EXCHANGE REACTIONS IN

LIQUID SULFUR DIOXIDE

by

Rowland Edward Johnson

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APPROVED:

Redacted for Privacy
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Professor of Chemistry

In Charge of Major

Redacted for Privacy
_____

Head of Department of Chemistry

Redacted for Privacy
_____

Chairman of School Graduate Committee

Redacted for Privacy
_____

Dean of Graduate School

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Also we would like to acknowledge the help given by Dr. J. L. Huston in solving many of the experimental difficulties.

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EXCHANGE REACTIONS IN LIQUID SULFUR DIOXIDE

I. INTRODUCTION

Historically, the study of the reactions of acids[1]
and bases in solution have almost always involved water as
a solvent. As a result of this, the general theory of
acid-base phenomena which has been most commonly accepted
postulated the existence of hydrogen ions and hydroxide
ions in water; an acid was defined as a substance which, in
water, provided hydrogen ions, a base, in water, provided
hydroxide ions, and a neutralization reaction was the com-
bination of hydrogen and hydroxide ions to produce the
solvent, water.

In some cases, however, a substance, in water, may be
acidic or basic without furnishing hydrogen or hydroxide
ions. Furthermore, the solvent may be a liquid other than
water, or neutralization may take place in the absence of
any solvent. To obviate these difficulties, a number of
theories (14, pp.1-17) have been developed to supplement
and extend the hydrogen, hydroxide ion theory.

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1. The criteria of G. N. Lewis (13, p.302) for the acidic
    or basic nature of a substance are its ability to
    undergo:
    a) Neutralization reactions
    b) Titration with indicators
    c) Displacement reactions
    d) Catalytic action

Perhaps the most general of these is the Lewis Theory
(14, p.16) which states that an acid is a substance which
can accept a pair of electrons, a base is a substance which
can donate a pair of electrons, and neutralization involves
the formation of a coordinate bond between the acid and
the base. (In addition, of course, any substance which
provides an electron-pair acceptor is classed as an acid;
in the water system, both hydrogen ion and hydrogen chlo-
ride are acids.) In the present report, we are concerned
specifically with the application of these ideas to liquid
sulfur dioxide as a solvent and some of its acids and
bases.

II. THEORY

A. PRESENT STATUS. The sulfur dioxide acid-base system has been developed primarily by Jander and his co-workers (9, pp.209-306). They postulate the existence of thionyl ions and sulfite ions in liquid sulfur dioxide analogous to hydrogen and hydroxide ions in water:

$$2 SO_2 \rightleftharpoons SO^{++} + SO_3^= \tag{1}$$

In this system, the thionyl ion acts as an electron acceptor; in the Lewis sense, it is an acid and Jander considers thionyl compounds in sulfur dioxide to be acidic analogues ("Saurenanaloge") of hydrogen-ionizing compounds in water (9, pp.209-210). He envisages the ionization of thionyl chloride as represented by Equation (2):

$$SOCl_2 \rightleftharpoons SO^{++} + 2Cl^- \tag{2}$$

His basis for this is the increased conductivity of a solution of thionyl chloride in sulfur dioxide over the pure solvent and other experimental work discussed below.

Likewise, a sulfite compound, such as tetramethyl-ammonium sulfite which is one of the more soluble sulfites, produces sulfite ions in solution and acts as a base according to Jander.

$$(Me_4N)_2SO_3 \rightleftharpoons 2 Me_4N^+ + SO_3^= \tag{3}$$
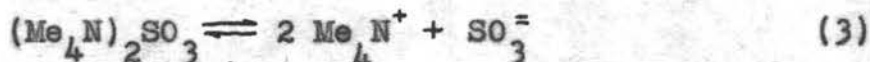
A number of classical reactions have been studied by these workers to establish their theory. Neutralization, a typical acid-base reaction, has been studied with various

acids and bases in liquid sulfur dioxide; Equation (4) is
typical of their concept of this reaction (9, p.210):

$$(Me4N)_2SO_3 + SOCl_2 \longrightarrow 2SO_2 + 2Me_4N^+ + 2Cl^- \quad (4a)$$

or

$$SO_3^= + SO^{++} \longrightarrow 2SO_2 \quad (4b)$$
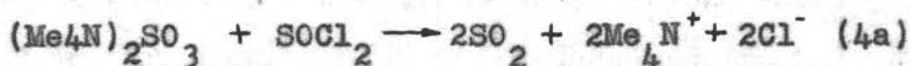
Such reactions were studied by a conductimetric method of
titration; no data are given but it is implied from the
experimental procedure that the reaction was rapid. This
indicates an ionic reaction, (4b) above, since ionic
reactions are rapid and may be studied conductimetrically.

In addition, many displacement reactions have been
studied as typical of acid-base phenomena. In one example,
thionyl bromide and potassium chloride were produced from
the addition of thionyl chloride to potassium bromide
dissolved in liquid sulfur dioxide. From these consider-
ations, Jander and his coworkers felt confident in believ-
ing in the existence of sulfite ions from sulfite com-
pounds and thionyl ions from thionyl compounds in liquid
sulfur dioxide.

B. DIFFICULTIES WITH PRESENT STATUS. Jander's
theory has gained a limited amount of acceptance
(6, pp.482-487) but has not met with unqualified approval.
In Jander's work, one notes, for example, different values
for the specific conductance of pure sulfur dioxide; in
one table (9, p.211) the value is 1×10^{-7} reciprocal ohms

at 0° C. (Other workers (4, p.572; 18, p.516) agree with
this value.) In another table (9, p.237), however, the
value given is ~8 X 10^{-7} reciprocal ohms, temperature un-
stated. In this latter table, the specific conductance
of a 0.1 M solution of thionyl chloride is listed as
1.1 X 10^{-6} reciprocal ohms at -19°C. One wonders then if
the difference between these two latter values is real
or due to an experimental error; one is led to believe
that only a very small amount of ionization, of the type
represented by Equation (2), takes place.

Jander's theory has also been criticized by Bateman,
Hughes, and Ingold (3, pp.244-246). These authors feel
that the neutralization of a sulfite and a thionyl com-
pound can take place without the presence of thionyl ions,
for example, by the reaction mechanism of Equation (5) or
(6) or both:

$$SOCl_2 \rightleftharpoons SOCl^+ + Cl^- \tag{5a}$$

$$SOCl^+ + SO_3^= \longrightarrow 2SO_2 + Cl^- \tag{5b}$$

$$SOCl_2 + SO_3^= \longrightarrow 2SO_2 + 2Cl^- \tag{6}$$
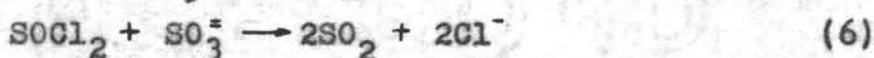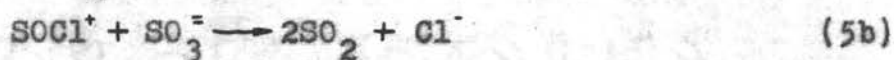
Such a first step ionization as (5a) may explain the reac-
tion of thionyl chloride with hydroxyl organic compounds
wherein a chlorosulfinylate is formed:

$$ROH + SOCl_2 \longrightarrow ROSOCl + HCl \tag{7}$$
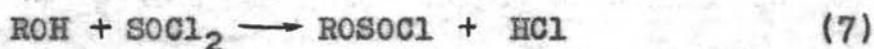
This reaction is known to occur (3, p.244). Thus the
neutralization which Jander explains by Equation (4b) may

also be explained in ways which do not postulate the existence of thionyl ions.

Furthermore, these authors seem to have proved that some of Jander's experimental work on triethyl amine in liquid sulfur dioxide (a base, analogous to ammonium hydroxide in water) was completely wrong (3, pp.244-247); this work is under investigation in our Laboratory also and the results obtained uphold the work of Bateman, Hughes, and Ingold[1]. On the basis of what now seems to be invalid data, Jander has drawn conclusions (9, pp.224-227) to help prove his acid-base theory of sulfur dioxide.

It is evident from the above that the existence in liquid sulfur dioxide solutions of the ions postulated by Jander is in doubt. Indeed, Jander's entire theory is open to question as the best explanation to fit the experimental data. It was felt that experiments specifically designed to prove or disprove the existence of thionyl ions from dissolved thionyl compounds, together with a general study of the ratio of the forward and back reactions of the equilibria of Equations (1) and (2) (if these rates are measurable) would go far toward helping clarify the whole situation. Further experiments designed to test the existence of sulfite ions in a tetramethylammonium sulfite solution seemed particularly inviting since these

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1. R. H. Herber and T. H. Norris, private communication.

solutions have an unusually high specific conductance
(2×10^{-4} reciprocal ohms at -19°C for a 0.002 M solution
(9, p.236)) and hence presumably a relatively high degree
of ionization.

C. APPLICATION OF RADIOACTIVE TRACERS. If, when
thionyl chloride is dissolved in liquid sulfur dioxide,
thionyl ions are produced according to the reactions of
Equations (1) and (2), there should be an exchange of
thionyl ions between solvent and solute. It is evident
that such an exchange may be tested by labeling either the
solvent or solute with a tracer such as radioactive S^{35}
and seeking the tracer in the unlabeled material after a
period of contact. Such a procedure may be applied also,
of course, to sulfite ions and a sulfite compound.

In spite of the objections to Jander's theory, we
felt that the exchange reactions between thionyl chloride
and sulfur dioxide would proceed rapidly, perhaps immeas-
urably fast. An immeasurably fast rate might be due to a
large equilibrium concentration of ions (unlikely because
of the small specific conductance of thionyl chloride in
sulfur dioxide) or more likely due to the rapidly revers-
ible equilibria (a typically ionic characteristic) of the
reactions of Equations (1) and (2). This latter possibil-
ity seemed plausible on the basis of Jander's conducti-
metric work.

A measurable rate, on the other hand, indicates, of course, a small equilibrium concentration of ions and in addition, a relatively slow rate of one or more of the equilibria of reactions (1) and (2). The slow establishment of the equilibrium concentration of thionyl ions (from either thionyl chloride or sulfur dioxide) and/or the slow recombination of the thionyl ions with sulfite ions (or chloride ions) would materially decrease the rate of exchange from that in the first case above. In this latter case, measurement of the rate of exchange, at various concentrations of the solute, will elucidate the relative rates of these equilibria, assuming the exchange to occur via them. It was hoped that kinetic data of this nature would serve to indicate the exchange mechanism, which might, for instance, involve $SOCl^+$ as an intermediate.

A third case presents itself, that of no appreciable exchange in a reasonable time. This indicates, as with the measurable rate above, a negligible concentration of ions and, furthermore, a negligible rate for one or both of the equilibria of Equations (1) and (2). Such a result would serve to invalidate Jander's whole general ionic concept of this solvent system.

The experimental procedure followed in our work was designed to test for the exchange of radiosulfur between solvent and solute (either a thionyl compound or

tetramethylammonium sulfite) and to determine the rate at
which such exchange occurred. To elucidate the dependence
of rate of exchange on specific conductivity, it was
proposed also to measure the rate of exchange between
thionyl bromide and sulfur dioxide. Thionyl bromide has
a specific conductance (1.2×10^{-5} reciprocal ohms at $-19^{\circ}C$
for a 0.1M solution (9, p.237)) about 10 times as great
as that of thionyl chloride. If the rate of exchange
depended upon the concentration of thionyl ions from thionyl
chloride, it was expected that the substitution of thionyl
bromide for the chloride would increase the rate, perhaps
by a factor of 10. To measure the heat of activation of
the exchange reaction, the exchange was to be measured at
various temperatures to find the temperature dependence.

III. EXPERIMENTAL OUTLINE

A. SULFUR DIOXIDE - THIONYL CHLORIDE. The original procedure proposed for a study of this system involved the use of labeled sulfur dioxide and inactive thionyl chloride with sulfur dioxide in excess, that is, as the solvent. (Because sulfur dioxide and thionyl chloride are miscible in all proportions, either may act as solvent depending upon which is in excess. Jander's work treats sulfur dioxide as the solvent.) A small amount of thionyl chloride and a 10-fold excess of sulfur dioxide were mixed and sealed in a glass bomb tube and allowed to react for a determined length of time. At the end of the run, the thionyl chloride was examined for activity as a measure of exchange. The difficulty of separating a large amount of active sulfur dioxide from a small amount of thionyl chloride deterred us from following this line of work; the procedure gave erratic and unreliable results and was very time-consuming.

After one unsuccessful attempt, radioactive thionyl chloride was prepared and used with inactive sulfur dioxide for the remainder of these experiments. Equation (8) represents the reaction.

$$S^*OCl_2 + SO_2 \rightleftharpoons SOCl_2 + S^*O_2 \qquad (8)$$
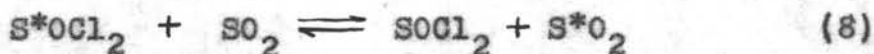
Any radioactivity that had appeared in the sulfur dioxide at the end of a run would represent exchange, it was a

relatively simple matter to remove a small amount of sulfur
dioxide from the bomb and examine it for activity. Runs
were made at various concentrations of thionyl chloride in
sulfur dioxide (some even with thionyl chloride as the
solvent) and at different temperatures in an effort to
determine the rate-dependence on concentration and the
activation energy for the reaction.

B. SULFUR DIOXIDE - THIONYL BROMIDE. It was hoped
that radioactive thionyl bromide could be prepared by a
simple displacement reaction between radioactive thionyl
chloride and potassium bromide. The reaction would be
carried out in liquid sulfur dioxide which would also act
as the solvent in any exchange that occurred between the
thionyl bromide (after it was produced) and sulfur diox-
ide. The method proved useless because an immeasurably
fast exchange appeared to occur between the thionyl com-
pound and sulfur dioxide when the displacement reaction
took place.

Instead, inactive thionyl bromide was prepared and
used with radioactive sulfur dioxide as a solvent. The
separation of these two was relatively easy because of
the difference in boiling points; boiling point of sulfur
dioxide is -10°C (20, p.162), boiling point of thionyl
bromide is 137° C (15, p.2597). Exchange was represented
by appearance of activity in the thionyl bromide.

C. SULFUR DIOXIDE - TETRAMETHYLAMMONIUM SULFITE.
Tetramethylammonium sulfite was prepared from tetramethyl-
ammonium hydroxide by reaction with sulfur dioxide.
Radioactive sulfur dioxide was used as a solvent; experi-
ments were carried out at a low temperature and in as short
a time as practical in an endeavor to reduce the amount of
exchange.   The solid sulfite that remained after the
sulfur dioxide was evaporated off was examined for
activity as a measure of exchange.

IV. EXPERIMENTAL PROCEDURE

A. INTRODUCTORY REMARKS. The radioactive sulfur used in this experimental work was obtained, carrier-free, in neutron irradiated potassium chloride from the Atomic Energy Commission. The isotope used was S^{35}, a negative electron emitter whose particles have a maximum energy of 0.169 Mev and which decays with a half-life of 87.1 days (17, p.591). To recover the radiosulfur, the potassium chloride was dissolved in an aqueous solution of sodium hydroxide and bromine, carrier potassium sulfate was added and the sulfur precipitated as barium sulfate.

All activity determinations were made on sulfur as barium sulfate in a manner which did not differ greatly from a method used previously for radiocarbon (21, pp.133-135). Measurements were made with an end window counter (Tracerlab Model TGC-2, <2.0 milligrams per square centimeter mica). The samples were counted as thin layers of barium sulfate, 3-10 milligrams per square centimeter on cupped planchets. Corrections were applied for decay and self-absorption, the latter from an empirically determined curve. Samples were counted for a sufficiently long time so the relative error of the counts (due to the statistical nature of radioactive disintegration) never exceeded 1% (8, pp.199-212).

Since, almost without exception, the materials with which we worked were more or less volatile at room temperature, high vacuum techniques were extensively employed for the transfer of gases and liquids. Operations were carried out in an all-glass vacuum system at vacua of better than 10^{-5} mm Hg produced by a mercury diffusion pump (protected by a liquid nitrogen trap) backed by a mechanical pump. Pressures were measured by a McLeod gauge of conventional design. All stopcocks and ground joints subject to exposure to thionyl chloride or thionyl bromide were greased with Apiezon "L" grease, a high vacuum stopcock grease, unreactive to halogens; other stopcocks and joints were greased with Apiezon "N" grease, a freer flowing high vacuum grease.

A large amount of inactive sulfur dioxide was used in these experiments; special care was taken with its purification. The sulfur dioxide was drawn from a tank, labelled "SO_3-free", procured from the Ohio Chemical and Manufacturing Company. It was bubbled twice through concentrated sulfuric acid, passed through a tube of closely packed glass wool to remove spray, passed through a phosphorus pentoxide drying tube and collected as a liquid in the vacuum system. To remove any permanent gases, this liquid was pumped on so that considerable ebullience occurred, any permanent gases thus being swept out. The sulfur dioxide was then passed twice more

through phosphorus pentoxide and again collected as a
liquid. Finally, a portion, about one-half of the liquid,
was allowed to evaporate into a storage bulb; the remainder
was discarded. If any permanent gases remained in the
sulfur dioxide after this treatment, a cold finger on
the storage bulb was frozen with liquid nitrogen to
solidify the sulfur dioxide, and the bulb pumped to a
sufficiently low pressure.

B. PREPARATION OF RADIOACTIVE THIONYL CHLORIDE.
Radioactive thionyl chloride was prepared as indicated by
Equation (9) (22, p.303):

$$PCl_5(s) + S^*O_2(g) \longrightarrow POCl_3(l) + S^*OCl_2(l) \qquad (9)$$
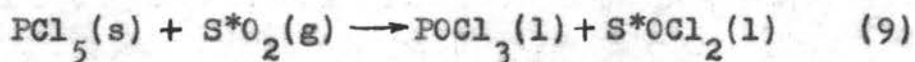
About five millimoles of analytical reagent grade
phosphorus pentachloride (about one gram, a 10-fold ex-
cess) were placed in a reaction tube, of 25 milliliters
capacity, on the vacuum system and evacuated. The system
also had storage bulbs of radioactive sulfur dioxide and
inactive thionyl chloride (Figure I). The radioactive
sulfur dioxide was prepared (free of sulfur trioxide)
from barium sulfate by the method of Johnson and Huston
(12, pp.1841-1842). The thionyl chloride used in this
experimental work was of Eastman White Label grade; it was
further purified, as suggested by Fieser (7, pp.381-382)
by fractional distillation from quinoline to remove any
acidic substances. The purified thionyl chloride was

collected and sealed in a bomb tube with a break tip
(such as in Figure I) and stored in the dark at room tem-
perature until needed.

After attaining a vacuum of better than 10^{-5} mm Hg
pressure, stopcocks A and E were closed and stopcock C
opened. Measuring the pressure on the mercury manometer,
about 0.5 millimoles of active sulfur dioxide, about
seven millicuries per millimole, were condensed into the
reaction tube with liquid nitrogen and stopcock D was
closed. The sulfur dioxide remaining in the vacuum line
was returned to the storage bulb with liquid nitrogen and
stopcock C was closed. The reaction bomb was removed at
ground joint 1 and allowed to stand, with occasional
shaking, for about two hours. A definite moistness in
the phosphorus pentachloride indicated that reaction had
occurred.

At the end of the two hours, the reaction bomb was
replaced on the vacuum system and the system again evac-
uated with stopcocks B, C, and D closed. The thionyl
chloride was frozen with liquid nitrogen and the break tip
cracked to pump off any air that might possibly be in the
thionyl chloride bomb. Finally, stopcock A was closed,
stopcock D opened, and the thionyl chloride, about 14
grams (120 millimoles), warmed and distilled into the re-
action bomb. At this point, the reaction bomb was again
removed from the line, with stopcock D closed, warmed,

and shaken briefly to mix. The reaction bomb now pre-
sumably contained about 4.5 millimoles of phosphorus
pentachloride, 0.5 millimoles of phosphorus oxychloride,
and about 120 millimoles of active thionyl chloride.

To purify the thionyl chloride, it was decided to
carry out three partial distillations; the phosphorus
oxychloride (boiling point is 105°C (22, p.238)) and
excess phosphorus pentachloride (a solid with negligible
vapor pressure (22, p.238)) would remain behind in the dis-
tillations. The reaction bomb was removed at ground joint
3 and replaced by the apparatus of Figure II. The appa-
ratus was evacuated with stopcocks A and E open. After
evacuation stopcock A was closed and D opened. Tube I was
cooled with liquid nitrogen until an estimated 90% of the
liquid in the reaction bomb had distilled into Tube I,
then the connecting tube at point A was sealed shut (with
a gas-oxygen flame). Tube I was warmed and Tube II cooled
until 90% of the liquid was again distilled, then point B
was sealed off. Finally a third 90% distillation was made
into the storage bomb and sealed off at point C.

To check for the presence of unreacted radioactive
sulfur dioxide, the activity of the 10% fraction remaining
in Tube I was compared with the activity of the most
volatile part of the final product, that is, a small
amount of the thionyl chloride was distilled off and count-
ed. The specific activities of the two samples counted

under comparable conditions were 32.4 and 30.6 counts per minute per milligram respectively. This agreement shows there is no fractionation of sulfur dioxide in these two samples. The possible presence of any phosphorus oxy-chloride remaining after these distillations was disregard-ed because in making use of the thionyl chloride in our experiments, only a small amount of the liquid was dis-tilled off and used; this would represent a negligible amount of the oxychloride.

The final yield was about 90 millimoles (about 75% yield) of a pale yellow liquid. This was stored in an all-glass bomb tube in the dark in the absence of air and water. The specific activity of the thionyl chloride was 4.00×10^3 counts per minute per milligram counted as barium sulfate, corrected to 1 March 1950. All experi-mental results from experiments which used this thionyl chloride are corrected for decay to this date; this in-cludes the S^*OCl_2 - SO_2 experiments (Tables III, IV, and V), the S^*OCl_2 - only experiments (Table VI), and S^*OCl_2 - SO_2 - KBr experiments (Table VII). Analysis of the product gave the following results: sulfur, calcu-lated 26.9%, found 26.2%; chlorine, calculated 59.6%, found 58.5%. The vapor pressure, as measured with a sulfuric acid manometer, gave a pressure of 30 mm Hg at 0°C, literature value (1, p.721) is 36 mm Hg at 0°C.

C. PREPARATION OF THIONYL BROMIDE. Thionyl bromide
was prepared from thionyl chloride and potassium bromide
by a method suggested by Jander. Equation (10) represents
the reaction:

$$SOCl_2 + 2KBr \longrightarrow SOBr_2 + 2KCl \qquad (10)$$
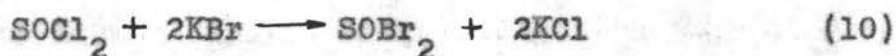
This proceeds because the solubility of potassium bromide
in liquid sulfur dioxide is greater than that of potassium
chloride (3, p.231).

One hundred grams (840 millimoles) of C. P. potassium
bromide was ground with a mortar and pestle until it
passed a 30 mesh screen. This was placed in a 125 milli-
liter flask and a break tip blown on the neck of the flask.
The flask and contents were evacuated while surrounded with
boiling water to drive off adsorbed air and water. The
pumps were closed off and 16 grams (130 millimoles) of
thionyl chloride, prepared as previously described, plus
about 38 grams (590 millimoles) of sulfur dioxide were
distilled into the potassium bromide with liquid nitrogen
and the reaction flask sealed. The six-fold excess of
potassium bromide was used to insure a more complete re-
action.

After warming, the flask was placed on a mechanical
shaker at room temperature. As the reaction proceeded,
the liquid in the flask turned bright orange, the color of
thionyl bromide (15, p.2597). At the end of four hours,
the color change had ceased and it was felt that the

reaction was complete.

The reaction flask was resealed to the vacuum system
which had a sulfuric acid manometer and a container to
receive the sulfur dioxide (and any unreacted thionyl
chloride). The system was evacuated, the pumps closed
off from the system, and the break tip on the flask
cracked. The sulfur dioxide was distilled off with liquid
nitrogen; the distillation proceeded rapidly at first but
slowed after most of the sulfur dioxide had been distilled
off. When the vapor pressure of the liquid in the re-
action flask fell to about 20 mm Hg at room temperature,
the sulfur dioxide collector was replaced with a break tip
bomb tube in which the thionyl bromide was to be stored
until needed. (The vapor pressure of thionyl bromide at
room temperature is about 6 mm Hg (16, p.148).)

The reaction flask was now warmed to about 40°C and
the thionyl bromide collected with liquid nitrogen in the
bomb tube. This distillation was very slow because the
thionyl bromide was spread throughout the large amount of
potassium bromide and chloride in the reaction flask; no
attempt was made to complete this distillation because of
the unreasonably long time that it would have taken. After
collecting as much as possible, the collector bomb tube was
closed off from the reaction flask and opened to the
manometer and pumps. Pumping continued, with agitation of
the thionyl bromide, until the vapor pressure reached 10 mm

Hg pressure with the residual liquid at room temperature. We feel that the excess vapor pressure is due to dissolved sulfur dioxide; the procedure developed for using the thionyl bromide in our experimental work minimizes the effect of any such residual sulfur dioxide.

The final yield was about 12 grams (60 millimoles) or about 45%. Analysis of the product gave the following results: sulfur calculated 15.4%, found 13.9%; bromine calculated 77.0%, found 78.2%. A qualitative test showed only a very small amount of chloride present. In using the thionyl bromide in an experimental run, a three-fold excess was drawn from the stock and evaporated to the desired amount; the vapor pressure of the thionyl bromide, after this treatment, was 7 mm Hg.

D. PREPARATION OF TETRAMETHYLAMMONIUM PYROSULFITE.[1] Tetramethylammonium pyrosulfite was prepared by two methods suggested by Jander (10, pp.304-307; 11, p. 67; see also 2, pp. 59-60); the raction is given by Equation (11).

$$2Me_4NOH + 2SO_2 \longrightarrow (Me_4N)_2S_2O_5 + H_2O \qquad (11)$$
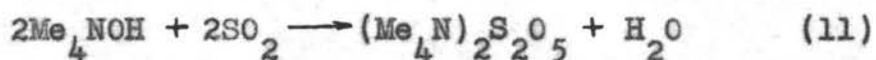
Preparation by the first method was carried out in a high vacuum apparatus (Figure III). About 20 milliliters of 10% tetramethylammonium hydroxide solution

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1. Tetramethylammonium sulfite crystallizes with one molecule of sulfur dioxide to give the pyrosulfite, $(Me_4N)_2S_2O_5$.

(Eastman White Label grade) was placed in arm A and frozen. The apparatus was evacuated and stopcock 1 closed. Arm C was cooled with a Dry Ice-acetone bath and the hydroxide solution warmed to room temperature. As much water as possible was removed from the solution; tetramethylammonium hydroxide forms a number of different hydrates and it is impossible to form the anhydrous salt (19, pp.958-960). After dehydration, stopcock 2 was closed, arm C removed, dried, and replaced. The apparatus was again evacuated and sulfur dioxide condensed as a liquid with a Dry Ice-acetone bath around the salt in arm A. A cloudy, yellow-orange solution resulted. The sulfur dioxide was distilled off and the system evacuated to remove the water remaining on the salt. Sulfur dioxide was again condensed as a liquid in arm A to dissolve the salt; the solution was now practically free of cloudiness.

To remove the residual suspended matter, arm B was cooled with a Dry Ice-acetone bath and the liquid solution poured from A to B through the sintered glass filter. The sulfur dioxide was then distilled back to A and repoured under the same conditions until A was free of the salt. The clear orange-yellow solution in B was evaporated and finally exhaustively pumped to dryness.

This series of operations was carried out a number of times; the products were combined and mixed and recrystallized from liquid sulfur dioxide to insure a homogeneous

sample. Analysis showed 20.6% sulfur (gravimetric) and 18.6% sulfur (as sulfite); calculated sulfur is 21.9%. The percent ratio of sulfite sulfur to total sulfur is 90.4%. This preparation will be called "Prep I".

After considerable difficulty with the apparatus used in the preceding preparation, specifically with the sintered glass filter becoming plugged, a more simplified procedure and apparatus were adopted for the second preparation. A large tube containing about 30 milliliters of 10% tetramethylammonium hydroxide was attached to the vacuum system and evacuated. Purified sulfur dioxide gas was admitted to the tube and allowed to dissolve with agitation of the solution until the liquid was saturated. The solution was evaporated to dryness by pumping off the water; liquid sulfur dioxide was condensed in the tube with a Dry Ice-acetone bath to dissolve the salt. At this point, the salt gave a cloudy orange-yellow solution.

To remove the insoluble material, the cloudy suspen- sion was allowed to settle and the clear supernatant liquid decanted, in the presence of air, into a second reaction tube; this latter tube contained boiling sulfur dioxide to minimize contact with air. This procedure was repeated twice. While the method may appear somewhat questionable, analysis showed a reasonably pure product. This is called "Prep II" and gave, upon analysis, 19.9%

sulfur (gravimetric) and 18.1% sulfur (as sulfite);
calculated sulfur is 21.9%. The percent ratio of sulfite
sulfur to total sulfur is 91.1%.

E. RADIOACTIVE SULFUR DIOXIDE - THIONYL CHLORIDE
EXPERIMENTS. Preliminary exchange experiments, using
labeled sulfur dioxide appeared to indicate a rapid ex-
change, but yielded erratic and questionable results. It
therefore seemed best to prepare labeled thionyl chloride,
in the hope of getting better data, as indicated in the
Experimental Outline section. The foregoing preliminary
results suggested the exchange process itself as a pre-
parative method:

$$SOCl_2 + S^*O_2 \rightleftharpoons S^*OCl_2 + SO_2 \qquad (12)$$
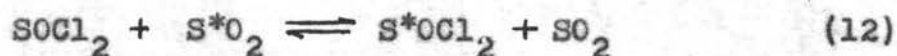
A small amount of highly active sulfur dioxide was mixed
with a relatively large amount of thionyl chloride and the
mixture was allowed to stand at room temperature for
activity equilibration. It was felt that equilibration
would be rapid, a matter of hours, and that the difference
in the vapor pressures of the sulfur dioxide and the
thionyl chloride (boiling point is $78.8^{o}C$ (20, p.162)
would allow a clean separation of the products. It was
necessary for our work to have as little radioactive sulfur
dioxide as possible present as an impurity in the thionyl
chloride; such an impurity would appear as an instantaneous
exchange in an experimental run.

Although unsuccessful as a preparative method, this mixture with thionyl chloride as a solvent provided a considerable amount of data to compare with our other experimental work which was performed with sulfur dioxide as solvent.

A break-tip bomb tube was used as a reaction vessel; to this was sealed a bomb tube of thionyl chloride containing about 10 grams (90 millimoles) purified as previously described. These two bomb tubes together were attached to the vacuum system which also held a storage bulb containing the previously prepared radioactive sulfur dioxide. The system was evacuated and the thionyl chloride frozen with liquid nitrogen. The break tip on the thionyl chloride bomb was cracked and any permanent gases present pumped off; the pumps were then closed off.

The storage bulb was now opened to the system and, cooling the reaction bomb tube with liquid nitrogen, the sulfur dioxide (about four millimoles whose activity was 6000 counts per minute per milligram counted as barium sulfate) was transferred to the bomb tube. Meanwhile, the thionyl chloride was warmed to room temperature and distilled into the reaction tube. Finally, the reaction bomb was sealed off, warmed to room temperature, and wrapped to prevent photodecomposition while the reaction proceeded. The mole ratio of sulfur dioxide to thionyl chloride was about 1:22.

It was decided that 14 days reaction time was
sufficient for the reaction of Equation (11) to reach
equilibrium; at equilibrium, 90/94 of the activity would
be present in the thionyl chloride. At the end of this
time, two break tip bomb tubes were sealed to the reaction
tube and the system evacuated and sealed off from the
vacuum pumps. The reaction bomb tip was cracked and an
estimated one quarter of the reaction mixture was distilled
into one of the empty bomb tubes by cooling it with liquid
nitrogen. This fraction was called the "sulfur dioxide
fraction" and it was hoped that it contained virtually all
of the sulfur dioxide. (In addition, it contained about 20
millimoles of thionyl chloride.) The three quarters
residue from this distillation, the "thionyl chloride
fraction" was presumably free of sulfur dioxide; it was
collected and sealed off in the other empty bomb tube, to
be stored until needed further.

An analysis of the thionyl chloride fraction shortly
after the separation showed that but little exchange had
taken place; experiments were undertaken to determine the
exact specific activity of the thionyl chloride.

To determine the specific activity of the thionyl
chloride and to test for the presence of radioactive
sulfur dioxide in the thionyl chloride fraction, all but
a few drops (about 1%) of this fraction was distilled to a
new bomb tube; the 1% remainder was distilled into aqueous

sodium hydroxide, oxidized with bromine water, and pre-
cipitated and counted as barium sulfate. We considered
such a distillation as certain to remove any sulfur dioxide
which might be present and leave essentially pure thionyl
chloride. Such a separation was made 14 days after the
initial 1/4 - 3/4 separation and repeated 21 days later
(a total of 35 days after the initial separation). These
two samples of pure thionyl chloride are designated as
"$SOCl_2$ #1" and "$SOCl_2$ #2" respectively in Table I.

The above procedure would give the activity of pure
thionyl chloride; as a basis of comparison it was
necessary to measure the activity of the liquid from which
the thionyl chloride was taken and which conceivably might
contain some active sulfur dioxide. Samples, again about
1%, were taken by pouring some of the liquid, in the
absence of air, into a small container blown onto the bomb
tube. The container was sealed off from the bomb, cracked,
and the contents absorbed quantitatively in sodium hydrox-
ide and treated as above. Two samples were taken, one
each on 14 days and 35 days after the original 1/4 - 3/4
separation, that is, at the same time as the pure thionyl
chloride samples were taken. These two liquid samples are
designated "Equilibrium Mixture #1" and "Equilibrium Mix-
ture #2" respectively in Table I.

TABLE I

Activity of samples from "SOCl$_2$ fraction"

Sample	Days After 1/4 - 3/4 Separation	Specific Activity (cpm/mg)	% Exchange
SOCl$_2$ #1	14	2.65[a]	<1
SOCl$_2$ #2	35	2.65	<1
Equilibrium Mixture #1	14	14.9	-
Equilibrium Mixture #2	35	24.4	-

a. If complete activity equilibration had taken place, the specific activity of the pure thionyl chloride would have been 280 counts per minute per milligram.

From the data in this table, we may draw two conclusions. In the first place, the similarity of the activities of the two thionyl chloride samples shows that no appreciable exchange has taken place in 21 days; this is the mixture from which most of the sulfur dioxide has been removed and the S*O$_2$:SOCl$_2$ mole ratio is approximately 1:350. We may assume also that there has been no exchange in the 14 days between the time of the 1/4 - 3/4 separation and the time that the first thionyl chloride sample was taken. Secondly, there has been less than 1% exchange in the 14 days between the original mixing of the 4 millimoles of sulfur dioxide and the 90 millimoles of thionyl chloride (a 1:22 mole ratio) and the 1/4 - 3/4 separation. The small specific activity of the "pure" thionyl chloride

might perhaps be due to a small residual amount of sulfur dioxide; in any case, 1% may be considered an upper figure for the exchange.

The discrepancy in the specific activities of the two equilibrium mixture samples might be due to different amounts of vapor (richer in the more volatile, more active sulfur dioxide) trapped off when samples were drawn. It might also be noted that the separation of the original reaction mixture into a "thionyl chloride fraction" and a "sulfur dioxide fraction" was clean-cut enough, as shown by the specific activity of the liquid thionyl chloride of about 20 counts per minute per milligram due to residual sulfur dioxide as compared to an expected specific activity of 280 counts per minute per milligram for the thionyl chloride itself.

To complete this study of thionyl chloride as a solvent, the "sulfur dioxide fraction" was analysed as above; the mole ratio in this fraction of $S^*O_2:SOCl_2$ was about 1:5 (that is, 4 millimoles of sulfur dioxide to about 20 millimoles of thionyl chloride). The results are given in Table II.

TABLE II

Activity of Samples from "SO$_2$ fraction"

Sample	Days After 1/4 - 3/4 Separation	Specific Activity (cpm/mg)	% Exchange
SOCl$_2$	35	3.2[a]	~1
Equilibrium Mixture	53	910	-

a. If complete activity equilibration had taken place, the specific activity of the pure thionyl chloride would have been 280 counts per minute per milligram.

The fact that the activity of "pure" thionyl chloride present for 35 days at this mole ratio has not increased significantly over the value cited in Table I indicates negligible exchange at this concentration.

F. SULFUR DIOXIDE - RADIOACTIVE THIONYL CHLORIDE EXPERIMENTS. A majority of these experiments were carried out at a 1:10 mole ratio of SOCl$_2$:SO$_2$; the quantities of materials involved at this ratio were convenient to handle and the separation procedure posed no great problem. However, runs were also carried out at mole ratios of about 1:50 and 1:200 of SOCl$_2$:SO$_2$ both to determine the effect, if any, of concentration on rate and to measure the rate at a concentration similar to that at which Jander has measured the conductance of thionyl chloride in sulfur dioxide (namely 0.1 M, a 1:250 mole ratio). The following

experimental procedure was developed for the 1:10 mole
ratio runs and modified as needed for the more dilute runs.

Several exploratory runs were necessary to refine the
procedure to a point where the blank for a run, that is,
the apparent exchange for a bomb separated only minutes
after it was made, was less than 10%. A number of runs
were then made for short periods of time, up to a week,
but no appreciable exchange was found. A set of four
bombs was then prepared; we planned to open these over a
sufficiently long period of time to detect any very slow
exchange.

Runs were carried out in small glass bombs of about
five milliliters volume constructed from a 10/30 $
ground joint as indicated by Figure IV(a). In a run, one
of these was attached by means of the 12/30 ground joint
to the vacuum system which also had storage and dosage
bulbs for radioactive thionyl chloride and inactive sulfur
dioxide and a mercury manometer. On attaining a high
vacuum in the system, the pumps were closed off and about
5.5 millimoles of sulfur dioxide (measured with the
manometer from a known dosage volume) were condensed into
the bomb tube. Because thionyl chloride attacks mercury,
the thionyl chloride was dosed out in an almost all glass
apparatus. (A small amount of contact with stopcock
grease was unavoidable). The storage bulb of thionyl
chloride was cooled with a water-ice bath so its vapor

pressure was accurately determined. Thionyl chloride was allowed to evaporate at this vapor pressure into its previously evacuated dosage bulb for exactly 10 minutes; the dosage bulb was then closed off from the thionyl chloride storage bulb and opened to the bomb and the thionyl chloride distilled into the bomb with liquid nitrogen. Several tests with this empirical procedure showed that the dose was 0.542 $\pm$ .004 millimoles of thionyl chloride. The bomb was sealed off at point A, warmed to room temperature, placed in a blackened tube to prevent photodecomposition of the thionyl chloride, and set in a 25.0 $\pm$ 0.1° C water bath thermostat until ready to be analysed.

Separation was carried out in the apparatus represented by Figure V. By means of its ground joint, the bomb was very carefully attached to the female 10/30 $\mathfrak{T}$ ground joint; the capillary tip of the bomb was bent at such an angle as to be broken by rotating the bomb in the female ground joint until the capillary tip impinged on a bubble blown on the inside wall of the female joint. A collector test tube, containing about 10 milliliters of 1 N sodium hydroxide, with a seal-off point and a 12/30 $\mathfrak{T}$ male ground joint was attached to the other arm of the apparatus. The arms were attached to a flask of about 500 milliliters capacity; this volume of sulfur dioxide at a vapor pressure

of 2 cm. Hg (its vapor pressure at Dry Ice temperature)
will give about 100 milligrams of barium sulfate.

The bomb tube and sample were cooled with a Dry Ice-
acetone bath and the sodium hydroxide was frozen with
liquid nitrogen. The system was evacuated with all
stopcocks open; at a sufficiently low pressure, stopcock
C was closed and the bomb rotated in the ground joint to
crack off the capillary tip. After allowing the bomb
sample to come to pressure equilibrium, stopcock A and B
were closed and stopcock C opened for exactly three
minutes; this allowed a small amount, about 10%, of the
sulfur dioxide to evaporate into the 500 milliliter flask;
a smaller amount of thionyl chloride was carried over also,
of course.

Stopcock A was next opened and the contents of the
flask distilled onto the frozen sodium hydroxide; this
tube was then sealed off and warmed to room temperature.
A new collector test tube was placed on the apparatus at
the 12/30 joint and, after evacuation, the remainder of
the sample distilled from the bomb into the collector which
was sealed off and warmed to room temperature. The first
collector contained a sample of practically pure sulfur
dioxide from the bomb; the other contained a mixture of
sulfur dioxide and thionyl chloride. After shaking each
to absorb and hydrolyse the contents, they were cracked
open, the contents oxidized with bromine, precipitated,

and counted separately as described before. The results
of these runs are tabulated in Table III; as mentioned
below, at 100% exchange, the specific activities of the
thionyl chloride and sulfur dioxide fractions would be
equal and this holds true for all thionyl chloride and
thionyl bromide runs described here. Figure VIII shows
graphically the variation of log (100 - % exchange) with
time.

TABLE III

Data from $S^*OCl_2 : SO_2$ 1:10 runs at 25°C

Run	Time in Hours	Mole Fr. $SOCl_2$	Sp. Act. SO_2[a] Fr. (cpm/mg)	Sp. Act. $SOCl_2$[a] Fr. (cpm/mg)	% Exchange
--	0	--	-	-	3[b]
1	137	0.089	19.6	395	5.3
2	639	0.088	56.4	346	17.3
3	1817	0.088	128	362	37.0
4	3012	0.087	58.5	388	16.0

a. Decay corrected to 1 March 1950
b. Extrapolated.

For the sake of clarity, a complete sample calcula-
tion of a percent exchange is given here. Let us consider
run #1 above. The mole fraction of thionyl chloride in
0.089; this represents the standard dose of 0.542 milli-
moles. The mole fraction of sulfur dioxide is then 0.911
and this is equivalent to 5.55 millimoles of sulfur
dioxide. The total number of millimoles in the sample
is 6.09; this will produce 1420 milligrams of $BaSO_4$ of

which 126 milligrams is due to thionyl chloride and about
1290 milligrams is due to the sulfur dioxide. As men-
tioned before, the separation procedure gives a sulfur
dioxide fraction containing the equivalent of 100 milli-
grams of $BaSO_4$; the remainder, 1320 milligrams, is
collected in the thionyl chloride fraction.

SO_2 Fraction: 100 mg. X 19.6 cpm/mg . . 0.02×10^5 cpm
$SOCl_2$ Fraction: 1320 mg. x 395 cpm/mg . $\underline{5.21 \times 10^5}$
Total experimental activity . . . . . . $\overline{5.23 \times 10^5}$ cpm

Calculated Total activity: Pure $SOCl_2$ has an activ-
ity of 4.00×10^3 cpm/mg counted as $BaSO_4$.
4000 cpm/mg X 0.542 mmoles X 233 mg/ mmole . .
5.06×10^5 cpm

This difference of 3% between the calculated and experi-
mental total activities is quite reasonable as an experi-
mental error. The difference between calculated and ex-
perimental total activities were, in general, in line with
this figure.

If 100% exchange had taken place, the activity would
have been distributed on a mole fraction basis, that is,
the specific activities of the sulfur dioxide and thionyl
chloride would have been equal but 0.542/6.09 of the
activity would have remained with the thionyl chloride and
5.55/6.09 of the activity would have gone to the sulfur
dioxide. We can then calculate the specific activity of
the sulfur dioxide at 100% exchange and compare it with
the actual specific activity found experimentally to

determine the percent exchange.

5.55/6.09 . . . . . 0.911

For 100% exchange:
Specific Activity of the SO_2 . $\dfrac{0.911 \times 5.23 \times 10^5 \text{ cpm}}{1290 \text{ mg}}$

. 370 cpm/mg

Actual % Exchange . . . . $\dfrac{19.6 \text{ cpm/mg}}{370 \text{ cpm/mg}} \times 100$

. . . . 5.3%

The runs made at $61 \pm 1^\circ C$ were similar to the runs at $25^\circ C$ except that the bomb tube was sealed inside a thick walled tube containing some liquid sulfur dioxide to protect the capillary tip from breaking under the high pressures developed by the reaction mixture. These runs were made over a shorter period of time in expectation of a more rapid rate of exchange. A series of three bombs were run; their results are given in Table IV, Series 1.

TABLE IV

Data from $S^*OCl_2:SO_2$ 1:10 runs at $61^\circ C$

Run	Time in Hours	Mole Fr. $SOCl_2$	Sp. Act. SO_2[a] Fr. (cpm/mg)	Sp. Act. $SOCl_2$[a] Fr. (cpm/mg)	% Exchange
			Series 1		
–	0	–	–	–	8[b]
1	138	0.090	42.3	372	12.1
2	407	0.090	78.1	427	19.4
3	1149	0.089	63.3	384	17.5
			Series 2		
1	427	0.092	18.9	383	5.3
2	767	0.092	28.1	385	7.8

a. Decay corrected to 1 March 1950.
b. Extrapolated.

It was felt that the data of series 1 were insufficient, two more runs were made, results given in Table IV, Series 2. These two series were not directly comparable because of differences in the blanks. These results are shown graphically in Figure IX.

It was planned to make the more dilute runs by decreasing the amount of thionyl chloride by factors of 5 and 20 to 0.11 millimoles and 0.027 millimoles for the 1:50 and 1:200 runs respectively. Preliminary experiments showed an excessive blank when using such small quantities of thionyl chloride; it was decided instead to increase the amount of sulfur dioxide and use a different type of bomb for the runs. This bomb is shown in Figure IV(b).

The bomb was attached to the vacuum system by the 12/30 ground joint and evacuated. Sulfur dioxide was condensed as a liquid, by means of a Dry-Ice-acetone bath, into a tube marked to hold 4.0 milliliters (about 6.4 grams, 100 millimoles). This sulfur dioxide was transferred, by liquid nitrogen, to the bomb and a dose (0.54 millimoles for the 1:200 run, 2.2 millimoles for the 1:50 run) of thionyl chloride added to the bomb. The bomb was sealed off at point A, warmed to room temperature and kept in the dark at $25.0 \pm 0.1^{\circ}C$.

Eight 10/30 ground joints, each with a capillary breaktip and a sealoff point, were incorporated into the bomb. To take a sample of the sulfur dioxide for activity

analysis, one of the ground joints would be attached to the separation apparatus, described above in the section on 1:10 runs, and evacuation and cracking of the tip carried out as above. When the sulfur dioxide sample (about 0.5% of that present) had been drawn off, the bomb was sealed off at the point below the break-tip ground joint and returned to the water-bath. The procedure enabled us to use the same reaction mixture for eight determinations; after taking the eighth sample, the remainder of the reaction mixture was removed and an activity analysis and gravimetric sulfate determination performed to check the quantities of the reactants.

Analysis of the 1:50 bomb showed that the actual mole ratio of $SOCl_2:SO_2$ was 1:58. The activity of the final residue was 72.2 counts per minute per milligram; this is the activity of the sulfur dioxide samples for 100% activity equilibration. Two 1:200 bombs were run: Bomb #1 had an actual mole ratio of 1:161; the specific activity of the sulfur dioxide for 100% equilibration would be 25.4 counts per minute per milligram. Bomb #2 had an actual mole ratio of 1:205 and the activity of its sulfur dioxide would be 20.7 counts per minute per milligram. Results of these three bombs are given in Table V and graphed in Figures X and XI.

TABLE V

Data on 1:50 and 1:200 Runs at 25°C

Run	Time in hrs.	Sp. Act. of SO_2[a] (in cpm/mg)	% Exchange
1:50	0	-	5[b]
	15	5.4	7[c]
	112	4.44	6.1
	566	5.88	8.1
	1022	14.0	19.4
	1335	5.84	8.1
	1503	8.15	11.3
	1673	9.45	13.1
1:200 Bomb #1	0	-	7[b]
	61	1.55	6.1
	154	3.53	13.9
	522	4.66	18.3
	903	8.40	33.1
	1003	3.95	15.5
1:200 Bomb #2	0	-	18[b]
	69	4.00	19.3
	717	6.30	30.4
	1171	6.74	32.6
	1483	3.33	16.1
	1652	3.44	16.6
	1831	4.72	22.8

a. Decay corrected to 1 March 1950.
b. Extrapolated.
c. Very poor counting sample.

Thionyl chloride is known to decompose with time in a manner represented by Equations (13) and (14) (5, p.60; 22, p.306).

$$SOCl_2 \longrightarrow SO + CL_2$$

$$2SO \longrightarrow S + SO_2 \tag{13}$$

$$4SOCl_2 \longrightarrow S_2Cl_2 + 2SO_2 + 3Cl_2 \tag{14}$$

In each of these decompositions, if radioactive thionyl chloride is the starting material, a more volatile radio-sulfur compound is one of the products. This would appear as an apparent exchange when the separation is made at the end of a run.

To determine whether or not such decomposition might be taking place, small amounts of radioactive thionyl chloride (equal to the amount of thionyl chloride in a normal 1:10 run) were sealed in several small glass ampules and stored in the dark at $25^{\circ}C$ and $61^{\circ}C$ for various lengths of time. At the end of the run, the thionyl chloride ampule was sealed in an apparatus as shown in Figure VII. The apparatus was evacuated, about 5.5 milli-moles of sulfur dioxide (the amount used in a 1:10 run) was dosed in and condensed below point B, and the apparatus sealed off at A. The apparatus was shaken to break the thionyl chloride ampule, and the thionyl chloride also distilled over into the leg below point B. This leg was then sealed off at B and treated thereafter as a normal 1:10 run bomb except that it was stored at Dry Ice tem-perature or colder until separation was made, and the time between preparation of the bomb and separation never

exceeded 24 hours. These two precautions held to a minimum any exchange that might occur. Thus, any "exchange" found in these runs would be only apparent exchange; it would actually be due to the decomposition of the radioactive thionyl chloride. The results of this work are given in Table VI.

TABLE VI

Data from $SOCl_2$ - only runs

Time in hours	Mole Fr. $SOCl_2$ [a]	Sp. Act. SO_2 Fr. (cpm/mg)	Sp. Act. $SOCl_2$ Fr. (cpm/mg)	% Exchange
		Runs at 25°C.		
432	0.089	30.0	364	8.5
1153	0.090	33.2	429	8.3
1827	0.089	49.4	482	11.0
2515	0.090	34.6	440	8.4
		Runs at 61°C.		
579	0.090	35.8	445	8.6
888	0.089	38.0	409	9.9
1034	0.095	40.5	419	10.3

a. After mixing with inactive sulfur dioxide at end of run.

These runs show that the decomposition of thionyl chloride alone is negligible over the periods of time in which our experimental runs were made. Another possibility must be considered, namely, that thionyl chloride decomposes more rapidly in a sulfur dioxide solution. The reactions of sulfur and sulfur monochloride in the presence of chlorine are rather complicated (22, pp.297-300) but, in the hope of finding elemental sulfur from

the decomposition of thionyl chloride, the inside walls
of the bombs from the 1:10 run for 3000 hours at 25°C
and from the 1:50 and the two 1:200 runs were monitored
for radioactivity. Elemental sulfur, if present in the
reaction mixture, would be expected to deposit on the
walls; although the activity of the original thionyl
chloride was great enough so the sulfur from as little as
10% decomposition could be detected, no activity was found
on the walls of the bomb tubes. Any appreciable decompo-
sition, then, must be by a mechanism which does not pro-
duce sulfur or any other non-volatile sulfur compound,
still containing the radioactivity.

G. SULFUR DIOXIDE - POTASSIUM BROMIDE - RADIOACTIVE
THIONYL CHLORIDE EXPERIMENTS. It was originally intended
to study the thionyl bromide - sulfur dioxide system
using radioactive thionyl bromide prepared by a method
of Jander (9, p.232) as indicated by Equation (15):

$$S^*OCl_2 + 2KBr \longrightarrow S^*OBr_2 + KCl \quad \text{(in liquid } SO_2) \quad (15)$$
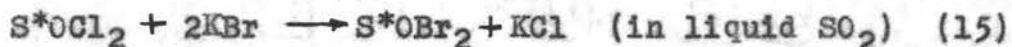
We have found this reaction fast and, by mixing the
correct proportions of radioactive thionyl chloride and
sulfur dioxide in the presence of potassium bromide, it
appeared, beforehand, that exchange would proceed mainly
between the sulfur dioxide and the thionyl bromide. The
same bomb could be used as a reaction vessel for the re-
action of Equation (13) and then contain the reaction

mixture for the exchange experiment.

Exploratory experiments were carried out to measure
the zero time blank for the reaction; the procedure was
similar to that used in the 1:10 runs described in the
thionyl chloride - sulfur dioxide section except that
about 350 milligrams (a 3-fold excess) of crystalline
C. P. potassium bromide was added to the reaction bomb
before it was put on the vacuum system. After being
filled and sealed off, the bomb was warmed to room tem-
perature for about ten minutes and shaken. It was then
held at liquid nitrogen temperature until separated;
separation was effected, as with the thionyl chloride
bombs, on the apparatus of Figure V. After some diffi-
culties with initial runs, such as bombs run with an in-
sufficient amount of potassium bromide, a series of four
bombs was run; the results are given in Table VII.

TABLE VII

Data from S^*OCl_2 - SO_2 - KBr Runs

Run	Mole Fr. $SOBr_2$[a]	Sp. Act. SO_2[b] Fr. (cpm/mg)	Sp. Act. $SOBr_2$[b] Fr. (cpm/mg)	% Exchange
1	0.091	166	388	45
2	0.084	883	252	300
3	0.092	622	334	175
4	0.092	340	356	96

a. Assuming 100% conversion from thionyl chloride.
b. Decay corrected to 1 March 1950.

The results were rather discouraging from the standpoint of a preparation of radioactive thionyl bromide. These four runs were made in an identical manner insofar as experimentally possible; the high activities of the more volatile sulfur dioxide fraction indicate some phenomena other than a simple catalysed exchange process.

H. RADIOACTIVE SULFUR DIOXIDE - THIONYL BROMIDE EXPERIMENTS. As mentioned previously, exchange experiments were to be run on mixtures of thionyl bromide and sulfur dioxide, in contrast to thionyl chloride and sulfur dioxide, in an attempt to correlate the difference (if any) of rates of exchange with the ten-fold difference in specific conductivity of the two solutes dissolved in sulfur dioxide. The use of a less volatile, non-radioactive solute in these experiments necessitated some

changes in the experimental techniques.

The vapor pressure of thionyl bromide is so low as to render prohibitive its dosage by gaseous methods as used with thionyl chloride. Instead, thionyl bromide was dosed out as a liquid. One end of a short piece of capillary tubing was sealed to the vacuum system; the other end was sealed off. From the molecular weight and density of thionyl bromide and the diameter of the capillary bore, we calculated the length of capillary necessary to give 0.5 millimoles of thionyl bromide; this length was so marked with a scratch. Experimental determinations of the weight of thionyl bromide delivered from this volume show that it will contain $0.499 \pm .002$ millimoles of thionyl bromide.

In practice, about a four-fold excess of thionyl bromide was condensed into the capillary by means of liquid nitrogen from the stock of thionyl bromide. The storage bulb was closed off and the capillary opened to the vacuum pumps; on gradual warming to room temperature, any volatile compounds present were distilled off, the thionyl bromide melted and ran down to fill the capillary tubing. Pumping continued, then, until the level of the thionyl bromide dropped, by evaporation, to the scratch mark.

The procedures of filling the bomb, sealing, etc.,

follow the procedures used with the 1:10 thionyl chloride runs (except, of course, radioactive sulfur dioxide was used here); the separation procedure followed was different, however, and the apparatus of Figure VI was used. The bomb was carefully attached to the 10/30 ground joint and two test tubes, each with about 10 milliliters of 1N sodium hydroxide, were attached, by means of ground joints, to ground joints 1 and 2 and cooled by liquid nitrogen. All stopcocks were opened and the system evacuated. Stopcocks B and D were closed and stopcock C turned so the bomb was connected to the 185 milliliter flask. The reaction mixture was momentarily cooled with liquid nitrogen (to prevent any bumping of the reaction mixture when the tip of the bomb was cracked off), the bomb was rotated to crack the tip, and an ice bath placed around the flask and bomb as shown. The ice bath was used to provide reproducible conditions; it was deemed impossible to remove all of the sulfur dioxide from the thionyl bromide. However, a small amount, unvarying from run to run, would appear only as a blank in the experiment. About 10 minutes were necessary for the bomb and flask to reach pressure equilibrium.

The amount of sulfur dioxide in the bomb was sufficient to produce almost one atmosphere pressure in the flask; this was too high a pressure to remove enough of

the sulfur dioxide from the thionyl bromide, which, being
relatively non-volatile, remains behind in the bomb.
Consequently, it was necessary to distill the sulfur
dioxide into one of the sodium hydroxide collector tubes,
after closing stopcock C and opening D. Stopcock D was
closed after all of the sulfur dioxide was distilled from
the flask, and C opened to the flask again for another ten
minutes; this reduced the amount of sulfur dioxide in the
thionyl chloride to a reasonable value. At the end of the
ten minutes, stopcock A was closed and C reversed so the
thionyl bromide distilled into the second sodium hydroxide
collector tube. Stopcock D was also opened and the small
amount of sulfur dioxide present in the flask was added to
that already in collector tube 1.

The results of a number of runs made at $25^{\circ} \pm 0.1^{\circ}C$
at an approximately 1:10 mole ratio of $SOBr_2:SO_2$ are given
in Table VIII.

TABLE VIII

Data from $SOBr_2$ - S^*O_2 runs

Run	Time in hours	Mole Fr. $SOBr_2$	Sp. Act. $SOBr_2$ Fr. (cpm/mg)	Sp. Act. SO_2 Fr. (cpm/mg)	% Exchange
Blank	0	0.081	17.9	412	4.7 ⎫
Blank	0	0.085	18.8	387	5.2 ⎬ Ave.
Blank	0	0.085	11.9	392	3.3 ⎭ 4.4
1	71	0.089	18.2	401	4.9
2	170	0.092	20.3	400	6.1
3	491	0.091	19.6	389	5.4
4	503	0.093	25.8	422	6.6
5	701	0.092	30.6	407	8.1
6	816	0.092	30.1	409	7.9

These data seem to indicate a very slight exchange, a
matter of less than 4% in 800 hours (this represents a
half-time of activity equilibration greater than 10,000
hours). Unfortunately, this experiment cannot be extended
because, contrary to Jander's data (3, p.259), thionyl
bromide decomposes in liquid sulfur dioxide. We have
noticed a deepening of the color of dissolved thionyl
bromide after two weeks and a slight cloudiness when aged
solutions are cooled with Dry Ice which does not appear
with a new solution. These observations would seem to
indicate decomposition of the thionyl bromide; our experi-
ments are valid, nonetheless, since a slight decomposition,
as much as 20-25%, would not materially affect the percent
exchange. In these experiments, we are looking for radio-
activity in the thionyl bromide; a decomposition, while

changing the mole ratio slightly, would not materially add activity to the thionyl bromide fraction.

I. TETRAMETHYLAMMONIUM PYROSULFITE EXPERIMENTS. Since tetramethylammonium pyrosulfite is a solid at room temperature, exchange experiments involving it were far simpler; separation of solvent from solute involved a simple distillation. We found the rate of exchange too fast to measure even at Dry Ice temperatures; for this reason only three experimental runs were made.

Run #1 was made with Preparation #2 described above; 160 milligrams (0.55 millimoles) were placed in a reaction bomb vessel and attached, by means of a ground joint, to the vacuum system. The system was evacuated and about one milliliter of liquid radioactive sulfur dioxide (22 millimoles) dosed in, measured with a dosage volume and a mercury manometer. The reaction vessel was closed off, agitated to hasten solution, and warmed to $-21^{\circ}C$, at which temperature it remained for $2\frac{1}{2}$ hours. At the end of this time, an aliquot of the sulfur dioxide was removed for activity analysis; the remainder was distilled back to the storage bulb by means of liquid nitrogen. The tetramethylammonium pyrosulfite was removed from the reaction vessel, dissolved in sodium hydroxide, oxidized, and precipitated as described before. The sulfur dioxide underwent the same treatment.

Run #2 was made under the same conditions with material from Preparation #2 except that the solution was not allowed to warm above Dry Ice temperature and, further, the addition of the sulfur dioxide to the salt, the dissolving process, and the removal of the sulfur dioxide were expedited so the total time of contact of solute and solvent was only 20 minutes. Run #3 was identical with Run #2 except that Preparation #1 was used.

It will be remembered, from the analyses of these two preparations given above in one of the preceding sections, that not all of the sulfur in our tetramethylammonium pyrosulfite exists in the +4 state; undoubtedly a certain unavoidable amount of oxidation occurs in its preparation. The experiments described above are designed to measure the exchange of radioactive sulfur dioxide with sulfite sulfur; it is reasonable, therefore, to compute the percent exchange on the basis of the percent of sulfite sulfur, compared to total sulfur present in the compound. These results are given in Table IX.

TABLE IX

Data from Tetramethylammonium Pyrosulfite Runs

Run	Salt Used	Time in minutes	Sp. Act. SO_2 cpm/mg	Sp. Act Salt cpm/mg	% Exchange
1	#2[a]	155	144	132	100
2	#2	20	105	91.0	95
3	#1[b]	20	105	75.3	80

a. Percent ratio of sulfite sulfur to total sulfur was 91.1%.
b. Percent ratio of sulfite sulfur to total sulfur was 90.4%.

These results appear to represent practically complete exchange in the time of the experiments. Experimental difficulties precluded a shorter time of run, the desirability of which is indicated by the result obtained in Run #3.

V.   DISCUSSION OF RESULTS

A.   SULFUR DIOXIDE - POTASSIUM BROMIDE - THIONYL CHLORIDE EXPERIMENTS.   While not wholly germane to the main investigation, we nevertheless felt that the results of the experiments of mixing sulfur dioxide and potassium bromide with active thionyl chloride were very interesting. For any equilibrium exchange process, the maximum possible exchange is 100%, corresponding to complete randomization of the activity.   One might conceive possibly of a mechanism which would transfer activity essentially irreversibly from the thionyl chloride to the sulfur dioxide; such a process, however, would yield a specific activity for the sulfur dioxide fraction not more than about 10% greater than that of the thionyl chloride fraction because of the large mole excess of sulfur dioxide in the system, i.e., an apparent exchange of 110%.   The results of runs 2 and 3 (see Table VIII) show a much greater value than this, 300% and 175% respectively. The only reasonable explanation of these results would appear to lie in the formation, in this reaction, of some radioactive sulfur-containing compound more volatile than sulfur dioxide. Since the specific activity of the sulfur dioxide was measured by distilling off a small portion, such material would concentrate in this fraction and thus lead to a high apparent exchange rate. However, this

explanation is not completely satisfying. Granted that
thionyl bromide is less stable than thionyl chloride and
might decompose into various amounts of sulfur, sulfur
monoxide, sulfur monobromide, sulfur dioxide, and bromine,
still the decomposition could not proceed to a very great
extent in as short a time as ten minutes. Moreover, our
experimental work, in preparing thionyl bromide from
thionyl chloride by this reaction, agrees with Jander's
observation (3, p.232) that the reaction proceeds as
Equation (15) is written. It is hoped that further ex-
periments may be carried out later on this system.

B. TETRAMETHYLAMMONIUM PYROSULFITE EXPERIMENTS. On
first considering the tetramethylammonium pyrosulfite
experiments, it would seem that Jander's theory has been
upheld; a rapid exchange has taken place upon the mere
solution of the salt in sulfur dioxide. Unfortunately,
however, at least one other very likely alternative
mechanism may be postulated to account for the exchange,
without the necessity of postulating the existence of
sulfite ions from liquid sulfur dioxide by the equili-
brium of Equation (1). Since the salt, in solution,
ionizes to pyrosulfite ions, these ions may exchange
activity in a manner represented by the ionic equilibrium
of Equation (16):

$$SO_3^= + S^*O_2 \rightleftharpoons S^*SO_5^= \rightleftharpoons S^*O_3^= + SO_2 \qquad (16)$$
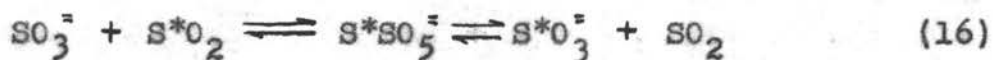
This mechanism does not, of course, prohibit the existence of sulfite ions from sulfur dioxide but even if such an equilibrium exists, it seems likely that the radio-active exchange occurs, in the main, as indicated above with solvent sulfur dioxide exchanging with the sulfur dioxide from the pyrosulfite ions. Thus, because of the possibility of Equation (16), the results cannot be taken to indicate definitely either the presence or the absence of sulfite ions from the liquid sulfur dioxide.

The exchange might also take place in another manner. Namely, on dissolution of the salt, the pyrosulfite ion dissociates into a sulfite ion and sulfur dioxide without an equilibrium as in Equation (16). On recrystallizing the salt then, the sulfur dioxide molecule entering the pyrosulfite has exchanged with the solvent sulfur dioxide, and, unless the sulfite ion has also exchanged (with solvent sulfite ions), the maximum possible exchange would be 50%. The experimental results exclude this possibility.

This experiment was not repeated with any other soluble sulfite because it was felt that the same results would be obtained.

C. THIONYL CHLORIDE AND THIONYL BROMIDE EXPERIMENTS. Any equilibrium exchange experiment must follow a first order rate law (8, pp.285-288). This implies that plots such as those of Figures VIII, IX, X, and XI should give

straight lines. Since it is evident that such is not
the case in these graphs, the question of the reliability
of the thionyl chloride data immediately arises. It would
seem important to dispose of this point before further
discussion.

It is apparent from the data that there is a not in-
considerable zero time "blank" in these experiments. For
the data to be reliable, this blank must be reproducible
within a given series of runs. Preliminary experiments
had appeared to indicate such a reproducibility and it is
felt that the data themselves also indicate this.

In the first place, it will be noted that each of the
plots gives for the most part a relatively smooth curve:
the points do not appear to scatter at random. In each
case the apparent percent exchange initially increases
smoothly with time; an extrapolation back to zero time
never gives a negative apparent exchange. Further, the
apparent reversal of exchange, strange as it may be in
itself, occurs without exception in all the above curves.
This would seem to indicate the same process, whatever it
may be, taking place in each bomb.

Further evidence derives from the $SOCl_2$-only runs,
for which data are given in Table VI. These runs show a
maximum spread of 2.7% in an average of 9.0% for 2500
hours at $25^{\circ}C$ and a maximum spread of 1.7% in an average

of 9.6% for 1030 hours at 61°C. These runs were made in
an identical manner with the 1:10 $SOCl_2:SO_2$ runs except
that the thionyl chloride was stored by itself for various
lengths of time before mixing with sulfur dioxide. It
would seem that the apparent exchange does not appear
until the thionyl chloride is in contact with sulfur
dioxide for some time.

On the basis of the foregoing, it is to be concluded
that the results shown in the graphs represent real
effects.

The lack of straight lines in the plots indicates that
we cannot, however, be dealing here with any straight-
forward, simple exchange process: complications, which are
present, evidently remain to be explained. It seems
possible the effects are to be ascribed to a slow decompo-
sition of the labeled thionyl chloride, which shows up as
apparent exchange. To explain the specific results
observed, one might suppose the decomposition of thionyl
chloride to occur as a two step process as represented
by Equation (13), first into chlorine and sulfur monoxides
and then the latter into sulfur dioxide and sulfur. The
formation of active sulfur monoxide, with a greater vapor
pressure than sulfur dioxide, would enhance the apparent
exchange. If we further assume the decomposition of the
sulfur monoxide to be an auto-catalytic process, the

decrease in apparent exchange with time is explained.
This should, however, produce an active sulfur residue
in the reaction vessels and since none such was found,
still further assumptions are necessary. One might
suppose that in the actual process of decomposing, the
sulfur monoxide undergoes a rapid exchange with the sol-
vent sulfur dioxide. The residual sulfur formed would
then be of undetectibly low activity. All this is
admittedly highly speculative, although it does explain
the experimental results. Quite apart from any such ex-
planations, however, we have the one conclusion, important
for our purposes, that the true exchange rate can be no
higher than that corresponding to the lowest apparent ex-
change rate, i.e., those points on the thionyl chloride
exchange curves farthest to the right.

We may then say that the exchange is exceedingly slow
between thionyl chloride and sulfur dioxide from a
$SO_2:SOCl_2$ mole ratio of 1:350 to one of 200:1. Minimum
half-times of exchange may be calculated for the various
runs; these results are given in Table X.

TABLE X

Half-times for $SOCl_2$ runs

Mole Fr. SO_2:$SOCl_2$	Time in Hours	% Exchange	Calculated Half- time in hours
1:350	840	1	6×10^4
1:20	334	1	2×10^4
1:5	840	1.1	5×10^4
10:1	3012	16.0	1×10^4
50:1	1673	13.1	8×10^3
200:1[a]	1003	15.5	4×10^3
200:1[b]	1831	22.8	5×10^3

a. Bomb #1
b. Bomb #2

Hence we reach the important conclusion that Jander's theory of acid-base chemistry in liquid sulfur dioxide cannot be accepted in its entirety. Specifically, his concept of thionyl ions from both solute thionyl chloride and solvent sulfur dioxide must be incorrect.

Alternative explanations to those given by Jander seem necessary in order to explain his experimental results. His neutralization reaction between tetramethylammonium pyrosulfite and thionyl chloride would proceed by sulfite ions reacting with thionyl chloride molecules, or perhaps thionyl chloride ions, $SOCl$. The possibility that thionyl chloride ions exist in liquid sulfur dioxide

is under investigation in our Laboratory; the proposed
method of study consists of mixing chlorine-labeled
tetramethylammonium chloride with thionyl chloride in
sulfur dioxide. The appearance of radioactive chlorine
in the thionyl chloride would indicate its ionization; at
the present time, this work has not been completed to a
point where data are available.

The results obtained from the thionyl bromide and
active sulfur dioxide runs (see Table VIII) corroborate
the results of the tionyl chloride experiments; even
though the thionyl bromide solution has a ten-fold greater
specific conductance, the exchange is also very slow.
(Here, there seems to be no question of the reproducibility
of results; the three blank runs given in Table VIII show
this procedure to be eminently reliable.) A calculation
from the data gives a lower limit for the half time of
equilibration of about 1×10^4 hours; it is interesting
that this is so similar to the figure quoted above in
Table X for the 1:10 thionyl chloride runs at 25° C. In
fact, all the runs give values of half-times of the same
order of magnitude. Just how much significance is to be
attached to this is not entirely clear at this point, in
view of the uncertain character of the figures themselves.

D. GENERAL CONCLUSIONS. The conclusion we reach
from this work is that Jander's theory of sulfur dioxide
chemistry is no longer tenable as a whole; specifically
his postulates concerning the existence of thionyl ions
both from thionyl compounds in liquid sulfur dioxide and
from the sulfur dioxide itself must be incorrect. Further
work is needed to determine the actual species present
due to thionyl chloride when it dissolves in sulfur dioxide,
that is, to determine whether or not an appreciable
ionization of chloride ions occurs.

We have shown rather conclusively that an extensive
ionization of tetramethylammonium pyrosulfite occurs when
it is dissolved in liquid sulfur dioxide, without being
able experimentally to prove or disprove the existence of
sulfite ions from the solvent sulfur dioxide. It is un-
likely that additional work would serve to elucidate this
problem further.

VI. SUMMARY

1. The exchange of sulfur between tetramethyl-ammonium pyrosulfite and sulfur-labeled sulfur dioxide as a solvent occurs immeasurably fast even at $-78^{\circ}C$.

2. The sulfur of thionyl chloride exchanges very slowly with liquid sulfur dioxide in the range of mole ratios of $SOCl_2:SO_2$ of 350:1 to 1:200 at 25° C.

3. The sulfur of thionyl chloride exchanges very slowly with liquid sulfur dioxide when present in a mole ratio of 1:10 $SOCl_2:SO_2$ at $61^{\circ}C$.

4. The sulfur of thionyl bromide exchanges very slowly with liquid sulfur dioxide when present in a mole ratio of 1:10 $SOBr_2:SO_2$ at $25^{\circ}C$.

5. Jander's conclusions concerning the existence of both thionyl ions from solute thionyl compounds and thionyl ions from solvent liquid sulfur dioxide cannot be correct.

6. The displacement reaction between thionyl chloride and potassium bromide in liquid sulfur dioxide may not be as straightforward under some conditions as Jander would indicate.

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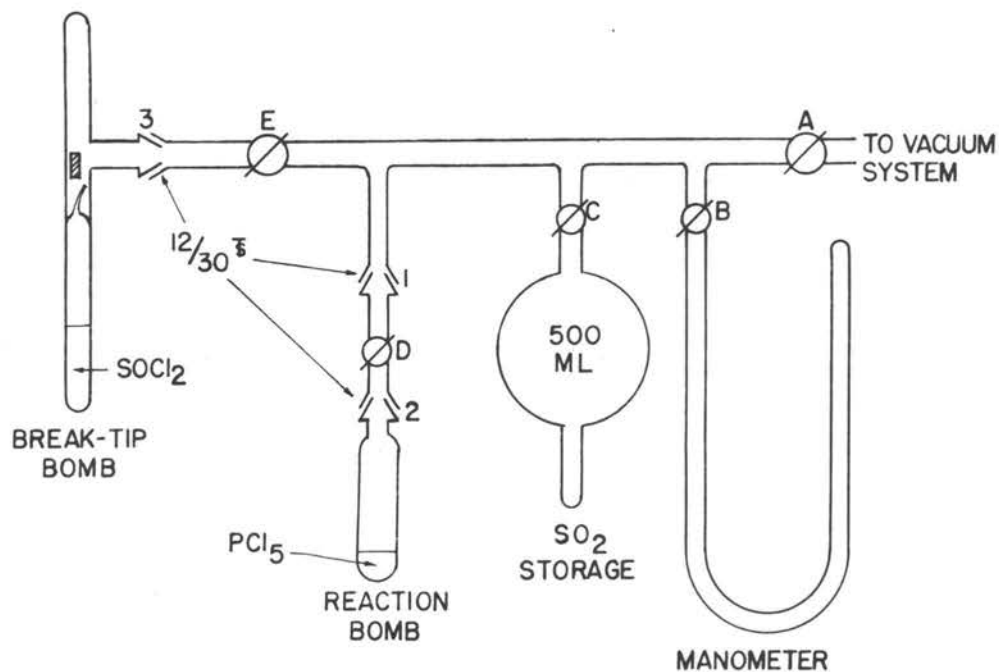APPENDIX

FIGURE I

APPARATUS FOR S*OCl₂ PREPARATION

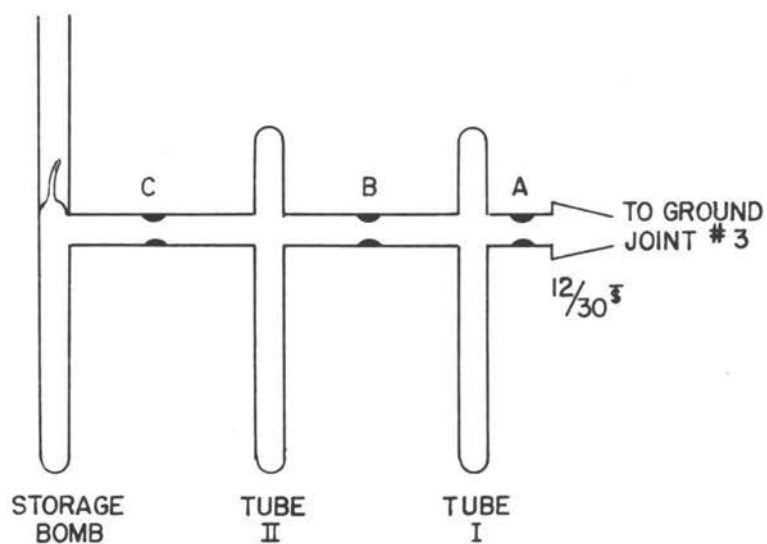# FIGURE II

APPARATUS FOR PURIFICATION OF S*OCl₂

FIGURE III
APPARATUS FOR TETRAMETHYLAMMONIUM
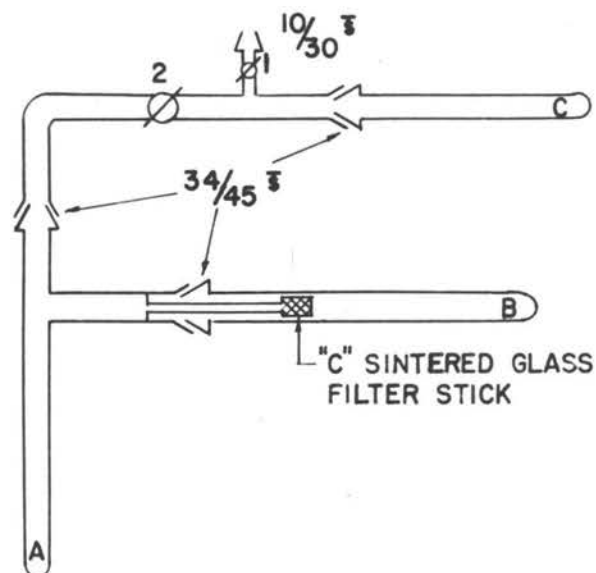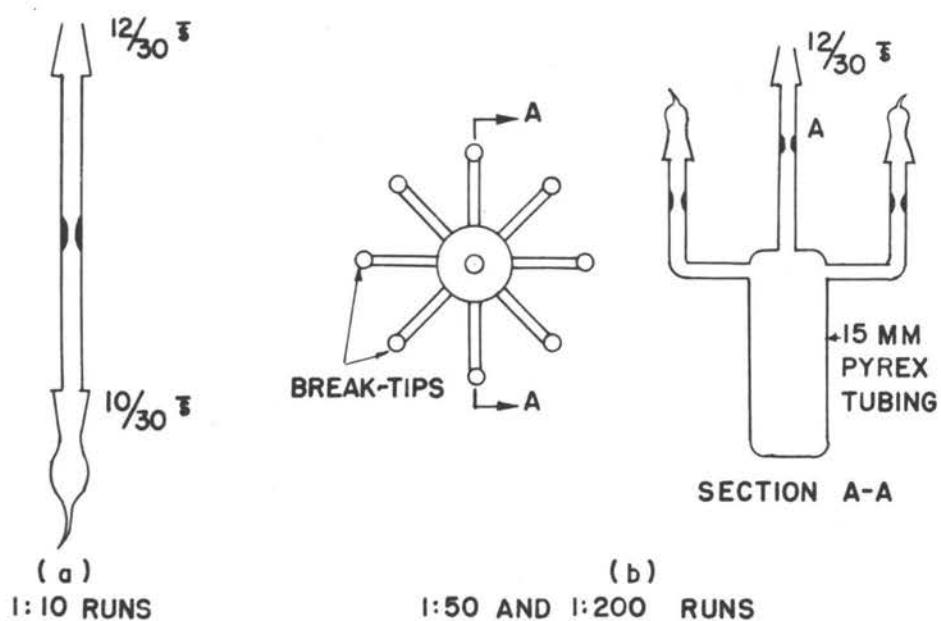## PYROSULFITE PREPARATION

FIGURE IV
BOMBS USED IN RUNS

(a)
1:10 RUNS

(b)
1:50 AND 1:200 RUNS

FIGURE V

SEPARATION APPARATUS - $SOCl_2$
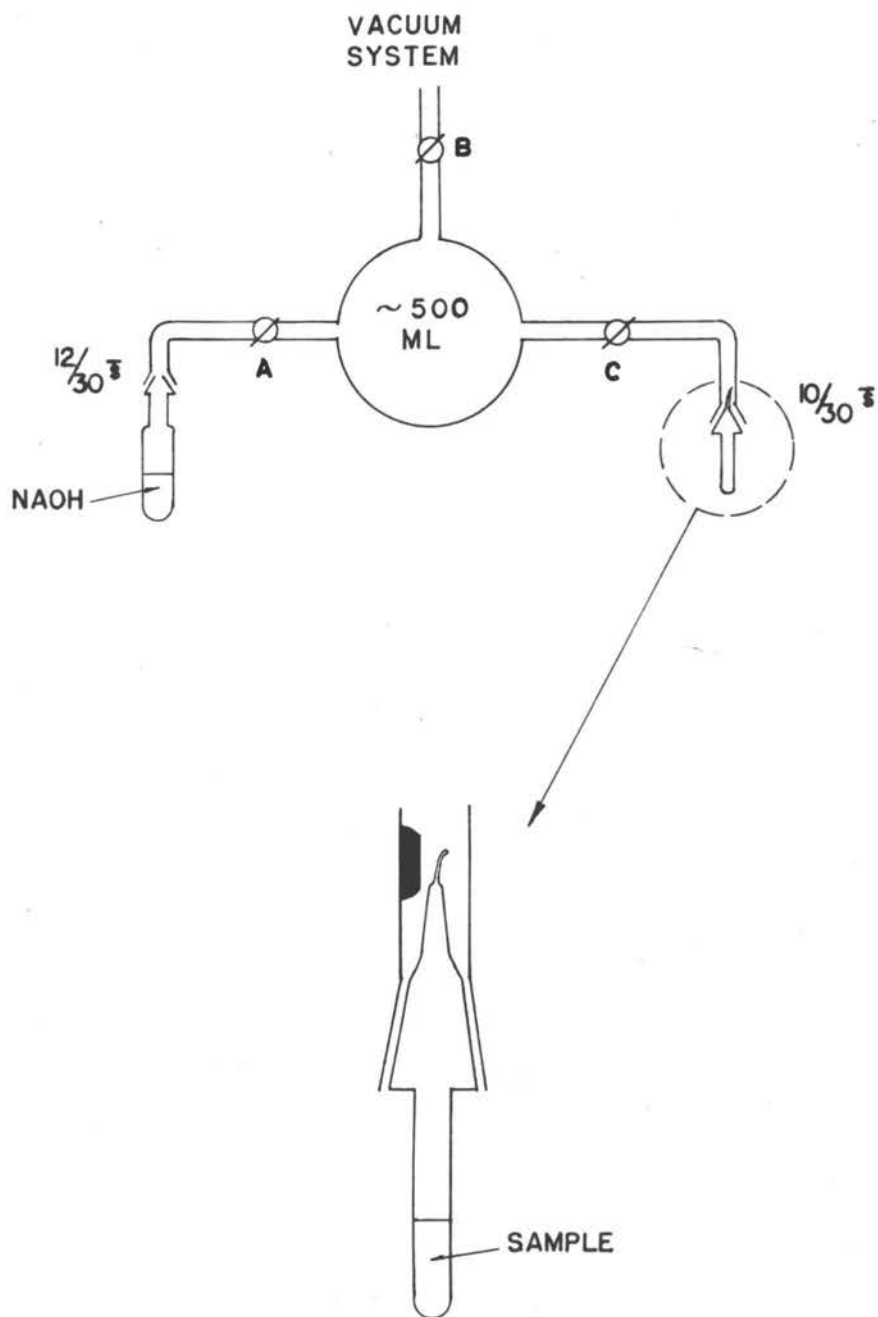
FIGURE VI
SEPARATION APPARATUS – SOBr$_2$

TO VACUUM
SYSTEM

A

B   D

C

185
ML

10/30 ꞃ

12/30 ꞃ

1   2

ICE BATH
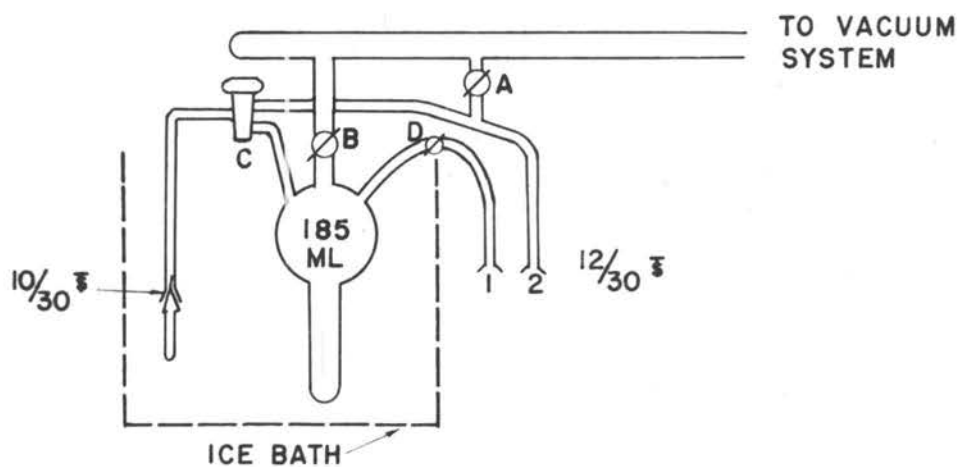
FIGURE VII
ANALYSIS OF SOCl$_2$–ONLY BOMBS

12/30 ꞃ

A

B

SOCl$_2$
AMPULE

10/30 ꞃ
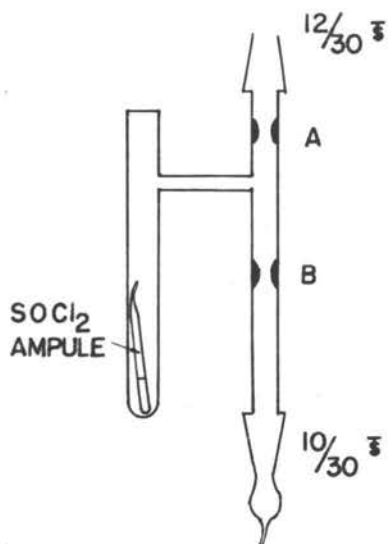
FIGURE VIII
LOG (100-% EXCHANGE)   VS   TIME
SOCl₂ : SO₂   1:10   25°C
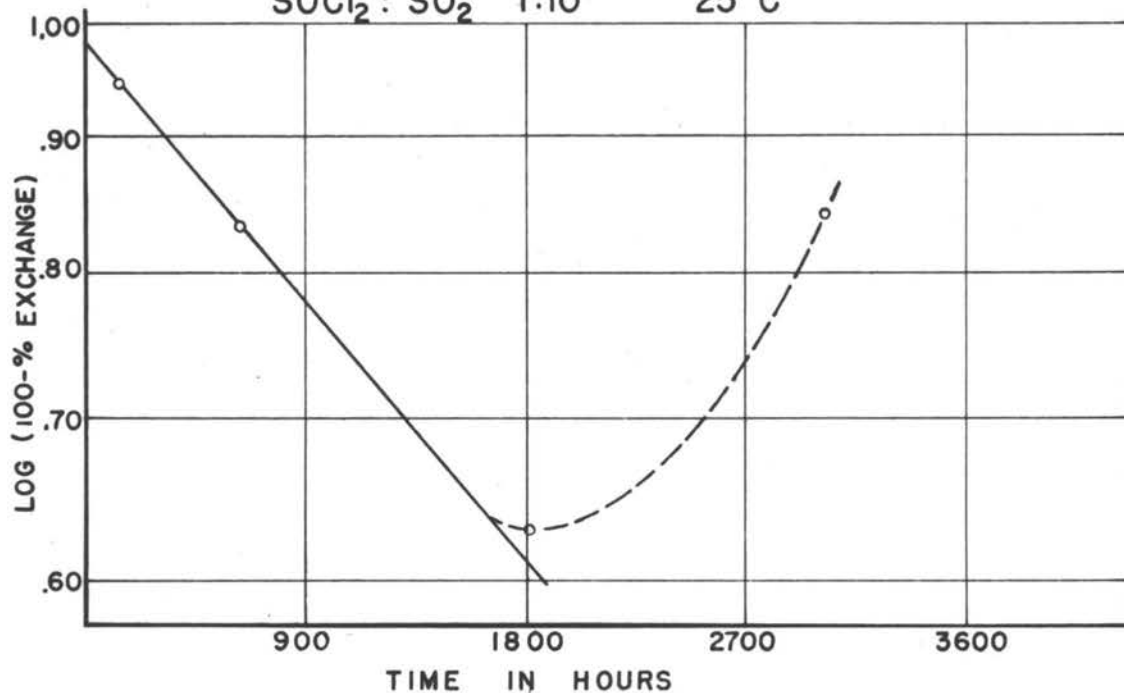
FIGURE IX
LOG (100-% EXCHANGE)   VS   TIME
SOCl₂ : SO₂   1:10   61°C
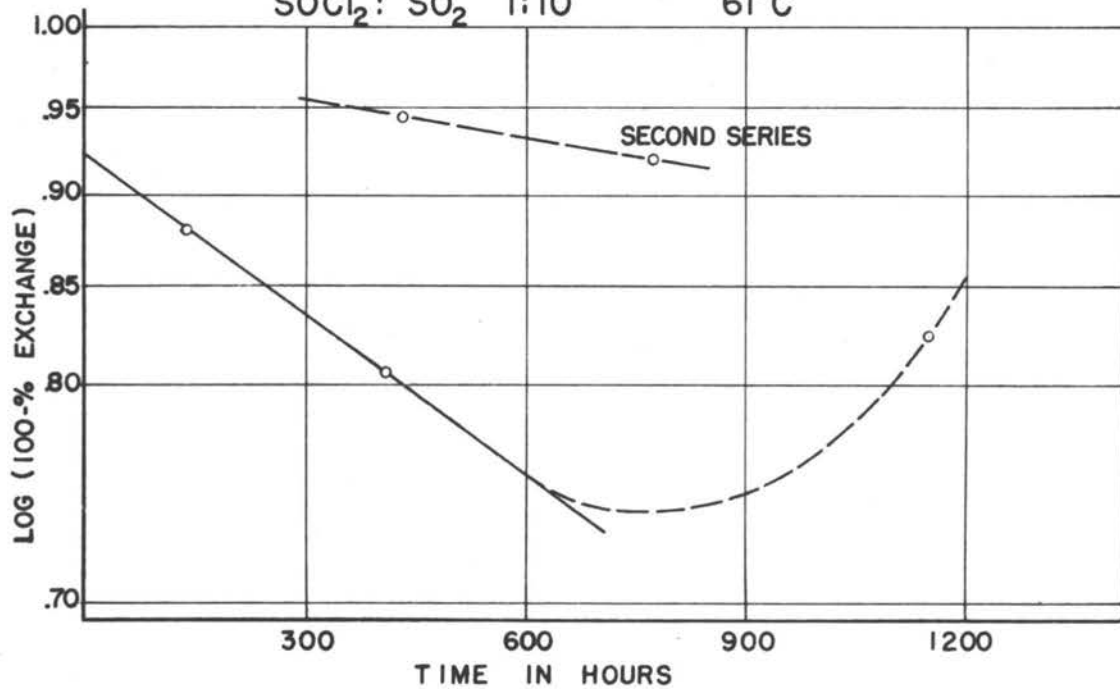
FIGURE X
LOG (100-% EXCHANGE) VS TIME
SOCl₂ : SO₂   1:50   25°C
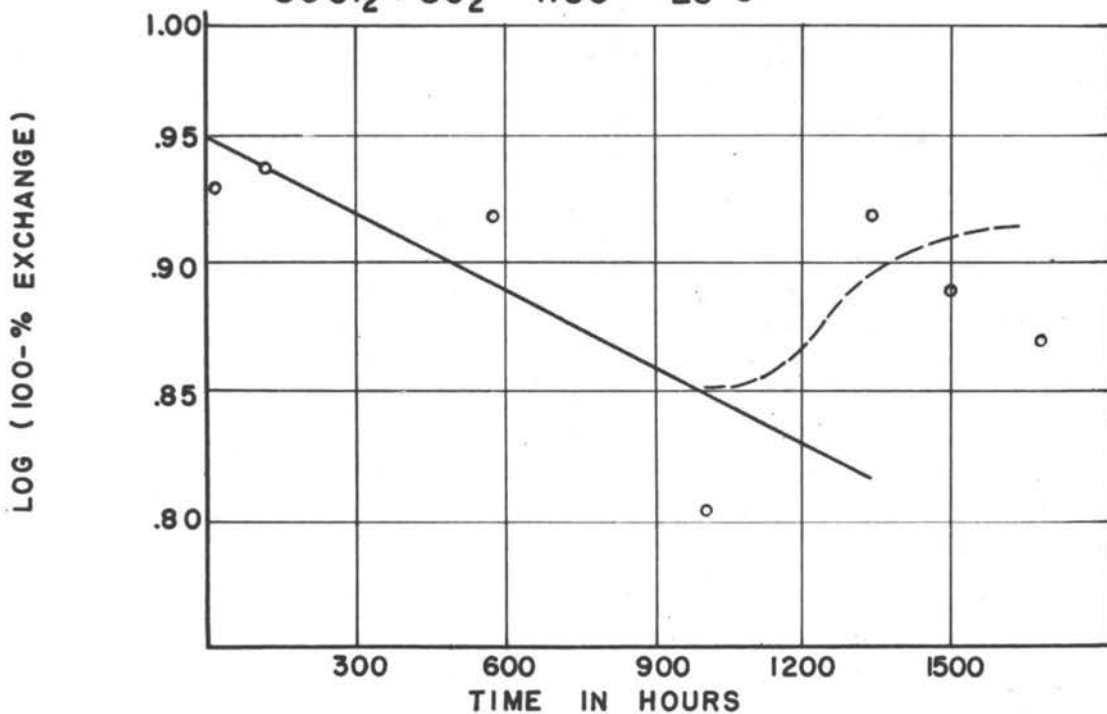
FIGURE XI
LOG (100-% EXCHANGE) VS TIME
SOCl₂ : SO₂   1:200   25°C