d)	127.0	0.000403	0.435	0.300	26.9	1.23 2.22 2.51 3.01 3.22 15.59(calc)	23.67 23.57 23.65 22.90 23.87	7.89 14.20 16.1 19.3 20.7
13	2 4 6 8 00 d)	118.0	0.305	0.433	0.0100	67.3	0.214 0.336 0.616 0.832 2.97 (calc)	66.15 62.48 58.29 50.64	7.21 11.3 20.7 28.0
14	10 15 20 1002c) ∞d)	118.0	0.305	0.434	0.0100	193 <b>.</b> 5	1.36 3.05 4.29 5.17 8.08 8.52(calc)		16.0 35.8 50.4 60.7

TABLE II (Cont'd.)

				4.040 A	T LOOTO A	•/			
Run	Time (min)	Vol. (ml)	(mols/1)	H2S (mols/l)	(mols/1)	Speci	fic Activities	1	% Exchg.a)
				1. T	55	(CS2) b)	(H2S)+	(CS <sub>2</sub> ) <sub>±</sub>	1.16
15	2 4 6 8 00 d)	118.0	0.433	0.0100	0.309	66.6	23.71 24.88 29.88 35.03 65.5 (calc)	68.39 66.48 65.83	36.2 38.0 45.6 53.5
16	2 4 6 8 00 <sup>d</sup> )	118.0	0.433	0.0100	0.309	187.7	69.73 90.76 103.1 118.7 184.7(calc)		37.8 49.1 55.8 64.3
17	120 180 420 630 ∞ <sup>d</sup> )	150.0	0.0048	0.0922	0.0907	27.2	1.35 1.79 5.54 7.44 18.00(cale)	26.06 26.44 24.59 25.36	7.50 9.94 30.8 41.3
18	120 240 620 1340 2880 ∞d)	150.0	0.00048	0.0922	0.0907	26.6	0.583 0.591 0.879 1.33 3.76 17.6 (calc)	24.64 26.10 24.72 21.51 20.35	3.31 3.36 4.99 7.56 21.4

TABLE II (Cont'd.)

## TABLE III

### HYDROGEN SULFIDE - CARBON DISULFIDE EXCHANGE EXPERIMENTS IN BENZENE: OBSERVED RATES AND CALCULATED RATE CONSTANTS

## Temp. = $10.0 \pm 0.1^{\circ}C$

Run	(mols/l)	(mols/l)	(mols/1)	Rate X 103 (g-atoms/1-min)	Complexa) (mols/l)	k (g-atoms/mol-min)
1	1.41	0.430	0.300	32.2	0.169	0.190
2	0.643	0.424	0.296	21.4	0.116	0.184
3	0.441	0.442	0.304	13.5	0.0976	0.138
4	0.147	0.436	0.297	6.45	0.0421	0.153
5	0.102	0.388	0.301	5.19	0.0287	0.181
6	0.0458	0.397	0.302	3.61	0.0140	0.258
7	0.0092	0.432	0.311	0.955	0.00319	0.299
8	0.0040	0.432	0.311	0.386	0.00140	0.276
9	0.000428	0.434	0.308	0.0223	0.000148	0.151
10	0.000428	0.434	0.308	0.0205	0.000148	0.139
11	0.000399	0.435	0.306	0.0270	0.000139	0.194
12	0.000403	0.435	0.300	0.0147	0.000138	0.107
13	0.305	0.433	0.0100	0.700	0.00341	0.205
14	0.305	0.434	0.0100	0.855	0.00341	0.252
15	0.433	0.0100	0.309	0.702	0.00343	0.205
16	0.433	0.0100	0.309	0.880	0.00343	0.257
17	0.0048	0.0922	0.0907	0.0549	0.000156	0.352
18	0.00048	0.0922	0.0907	0.00566	0.0000156	0.363

a) Complex concentrations are calculated assuming the formation of the bithiocarbonate,  $(Et_3NH)(HCS_3)$ , with an association constant, K = 4.0 12/mole<sup>2</sup>.



It is perhaps worth noting that the triethylamine concentration range spanned by the data shown in Figure 4 far exceeds that covered in Mickelsen's work with liquid hydrogen sulfide (going down to about 4 X  $10^{-4}$  <u>M</u> in contrast to a minimum concentration of about 5 X  $10^{-2}$  <u>M</u> in the earlier work). Unfortunately, however, the maximum concentration observed (1.41 <u>M</u>O falls somewhat short of the maximum of about 7 <u>M</u> in Mickelsen's work, a factor of significance in connection with the interpretation of the present data shortly to be offered. This maximum was set by the saturation solubility of hydrogen sulfide in benzene (about 0.6 <u>M</u>), since the amount of stock hydrogen sulfide solution used to obtain the 0.4 <u>M</u> hydrogen sulfide concentration used in these experiments automatically set a limit to the amount of triethylamine that could be added.

3. <u>The Rate Law for the Hydrogen Sulfide - Carbon</u> <u>Disulfide Exchange in Triethylamine-Containing Benzene Solution.--</u> Were the rate law for the foregoing exchange reaction of the general form

Rate = 
$$k(Et_2N)^{X}(H_2S)^{Y}(CS_2)^{Z}$$
 (20)

one would have expected, for the plot shown in Figure 4, to have obtained a straight line with a slope corresponding to the order of the reaction with respect to triethylamine. That is, the slope would have indicated the value of the exponent x

in equation (20). Clearly, the curvature displayed in Figure 4 indicates, that, in fact, no situation of this type exists, the exchange rate quite evidently not being related to the concentrations of triethylamine in any such simple manner as that depicted by equation (20). Rather the shape of the plot would appear to suggest a shifting equilibrium, the exchange rate depending on a complex in the solution whose concentration in turn depends on triethylamine concentration, but to a smaller and smaller extent as, with increasing triethylamine concentration, the complex formation equilibrium is shifted towards a greater degree of association, tending more and more to use up the triethylamine. Thus both on the basis of color formation and of the exchange results we appear to have here again, as did Mickelsen for liquid hydrogen sulfide solutions. a clear suggestion of the formation in solution of some complex species (one or more). One finds little difficulty in imagining thiocarbonate formation to be involved.

In an attempt to obtain an indication of the rate dependence on hydrogen sulfide and carbon disulfide, and hence the nature of the above suggested complex (or complexes), four experiments were done at lower concentrations than those involved in the experiments plotted in Figure 4. These experiments (Nos. 7, 13, 14, 15, and 16) have been retabulated in Table IV, together with an experiment at the

higher concentrations, included for the sake of comparison. In these experiments, one of the reactants at a time was reduced to a concentration of about 0.0100 M, the other two reactants being kept, one, at about 0.30 M, the other at about 0.43 M. Thus for each experiment the product of the three reactant concentrations remained a constant. There is one run for triethylamine at about 0.01 M and two each for hydrogen sulfide and carbon disulfide, respectively, at this concentration.

#### TABLE IV

### HYDROGEN SULFIDE - CARBON DISULFIDE EXCHANGE IN BENZENE: RATE DEPENDENCE ON REACTANT CONCENTRATIONS

Run	(mols/l)	(mols/l)	(mols/l)	(g-atoms/1-min)
3	0.441	0.442	0.304	13.5
7	0.0092	0.432	0.311	0.955
13	0.305	0.433	0.0100	0.700
14	0.305	0.434	0.0100	0.855
15	0.433	0.0100	0.309	0.702
16	0.433	0.0100	0.309	0.880

A most interesting result is to be observed in Table IV. It may be seen that the lowering of either hydrogen sulfide or of carbon disulfide concentration to about 0.010 <u>M</u> has almost the same effect rate-wise, as does the lowering of triethylamine concentration to this level. Put another way, it appears that, so long as the product of all three reactant concentrations remains constant, no matter which one has the

low value, the exchange rate remains substantially constant. This observation immediately suggests a completely symmetrical rate dependence on the concentrations of the three reactants. Such a conclusion would appear, in turn, to imply, not only that all three materials are involved in formation of the complex (an assumption already implicit in the hypothesis of thiocarbonate formation, of course), but also that they are all three involved in the same proportions, 1:1:1, or 2:2:2, etc. Clearly the simplest and most reasonable assumption to make in the light of this last conclusion is that the exchange rate depends on the concentration of some complex species in solution which contains in its make-up one mole of each of the reactants, for each mole of complex formed. A plausible postulate for such a species would be the bithiocarbonate, (Et3NH)(HCS3). Thus we may take the complex to be a product of the reversible equilibrium

$$Et_{3N} + H_{2S} + CS_{2} \Longrightarrow (Et_{3}NH)(HCS_{3})$$
(21)

The exchange rate is then assumed to depend on the rate of dissociation of this complex according to a first order rate law. Thus, if we designate the complex concentration as x, and the three reactant concentrations (as initially measured out) as a =  $[Et_3N]$ , b =  $[H_2S]$  and c =  $[CS_2]$ , we may write the two following expressions governing, respectively, the exchange

rate and the equilibrium concentration of complex in solution:

Rate = 
$$kx$$
 (22)

$$x = \frac{x}{(a-x)(b-x)(c-x)}$$
 (23)

In order to provide a test of the foregoing postulated rate law, the exchange rates observed in all eighteen runs given in Table II were subjected to a least squares analysis in the manner described in Section III. Thus it has been possible to arrive at values for the two constants, k and K, which best fit the data. The values so obtained are k = 0.190 g-atoms/mole-min and K = 4.0 12/mole2. Now inspection of equation (22) shows that by making a log-log plot of the observed exchange rates versus complex concentrations, one should obtain a straight line of unit slope. Figure 5 shows such a plot, complex concentrations having been calculated on the basis of K = 4.0. The straight line drawn in the figure corresponds to the specific rate constant value, k = 0.190. As may be seen, the experimental points scatter moderately closely about this line, an observation which one may take as providing reasonably satisfactory evidence in support of the suggested reaction mechanism and rate law.

The five runs discussed in connection with Table IV appear in Figure 5 as the cluster of points at log(complex) $\approx$  -2.5.



The closeness of the cluster shown in the figure again attests to the conclusions already drawn in connection with these runs. On the other hand, at lower complex concentrations the plotted points appear to show greater scatter. Whether this might represent a systematic deviation, thus indicating an incomplete adequacy for the suggested reaction interpretation, is a matter which will be treated further in Section V. In the meantime, however, it may be noted that the slowness of the experiments at the lowest concentrations gave rise to certain experimental difficulties. For one thing, with half-times of about eight days, there was always the possibility that the refrigerated thermostat may not have stayed exactly on temperature at all times. This possibility suggests itself since, during the course of this work, the bath was, in fact, observed occasionally to "stick" in the "On" position (i.e. with the refrigeration unit running and the bath becoming colder). In no instance, however, was it ever observed to "unstick" itself after such an event. Hence on the basis of the fact that, whenever the bath temperature was checked during any of the runs in Tables II and III, including those under discussion, it was always exactly at temperature, one is inclined to doubt that any such "sticking", with consequent temporary lowering of temperature, had occurred. A further, more direct, check on this point, however, is provided by the

fact that four different runs were made at the lowest triethylamine concentration (at the higher  $H_2S$  and  $CS_2$  concentrations; cf. Experiments 9-12). Despite the fact that these experiments were carried out at different times, they may be seen to cluster reasonably closely in Figure 5.

A second feature in connection with the low concentration, long time runs which might conceivably make for the possibility of greater scatter, is concerned with the possibility of a slow loss of hydrogen sulfide from the reaction flasks. While the experiments were carried out in flasks equipped with well-fitting, standard taper, ground glass stoppers, no grease was used because of the solvent character of the benzene. Hence the possibility of such loss cannot be ignored. However, the effect is probably not a large one, an actual check in the case of Experiment 9 showing, from the beginning to the end of the run (four days), a hydrogen sulfide loss of only about 18%. Clearly the scatter observed in Figure 4 is significantly greater than any such figure as this.

As a further aid in attempting to visualize the adequacy of the reaction interpretation presented, it is finally convenient to consider both the last column of figures in Table III and the plot given in Figure 6. The former consists of apparent specific rate constants, calculated by dividing the computed complex concentrations (based on K = 4.0) into the



observed exchange rates. The k values listed appear to show a fairly reasonable constancy, with an average value of 0.217, not far from the least squares value of 0.190. The most noticeable deviation from constancy appears to be shown by Experiments 17 and 18 which involved lower hydrogen sulfide and carbon disulfide concentrations than most of the rest of the experiments. These are the same runs which appear to give high rates at  $log(complex)\approx -3.8$  and -4.8 in Figure 5. Figure 6 represents a re-plotting of the experimental points shown in Figure 4, the solid and dashed lines this time, however, being drawn in terms of the postulated rate law, with the specific rate constant and equilibrium constant having the already indicated respective values of 0.190 and 4.0. Again the fit of the points in general appears reasonably good except for the two points at  $(H_2S) \approx (CS_2) \approx 0.09$  M.

It seems clear that the interpretation of these results in terms of the formation of a complex involving all three reactants (presumably a thiocarbonate) is a reasonable one. It further seems clear that the specific hypothesis of the formation of the species (Et<sub>3</sub>NH)(HCS<sub>3</sub>), with the exchange rate governed by the rate of dissociation of this substance (in a first order process), fits the results moderately satisfactorily, although a certain number of the experiments do not fit quite so well as one might have liked. While this apparent lack of

fit may be strictly experimental in character, it is, of course, possible that it may, in fact, indicate at least a partial inadequacy of the reaction scheme offered in this section. As already mentioned, this point will be treated further in the next section.

### V. DISCUSSION

The results presented in the preceding section appear clearly to suggest the reversible formation of some thiocarbonate species in benzene solution, just as Mickelsen (12,p.95-119) observed in his research dealing with liquid hydrogen sulfide solutions. Clearly the present results are at least in qualitative agreement with the earlier ones.

Mickelsen offered three alternative exchange models (as described in Section I), between which, on the basis of his results, he was unable to make a choice. While the interpretation of the present results conforms to none of these three models, exactly, it is related fairly closely to the first two, which are themselves related rather closely to each other. On the other hand, however, if one assumes essentially the same mechanism for the benzene solution reaction as for the liquid hydrogen sulfide one, it does appear possible now, on the basis of the present data, to present a quite good case against the validity of Mickelsen's third postulated mechanism, which involved the unexpected thiocarbonate species,  $(Et_3NH)(HC_2S_5)$ .

Mickelsen assumed the equilibrium constant for the formation of this last complex to be large enough so that the formation equilibrium would lie essentially completely towards the side of complex formation. Hence the amount of complex

formed was assumed, in his treatment, to be directly related to the amount of the limiting reactant present, whichever that might be. If, in connection with the present results, we make a similar assumption, it is immediately found that the model fails to provide an adequate interpretation of the data. The first evidence to this effect has already been presented in connection with the discussion of the material treated in Table IV. Here it was shown that if any one of the three reactants involved in this research were present at the limiting concentration of about 0.01 M, essentially the same exchange rate was always obtained. It will be apparent that, on the assumption that the species (Et3NH)(HC2S5) is being formed, a limiting CS2 concentration of 0.01 would yield a complex concentration of only 0.005, in contrast to complex concentrations of 0.01 for either H2S or Et3N at 0.01 M. Hence limiting CS2 in Table IV should have shown only half the rate shown when the other two species were limiting. Clearly such is not the case.

Further evidence against formation of the species  $(Et_3NH)(HC_2S_5)$  is to be found when one considers all eighteen of the present experiments together. Thus Table V presents, for all these runs, a listing of concentrations of the hypothetical complex,  $(Et_3NH)(HC_2S_5)$ , calculated on the basis of the concentration of the limiting reactant in each case
## TABLE V

## COMPARISON OF RATE CONSTANTS RELATED TO FORMATION OF THE ALTERNATIVE COMPLEXES (Et3NH)(HC2S5) AND (Et3NH)(HCS3)

Run	(Et3NH)(HC2S5)	a) Rate X 10 <sup>3</sup>	kib)	kc)
	(moles/1)	(g-atoms/l-min)	(g-at/mol-min)	(g-at/mol-min)
1	0.150	32.2	0.215	0.190
2	0.148	21.4	0.144	0.184
3	0.152	13.5	0.0888	0.138
4	0.147	6.45	0.0439	0.153
5	0.102	5.19	0.0509	0.181
6	0.0458	3.61	0.0788	0.258
7	0.0092	0.955	0.104	0.299
8	0.0040	0.386	0.0965	0.276
9	0.000428	0.0223	0.0521	0.151
10	0.000428	0.0205	0.0479	0.139
11	0.000399	0.0270	0.0677	0.194
12	0.000403	0.0147	0.0365	0.107
13	0.00500	0.700	0.140	0.205
14	0.00500	0.855	0.171	0.252
15	0.0100	0.702	0.0702	0.205
16	0.0100	0.880	0.0880	0.257
17	0.0048	0.0549	0.0114	0.352
18	0.00048	0.00566	0.0118	0.363

- a) Calculated on the basis of K(ass'n) >> 1.
- b) Calculated on the basis of Rate =  $k^{\dagger}$  [(Et<sub>3</sub>NH)(HC<sub>2</sub>S<sub>5</sub>)].
- c) Calculated on the basis of Rate = k[(Et<sub>3</sub>NH)(HCS<sub>3</sub>)] (with K(ass'n) = 4.0).

(see Table II or III for these figures). In column three of this table the exchange rates are retabulated from the previous section. In the next column, now, are presented apparent values of specific rate constants computed on the basis of the rate law

Rate = 
$$k^{1}$$
 (Et<sub>3</sub>NH)(HC<sub>2</sub>S<sub>5</sub>) (24)

In the last column, apparent specific rate constants derived from the reaction mechanism interpretation offered in Section IV, (involving the assumption of formation of the thiocarbonate species (Et<sub>3</sub>NH(HCS<sub>3</sub>)) have also been retabulted for the sake of comparison. Clearly, while the spread among these last constants is considerably greater than one might have desired (0.107 to 0.363, a 3.4-fold range), the spread among the apparent k values associated with the species (Et<sub>3</sub>NH)(HC<sub>2</sub>S<sub>5</sub>) is far greater, going from a low of 0.0114 to a high of 0.215, approximately a nineteen-fold range. Certainly no constancy could be claimed for such a set of figures.

On the basis of the foregoing discussion, then, it seems safe to conclude that Mickelsen's third alternative reaction mechanism involving the assumed formation of the rather unexpected thiocarbonate species, (Et<sub>3</sub>NH)(HC<sub>2</sub>S<sub>5</sub>), may now be ruled out (always assuming, of course, the same reaction mechanism in both the solutions involved in Mickelsen's

research and those here involved, an assumption which does not appear too unreasonable). This conclusion probably constitutes the one result of most clear-cut value to be derived from the present research.

What now of Mickelsen's other two postulated interpretations? Unfortunately, the situation in this area is considerably more clouded than that discussed in the foregoing paragraphs, and, for reasons which will shortly be made clear, must probably remain so for the present. A certain amount of discussion relative to this matter may, however, be somewhat revealing.

The reaction interpretation presented in Section IV of the present work consisted of the assumption of an equilibrium leading to formation of the complex, triethylammonium bithiocarbonate, in solution, and an exchange rate governed by the rate of dissociation of this material, leading to a rate law first order in its concentration, this concentration in turn being computable from an equilibrium constant expression. Thus:

$$Et_3N + H_2S + CS_2 \Longrightarrow (Et_3NH)(HCS_3)$$
 (25)

$$(= \frac{x}{(a-x)(b-x)(c-x)}$$
 (26)

Rate = kx (27)

Here the symbols have the same significance as before, viz.

- x = equilibrium concentration of (Et<sub>3</sub>NH)(HCS<sub>3</sub>)
- a = initial concentration of Et<sub>2</sub>N
- b = initial concentration of H2S
- c = initial concentration of CS2

Now the only way in which Mickelsen's reaction interpretations differ from the above is that they postulate a second equilibrium, involving formation of the normal thiocarbonate species, with a larger and larger proportion of this being formed as triethylamine concentration is increased. The normal thiocarbonate is assumed either to exchange (again presumably by dissociation) more slowly than the acid thiocarbonate, or, alternatively, not to exchange at any significant rate at all. (These last alternative assumptions represent, it may be noted, the only difference between Mickelsen's two interpretations). Thus in terms of such a picture, one may, in addition to Equation (25) above, and in place of Equations (26) and (27), write the following:

$$2Et_{3}N + H_{2}S + CS_{2} \longrightarrow (Et_{3}NH)_{2}(CS_{3})$$
(28)

$$K_1 = \frac{x_1}{(a-x_1-2x_2)(b-x_1-x_2)(c-x_1-x_2)}$$
 (29)

$$K_2 = \frac{x_2}{(a-x_1-2x_2)^2(b-x_1-x_2)(c-x_1-x_2)}$$
(30)

$$Rate_1 = k_1 x_1 \tag{31}$$

 $Rate_2 = k_2 x_2 \tag{32}$ 

Rate = 
$$Rate_1 + Rate_2 = k_1x_1 + k_2x_2$$
 (33)

Here, in addition to the symbols previously defined,

x1 = equilibrium concentration of (Et<sub>3</sub>NH)(HCS<sub>3</sub>) x2 = equilibrium concentration of (Et<sub>3</sub>NH)<sub>2</sub>(CS<sub>3</sub>)

It is appropriate now to consider whether a treatment along these lines might conceivably represent a better interpretation of the results of the present research than that offered in Section IV, where the spread among the apparent specific rate constants, for example, listed in Table III, is probably somewhat greater than one might have desired. In particular, one might ask whether the results of experiments 17 and 18, which were at lower hydrogen sulfide and carbon disulfide concentrations than most of the rest of the experiments, and which appear particularly to deviate from the rest, can be taken as indicating the need for consideration of the above two equilibria treatment.

In order to examine this matter, let us assume that, in fact the above two equilibria situations are involved in the benzene solutions. At low triethylamine concentration, the concentrations of complexes formed,  $x_1$  and  $x_2$ , must be

small compared to the concentrations of hydrogen sulfide and carbon disulfide, simply on the basis of stoichiometry. If we further assume that K1 and K2 are not too large (Mickelsen indicated values of 6.5 and 0.8 for his first exchange model), one may estimate that the total complex concentration is also probably relatively small compared even to the triethylamine concentration. Under these circumstances one may, to a first approximation, neglect all the subtractive terms in Equations (29) and (30) and thus obtain, on rearrangement, the approximate expressions

$$x_1 \approx K_1 abc$$
 (34)  
 $x_2 \approx K_2 a^2 bc$  (35)

Further expressions analogous to Equations (34) and (35) could be derived if one were to consider the formation of complexes in which the stoichiometry might conceivably include two hydrogen sulfides, two carbon disulfides, or even two molecules each of the three reactants. The corresponding complex concentrations for such cases would then be given approximately by the expressions

$$x_3 \simeq K_3 ab^2 c$$
 (36)

$$x_h \approx K_h a b c^2$$
 (37)

 $x_{4} \approx K_{4}abc^{2}$  $x_{5} \approx K_{5}a^{2}b^{2}c^{2}$ (38)

Now if the exchange rate were to depend on the concentration of any one of the foregoing complexes alone, then, at low triethylamine concentrations, the rate should be proportional to the corresponding concentration product, abc,  $a^{2}bc$ , etc. On the other hand, if the rate depended, for example, on two complex concentrations, then it should be proportional to some linear combination of the two corresponding products. It is appropriate, therefore, to see how these products actually do vary with the exchange rate. To this end a comparison has been made involving two of the low triethylamine concentration experiments which seemed somewhat poorly accomodated, relative to each other, by the interpretation offered in Section IV. The data dealing with this comparison are presented in Table VI.

Consideration of the material in Table VI is quite suggestive. While the exchange rate in Experiment 9 is less than that in Experiment 17, the value of the product abc is greater in (9) than in (17). Clearly this is consistent with the already indicated apparent shortcoming of the reaction interpretation presented in Section IV, which simply postulates formation of the species ( $Et_3NH$ )( $HCS_3$ ). Consider now the product  $a^2bc$ , corresponding to formation of the normal thiocarbonate species, ( $Et_3NH$ )<sub>2</sub>CS<sub>3</sub>. It may be seen that here the value of the product has decreased rather than increased, as

#### TABLE VI

#### COMPARISON OF REACTANT CONCENTRATION PRODUCTS WITH RATES AT LOW TRIETHYLAMINE

17	2
5.49	2.23
4.8	0.428
0.0922	0.434
0.0907	0.308
4.01	5.72
1.93	0.245
3.70	24.8
3.64	17.6
1.61	3.27
	<u>17</u> 5.49 4.8 0.0922 0.0907 4.01 1.93 3.70 3.64 1.61

did the product abc, in going from (17) to (9). The decrease is, moreover, even greater, relatively speaking, than is the decrease in exchange rate. Thus while postulation of formation of the substance  $(Et_3NH)_2CS_3$  alone would obviously fit the data much more poorly even than does the assumption of bithiocarbonate formation alone, it will be apparent that a rate depending on some linear combination of the two terms abc and  $a^2bc$ , and thus of the two forms of thiocarbonate, would greatly improve the fit of the data, at least so far as these two experiments are concerned. Thus a rate law of the very type proposed by Mickelsen is quite evidently also here suggested by the present data.

In contrast to the above conclusion, it may be seen from Table VI that any of the products  $ab^2c$ ,  $abc^2$  or  $a^2b^2c^2$ increase considerably in going from (17) to (9). Hence any one of these would give a much poorer fit to the data than does the product abc associated with the mechanism already advocated (the product  $abc^2$  corresponds to the species (Et<sub>3</sub>NH)(HC<sub>2</sub>S<sub>5</sub>) involved in Mickelsen's third model, already ruled out in earlier discussion). Furthermore, no improvement in the fit of the data could ever be achieved by any combination of any one of these other products with the product abc. Obviously any such linear combination of two products must involve the product  $a^2bc$ . Certainly the most reasonable such combination would be abc and  $a^2bc$ , corresponding to bithiocarbonate and the normal thiocarbonate.

It will be apparent that a more quantitative attempt to fit all the present experimental data in terms of the rate law represented by equation (33), with accompanying derivation of values for the four constants  $K_1$ ,  $K_2$ ,  $k_1$  and  $k_2$ , would have been highly desirable. Such a procedure would naturally have facilitated comparison of the present results with those obtained by Mickelsen. After a preliminary attempt in this direction had been made, however, it soon became apparent

that the mathematical complexities involved were, unfortunately, very formidible, indeed. In view of the limited scope of the present investigation, as reflected, for example, in the fact that the rate effect of triethylamine alone was studied in detail, hydrogen sulfide and carbon disulfide having been examined in only a cursory manner, it was not felt that the effort involved could be justified. Rather it would appear that more detailed experimental data should first be in hand. In this connection it should also be noted that Mickelsen's own data actually require more detailed analysis before any comparison with the present results would be entirely meaningful. Thus Mickelsen's so-called first two exchange models are in truth but one model with two different sets of trial values of the four constants, K1, K2, k1 and ko, both of which sets appear to fit the experimental results about equally well. Clearly, therefore, neither of these sets gives an optimum fit to the data, and hence some type of data fitting process, such as a least squares procedure would certainly seem called for.

The foregoing comparison of the present results with those obtained by Mickelson has been concerned almost entirely so far with the form and nature of the rate law and reaction mechanism in the two cases, without regard to any quantitative comparison of the actual exchange rates. Such a comparison

would seem, therefore, now to be called for.

In order to make this comparison, it is, of course, necessary to correct the actually observed rates to some common set of conditions. As a basis for the comparison, therefore, we will choose a set of reactant concentrations falling in the general range involved in Mickelsen's work and a temperature corresponding to the present work. Correction for concentration will be made as follows: (a) for Mickelsen's rates, on the basis of his third reaction model (valid in the reactant concentration range stipulated, even though invalid over a more general range); and (b) for the present results, on the basis of the bithiocarbonate rate law presented in Section IV. As will be seen the first correction is a minor one, the "corrected" rate amounting for all practical purposes almost to an actually observed value. The latter correction, however, is of much more questionable validity since it involves extrapolation of observed rates to much higher hydrogen sulfide concentrations than any dealt with in the present investigation. This point will be returned to after the data themselves have been presented. Correction of Mickelsen's data (the bulk of his experiments were at -23°C) to the temperature of the present research (10°C, necessary because of the freezing point of benzene at 590), is easily made on the basis of his

reported activation energy of 18.4 kcal/mole. Substitution of this figure in the Arrhenius equation

$$k = Aexp(-E_p/RT)$$
(39)

immediately leads to the value 74.6 for the ratio of the exchange rates at the two temperatures.

To proceed with the comparison, then, let us arbitrarily choose a triethylamine concentration of 0.349 molar and a carbon disulfide concentration of 0.510 molar. To conform, as stipulated, to the reactant concentration range involved in Mickelsen's work, it is necessary, of course, to base our comparison on a hydrogen sulfide molarity corresponding to the pure liquid (at  $10^{\circ}$ ). To calculate this quantity one must know the density of the liquid. This may be approximately estimated using the following equation, which has been reported as valid in the low temperature range -82 to  $-63^{\circ}$ C (18,p.22):

$$d_{j}^{t} = 0.866 - 0.001629t$$
 (40)

where

t = temperature in degrees Centigrade

Substitution in this equation yields an indicated density at  $10^{\circ}$ C of 0.850 g/l. Use of this figure, then, finally leads to a calculated approximate molarity for pure hydrogen sulfide at

# 10°C of 24.9 M.

Mickelsen reported his concentrations in terms of molalities (moles of solute per 1000 g of solvent), but this factor is of little significance since he derived from his data, and reported, a first order specific rate constant, which is naturally independent of reactant concentration units. This constant, k' = 0.025 g-atoms/mole-min, makes possible the calculation of the rate which Mickelsen would have observed at any particular pair of triethylamine and carbon disulfide concentrations falling within the range for which the rate law with which it is associated may be valid. The constant does, however, correspond to rates in pure hydrogen sulfide, a fact which accounts for the necessity for the indicated molarity of 24.9 recorded above.

Mickelsen's third model involved formation of the hypothetical thiocarbonate species,  $(Et_3NH)(HC_2S_5)$ , in a concentration limited simply by the concentration of the limiting reactant present, the formation reaction being assumed to go essentially to completion. On this basis, the above concentrations would predict a thiocarbonate complex concentration of  $\frac{1}{2} \times 0.510 = 0.255$  molar. The exchange rate which would have been observed at these concentrations (at -23°C) would, therefore, have been (cf. equation (24)) (0.025)(0.255) =  $6.38 \times 10^{-3}$  g-atoms/liter-min. Finally, at  $10^{\circ}C$ , Mickelsen's observed rate would have been (6.38  $\times 10^{-3}$ )(74.6) = 0.476 g-atoms/liter-min. In connection with this value, let us again emphasize that, despite the apparent "corrections" involved and the general invalidity of the rate law used, the figure given represents essentially the rate which Mickelsen would actually have observed (on the average), had he done an experiment under the exact chosen conditions. This follows since his range of experimentation actually spanned these conditions, both concentration-wise and temperature-wise.

Let us see now what exchange rate the present results would suggest for these conditions. Here all that can be done for the present, is to extrapolate the observed rates to the much higher hydrogen sulfide concentration in Mickelsen's work, on the basis of the bithiocarbonate rate law (cf. equations (25) - (27)). At the indicated molarities of the three reactants, one may employ equation (26), using K = 4.0, to calculate an equilibrium bithiocarbonate complex concentration of 0.332 M. Multiplication of this figure by the previously quoted specific rate constant for this rate law (0.190 g-atoms/mole-min) leads to an "expected" rate of 0.0631 g-atoms/liter-min. Thus the rate of 0.476 for Mickelsen's results is greater than the present figure by a factor of about 7.5

It is of some interest to find the two foregoing rate figures as close to each other as they are. Clearly such a finding suggests the same general process to be occurring in benzene solution as was observed in the liquid hydrogen sulfide solutions. Just how significant the difference, such as it is, must be considered to be is not entirely plain at this juncture. Thus, for example, with the solvents involved having the quite different dielectric constants of  $\approx 8.0$ (H<sub>2</sub>S at -61°) and 2.28 (benzene at 20°), it is not at all obvious that one would necessarily expect the same values for the specific rate constants in both cases. (Note that no assumptions relative to any similarity of equilibrium constants in the two solvents were involved in the above comparison).

Despite these points, it is of some interest to observe, however, that modification of the proffered "bithiocarbonate interpretation" of the present data to a form to include the normal thiocarbonate (i.e. the model covered in equations (25) and (28) - (33)), might quite possibly bring the above two rate figures into closer agreement. This follows since the curvature of Figure 4 could be accounted for, at least in part, in terms of a shifting of complex form from the more rapidly exchanging bithiocarbonate to the less rapidly exchanging normal thiocarbonate with increasing triethylamine

concentration. Hence one might find a lower value than 4.0 for the bithiocarbonate association constant K<sub>1</sub>, the rather high value having been necessary in the unmodified interpretation to account for the curvature. This in turn would mean a greater percentage increase in complex concentration for the extrapolation, involved in the above comparison, from the hydrogen sulfide concentration range associated with the present research to that involved in Mickelsen's research. The fact, incidentally, that the "complex" would actually consist of a mixture of the two complex species, both the normal and the bithiocarbonate, would not affect the matter, since, so long as triethylamine concentration remains constant, the proportions of the two species in the mixture would also remain constant. This may immediately be seen by considering the equilibrium

$$(Et_3NH)(HCS_3) + Et_3N \Longrightarrow (Et_3NH)_2(CS_3)$$
(41)

Thus, with a greater increase in complex concentration from low to high hydrogen sulfide concentration, one would have obtained, as a result of the above correction procedure, a higher "expected" rate on the basis of the present results, but at Mickelsen's concentrations. Hence the suggested possibility of a closer agreement with the figure derived from Mickelsen's work.

This last point again suggests, as did an earlier phase of this discussion, the possibility that the two equilibria interpretations (Equations (25) and (28)) of the process here studied might possibly turn out to be preferable to that offered in Section IV. It is to be hoped that accumulation of additional experimental data will ultimately facilitate further exploration of this matter.

Finally it seems appropriate to return briefly to a point touched on in the Introduction to this thesis, namely a partial discussion of the extent of validity of the socalled solvent systems theory of acid-base behavior. If we grant, as seems but reasonable, that reaction of triethylamine, carbon disulfide and hydrogen sulfide to form a thiocarbonate is an acid-base type process, it seems clear that the apparent finding of essentially the same such process in the inert solvent benzene as in the "ionizing" solvent, hydrogen sulfide, constitutes a definite reflection on the utility of the solvent systems picture. Clearly we see here an illustration of the greater value of a more general concept of acid-base behavior such as that involved in the Lewis interpretation of such phenomena.

## VI. SUMMARY

The radioactive tracer sulfur-35 has been used to study certain phases of the kinetics of the isotopic exchange reaction between hydrogen sulfide and carbon disulfide in the inert, nonaqueous solvent benzene, both in the absence and in the presence of triethylamine. This investigation serves to supplement earlier results obtained in a study of the same reaction in liquid hydrogen sulfide itself as solvent.

Both the earlier work in liquid hydrogen sulfide and other research involving benzene as solvent had indicated a complete absence of any significant exchange between these two materials in the absence of triethylamine. The present investigation has confirmed this result for benzene solution. Just as in liquid hydrogen sulfide, however, the presence of triethylamine leads to measurable exchange rates, the observed half-times ranging from about five munites to about eight days at  $10^{\circ}C$ .

Analysis of the data suggests again, as for liquid hydrogen sulfide, the formation of thiocarbonate in solution, with the exchange rate depending on the rate of dissociation of such a species, (one or more). It has been shown that the present data can be interpreted reasonably adequately in terms of formation of the specific species, (Et<sub>3</sub>NH)(HCS<sub>3</sub>),

the rate then being given by the expression

Rate = 
$$k[(Et_3NH)(HCS_3)]$$

and the complex concentration being governed by the equilibrium constant expression

$$K = \frac{\left[(Et_{3}NH)(HCS_{3})\right]}{\left[Et_{3}N\right]\left[H_{2}S\right]\left[CS_{2}\right]}$$

The observed values for the two constants at  $10^{\circ}$ C are K = 4.0  $1^{2}$ /mole<sup>2</sup> and k = 0.190 g-atoms/mole-min.

Further consideration of the data make possible a definite elimination of the formation in benzene of any such species as the complex  $(Et_3NH)(HC_2S_5)$  suggested as a possibility in the earlier liquid hydrogen sulfide research. The possibility that the complexes involved in benzene might consist, however, both of bithiocarbonate and the normal thiocarbonate,  $(Et_3NH)(HCS_3)$  and  $(Et_3NH)_2CS_3$ , is a more real one. Further work bearing on this point would be of value.

Quantitatively, the present rates appear to be slower by a factor of about 7.5 than those observed in liquid hydrogen sulfide. This comparison rests, however, on a rather uncertain extrapolation of the rates here observed to the high hydrogen sulfide concentration corresponding to the liquid hydrogen sulfide solutions, so that the difference could be more illusory than real. It might, for example, be derived, at least partly, from the lack of consideration of the possible participation of the normal thiocarbonate in the exchange process. In view of the rather different character of the two solvents, benzene and hydrogen sulfide, however, it is not felt that considerations relative to this apparent difference should be pressed too far.

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