

AN ABSTRACT OF THE THESIS OF

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(Name) (Degree) (Major)

Date thesis is presented March 19, 1965

Title THE HIGH TEMPERATURE RADIOSULFUR EXCHANGE
REACTION OF SULFUR DIOXIDE WITH CONCENTRATED
SULFURIC ACID AND AMMONIUM BISULFATE

Abstract approved [REDACTED]
(Major professor)

The present study has consisted primarily of an investigation of the rates of isotopic sulfur exchange between sulfur dioxide and various sulfur (VI) solutions, both 100% H_2SO_4 and, in particular, related ammonia-containing sulfur (VI) solutions. One of the main objects of the work was to obtain a comparison between exchange rates in such systems and those previously observed in aqueous acid systems. The exchange was studied at temperatures from 167.5°C to 225.3°C, the sulfur (VI) systems examined including: (1) 100% H_2SO_4 ; (2) fused ammonium bisulfate; (3) mixtures of ammonium bisulfate and 100% H_2SO_4 ; and (4) a 1:1 mixture of ammonium bisulfate and 84.5% H_2SO_4 . The observed rates were all conveniently measurable throughout the indicated temperature range.

Previous studies of exchange rates between sulfur dioxide and either concentrated sulfuric acid solutions or fused ammonium bisulfate have shown in both cases the reaction to be first order in

the amount of sulfur dioxide and proportional to the fraction of it dissolved in the solution, viz.:

$$\text{Rate} = k (\text{SO}_2) \quad (1)$$

where (SO_2) represents dissolved sulfur dioxide concentration. The results showed, however, a wide variation of the rate constants for different types of solutions. In an attempt to account for this wide variation, an effort has now been made to interpret both the present results as well as previous data in terms of sulfur dioxide activities rather than concentrations. To this end equation (1) has been re-written in the form

$$\text{Rate} = k_a \gamma (\text{SO}_2) \quad (2)$$

where γ is the activity coefficient of sulfur dioxide in the solutions.

In order to calculate the rate constants based on sulfur dioxide activities (k_a), the concentration rate constants (k) and activity coefficients (γ) were first calculated. The latter quantities were computed from the relationship:

$$\gamma = P/P' \quad (3)$$

where P is the actual partial pressure of solute SO_2 over a solution at the composition of interest and P' is the calculated ideal solution (Raoult's law) partial pressure at the same composition. Values of P in equation (3) were calculated directly from sulfur dioxide distribution coefficients between gas phase and solution on

the basis of the ideal gas equation, Henry's law having been found valid in these systems. The distribution coefficients were either obtained from the present exchange results or, for some of the previous data, were estimated by interpolation or extrapolation from data measured under slightly different conditions.

A comparison between the two types of rate constants, k and k_a , shows that, while the constants, k , vary drastically from one solution to another, the activity constants, k_a , vary among themselves to only a modest degree. A striking example of this feature is provided by comparison of exchange rates at 225.3°C in fused ammonium bisulfate and in the 1:1 mixture of ammonium bisulfate with 84.5% H_2SO_4 . Here the constants k differ by a factor of 32 while the k_a values differ by only a factor of two. This comparison shows clearly the merits of interpreting the rate as first order in sulfur dioxide activity rather than concentration.

Apparent activation energies, frequency factors and activation entropies, both for k values and k_a values, have been calculated for the systems: (1) fused ammonium bisulfate; (2) 100% H_2SO_4 ; and (3) 1:1 ammonium bisulfate and 84.5% H_2SO_4 . It was found that, even though the k_a values themselves showed good accord among themselves as compared to the k values, these related kinetic parameters failed to reflect this accord. Thus important variations among the k based parameters appear to persist with the k_a based

parameters. It is suggested that the basis for this lack of concordance among the latter parameters may be related to the fact that the activity coefficients of the sulfur (VI) exchanging species and of the activated complexes have not been adequately taken into account.

Since the sulfur (VI) concentration in the solutions varied but little from case to case, it was not possible to test the rate dependence on this factor. However, previous work has demonstrated a first order dependence of rate on bisulfate ion in aqueous acid, and it has been assumed the same dependence prevails in the present solutions. If this assumption is valid, the relative constancy of k_a values observed, as the ratio of bisulfate ion concentration to unionized H_2SO_4 concentration changes drastically from one solution to another, implies that the rate must be approximately first order in both of these sulfur (VI) species and must have, for exchange with either, approximately the same specific rate constant. Hence it is tentatively proposed that the exchange rate may be, at least approximately, described, for all the solutions here examined by the rate law

$$\text{Rate} = k_2 \gamma (\text{SO}_2) [(\text{HSO}_4^-) + (\text{H}_2\text{SO}_4)]$$

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SULFURIC ACID AND AMMONIUM BISULFATE

by

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A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1965

APPROVED:

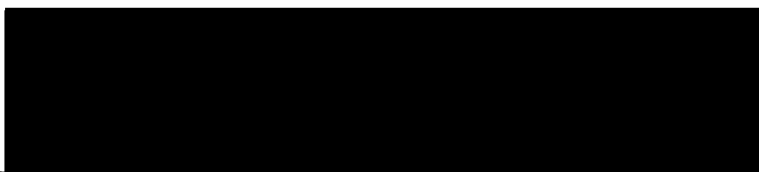


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Typed by Lois Shrader and Muriel Davis

ACKNOWLEDGMENT

The writer wishes to express her indebtedness and gratitude to Dr. T. H. Norris for his help, guidance and encouragement throughout the course of this research.

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THE HIGH TEMPERATURE RADIOSULFUR EXCHANGE REACTION OF SULFUR DIOXIDE WITH CONCENTRATED SULFURIC ACID AND AMMONIUM BISULFATE

I. INTRODUCTION

Radioactive tracers have been used as an aid in the investigation of various chemical phenomena for many years. Due to the low penetrating power of its beta rays and its relatively long half-life of 87.1 days, sulfur-35 is an especially convenient material to work with and so has been extensively used as a tracer. In particular, this isotope has been used for the study of the rates of a wide range of isotopic exchange reactions under a variety of conditions.

In 1939, the exchange of oxygen atoms between sulfur (IV) and sulfur (VI) compounds was first studied by Voge (18) using S-35. He investigated the reaction between aqueous sulfite and sulfate at 100°C, finding no exchange in 36 hours, either in basic or 0.1N acid solution. He also observed no exchange between sulfur dioxide and sulfur trioxide gases in 17 hours at 280°C, the addition of water vapor leading to only about 10% exchange under these conditions. He did, however, observe a slow exchange between these two gases when he raised the temperature to 335°C, the rate being accelerated by the presence of water or of platinized asbestos.

In 1946, Huston (9, p. 1-48) studied in detail the kinetics of the exchange reaction between sulfur dioxide and sulfur trioxide, and observed the rate to be conveniently measurable in

in the range 400-440° C.

These results led Harmon (6, p. 1-16) to study the exchange between sulfur dioxide and concentrated sulfuric acid and he observed the following: (1) at room temperature, no exchange in 48 hours; (2) at 100° C, 5% exchange in 48 hours; (3) at 280° C, complete exchange in less than five hours. This reaction between sulfur dioxide and concentrated sulfuric acid was found to proceed at a conveniently measurable rate in the range 160-210° C by Norris (16). In succeeding studies by Masters and Norris (12) and by Doherty (2, p. 1-37), the reaction was found to be first order in sulfur dioxide and one-half order in water concentration in the range 85-98% sulfuric acid.

McDonald (13, p. 1-138) carried out a detailed study for the systems involving sulfuric acid over the entire concentration range from dilute aqueous solutions up to 100% acid, and beyond, into the fuming range. He found that the sulfur exchange between sulfur dioxide and sulfuric acid occurs at a conveniently measurable rate in the vicinity of 174° C. His kinetics study showed the reaction to be first order in sulfur dioxide concentration, the following rate law being obeyed over the entire concentration range from dilute aqueous solutions up to 100% sulfuric acid:

$$\text{Rate} = k_1(\text{SO}_2)(\text{HSO}_4^-) + k_2(\text{SO}_2)(\text{H}_2\text{SO}_4)$$

In aqueous acid, the second term in this rate law is unimportant.

At 174°C the constants k_1 and k_2 have the values

$$k_1 = 1.06 \times 10^{-4} \text{ l mole}^{-1} \text{ min}^{-1}$$

$$k_2 = 1.48 \times 10^{-5} \text{ l mole}^{-1} \text{ min}^{-1}$$

McDonald's study showed the exchange rate to increase with increasing sulfuric acid concentration, reaching a maximum at about 76-80% sulfuric acid and thereafter declining to 100% acid. The fact that the maximum rate does not occur at a one to one mole ratio of water to sulfuric acid (84.5%) indicates that the maximum bisulfate ion concentration occurs on the water side of this point, a feature related by this investigator to incomplete transfer of hydrogen ions from H_2SO_4 to H_2O molecules at a 1:1 ratio of the two.

The author (1, p. 1-50) studied the exchange between sulfur dioxide and fused ammonium bisulfate at the two temperatures, 169.5°C and 194.8°C. This system is of particular interest in that it presents a parallel to a 1:1 mole ratio water-sulfuric acid solution, which may be thought of as hydronium bisulfate, the ammonia having replaced the water. Hence comparison of the rates in the two systems has been of some interest. It was found that the exchange in the fused ammonium bisulfate occurs at conveniently measurable rates at both temperatures. Study of the kinetics showed the reaction to be first order in the amount of sulfur

dioxide used and proportional to the fraction dissolved in the fused salt, in accordance with the rate expression

$$\text{Rate} = k(\text{SO}_2)F'$$

The values of k found were $7.31 \times 10^{-3} \text{ hr}^{-1}$ at 169.5°C and $3.04 \times 10^{-2} \text{ hr}^{-1}$ at 194.8°C . The temperature coefficient of the rate at 169.5°C was 1.8 per 10° , corresponding to an activation energy of 23.2 kcal/mole. By application of Doherty's calculation method (see Section III), the solubility of sulfur dioxide in the fused salt was determined in terms of a distribution coefficient, c , representing the ratio of gas concentration in the liquid to that in the gas phase. The values found were $c = 19.0$ at 169.5°C and 10.61 at 194.8°C .

A comparison of this last reaction with the previously studied exchange between sulfur dioxide and aqueous sulfuric acid was made by assuming the same rate law to prevail as that found for reaction between sulfur dioxide and bisulfate ion in the aqueous acid medium, viz.

$$\text{Rate} = k_1(\text{SO}_2)(\text{HSO}_4^-)$$

The concentration of bisulfate ion was computed by assuming the fused salt to be fully ionized. The activation energy associated with the k_1 rate law was calculated, making possible the expression of k_1 for the fused ammonium bisulfate system as

$$k_1 = 6.15 \times 10^4 e^{-23,600/RT} \ell \text{ mole}^{-1} \text{ sec}^{-1}$$

The entropy of activation deduced from these data was -39.4 calories degree⁻¹ mole⁻¹. On the basis of the above formula, one may calculate that, for 174.0°C , the value of k_1 for fused ammonium bisulfate would be $1.073 \times 10^{-5} \ell \text{ mole}^{-1} \text{ min}^{-1}$, a figure to be compared with that given by McDonald for aqueous acid, viz., $1.06 \times 10^{-4} \ell \text{ mole}^{-1} \text{ min}^{-1}$. Thus it may be seen that, on the basis of these constants, the rate in fused ammonium bisulfate appears to be about ten times slower than in the aqueous acid.

In this system, it was gratifying to find that, as anticipated, the exchange occurred, at least qualitatively, at a roughly comparable rate to that found with sulfuric acid, but, more quantitatively, a puzzle was presented by the fact that the rate constant appeared to be about ten times smaller.

In the present work, an attempt has been made to clarify this situation by carrying out experiments in mixed ammonium bisulfate-sulfuric acid systems as well as further experiments both in pure ammonium bisulfate and in 100% sulfuric acid. Mixtures of ammonium bisulfate and 100% sulfuric acid, i. e. systems with $\text{NH}_3:\text{H}_2\text{SO}_4$ mole ratios of less than 1:1, for example, were of interest in that they present a parallel to compare to aqueous sulfuric acid solutions of acid concentration greater than that of 84.5%, the 1:1 $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$ mole ratio concentration.

The exchange reactions involved in the present research were the following: (1) sulfur dioxide and ammonium bisulfate at 169.5°C and 225.3°C; (2) sulfur dioxide and 2.05:1 (mole ratio) ammonium bisulfate and 100% H_2SO_4 mixture at 194.4°C; (3) sulfur dioxide and 1:4 ammonium bisulfate and 100% H_2SO_4 mixture at 194.4°C; (4) sulfur dioxide and 100% H_2SO_4 at 167.5°C, 194.4°C and at 225.3°C; (5) sulfur dioxide and 1:1 ammonium bisulfate and 84.5% H_2SO_4 at 167.5°C, 194.4°C and at 225.3°C.

II. EXPERIMENTAL

Preparation of Reactants

Sulfur Dioxide

A material of 99.98 percent minimum purity was obtained from the Matheson Company, Inc., in a steel cylinder. It was transferred to the vacuum system through two bubblers of concentrated sulfuric acid to remove sulfur trioxide, passed through a tube of phosphorous pentoxide to eliminate water and collected in a liquid nitrogen trap. The frozen material was then allowed to melt and the liquid sulfur dioxide was distilled, the middle fraction (about half) being saved for use as the stock supply. The other two fractions were passed to the hood and discarded.

Sulfur-35

This material was obtained as carrier-free sulfuric acid in dilute hydrochloric acid from the Oak Ridge National Laboratory of the U. S. Atomic Energy Commission.

Sulfur-35 Labeled Ammonium Bisulfate

Ammonium bisulfate (Baker & Adamson, Reagent Grade) was dissolved in distilled water and small amounts, usually pipetted

using micropipettes of 10-100 λ , of the above described radioactive sulfuric acid solution were added. The solution, after that, was evaporated in an oven ($\approx 100^{\circ}\text{C}$) for about a week to dryness. To test the dryness of ammonium bisulfate, a weighed amount of the dried ammonium bisulfate (o. 500g) was put in the oven overnight and then weighed again. The second weight was again 0.500g. The material was stored in a covered beaker in a calcium chloride dried dessicator when not in use. Specific activities between 92 and 652 c. p. m. per mg, counted as barium sulfate, were obtained. Labeled ammonium bisulfate was mixed with inactive sulfuric acid (different quantities and concentrations) to prepare the radioactive mixtures studied in this work. Specific activities between 61 and 234 c. p. m. per mg as barium sulfate were obtained in the case of the 2.05:1 NH_4HSO_4 and 100% H_2SO_4 mixture, between 58 and 75 c. p. m. per mg as barium sulfate in the case of 1:4 NH_4HSO_4 and 100% H_2SO_4 mixture and between 60 and 203 c. p. m. per mg as barium sulfate in the case of the 1:1 NH_4HSO_4 and 84.5% H_2SO_4 mixture.

Sulfur-35 Labeled Concentrated Sulfuric Acid

This material was prepared by dissolving a small amount of S-35 carrier-free sulfuric acid in a milliliter or so of concentrated sulfuric acid (Baker and Adamson, Reagent Grade, 95.5-96.5%), after which the solution was evaporated, using an infrared lamp

until white fumes formed. This small amount of high specific activity labeled concentrated acid was then used as a source of activity to label a larger, stock concentrated sulfuric acid solution (Baker and Adamson, Reagent Grade, 95.5-96.5%) which was then used for preparing 100% sulfuric acid as described below. Different amounts of the high specific activity concentrated acid were added, according to the ultimate specific activity needed.

Sulfur-35 Labeled 100% Sulfuric Acid

The "Fair and Foggy" method of Kunzler (11) was followed. In this method increments of concentrated sulfuric acid are added to fuming sulfuric acid as long as fog or mist is formed when moist air is passed over the surface of the acid ("foggy"). Just as soon as fog is no longer observed ("fair"), the operation is stopped. According to Kunzler (11), the acid samples so prepared have a sulfuric acid concentration of exactly 100% within an accuracy of a few hundredths of a percent, depending on the care taken in the preparation and one's ability to detect the presence of the fog.

As actually done, sulfur-35 labeled concentrated acid (prepared as described in the previous section) was added to inactive fuming sulfuric acid (Baker Analyzed, Reagent Grade, 20-23% SO_3). The operation was carried out in a two neck flask of 500 ml volume. A magnetic stirrer with a Teflon covered magnetic stirring bar

was used for stirring the solution. The concentrated sulfuric acid was transferred into the flask through one of its necks via a funnel equipped with a Teflon stopcock and inlet tube with an "inner part" ground joint of the same size as the "outer part" ground joint of the neck of the flask. No grease was used in any part of this operation. Teflon stopcocks were found the only kind of stopcocks suitable to be used in contact with sulfuric acid, for they need no grease and they are not attacked by the acid. The other neck of the flask was stoppered by a rubber stopper having a glass tube inserted in its center (~15 cm long and 6 mm outer diameter). Attached to this glass tube was a piece of rubber tubing, closed with a pinch clamp at its end. The presence or absence of fog was detected by exhaling through the rubber tubing into the flask. The solution was shaken well before introducing each puff. The ends of the tubes through the two necks were kept always above the level of the liquid in the flask.

Several preparations of this sort were done. Following a preparation, the two neck flask was transferred to and opened in a dry box, in which all subsequent transfers of the acid were made (except for a few transfers done in the vacuum system). Due to the difficulty of keeping the concentration of sulfuric acid at its original value, the acid was transferred from the two neck flask into a 200 ml round flask (see Figure 2, part 1) equipped with stoppered ground joint at one end and a Teflon stopcock at the other end

(part 2 of Figure 2). Then, with the apparatus horizontal, this ground joint was sealed off in the open air at point a (Figure 2), the stopcock meanwhile being kept open and attached via rubber tubing to a barium oxide drying tube which had its other end exposed to the open air. In the case of each preparation, the acid was thereafter kept in and dispensed from this 200 ml flask (see Run Procedure), the flask being kept either in the dry box or stored in a dessicator over calcium chloride. After each preparation and also at the time of filling of any particular batch of reaction bombs, samples of the acid were taken in triplicate, initially by decantation from the original two neck flask, later by withdrawal from the 200 ml flask through the bomb filling arrangement described in the Run Procedure section. Samples of estimated amount were put into weighing bottles. The closed weighing bottles were then removed from the dry box, weighed and then titrated with base as described in the following section on Chemical Analysis. After the initial trials with the procedure, all new preparations were found to have a concentration of 99.9-100.0%. In the subsequent titration of preparations which had been used for filling previous sets of reaction bombs, it was occasionally found that the concentration had dropped below 99.9%, water evidently having been absorbed. All such preparations were discarded, and only acid actually titrated as having 99.9-100.0% concentration at the time of filling the bombs was used for the

experiments. The specific activities of the acid preparations were between 76 and 1900 c. p. m. per mg as barium sulfate.

Sulfuric Acid of 100% Concentration (Inactive)

The same "Fair and Foggy" method described above was followed, with the difference that the concentrated sulfuric acid used in this case was unlabeled. Acid transfer, storage and titration procedures were also exactly the same, acid samples, for example, being always checked for concentration by titration in triplicate at the time of filling of any particular batch of bombs.

Sulfuric Acid of 84.5% Concentration

This material (inactive) was prepared by dilution of concentrated sulfuric acid (Baker and Adamson, Reagent Grade, 95.5-96.5%) with distilled water. The concentration of the acid was determined initially by titration and then the dilution was made by using weighed quantities of water and of acid, all transfers being made in the dry box. After each preparation three samples were transferred, in the dry box, into previously weighed weighing bottles for titration. Three samples were also taken at the time of filling of any particular batch of reaction tubes. The closed weighing bottles were then taken out of the dry box, weighed and the acid was titrated with base following the method described on page 13 in

Chemical Analysis. The prepared material was kept in and (by decantation) dispensed from a glass stoppered Erlenmeyer flask. This flask was kept either in the dry box or over calcium chloride in a dessicator.

Chemical Analysis

The concentration of sulfuric acid was determined by potentiometric titration with a standard solution of 1 normal sodium hydroxide which was prepared from Uni-Tech volumetric concentrate solution¹ of the base. Triplicate samples were obtained from the acid under consideration. These were weighed in closed weighing bottles and then titrated. A Beckman Model H2pH meter² with glass indicator electrode and a calomel reference electrode was used to detect the end point.

Run Procedure

General

The run procedure was basically the same for all runs except for a few differences that arose from the variation in the nature of

¹ Available from Uni-Tech Chemical Manufacturing Company, Panorama City, California

² Available from Beckman Instruments, Inc., South Pasadena, California.

the sulfur (VI) exchanging reactant species in different cases. All the exchange experiments were carried out in sealed Pyrex glass tubes. Exchange reactions of sulfur dioxide (always inactive) with the following reactants (labeled) were studied: (1) pure ammonium bisulfate (see Table III A); (2) two mixtures of ammonium bisulfate and 100% sulfuric acid at respective mole ratios (salt to acid) of 2.05 to 1 and 1 to 4 (see Table III B); (3) pure 100% sulfuric acid (see Table III C); (4) a mixture of ammonium bisulfate and 84.5% H_2SO_4 with a mole ratio of 1 to 1 (see Table III D). Ammonium bisulfate was the S-35 labeled species both in mixtures (2) and (4) (inactive sulfuric acid being used in both cases), and (naturally) in case (1), the pure ammonium bisulfate exchange reactions. Labeled 100% sulfuric acid was used in case (3), the pure 100% sulfuric acid exchange reactions.

Due to the sensitivity of concentrated sulfuric acid to moisture, operations of filling the exchange tubes with the acid (all concentrations) and removal of acid samples from the stock for titration were done in a dry box in all cases except a few where vacuum system transfers were done. The dry box was of standard design, equipped with a circulating pump that allowed the dry air to pass successively through the drying agents: calcium sulfate, barium oxide and phosphorus pentoxide, then into the dry box and finally back to the drying agents again. A dewar flask full of liquid nitrogen was

installed in the dry box prior to its closure from the atmosphere so that the slow evaporation of liquid nitrogen kept a positive pressure inside the box. The atmosphere in the dry box was usually recycled through the drying agents for about 12 hours before the exposure of sulfuric acid to the atmosphere of the dry box.

To transfer the sulfur dioxide gas into the exchange tubes and also to separate it from the solutions after the exchanges were finished, a vacuum system of standard design was used. A mechanical pump and a mercury diffusion pump, pumping through a liquid nitrogen cooled trap were used to evacuate the system to a pressure of less than 10^{-5} mm of mercury. Pressures were measured with a McLeod gauge. In the case of the experiments involving pure ammonium bisulfate, the stopcocks were lubricated with Apiezon "N" or Apiezon "T" high vacuum grease³, the latter being especially useful during hot summer weather. In the case of the experiments involving sulfuric acid (both those with pure sulfuric acid and those with a mixture of sulfuric acid and ammonium bisulfate), Halocarbon⁴ stopcock grease (regular grade) was used to lubricate the stopcocks on the vacuum line, because the Apiezon grease was attacked by the acid.

³ Manufactured by Associated Electrical Industries, Ltd. for Apiezon Products Limited.

⁴ Available from Halocarbon Products Corp., 82 Burlews Court, Hackensack, N. J.

The exchange experiments themselves were carried out with the reaction tubes in a carefully controlled constant temperature bath, constructed especially for the purpose. The bath was of approximately thirty-five centimeters diameter and forty centimeter depth (inside dimensions). It was operated as an oil bath (Aeroshell oil 120W) and it consisted of a glass jar housed in an insulated metallic container with a Transite cover. Contained within the jar were: (1) two heaters, one of 500 watts for control and the other of 250 watts; (2) a stirrer; (3) a mercury thermometer; and (4) a temperature sensing element (resistance thermometer) connected to a Halikainen⁵ "Thermotrol" controller, which provided intermittent power to the control heater of 500 watts. The variations of temperature in this apparatus were checked with a National Bureau of Standards calibrated thermometer. In an initial testing out of this bath, a five junction iron-constantan thermocouple directly attached to a 10 mv. full scale strip chart recorder (the excess voltage bucked by a precision potentiometer) was used to record the variation of the temperature as a function of time in the thermostat. The temperature measurement and control was found to be good to about $\pm 0.1^\circ\text{C}$. Thereafter temperatures were monitored by means of a thermometer calibrated against the N. B. S. thermometer.

⁵ Halikainen Instruments, Berkeley, California.

Reaction Tubes

As indicated above all the exchange experiments in the research were carried out in sealed Pyrex glass tubes. The tubes were made in two shapes. Tubes of the type b (Figure 1) were used for the exchange of sulfur dioxide with ammonium bisulfate and those of the type a (Figure 1) were used for the exchange in sulfuric acid or for mixtures of sulfuric acid and ammonium bisulfate.

Ammonium Bisulfate Transference into Reaction Tubes

Ammonium bisulfate was always (in case of pure ammonium bisulfate or mixtures of the salt and sulfuric acid) transferred into the reaction tubes in the atmosphere of the laboratory. A previously weighed amount (± 0.1 mg) of the labeled salt (it was the labeled sulfur (VI) exchanging reactant in the cases of mixtures and, of course, as pure salt) was introduced into the reaction tube at point A (both Type a and Type b, Figure 1) before the ground joint C, shown in the figure, had been sealed on. The ground joint was then sealed to the tube.

Sulfuric Acid Transference into Reaction Tubes

Since concentrated sulfuric acid solutions could not be allowed to come in contact with the moist laboratory atmosphere, the

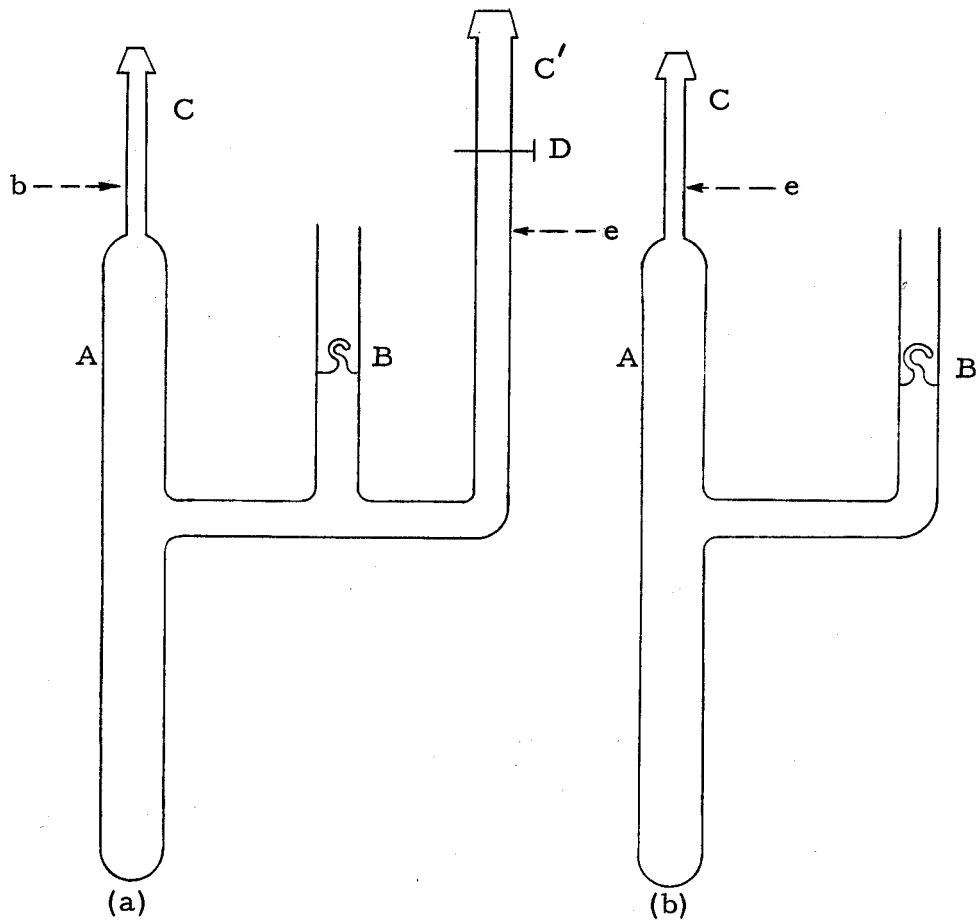


Figure 1. Exchange tubes.

operations of filling the exchange tubes with the acid (all concentrations) and removal of acid samples from the stock for titration were done in a dry box in all cases except for a few instances where vacuum system transfers were used.

Hand-made burettes with Teflon stopcocks (ungreased) were calibrated so as to transfer known volumes of sulfuric acid to the exchange bombs. The error in the weight of sulfuric acid transferred was about $\pm 1\%$, as established by weighing a number of test samples.

To lessen the exposure of sulfuric acid to the atmosphere of the dry box, two similar procedures were used. One of them was used to transfer 100% H_2SO_4 into the exchange tubes and the other was used to transfer the 84.5% H_2SO_4 into the reaction tubes. A third procedure was practiced where the vacuum line, instead of the dry box, was used for transferring the sulfuric acid into the exchange tubes. The last method was used to transfer sulfuric acid (100%) in the cases only of the three experiments 128, 130 and 131 (see Table III C, Batch VI, Groups XXX, XXXII and XXXIII). The dry box was used for all the rest of the experiments.

Figure 2 illustrates the apparatus used in the dry box for filling the reaction tubes with 100% sulfuric acid. It consisted of the following parts: (1) a round flask of 200 ml volume containing the sulfuric acid under consideration; (2) a Teflon stopcock (ungreased);

(3) an inner part ground joint of $\frac{20}{40}$ F size; (4) a matching ground joint (outer part); (5) an opening (1 cm outer diameter tubing) attached via rubber tubing to a barium oxide drying tube, which was exposed to the atmosphere of the dry box at its open end; (6) the body of the calibrated burette; (7) a Teflon stopcock (ungreased).

As previously was described (see p. 9, Sulfur-35 Labeled 100% Sulfuric Acid), the sulfuric acid was transferred from the two neck flask, in which the preparation of the acid had taken place, into the 200 ml round flask equipped with a stoppered ground joint at one end and a Teflon stopcock at the other end (part 2 of Figure 2).

After this, with the apparatus horizontal, the ground joint was sealed off (at point a of Figure 2) in the open air, while the stopcock was kept open but attached via rubber tubing to a barium oxide drying tube, which was exposed to the atmosphere of the laboratory at its open end. The body of the burette (part 6 of Figure 2) varied in size from one burette to another according to the volume of acid needed, though the tube connecting (6) to the ground joint (4) was always made from 6 mm outer diameter tubing. At the end of each operation of filling a batch of reaction tubes, the 200 ml container of sulfuric acid (parts 1 through 3 of Figure 2) was taken out of the dry box and broken (at point b in Figure 2). Part bc was then washed and dried in the oven. The leg of the stopcock 2 was first rinsed with water, then with chloroform, dried carefully with a pipe

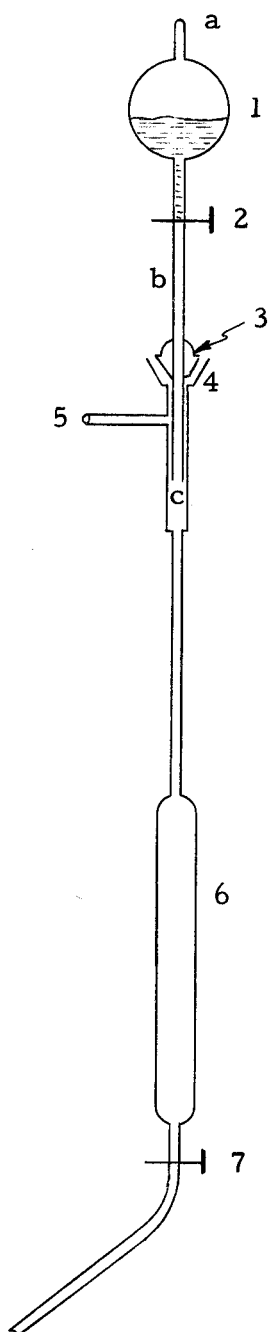


Figure 2. Burette design for transferring sulfuric acid to reaction tubes.

cleaner and kept in a dessicator over calcium chloride to be used in the next run, after the part bc was sealed to it again.

In the procedure used for filling the reaction tubes with 84.5% H_2SO_4 , the same style of burette (parts 4 through 7 of Figure 2) was used. Sulfuric acid, stored in an Erlenmeyer flask of 250 ml volume and stoppered with a glass stopper, was transferred into the burette through a capillary funnel, after which the capillary funnel was removed and the outer part ground joint (4 of Figure 2) was stoppered with an inner part ground joint cap. In the period between two runs, the closed Erlenmeyer flask of sulfuric acid was kept in a dessicator over calcium chloride.

In both of these first two techniques, the sulfuric acid was introduced into the reaction tube through ground joint C (Figure 1, type a). The acid used was labeled or unlabeled depending on whether the exchange was going to take place in the pure acid or in the mixture of the acid and the labeled salt which had already been introduced into the tube. The tube (Figure 1, type a) was stoppered with an outer part ground joint cap, greased with Halocarbon stopcock grease (regular grade). The tube (stopcock D closed) was then taken out of the dry box and it was now ready for transferring sulfur dioxide into it.

Each time the dry box was used for filling a batch of tubes,

three samples of the sulfuric acid under consideration were taken in previously weighed weighing bottles for weighing in titration. In almost all cases the concentrations found checked those expected within an experimental error of about $\pm 0.1\%$ (absolute). In those few cases where this was not so, the entire acid preparation was discarded.

In Figure 3, the apparatus employed to fill the reaction tubes with sulfuric acid in the procedure using the vacuum line instead of the dry box is illustrated. It consisted of the following parts: (1) a round flask of 200 ml volume containing the sulfuric acid stock (which was filled in the same way described previously in the explanation of Figure 1); (2, 3, 4) Teflon stopcocks (ungreased); (5, 8, 10) inner ground joints; (6) a point at which the reaction tube was sealed off; (7) a break-off tip (part of the reaction tube); (9) a high vacuum stopcock (greased with Halocarbon grease). The system was attached to the vacuum line through ground joint 5. To start with, stopcocks 2 and 9 were closed, and stopcocks 3 and 4 were open. After the system was evacuated to a good vacuum (the Teflon stopcocks held the vacuum reasonably well), stopcocks 3 and 4 were closed and after that stopcock 2 was opened. Then 2 was closed and 3 was opened until the sulfuric acid had filled the reaction tube to a mark previously scratched on it and, after that, the tube was sealed off at point 6 (see Figure 3). Then the tube was attached to the

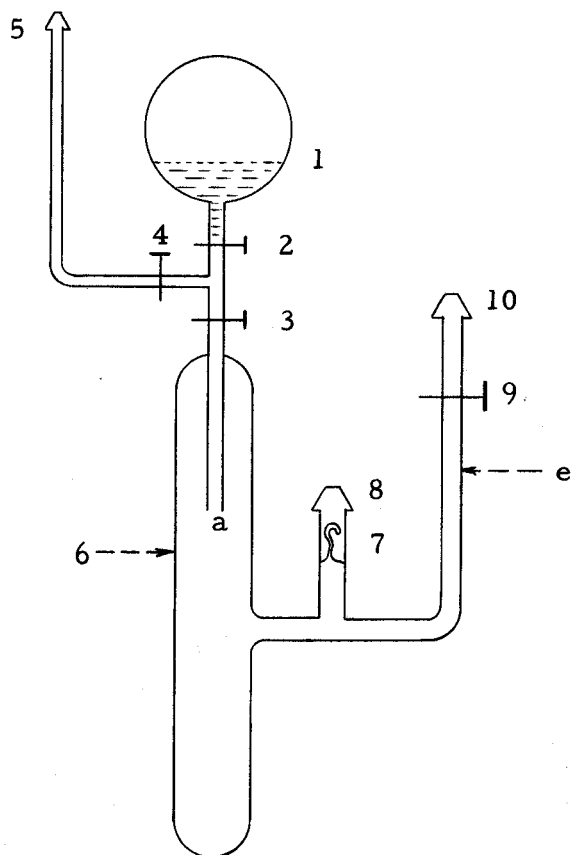


Figure 3. Apparatus design for transferring sulfuric acid to experiment tubes using the vacuum line.

vacuum line through ground joint 10, stopcock 9 was opened, the tube was evacuated, filled with sulfur dioxide and finally sealed off below stopcock 9. After the tube had been warmed to room temperature, it was weighed. For recovering the sulfur dioxide from the tube (after it was taken out of the thermostat), the tube was attached through ground joint 8 to the vacuum system. Then, after removal of the sulfur dioxide, the tube was detached from the vacuum system and cleaned thoroughly so that it might be reweighed. To this end, the tube was broken carefully into two parts just below break-tip 7, the parts of the break-tip being carefully saved. After removal of the sulfur (VI) residue for radioassay, the tube was then cleaned and reweighed. After allowing for the weight of sulfur dioxide used in the experiment, the weight of sulfuric acid was thus obtained.

As previously mentioned, this vacuum line technique was used to transfer sulfuric acid (100%) only in the case of the three experiments 128, 130 and 131 (see Table IIIC, Batch VI, Groups XXX, XXXII and XXXIII). Following these experiments, use of the method was discontinued because it was not found satisfactory. In one particular difficulty encountered, for example, a drop of acid would sometimes stick at point a (Figure 3) and fall down just at the time of sealing the tube off. This changed the concentration of sulfuric acid and consequently caused the loss of the experiment under consideration. In addition to this, one could avoid the time-consuming operation of

weighing each tube twice by transferring the sulfuric acid volumetrically in the dry box.

Sulfur Dioxide Transference into Reaction Tubes

The reaction tube, with the sulfur (VI) exchanging reactant in it, was attached to the vacuum line through a stopcock on the vacuum system to transfer the sulfur dioxide in. Ground joints C' (Type a, Figure 1), C (Type b, Figure 1) or 10 (Figure 3) on the reaction bombs were used for this connection. The stopcock on the vacuum line was opened and the tube was pumped on, with stopcock D (Type a, Figure 1) or 9 (Figure 3) open, at a pressure ($< 10^{-5}$ mm of mercury) for ~ 10 minutes. At this stage of the operation, ground joint C (Type a, Figure 1) was sealed off at point b (see Figure 1). Then, with the stopcock on the vacuum line closed, the contents of the tubes containing ammonium bisulfate were heated with an oil bath sufficiently either to fuse the pure ammonium bisulfate (tube type b, Figure 1) or, in case of salt-acid mixtures, to complete the solution process (tube type a, Figure 1). The temperature of the oil bath was varied from $\sim 150^\circ\text{C}$ in the case of pure ammonium bisulfate to $100\text{-}120^\circ\text{C}$ in the case of the mixtures. There was no need for this heating operation in the case of the pure 100% sulfuric acid as the exchanging reactant (in a tube of type a, Figure 1 or the type illustrated in Figure 3). Now the stopcock on the vacuum line was

opened and the tube was pumped on ($< 10^{-5}$ mm mercury) for a few minutes (3-5 minutes in most cases, 5-10 minutes with the pure fused ammonium bisulfate), after which the stopcock on the vacuum line was again closed. This procedure served to eliminate gases released by the solution or molten salt (as well as possibly some additional moisture in the latter case). At this point the question of some possible ammonium bisulfate decomposition under the experimental conditions described above arises, as well as the possibility of a slight water loss by the acid. This question is discussed at the end of this section. The acid, fused salt or the mixture of salt and acid was then frozen in liquid nitrogen, the stopcock on the vacuum line opened and the bomb again evacuated to $< 10^{-5}$ mm for a few minutes. The stopcock on the vacuum line was next closed. The amounts of sulfur dioxide used were measured by transferring the gas from the storage bulb to a dosing bulb of precisely known volume at a known temperature and pressure. Sulfur dioxide pressures were measured with a mercury manometer to ± 0.5 mm of Hg. The excess gas in the vacuum manifold outside the dosing bulb was then pumped off and the dosage amount of gas was frozen into the bomb with liquid nitrogen. Finally the stopcock on the vacuum line was closed and the tube was sealed off at point e (types a and b of Figure 1, and Figure 3) and removed from the vacuum system.

The dosing bulb was 27.0 ml volume for all experiments

preceding experiment no. 192. Starting with experiment no. 192, until the end of the work, a dosing bulb of 30.2 ml volume was used. The first dosing bulb was calibrated by filling with sulfur dioxide at known temperature and pressure and then absorbing the gas quantitatively in sodium hydroxide, precipitating, and weighing it as barium sulfate. This procedure was done three times, good checks between the results being obtained. The second dosing bulb was made from a 12 cm length of glass tubing (20 mm outer diameter) fitted with a high vacuum stopcock. With the stopcock open (ungreased), the bulb (already cleaned and dried) was attached to an aspirator via rubber tubing (thick wall) and evacuated. The stopcock was then closed and the bulb was weighed. The bulb was now filled with water by immersing the stopcock leg in a beaker full of distilled water and opening the stopcock. To complete the filling of the bulb with water, a capillary funnel extending down through the stopcock bore was used. The leg of the stopcock was dried by rinsing it with acetone. The bulb was now weighed again. The bulb was filled with water three times, giving water weights of 30.1960 g, 30.1971g and 30.1902g. The bulb was finally dried in the oven and then sealed to the vacuum system.

Considerable difficulty was encountered with the tubes filled with pure 100% sulfuric acid, in that they exploded when they attained room temperature after being sealed off from the vacuum

line. However, spraying the tubes generously with acetone just after sealing them off was found an adequate method for saving the tubes from breaking.

As previously mentioned in this section, the possibility of some decomposition of ammonium bisulfate, when it was fused and pumped on $< 10^{-5}$ mm Hg, was considered. In a previous work by the author (1, p. 14), this possibility was explored. A weighed amount of dried ammonium bisulfate (in an open container) was put in an oven overnight at 169.5°C and then weighed again. The loss in the weight of the sample was 0.207%. Another weighed amount of dried ammonium bisulfate was introduced into a tube supplied with a ground joint (the weight was measured by weighing the tube before and after introducing the ammonium bisulfate into it). The tube was attached to the vacuum system. The ammonium bisulfate was kept in an oil bath at $168-172^{\circ}\text{C}$ while being pumped to a pressure of $< 10^{-5}$ mm for about 10 minutes. The tube was weighed again. The loss in the weight of the sample was 3.25%. The same two tests were also carried out at 194.8°C . The loss of the ammonium bisulfate sample heated overnight in the oven was 0.857%, while the loss in the weight of the sample heated in the vacuo was 3.16%. In the present work the same two tests were carried out at 225.3°C . The weight of the ammonium bisulfate sample heated in the oven overnight decreased from 63.4358 to 62.6412 g, a weight loss of 1.253%, while the

weight of the sample heated in vacuo went from 3.7432 to 3.5930 g, a weight loss of 4.02%.

It may be noted that the foregoing tests were done under somewhat more drastic conditions than those applying to the filling of the reaction bulbs in the present work. It is also possible that at least some of the observed weight loss may have been due to release of trapped gases when the salt was fused (gas was visibly given off when the freshly melted salt was first exposed to the vacuum). In any case the weight loss was not large, and so the effect was not further considered, any possible small decomposition of the ammonium bisulfate occurring in the filling of the tubes being disregarded. A further question along the same lines relates to the possibility of loss of water by the sulfuric acid solutions in the filling process. This question was not explored experimentally, but in view of the low vapor pressures involved, it seems probable that the loss could not have been excessive. Hence this factor also was disregarded.

Reaction Tube Heating

After the sulfur dioxide had been introduced into the tubes as described above, the tubes were left for a time to attain room temperature. They were then put into the constant temperature oil bath for the duration of the experiment. In the bath the tubes were laid horizontally in a wire basket. The tubes were placed

horizontally so that the reaction liquid species (acid, fused salt or mixture of acid and salt) would spread out to give a maximum surface and a minimum thickness for the gas to diffuse through. This was done in an attempt to avoid any tendency towards control of the exchange rate by a slow diffusion process.

Separation of Reactants

After removing the exchange bombs from the thermostat, sulfur dioxide was recovered from the tube by attaching the break-off tip end (see Figure 1 and Figure 3) of the tube, containing a magnetically controllable breaker, to the vacuum line by means of a glass ground joint. The breaker consisted of an iron bar with a few drops of mercury, to increase its weight, encased in a glass tube. Also attached to the vacuum manifold was an absorption bomb, containing 1 N sodium hydroxide, through a ground joint. The exchange bomb was immersed in an oil bath of 40°C in the case of pure sulfuric 100% acid in the tube, of 150°C in the case of pure ammonium bisulfate, and 100-125°C in the case of mixtures of sulfuric acid and ammonium bisulfate. With the sodium hydroxide solution frozen in liquid nitrogen, the stopcocks through which the tubes were attached to the vacuum system were opened and the system evacuated to 10^{-5} mm of mercury. After the stopcock to the pump had been shut, the break-tip was then broken by raising the beaker with a magnet, and letting it fall. The gas passed through a disc of sintered glass (fine porosity) provided as a means

to filter out any particles of the solution, if there were any, carried by the gas, before it arrived at a trap of ice and water (see Figure 4). This trap was especially necessary in the case of having sulfuric acid (partially or totally) in the experiment tube, in order to trap any drops of acid carried by the gas, some of which apparently passed through the sintered disc. After that the gas was frozen by means of liquid nitrogen into the absorption bomb containing the sodium hydroxide solution, this bomb then being finally sealed off and removed from the vacuum line. Completeness of transfer of the gas to the absorption bulb was easily followed by use of a mercury manometer attached to the vacuum manifold. Completeness of separation using this procedure (91% apparent exchange) was attested to by experiments of essentially zero time duration (see Results section).

Radioactivity Assay

The exchanges were carried out using the isotope sulfur -35. This isotope emits beta particles of maximum energy 0.167Mev and has a half-life of 87.1 days (7).

Radiosulfur samples were assayed as barium sulfate following standard procedures described by Norris (17). For this purpose, labeled compounds, including the solutions of sulfur dioxide in sodium hydroxide (see the preceding section), were dissolved in water, oxidized with bromine water in the case of the sulfur dioxide

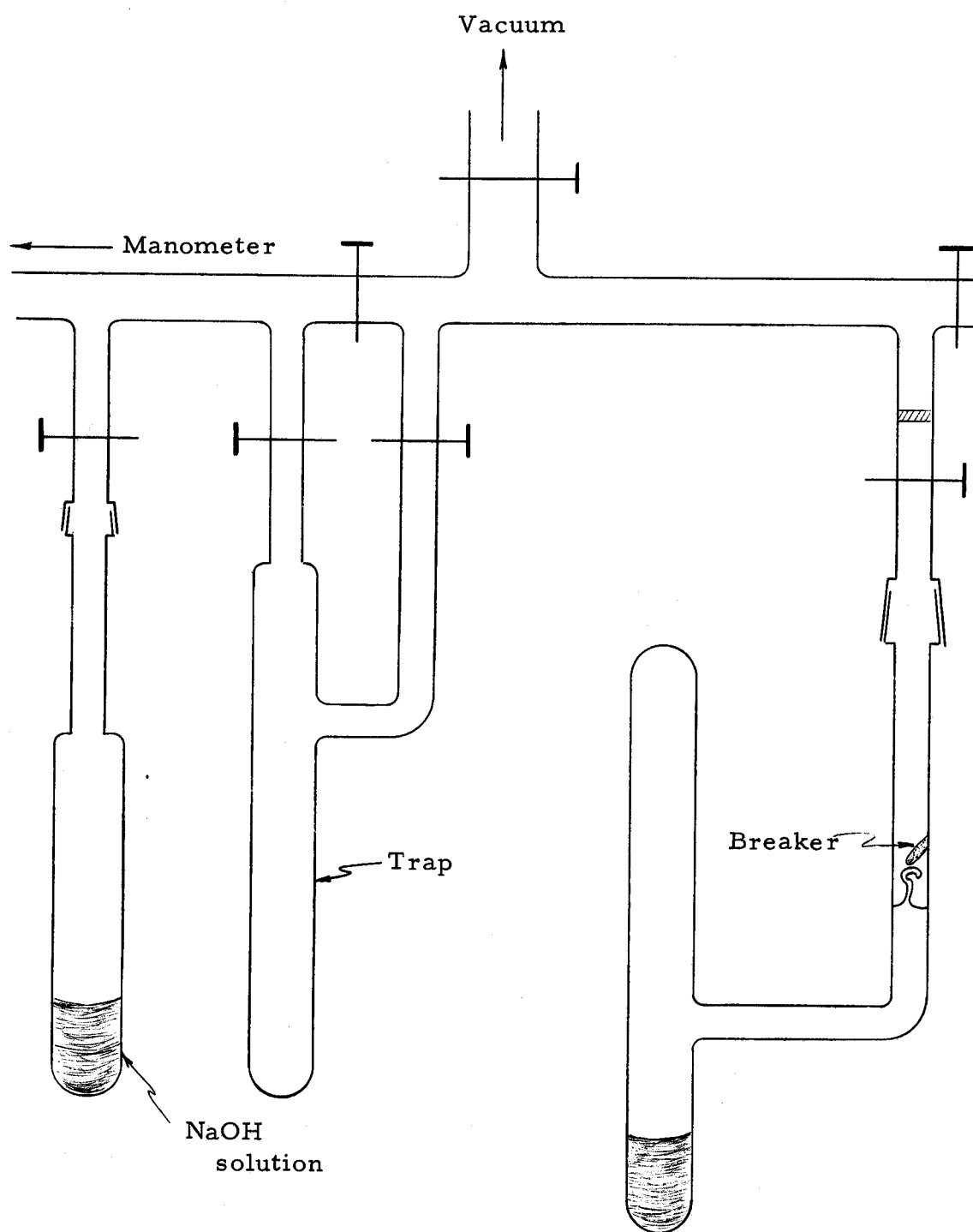


Figure 4. Separation system for break-tip tubes.

fractions, brought to a pH of ~ 1 with hydrochloric acid (no need for acid addition when sulfuric acid was present), heated to boiling and treated with 0.5 N barium chloride in order to precipitate barium sulfate. After digestion for half an hour at boiling temperature, the precipitate was collected in a sintered glass crucible by vacuum filtration. Crucibles of fine porosity were used for the precipitate obtained from the sulfur dioxide fractions to avoid losing some of the precipitate (usually small quantities of precipitate were obtained). A "medium" porosity crucible was used for the bulkier precipitates obtained from the sulfur (VI) fractions. The precipitate was washed several times with hot distilled water and finally slurried with acetone (U. S. P. grade), after it had been dried in an oven at 200°C. Appropriate amounts of the slurry were transferred to cupped, nickel-plated steel planchets (by means of an eye dropper) and dried under an infrared lamp. Duplicate planchets were made from each sample in every case. The weight of the precipitate on a planchet ranged between 7 to 170 mg. Measurements were made with an end window Geiger counter (Tracelab, Inc., Model TGC-2, with a 1.8 mg per square centimeter window) together with a Nuclear-Chicago Model 182 scaler. Two different tubes were used during the course of the work, but none of the calculations involved intercomparison of counting data obtained with the different tubes.

The second shelf in the counting arrangement (the nearest one

to the tube) was always used, so there was no need for corrections due to variation in geometry. Corrections were applied for background, decay, self-absorption and coincidence loss. The decay factor was obtained, when necessary, from the known half-life of 87.1 days (7). However in most of the experiments the decay correction was avoided by counting standard samples (initial activity samples, A_0 in Tables IIIA - IIID) at the same time as the related samples whose activities were being determined. All such related counts were made within, at most, a few hours of each other, hence the need for decay correction for the samples was eliminated. Self-absorption and coincidence corrections were made on the basis of curves previously prepared in this laboratory empirically. The latter correction was of material significance in only four cases (see Table III C, Group XXVII and XXVIII, and it was of a minute value in the rest of the experiments).

Each sample and the background were counted for at least nine minutes. This had the effect of insuring even for the weakest samples (the zero time samples excepted) a standard deviation in the determined counting rate of not more than 3%. For samples other than the weakest ones, especially the sulfur (VI) samples, the standard deviation was much smaller than this figure.

III. METHODS OF CALCULATION

The same methods of calculation described previously by the author (1, p. 16-22) in the case of the ammonium bisulfate study were followed throughout the present work. The rate, R , (in mmoles per hr), at which sulfur atoms appear to be transferred from the sulfur (VI) species to the sulfur (IV) species, must follow a first order course according to McKay (14) and Duffield and Calvin (3). The rate of exchange, R , is given by:

$$R = -2.303 \frac{ab}{(a+b)t} \log (1-F) \quad (1)$$

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

where $F = (\text{percent exchange})/100$ and t is the run time in hours.

The quantity b is the amount of the sulfur (VI) species (ammonium bisulfate and/or sulfuric acid) in a reaction bomb in millimoles, while a is equal to the amount of sulfur dioxide in millimoles. The latter quantity was calculated by applying the perfect gas law:

$$PV = n \underline{R} T \quad (2)$$

Here P is the pressure of sulfur dioxide dosed out and V is the volume of the doser used. At first the doser was of 27.0 ml volume and later a doser of 30.2 ml volume was used. \underline{R} is the gas constant. T is the absolute temperature at which the gas was dosed

out. So in this way n could be computed, which quantity was equal to a in equation (1).

As a practical matter, the observed exchange half-time, $t_{1/2}$, was used to calculate R . The value of $t_{1/2}$, the run time for which $F = 0.5$, was obtained from a graph of $\log(1-F)$ versus time for each set of experiments. For use of this quantity, one may obtain from equation (1) the relationship:

$$R = \frac{ab}{a+b} \cdot \frac{0.693}{t_{1/2}} \quad (3)$$

The value of F was computed in the same way done by Norris (17),

F is given by the formula:

$$F = \frac{S_t - S_o}{S_\infty - S_o} = \frac{S_t}{S_\infty} \quad (4)$$

where S_t is the specific activity of sulfur dioxide at time t , and S_o that of sulfur dioxide at zero time. The sulfur dioxide being initially inactive, $S_o = 0$. The value of S_t was taken to be identical with the observed value of the separated sulfur dioxide fraction, a procedure justified by the apparent completeness of reactant separation, a fact itself indicated by the absence of any apparent zero time exchange (see Results section). The planchets were weighed before use (see Section II) and after the barium sulfate had been dried. Thus the weight of the barium sulfate precipitated from sulfur dioxide and transferred to the planchets was known. Two

planchets were prepared from each sample. The activity of each planchet was measured with the Geiger counter three times, each time for three minutes. Corrections mentioned previously (see Section II) were taken into consideration to compute the specific activity in counts per minute per mg of barium sulfate. After that the average specific activity in counts/min-mg was calculated from the values found for the two planchets.

The quantity S_{∞} was the specific activity of the sulfur dioxide expected at infinite time. It was calculated from the measured initial specific activity of the sulfur (VI) fraction, A_0 , on the basis of the relative amounts of reactants used, random distribution of activity between sulfur (IV) and sulfur (VI) being assumed. This last assumption implies, of course, that S_{∞} was equal to the final specific activity of the sulfur (VI) fraction, A_{∞} . Hence one may write, for the purpose of the computation, the expression:

$$(a + b)A_{\infty} = (a + b)S_{\infty} = aS_0 + bA_0 \quad (5)$$

Here S_0 is the original specific activity of sulfur dioxide, equal to zero, and A_0 is the initial specific activity of sulfur in the sulfur (VI) fraction (ammonium bisulfate and/or sulfuric acid). Thus one obtains

$$S_{\infty} = A_0 \frac{b}{a + b} \quad (6)$$

The initial specific activity of the sulfur (VI) species, A_0 , was

measured by the same technique used for the measurement of S_t . For purposes of calculation of F , A_o was corrected, in a few cases, for decay, as necessary, to the time of the measurement of sulfur dioxide activities, S_t . In the majority of cases, however, the quantity, A_o , was actually directly measured in connection with and at the same time as the sulfur dioxide fractions from each particular batch of runs. In no case was any significant deviation of activity observed from that expected on the basis of decay from previously measured values.

As in the author's previous work (1, p. 1-50), it was again necessary to obtain values for the solubility of sulfur dioxide gas in the sulfur (VI)-containing solutions under the experimental conditions prevailing in each case. This was again done by means of the same method previously used by Doherty (2, p. 3-6). On the basis of previous results obtained in the study of the exchange between sulfur dioxide and sulfuric acid by Masters and Norris (12), Doherty (2, p. 1-37) and by McDonald (13, p. 1-138) and also those results obtained in the study of the exchange between sulfur dioxide and ammonium bisulfate by the author (1, p. 1-50), it was further assumed that the exchange reaction involves gas dissolved in the liquid phase, being first order, in this species, and hence has a rate proportional to the volume of the liquid phase and proportional to the gas pressure over the solution. This assumption is tantamount to the assumption of the validity of Henry's Law for these systems.

The justification for these assumptions lies essentially in the fact that the treatment described below "works", i. e., where one expects the experimental data to give a straight line plot, it is found that they do, in fact, do so.

On the basis of these considerations, then, one can write, as Doherty did, the tentative rate law:

$$R = k' \frac{(\text{amount of gas})(\text{volume of liquid sulfur (VI) species})}{(\text{total volume of gas} + \text{liquid sulfur (VI) species})} \quad (7)$$

where, for large gas volumes, the term

$$\frac{\text{amount of gas}}{(\text{total volume of gas} + \text{liquid sulfur (VI) species})}$$

is approximately proportional to the pressure of gas in the gas phase over the liquid sulfur (VI)-containing solutions. Equation (7) may be written

$$R = k' (\text{amount of gas}) R' \quad (8)$$

where R' corresponds to the ratio of liquid to total volumes in the reaction bombs:

$$R' = \frac{\text{volume of liquid sulfur (VI) species}}{\text{total volume of gas} + \text{liquid sulfur (VI) species}} \quad (8')$$

The validity of equation (7) rests on the double assumption that the volume of liquid may be neglected relative to the gas volume (i. e., R' is very small) and that the fraction of the total sulfur dioxide dissolved in the liquid phase is very small. As the liquid

is increased in relative volume (larger R') and the fraction of the gas dissolved increases, this equation will tend to be decreasingly valid. Thus Doherty (2, p. 4) in the treatment of his system, indicated that the constancy of k' held only approximately and then only for relatively large ratios of gas to liquid volume. It is assumed that the same situation applies in the present work and that k' is in fact a function of R' . Thus, with Doherty, we write as an expression containing a true rate constant

$$R = k (\text{amount of gas}) F' \quad (9)$$

where F' is the fraction of the total gas dissolved in the liquid sulfur (VI)-containing solution.

In order to find a relationship between F' and R' (and hence, ultimately, the gas solubility) it was assumed, as indicated above, that Henry's law applies in this system and that one may write (as Doherty did) a distribution coefficient c describing the distribution of the gas between the gas and liquid phases, thus:

$$c = \frac{\text{SO}_{2\ell} / \text{vol}_{\ell}}{\text{SO}_{2g} / \text{vol}_{g}} \quad (10)$$

Here the terms refer to the gas amounts in, and the volumes of the liquid sulfur (VI) species and the gas phases, respectively, according to whether subscript ℓ or g is given.

In order to obtain the desired relationship between F' and R' , one may proceed with the following self-explanatory steps, the first

representing simply a rearrangement of equation (10).

$$1 + \frac{\text{SO}_{2g}}{\text{SO}_{2l}} = \frac{\text{vol}_g}{c \text{ vol}_l} + 1 \quad (11)$$

$$\frac{\text{SO}_{2l} + \text{SO}_{2g}}{\text{SO}_{2l}} = \frac{\text{vol}_g + c \text{ vol}_l}{c \text{ vol}_l} = \frac{1}{F'} \quad (12)$$

$$F' = \frac{c \text{ vol}_l}{\text{vol}_g + c \text{ vol}_l} = \frac{c \text{ vol}_l}{\text{vol}_{\text{total}} - \text{vol}_l + c \text{ vol}_l}$$

$$\frac{c \frac{\text{vol}_l}{\text{vol}_{\text{total}}}}{1 - \frac{\text{vol}_l}{\text{vol}_{\text{total}}} + c \frac{\text{vol}_l}{\text{vol}_{\text{total}}}} = \frac{cR'}{1 - R' + cR'} \quad (13)$$

By equating equation (8) to equation (9),

$$k'(\text{amount of gas})R' = k(\text{amount of gas})F' \quad (14)$$

one is led directly, upon substitution of F' from equation (13), to the expression:

$$k' = k \frac{c}{1 - R' + cR'} \quad (15)$$

The reciprocal of equation (15) will be:

$$\frac{1}{k'} = \frac{1}{kc} [1 + (c - 1) R'] \quad (16)$$

Equation (16) can be used now to determine the solubilities of sulfur dioxide in the liquid sulfur (VI) species in terms of the

distribution coefficient c . Since a plot of $1/k'$ versus R' should yield, the temperature being kept constant, a straight line whose intercept at $R' = 1$ equals $1/k$ and intercept at $R' = 0$ equals $1/kc$, the value of c can be found when the values of the two intercepts at $R' = 1$ and $R' = 0$ are known.

For the foregoing purpose the observed values of $1/k'$ (calculated from equations (3) and (8) have been plotted versus R' at constant temperature. R' was varied by changing the amount of sulfur (VI) species used or by changing the size of the bomb.

Thus the calculation of c requires a knowledge of the volume of the liquid sulfur (VI) species at the temperatures under consideration, a quantity calculable from the known weight of sulfur (VI) species used on the basis of its density. As data are not available in the literature, however, it was necessary to measure these densities at the different temperatures under consideration.

For this purpose a glass pycnometer of about seven ml total volume was constructed. The body of this pycnometer was made from tubing of 10 mm outer diameter and about 5.5 cm in length. Connected to the end of this tube was a filling neck made from five mm inside diameter tubing, and about 10 cm in length, provided with a ground joint stopper at the top. Into the pycnometer was put a known weight (determined by weighing the pycnometer before and after filling of sulfur (VI) species). The pycnometer, stoppered, was then immersed

in the thermostat at the temperature concerned for a time. The pycnometer was then taken out of the thermostat and quickly scratched at the level of the liquid in the neck. The volume was then measured by filling the pycnometer with mercury to the mark and weighing the amount of mercury. The density of mercury was taken as 13.5340 g/ml at 25°C. The values of the densities measured are summarized in Table I. All the operations of transferring sulfuric acid into the pycnometers were done in the dry box (see Section II). It was also, in the present work, found necessary to know (see Section V) the densities of sulfuric acid under the same conditions of concentration and temperature at which Doherty (2, p. 1-37) worked. Doherty (2, p. 12) obtained estimations for these values by extrapolation to higher temperatures of the data appearing in International Critical Tables (4, p. 56-57). The values of the densities measured in this research are summarized in Table II.

TABLE 1. Reaction Medium Densities

Sulfur (VI) Reactant	Temp., °C	Density g/ml
pure NH_4HSO_4	225.3	1.617
2.05:1 NH_4HSO_4 ^(a) and 100% H_2SO_4	194.4	1.704
1:4 NH_4HSO_4 and 100% H_2SO_4	194.4	1.721
100% H_2SO_4	167.5	1.722
100% H_2SO_4	194.4	1.651
100% H_2SO_4	225.3	1.650
1:1 NH_4HSO_4 and 84.5% H_2SO_4	167.5	1.662
1:1 NH_4HSO_4 and 84.5% H_2SO_4	194.4	1.615
1:1 NH_4HSO_4 and 84.5% H_2SO_4	225.3	1.567

(a) The ratio shows the ratio in number of millimoles. So 2.05:1 NH_4HSO_4 and 100% H_2SO_4 means that the ratio of the number of millimoles of ammonium bisulfate to those of 100% sulfuric acid is as 2.05 to 1.

TABLE II. Acid Densities

% Acid	Temp. , °C	Density, Present Work, g/ml	Density, Pre- ^(a) vious Estimate g/ml
98.0	167.5	1.697	1.698
98.0	181.4	1.690	1.685
98.0	194.4	1.674	1.673
98.0	225.3	1.650	1.646
97.0	194.4	1.684	1.674
96.0	194.4	1.675	1.671
94.9	194.4	1.669	1.668
93.1	194.4	1.663	1.662
90.8	167.5	1.676	1.673
90.8	194.4	1.650	1.648
90.8	225.3	1.611	1.619
85.2	194.4	1.612	1.608

(a) Done by Doherty (2, p. 12)

IV. RESULTS

General

The experimental results are listed in Tables III A through VI. In the tables the data are presented in terms of "runs", "groups", and "batches". Each run represented an individual reaction tube and for each group several tubes (usually 3 or 4) were run for various time periods, but with nearly identical amounts of exchange reactants and tube volumes (so R' values were approximately the same) within the limits of experimental error. For each batch, several groups (usually 3) were done for various R' values, but all at the same temperature. The fractional exchange value for each run was calculated by the method described in Section III. The data from each group were then plotted as $\log(1-F)$ versus time. The good straight lines obtained show that the isotopic exchange must follow the expected first order rate law (cf. equation (1), Section III). A typical plot of $\log(1-F)$ versus time (for Batch VIII, Group XXXVIII, Table III D) is shown in Figure 5.

The straight lines of $\log(1-F)$ values versus time were drawn passing through the origin, essentially complete separation of reactants being assumed. This practice was justified by the author (1, p. 23) in the case of ammonium bisulfate (on the basis of zero

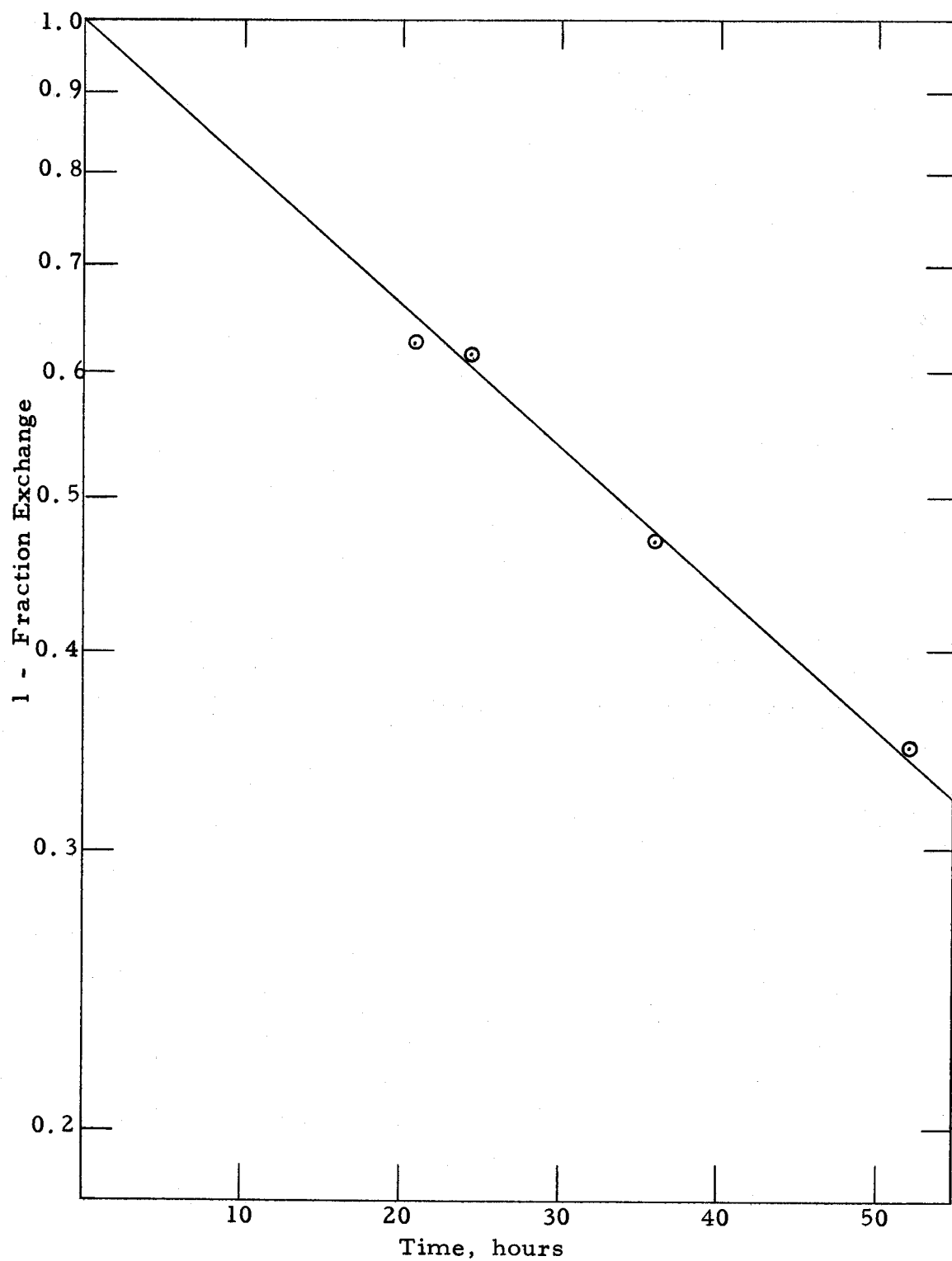


Figure 5. Typical plot of $\log(1-F)$ vs. time, Batch VIII, Group XXXVIII.

time experiment) and by McDonald (13, p. 50) in the case of sulfuric acid. To test the completeness of the separation of reactants in the case of using a mixture of sulfuric acid and ammonium bisulfate, two runs were made in the present work. In Run #127' (Batch IV, Group XXIV, Table III B), with 1:4 ammonium bisulfate and 100% sulfuric acid, the reactants were separated after five minutes in the thermostat, practically zero time, and the apparent exchange was 0.5%. In Run #211' (Batch IX, Group XXXXII, Table III D), with 1:1 ammonium bisulfate and 84.5% sulfuric acid, the reactants were separated after three minutes in the thermostat and the apparent exchange was 0.2%. The fraction of exchange was evidently close to zero in both experiments.

From each plot of $\log(1-F)$ versus time for each group, the value of the half-time, $t_{1/2}$, was found, and from it the rate of the reaction for the group was calculated by applying equation (3), Section III (See Tables, IVA-IVD). The value of k' for a group was calculated, after the calculation of the rate, by applying equation (8), Section III. Then, for each batch, the values of $1/k'$ of the various groups were plotted versus R' values and the best straight line (obtained by least squares) was drawn through the points. The straight lines for different batches are shown in Figures 6 through 16. As discussed in Section III, the straight line for each batch has an intercept at $R' = 1$ equal to $1/k$ and an intercept at $R' = 0$ equal

TABLE IIIA. Exchange Results, Pure Ammonium Bisulfate. ^(a)

Run ^(b) Number	Millimoles SO ₂	Millimoles ^(c) NH ₄ ⁺ SO ₄ [*]	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)	
					A ₀	A _t	S _t	S _∞		
Batch I, Group IX Experiments, 169.5°C. t _{1/2} = 105.0 hrs.										
77	1.014	60.0	37.0	0.25	208	196.5	0.981	205	0.0052	
78	1.016	60.0	37.0	110.0	203	203.2	108.7	199.6	0.545	
79	1.014	60.0	37.0	136.0	194.9	194.0	110.6	191.7	0.577	
81	1.014	60.0	37.0	47.0	194.9	194.2	47.7	191.7	0.249	
Ave.	1.014	60.0	37.0							
Batch I, Group X Experiments, 169.5°C. t _{1/2} = 111.0 hrs.										
66	0.287	42.3	9.6	71.5	111.6	119.7	41.0	110.8	0.370	
67	0.293	42.3	9.6	129.5	111.6	110.0	61.0	110.8	0.550	
67A	0.290	42.3	9.6	111.0	111.6	112.0	55.0	110.8	0.496	
Ave.	0.290	42.3	9.6							
Batch II, Group XI Experiments, 225.3°C. t _{1/2} = 188.0 hrs.										
241	0.615	2.11	33.0	13.13	652	683	32.7	505	0.0647	
242	0.612	2.11	31.4	15.33	652	667	54.5	505	0.1079	
244	0.613	2.11	34.9	96.9	652	581	147.2	502	0.293	
245	0.612	2.11	34.3	120.0	647	581	181.4	501	0.362	
Ave.	0.613	2.11	33.4							
Batch II, Group XII Experiments, 225.3°C. t _{1/2} = 92.5 hrs.										
247	0.340	2.11	16.00	47.7	647	615	150.2	557	0.270	
248	0.342	2.11	15.40	50.32	627	602	178.4	540	0.330	
249	0.342	2.11	16.0	62.7	627	595	201	540	0.372	
Ave.	0.341	2.11	15.80							
Batch II, Group XIII Experiments, 225.3°C. t _{1/2} = 43.9 hrs.										
250	0.340	6.33	15.50	22.8	535	525	144.3	508	0.284	
251	0.341	6.33	15.80	42.5	535	507	250	508	0.492	
254	0.341	6.33	15.0	15.08	537	534	108.0	510	0.212	
255	0.341	6.33	15.2	62.1	537	536	319	510	0.625	
Ave.	0.341	6.33	15.38							

TABLE IIIA. Continued^(a)

Run ^(b) Number	Millimoles SO ₂	Millimoles ^(c) NH ₄ [*] H ₂ SO ₄	Tube Volume, ml	Exchange Time, hrs.	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)	
					A ₀	A _t	S _t	S _∞		
Batch II, Group XIV Experiments, 225. 3°C. t _{1/2} = 10. 20 hrs.										
170	0. 586	43. 4	18. 50	9. 62	96. 6	92. 5	46. 3	95. 3	0. 486	
175	0. 571	43. 4	17. 70	10. 72	94. 3	92. 5	48. 1	93. 1	0. 517	
176	0. 581	43. 4	18. 10	13. 80	94. 4	91. 8	56. 4	93. 2	0. 605	
Ave.	0. 579	43. 4	18. 10							
Batch II, Group XV Experiments, 225. 3°C. t _{1/2} = 11. 40 hrs.										
172	0. 289	59. 9	12. 80	8. 33	96. 6	94. 4	38. 0	96. 1	0. 395	
173	0. 291	59. 9	13. 60	6. 60	94. 0	90. 5	30. 9	93. 5	0. 330	
184	0. 290	59. 9	12. 50	13. 60	92. 5	91. 9	51. 5	92. 0	0. 560	
Ave.	0. 290	59. 9	12. 97							
Batch II, Group XVI Experiments, 225. 3°C. t _{1/2} = 11. 40 hrs.										
174	0. 288	80. 4	11. 30	6. 87	96. 6	93. 7	33. 6	96. 2	0. 349	
182	0. 290	80. 4	11. 00	13. 80	92. 5	89. 8	51. 6	92. 1	0. 560	
183	0. 290	80. 4	11. 2	12. 0	92. 5	90. 3	47. 9	92. 1	0. 520	
Ave.	0. 289	80. 4	11. 17							

TABLE III.B. Exchange Results, Ammonium Bisulfate - 100% Sulfuric Acid Mixtures. (a)

Run ^(b) Number	Millimoles SO ₂	Millimoles ^(c) NH ₄ H ₂ SO ₄ *	Millimoles. 100% H ₂ SO ₄	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)
						A _o	A _t	S _t	S _∞	
Batch III, Group XVII Experiments, 194. 4°C. t _{1/2} = 20.5 hrs.										
102	0.290	45.1	22.1	22.5	17.0	176.0	176.0	83.6	175.2	0.477
103	0.290	45.1	22.1	22.5	9.0	173.2	179.7	46.3	172.4	0.269
104	0.290	45.1	22.1	22.5	37.0	176.0	175.2	122.6	175.2	0.700
Ave.	0.290	45.1	22.1	22.5						
Batch III, Group XVIII Experiments, 194. 4°C. t _{1/2} = 16.00 hrs.										
88	0.291	17.06	8.26	4.3	5.77	237	234	58.5	234	0.250
90	0.291	17.06	8.38	4.3	20.08	225	223	126.5	223	0.567
92	0.291	17.06	8.70	4.3	35.75	212	210	161.7	210	0.770
Ave.	0.291	17.06	8.45	4.3						
Batch III, Group XIX Experiments, 194. 4°C. t _{1/2} = 11.50 hrs.										
97	0.290	45.1	22.1	8.5	4.08	82.1	85.1	18.91	81.7	0.231
98	0.290	45.1	22.1	8.5	13.0	82.1	84.0	44.4	81.7	0.543
101	0.290	45.1	22.1	8.5	22.0	77.7	76.5	56.2	77.4	0.726
Ave.	0.290	45.1	22.1	8.5						
Batch III, Group XX Experiments, 194. 4°C. t _{1/2} = 9.67 hrs.										
107	0.294	45.1	22.1	5.8	6.67	141.9	139.8	50.6	141.3	0.358
105	0.292	45.1	22.1	5.8	12.0	143.6	142.0	85.9	143.0	0.601
106	0.292	45.1	22.1	5.8	10.83	61.0	63.6	31.6	60.7	0.521
108	0.290	45.1	22.1	5.8	20.03	60.7	62.8	44.6	60.4	0.738
Ave.	0.292	45.1	22.1	5.8						

TABLE IIIB. Continued^(a)

Run ^(b) Number	Millimoles SO ₂	Millimoles ^(c) NH ₄ H ₂ SO ₄	Millimoles 100% H ₂ SO ₄	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)
						A ₀	A _t	S _t	S _∞	
Batch IV, Group XXI Experiments, 194.4°C. t _{1/2} = 9.40 hrs.										
110	0.293	16.58	66.3	26	4.00	63.2	65.2	21.4	63.0	0.340
111	0.290	16.58	66.3	25	7.67	58.1	42.4	26.2	57.9	0.453
112	0.291	16.58	66.3	25	9.33	59.2	49.7	29.7	59.0	0.503
113	0.290	16.58	66.3	26	11.50	58.4	53.6	31.0	58.2	0.533
114	0.291	16.58	66.3	26	15.33	58.4	53.8	44.6	58.2	0.766
Ave.	0.291	16.58	66.3	25.6						
Batch IV, Group XXII Experiments, 194.4°C. t _{1/2} = 5.28 hrs.										
122	0.290	16.58	66.3	16.0	6.0	69.6	77.2	36.8	69.4	0.530
121	0.293	16.58	66.3	15.0	3.75	70.5	73.2	27.9	70.3	0.397
123	0.295	16.58	66.3	15.0	11.17	69.6	69.1	54.3	69.3	0.783
Ave.	0.293	16.58	66.3	15.33						
Batch IV, Group XXIII Experiments, 194.4°C. t _{1/2} = 3.60 hrs.										
118	0.291	16.58	66.3	8.8	6.33	73.6	76.1	51.5	73.3	0.703
120	0.293	16.58	66.3	9.0	4.50	73.3	69.6	40.5	73.0	0.555
117	0.291	16.58	66.3	9.2	3.25	74.5	75.6	37.6	74.2	0.507
119	0.293	16.58	66.3	9.5	1.75	73.3	76.4	20.9	73.0	0.286
Ave.	0.292	16.58	66.3	9.13						
Batch IV, Group XXIV Experiments, 194.4°C. t _{1/2} = 2.35 hrs.										
124	0.291	16.58	66.3	6.2	3.17	67.4	67.1	40.3	67.2	0.60
126	0.292	16.58	66.3	6.1	1.250	66.3	68.5	22.3	66.1	0.337
125	0.291	16.58	66.3	6.4	2.33	66.9	69.5	33.4	66.7	0.500
127	0.291	16.58	66.3	6.2	5.0	66.9	66.5	50.4	66.7	0.756
127'	0.291	16.58	66.3	6.23	0.0833	65.1	65.5	0.3	64.9	0.005
Ave.	0.291	16.58	66.3	6.23						

TABLE IIIC. Exchange Results, 100% Sulfuric Acid. (a)

Run ^(b) Number	Millimoles SO ₂	Millimoles ^(c) 100% H ₂ SO ₄	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)	
					A _o	A _t	S _t	S _∞		
Batch V, Group XXV Experiments, 167.5°C. t _{1/2} = 122.5 hrs.										
136	0.582	76.6	19.20	165	137.5	134.8	85.25	136.4	0.603	
137	0.582	76.6	19.20	113.1	137.5	145.2	64.6	136.4	0.474	
138	0.582	76.6	19.40	100.5	137.0	136.3	58.2	135.9	0.428	
139	0.582	76.6	19.0	93.0	125.5	123.0	53.7	124.5	0.431	
Ave.	0.582	76.6	19.2							
Batch V, Group XXVI Experiments, 167.5°C. t _{1/2} = 80.0 hrs.										
140	0.291	76.6	9.5	55.0	142.5	129.8	53.8	141.9	0.379	
142	0.291	76.6	9.7	106.0	128.5	119.0	76.8	128.0	0.600	
143	0.291	76.6	10.2	64.0	125.5	128.0	53.4	125.0	0.427	
Ave.	0.291	76.6	9.8							
Batch V, Group XXVII Experiments, 167.5°C. t _{1/2} = 70.5 hrs.										
141	0.289	76.6	7.0	47.0	131.1	120.1	50.5	130.6	0.387	
145	0.289	76.6	6.7	62.0	125.5	122.0	57.8	125.0	0.462	
145'	0.289	76.6	6.77	100.0	125.5	122.5	78.1	125.0	0.625	
147	0.291	76.6	6.60	59.0	1899	1839	819	1891	0.433	
Ave.	0.290	76.6	6.77							
Batch V, Group XXVIII Experiments, 167.5°C. t _{1/2} = 62.0 hrs.										
146	0.291	76.6	5.80	49.1	1900	1855	843.5	1892	0.446	
148	0.291	76.6	5.60	65.5	1900	1901	964	1892	0.510	
149	0.291	76.6	5.7	82.0	1900	1900	1142	1892	0.604	
Ave.	0.291	76.6	5.7							
Batch VI, Group XXIX Experiments, 194.4°C. t _{1/2} = 23.4 hrs.										
125'	0.290	91.0	26.0	3.5	145.9	145.6	13.04	145.5	0.0896	
126'	0.290	91.0	25.0	13.0	150.0	146.4	47.9	149.6	0.320	
127'	0.290	91.0	25.0	42.25	144.2	142.0	102.5	143.8	0.713	
Ave.	0.290	91.0	25.3							

TABLE III.C. Continued (a)

Run ^(b) Number	Millimoles SO ₂	Millimoles ^(c) 100% H ₂ SO ₄ *	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)	
					A _o	A _t	S _t	S _∞		
Batch VI, Group XXX Experiments, 194. 4°C. t _{1/2} = 15.00 hrs.										
131	0. 904	39. 9	8. 8	20. 3	76. 4	77. 3	45. 8	74. 7	0. 613	
Batch VI, Group XXXI Experiments, 194. 4°C. t _{1/2} = 14. 25 hrs.										
132	0. 285	76. 6	10. 9	27. 2	108. 4	103. 1	79. 3	108. 0	0. 734	
133	0. 290	76. 6	11. 5	16. 67	107. 9	101. 8	60. 0	107. 5	0. 558	
134	0. 287	76. 6	12. 0	15. 83	102. 0	99. 5	54. 0	101. 6	0. 531	
Ave.	0. 287	76. 6	11. 47							
Batch VI, Group XXXII Experiments, 194. 4°C. t _{1/2} = 11. 50 hrs.										
128	0. 485	122. 2	11. 9	12. 25	88. 8	84. 8	45. 6	88. 4	0. 516	
Batch VI, Group XXXIII Experiments, 194. 4°C. t _{1/2} = 12. 50 hrs.										
130	0. 481	90. 6	7. 2	20. 25	80. 9	77. 0	55. 0	80. 5	0. 683	
Batch VII, Group XXXIV Experiments, 225. 3°C. t _{1/2} = 3. 75 hrs.										
152	0. 582	76. 6	18. 0	3. 67	119. 3	122. 1	60. 0	118. 3	0. 507	
160	0. 586	76. 6	19. 10	2. 75	243	244	100. 2	241	0. 416	
161	0. 586	76. 6	18. 20	2. 40	243	247	83. 3	241	0. 346	
162	0. 586	76. 6	18. 40	5. 80	243	243	159. 3	241	0. 661	
Ave.	0. 585	76. 6	18. 42							
Batch VII, Group XXXV Experiments, 225. 3°C. t _{1/2} = 2. 32 hrs.										
154	0. 291	76. 6	10. 9	3. 45	119. 3	123. 8	75. 8	118. 8	0. 638	
156	0. 291	76. 6	10. 9	1. 70	119. 3	123. 7	46. 8	118. 8	0. 394	
157	0. 291	76. 6	10. 9	2. 40	119. 3	118. 8	60. 2	118. 8	0. 507	
Ave.	0. 291	76. 6	10. 9							
Batch VII, Group XXXVI Experiments, 225. 3°C. t _{1/2} = 1. 583 hrs.										
163	0. 292	76. 6	5. 90	1. 0	243	246	86. 1	242	0. 356	
164	0. 292	76. 6	6. 10	1. 450	243	242	109. 8	242	0. 454	
165	0. 292	76. 6	6. 0	2. 0	243	250	141. 0	242	0. 583	
Ave.	0. 292	76. 6	6. 0							

TABLE III D. Exchange Results, Ammonium Bisulfate - 84.5% Sulfuric Acid Mixtures.^(a)

Run (b) Number	Millimoles SO ₂	Millimoles ^(c) NH ₄ H ₂ SO ₄ *	Millimoles 84.5% H ₂ SO ₄	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)
						A _o	A _t	S _t	S _∞	
Batch VIII, Group XXXVII Experiments, 167.5°C. t _{1/2} = 48.5 hrs.										
217	0.324	27.4	27.4	15.2	36.0	172.3	173.0	69.1	171.3	0.403
218	0.324	27.4	27.4	14.9	45.03	175.3	171.6	84.0	174.2	0.482
219	0.325	27.4	27.4	14.40	48.0	172.5	169.0	83.0	171.5	0.484
220	0.325	27.4	27.4	15.10	52.25	171.2	168.3	92.1	168.3	0.541
230	0.325	27.4	27.4	15.0	69.0	160.0	156.9	99.2	159.0	0.624
Ave.	0.325	27.4	27.4	14.92						
Batch VIII, Group XXXVIII Experiments, 167.5°C. t _{1/2} = 33.4 hrs.										
221	0.324	27.4	27.4	8.7	20.9	167.1	162.1	62.0	166.1	0.373
224	0.325	27.4	27.4	8.8	24.15	167.1	162.8	63.3	166.1	0.381
227	0.323	27.4	27.4	8.9	36.0	160.0	156.5	84.5	159.0	0.531
228	0.325	27.4	27.4	8.8	52.0	160.0	156.0	103.9	159.0	0.653
Ave.	0.324	27.4	27.4	8.8						
Batch VIII, Group XXXIX Experiments, 167.5°C. t _{1/2} = 18.40 hrs.										
222	0.325	27.4	27.4	5.60	10.0	170.5	167.8	49.7	169.5	0.293
223	0.325	27.4	27.4	5.50	12.20	170.5	168.8	57.4	169.5	0.339
225	0.325	27.4	27.4	5.70	18.0	163.9	162.1	80.0	162.9	0.491
226	0.325	27.4	27.4	5.50	27.0	163.9	159.3	103.4	162.9	0.635
Ave.	0.325	27.4	27.4	5.58						
Batch IX, Group XXXX Experiments, 194.4°C. t _{1/2} = 7.65 hrs.										
212	0.325	27.4	27.4	13.40	7.08	186.5	184.4	84.2	185.4	0.454
213	0.325	27.4	27.4	13.60	13.40	186.5	183.5	129.6	185.4	0.699
214	0.325	27.4	27.4	14.00	8.17	181.4	179.9	95.1	180.3	0.527
215	0.325	27.4	27.4	13.20	9.0	181.4	181.8	99.8	180.3	0.554
Ave.	0.325	27.4	27.4	13.55						

TABLE III. Continued (a)

Run ^(b) Number	Millimoles SO ₂	Millimoles ^(c) NH ₄ H ₂ SO ₄	Millimoles 84.5% H ₂ SO ₄	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)
						A _o	A _t	S _t	S _∞	
Batch IX, Group XXXXI Experiments, 194. 4°C. t _{1/2} = 4.97 hrs.										
203	0.320	27.4	27.4	8.50	4.1	60.3	58.8	26.2	59.9	0.437
204	0.324	27.4	27.4	8.60	3.0	203	199.3	72.5	202.0	0.359
205	0.324	27.4	27.4	8.40	5.1	203	199.2	101.1	202.0	0.500
206	0.324	27.4	27.4	8.50	3.5	203	203	77.4	202.0	0.383
Ave.	0.323	27.4	27.4	8.50						
Batch IX, Group XXXXII Experiments, 194. 4°C. t _{1/2} = 2.25 hrs.										
208	0.326	27.4	27.4	4.50	3.0	198.2	193.4	116.4	197.0	0.591
209	0.326	27.4	27.4	4.80	3.50	198.2	194.3	130.3	197.0	0.661
210	0.326	27.4	27.4	4.70	2.0	197.4	195.7	83.1	196.2	0.424
211	0.326	27.4	27.4	4.3	2.53	197.4	195.2	107.9	196.2	0.550
211 [†]	0.326	27.4	27.4	4.58	0.05	196.6	193.0	0.4	195.4	0.002
Ave.	0.326	27.4	27.4	4.58						
Batch X, Group XXXXIII Experiments, 225. 3°C. t _{1/2} = 1.183 hrs.										
188	0.290	28.3	28.3	11.3	1.030	74.3	74.8	34.1	73.9	0.461
189	0.290	28.3	28.3	11.1	1.517	72.6	77.7	42.8	72.2	0.593
190	0.290	28.3	28.3	10.6	1.417	72.6	75.8	40.6	72.2	0.562
Ave.	0.290	28.3	28.3	11.0						
Batch X, Group XXXXIV Experiments, 225. 3°C. t _{1/2} = 0.800 hrs.										
194	0.323	27.4	27.4	7.8	1.017	68.4	67.4	39.6	68.0	0.582
196	0.323	27.4	27.4	7.8	0.767	68.1	72.6	33.6	67.7	0.496
200	0.322	27.4	27.4	8.7	0.633	60.3	58.7	24.8	59.9	0.414
201	0.322	27.4	27.4	8.4	0.867	60.3	58.5	31.4	59.9	0.524
Ave.	0.323	27.4	27.4	8.18						

TABLE IIID. Continued.^(a)

Run ^(b) Number	Millimoles SO ₂	Millimoles NH ₄ H [*] SO ₄	Millimoles 84.5% H ₂ SO ₄	Tube Volume, ml	Exchange Time, hrs	S. A. S(VI), cpm/mg ^(d)		S. A. SO ₂ , cpm/mg ^(d)		F ^(e)
						A ₀	A _t	S _t	S _∞	
Batch X, Group XXXXV Experiments, 225.3°C. t _{1/2} = 0.467 hrs.										
192	0.324	27.4	27.4	5.3	1.150	70.3	60.4	56.9	69.4	0.814
193	0.323	27.4	27.4	5.3	0.467	68.1	71.7	31.2	67.7	0.461
197	0.323	27.4	27.4	5.2	0.767	68.1	71.1	47.3	67.7	0.699
Ave.	0.323	27.4	27.4	5.27						

(a) All the results summarized in the Tables IIIA through IIID were calculated according to the methods described in Section III.

(b) The run number refers to the number of the experiment in the research note book. Missing numbers belong to broken tubes or to those experiments which were carried out with unlabeled material for the purpose of practicing some experimental technique.

(c) An asterisk indicates the reactant initially active.

(d) A₀ is the initial (experimentally measured) specific activity of the sulfur (VI) exchanging reactant, i. e. the specific activity of a mixture of sulfuric acid and ammonium bisulfate with the concentrations and mole ratios listed in each of the Tables IIIB and IIID, the specific activity of 100% sulfuric acid in Table IIIC and the specific activity of ammonium bisulfate in Table IIIA. A_t is the specific activity of the residual sulfur (VI) exchanging reaction after separation of SO₂ from the tube of the experiment. All specific activities were obtained as counts per minute per mg of barium sulfate. Activities for a given numbered experiment are given for the time of counting or, for the original sulfur (VI) reactant, corrected to that time.

(e) The fraction of radiosulfur exchanged, F, was calculated using the relation $F = \frac{S_t - S_0}{S_\infty - S_0}$, where S_t is the specific activity (cpm/mg) of sulfur dioxide at a time t. S_∞ is the specific activity of all the exchanging components if all the activity were completely randomized in the system under consideration. S₀ is the initial specific activity of SO₂=0. The value of S_∞ was calculated from the specific activity of the initially active component (i. e., the total sulfur (VI), mixture or pure substance, as the case might be) in the system and the known (dosed) quantities of all the exchanging species in the system

$$S_\infty = A_0 \frac{b}{a+b}$$

where a is the number of mmoles of SO₂ and b is the total number of mmoles of initially active sulfur (VI) exchanging reactant.

TABLE IVA. Exchange Rates, Pure Ammonium Bisulfate.

Batch Number	Group Number	Temp., °C.	Millimoles SO ₂ (average)	Millimoles NH ₄ H [*] SO ₄ (average)	Tube Volume, ml (average)	t _{1/2} , hrs	Rate, mmoles hr ⁻¹	R'	1/k', hrs
I(a)	I	169.5	1.022	20.01	37.1	197.5	3.41 × 10 ⁻³	3.66 × 10 ⁻²	10.97
	II	169.5	0.291	20.04	38.2	184.5	1.077 × 10 ⁻³	3.55 × 10 ⁻²	9.60
	III	169.5	1.021	60.08	36.6	180.0	3.86 × 10 ⁻³	0.1114	29.5
	IV	169.5	1.018	3.03	35.5	751.0	7.03 × 10 ⁻⁴	5.79 × 10 ⁻³	8.39
	V	169.5	0.293	60.01	9.6	101.0	2.00 × 10 ⁻³	0.425	62.2
	IX	169.5	1.014	60.0	37.0	105.0	6.58 × 10 ⁻³	0.1103	16.99
	X	169.5	0.290	42.3	9.6	111.0	1.800 × 10 ⁻³	0.307	49.4
II	XI	225.3	0.613	2.11	33.4	188.0	1.750 × 10 ⁻³	4.5 × 10 ⁻³	1.579
	XII	225.3	0.341	2.11	15.80	92.5	2.21 × 10 ⁻³	9.51 × 10 ⁻²	1.468
	XIII	225.3	0.341	6.33	15.38	43.9	5.13 × 10 ⁻²	2.93 × 10 ⁻²	1.948
	XIV	225.3	0.579	43.4	18.10	10.20	3.88 × 10 ⁻²	0.1707	2.55
	XV	225.3	0.290	59.9	12.97	11.40	1.754 × 10 ⁻²	0.329	5.44
	XVI	225.3	0.289	80.4	11.17	11.40	1.751 × 10 ⁻²	0.512	8.45

(a) Data for groups I, II, III, IV, and V are taken from the author's previous work (1, p. 39).

TABLE IVB. Exchange Rates, Ammonium Bisulfate - 100% Sulfuric Acid Mixtures.

Batch Number	Group Number	Temp., °C	Millimoles SO ₂ (average)	Millimoles NH ₄ H [*] SO ₄ (average)	Millimoles 100% H ₂ SO ₄ (average)	Tube		Rate, mmoles hr ⁻¹	R'	1/k', hrs
						Volume ml (average)	t _{1/2} , hrs			
III	XVII	194.4	0.290	45.1	22.1	22.5	20.5	9.76 x 10 ⁻³	0.192	5.70
	XVIII	194.4	0.291	17.06	8.45	4.3	16.00	1.247 x 10 ⁻²	0.379	8.83
	XIX	194.4	0.290	45.1	22.1	8.5	11.50	1.742 x 10 ⁻²	0.508	8.45
	XX	194.4	0.292	45.1	22.1	5.8	9.67	2.08 x 10 ⁻²	0.745	10.46
IV	XXI	194.4	0.291	16.58	66.3	25.6	9.40	2.14 x 10 ⁻²	0.1910	2.60
	XXII	194.4	0.293	16.58	66.3	15.33	5.28	3.83 x 10 ⁻²	0.320	2.45
	XXIII	194.4	0.292	16.58	66.3	9.13	3.60	5.60 x 10 ⁻²	0.536	2.79
	XXIV	194.4	0.291	16.58	66.3	6.23	2.35	8.55 x 10 ⁻²	0.785	2.67

TABLE IV C. Exchange Rates, 100% Sulfuric Acid.

Batch Number	Group Number	Temp., °C	Millimoles SO ₂ (average)	Millimoles 100% H ₂ SO ₄ (average)	Tube Volume, ml. (average)	t _{1/2} , hrs	Rate, mmoles hr ⁻¹	R'	1/k', hrs
V	XXV	167.5	0.582	76.6	19.20	122.5	3.26 x 10 ⁻³	0.227	40.5
	XXVI	167.5	0.291	76.6	9.80	80.0	2.51 x 10 ⁻³	0.445	51.6
	XXVII	167.5	0.290	76.6	6.77	70.5	2.84 x 10 ⁻³	0.644	65.8
	XXVIII	167.5	0.291	76.6	5.70	62.0	3.24 x 10 ⁻²	0.765	68.7
VI	XXIX	194.4	0.290	91.0	25.3	23.4	8.56 x 10 ⁻³	0.213	7.22
	XXX ^(a) Run No. 131	194.4	0.904	39.9	8.8	15.00	4.08 x 10 ⁻²	0.269	5.95
	XXXI	194.4	0.287	76.6	11.47	14.25	1.391 x 10 ⁻²	0.397	8.19
	XXXII ^(a) Run No. 128	194.4	0.485	122.2	11.90	11.50	2.91 x 10 ⁻²	0.610	10.17
	XXXIII ^(a) Run No. 130	194.4	0.481	90.6	7.20	12.50	2.65 x 10 ⁻²	0.747	13.56
VII	XXXIV	225.3	0.585	76.6	18.42	3.75	0.1072	0.247	1.348
	XXXV	225.3	0.291	76.6	10.90	2.32	8.68 x 10 ⁻²	0.417	1.399
	XXXVI	225.3	0.292	76.6	6.0	1.583	0.1274	0.758	1.739

(a) Groups XXX, XXXII and XXXIII consisted only of one run each because of experimental difficulties in filling the bomb tubes. The vacuum line filling procedure was used in three cases (see Run Procedure) and was soon discontinued as overly inconvenient.

TABLE IV. Exchange Rates, Ammonium Bisulfate - 84.5% Sulfuric Acid Mixtures.

Batch Number	Group Number	Temp., °C	Millimoles SO ₂ (average)	Millimoles NH ₄ HSO ₄ [*] (average)	Millimoles 84.5% H ₂ SO ₄ (average)	Tube Volume, ml (average)	t _{1/2} , hrs	Rate, m moles hr ⁻¹	R'	1/k', hrs
VIII	XXXVII	167.5	0.325	27.4	27.4	14.92	48.5	4.62 x 10 ⁻³	0.255	17.90
	XXXVIII	167.5	0.324	27.4	27.4	8.8	33.4	6.68 x 10 ⁻³	0.433	21.0
	XXXIX	167.5	0.325	27.4	27.4	5.58	18.40	12.17 x 10 ⁻³	0.683	18.26
IX	XXXX	194.4	0.325	27.4	27.4	13.55	7.65	0.0293	0.289	3.20
	XXXXI	194.4	0.323	27.4	27.4	8.50	4.97	0.0447	0.461	3.33
	XXXXII	194.4	0.326	27.4	27.4	4.58	2.25	0.1000	0.856	2.79
X	XXXXIII	225.3	0.290	28.3	28.3	11.00	1.183	0.1691	0.380	0.650
	XXXXIV	225.3	0.323	27.4	27.4	8.18	0.800	0.278	0.494	0.574
	XXXXV	225.3	0.323	27.4	27.4	5.27	0.467	0.475	0.767	0.521

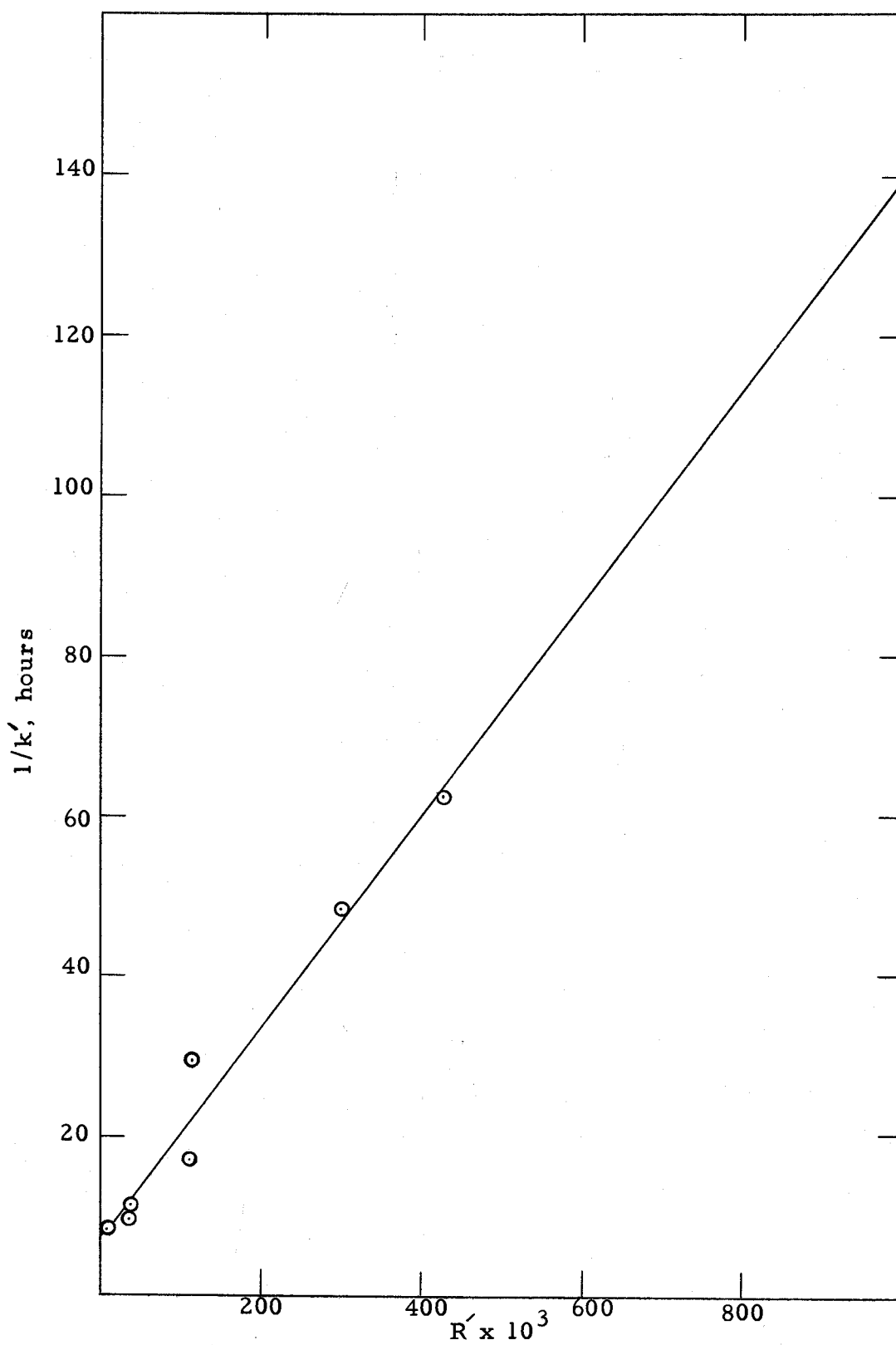


Figure 6. Rate-bomb volume dependency, pure NH_4HSO_4 at 169.5°C (Batch I).

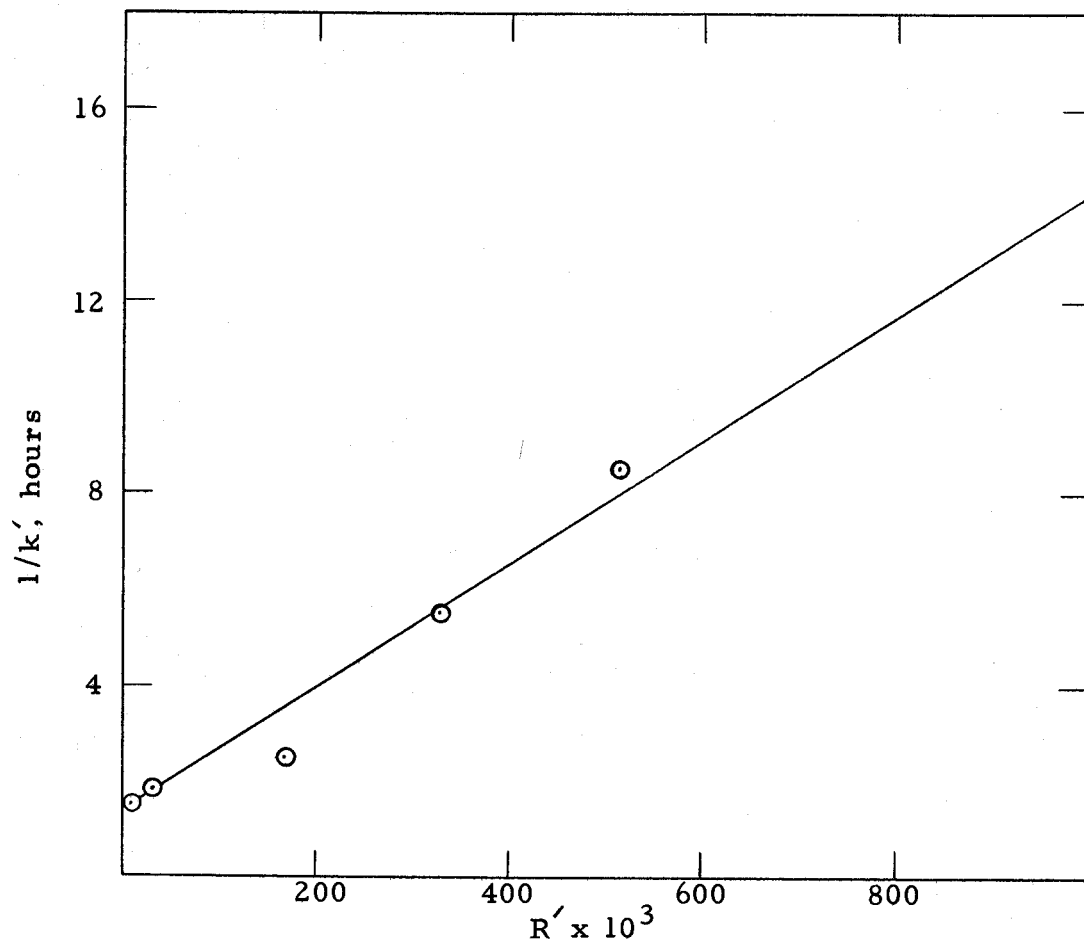


Figure 7. Rate-bomb volume dependency, pure NH_4HSO_4 at 225.3°C (Batch II).

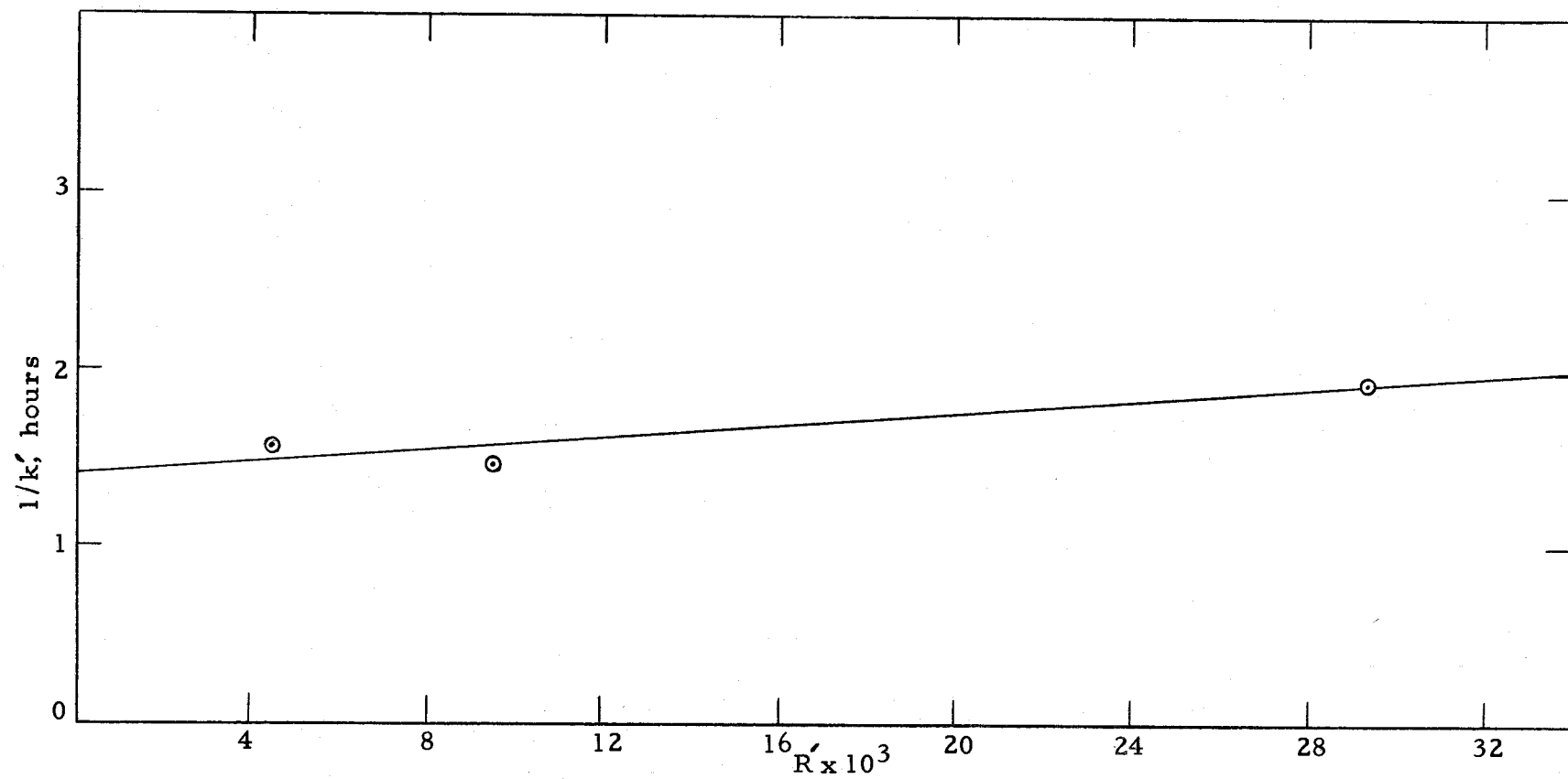


Figure 8. Rate-bomb volume dependency, pure NH_4HSO_4 at 225.3°C (Batch II, Continued).

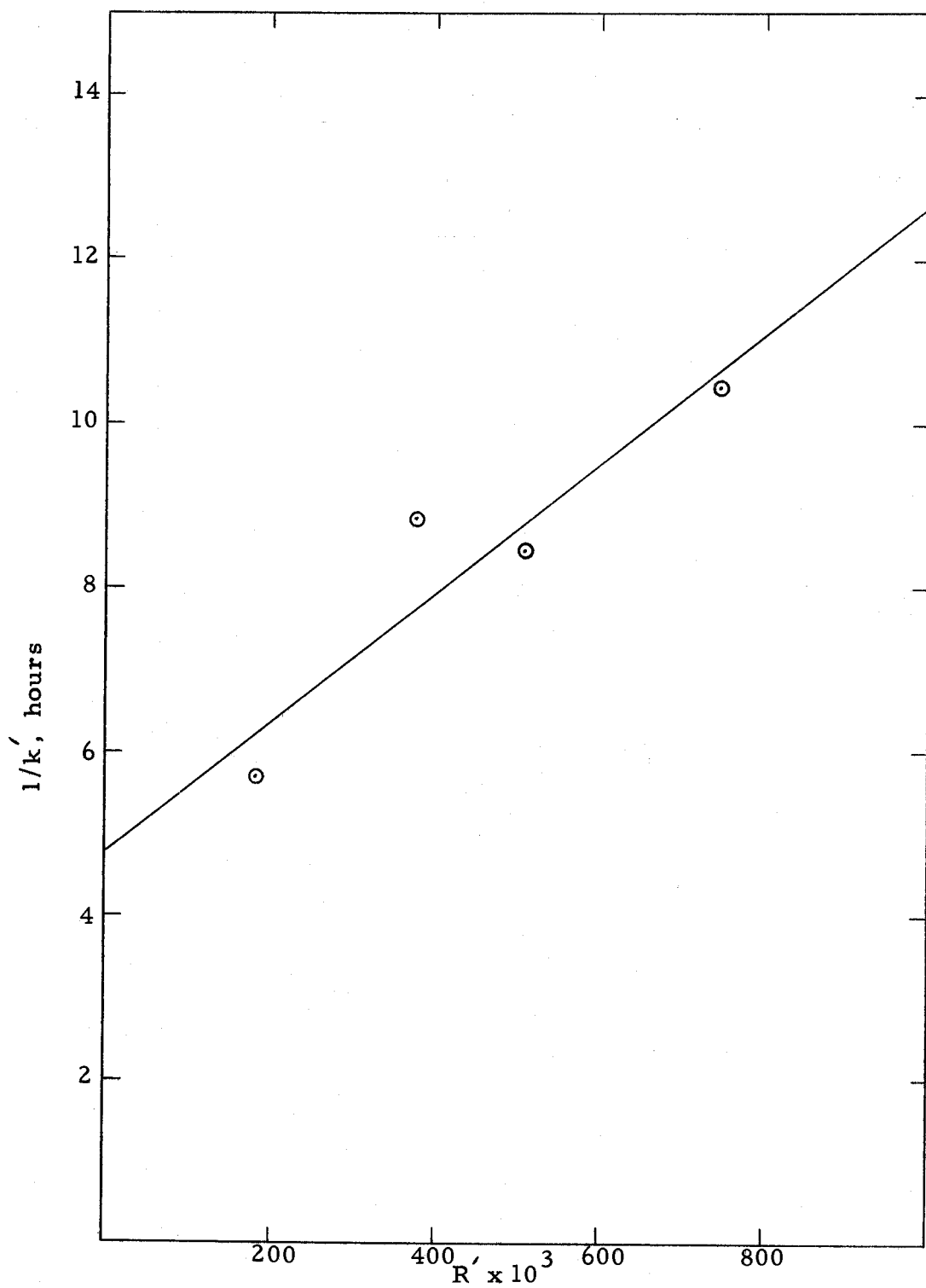


Figure 9. Rate-bomb volume dependency, 2.05:1 NH_4HSO_4 -
100% H_2SO_4 mixtures at 194.4° C (Batch III).

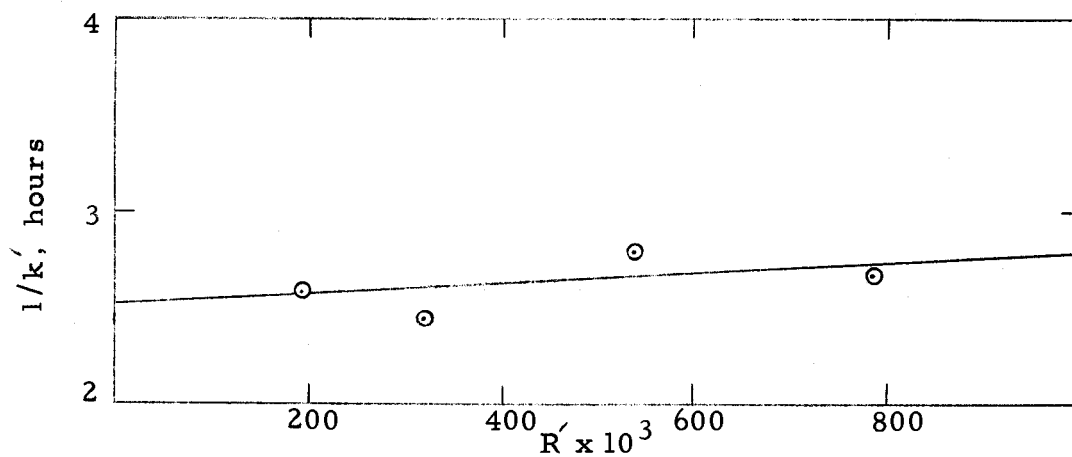


Figure 10. Rate-bomb volume dependency, 1:4 NH_4HSO_4 -100% H_2SO_4 mixtures at 194.4° C (Batch IV).

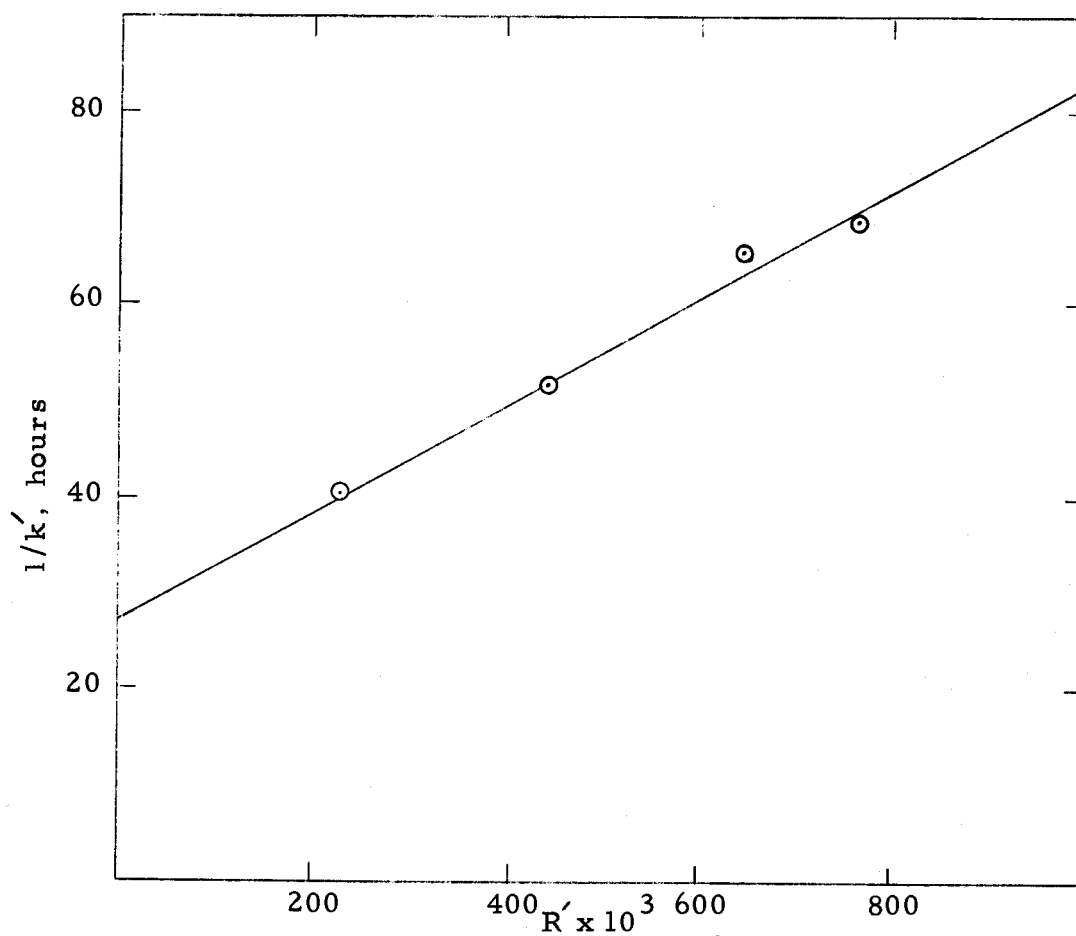


Figure 11. Rate-bomb volume dependency, 100% H_2SO_4 at 167.5° C (Batch V).

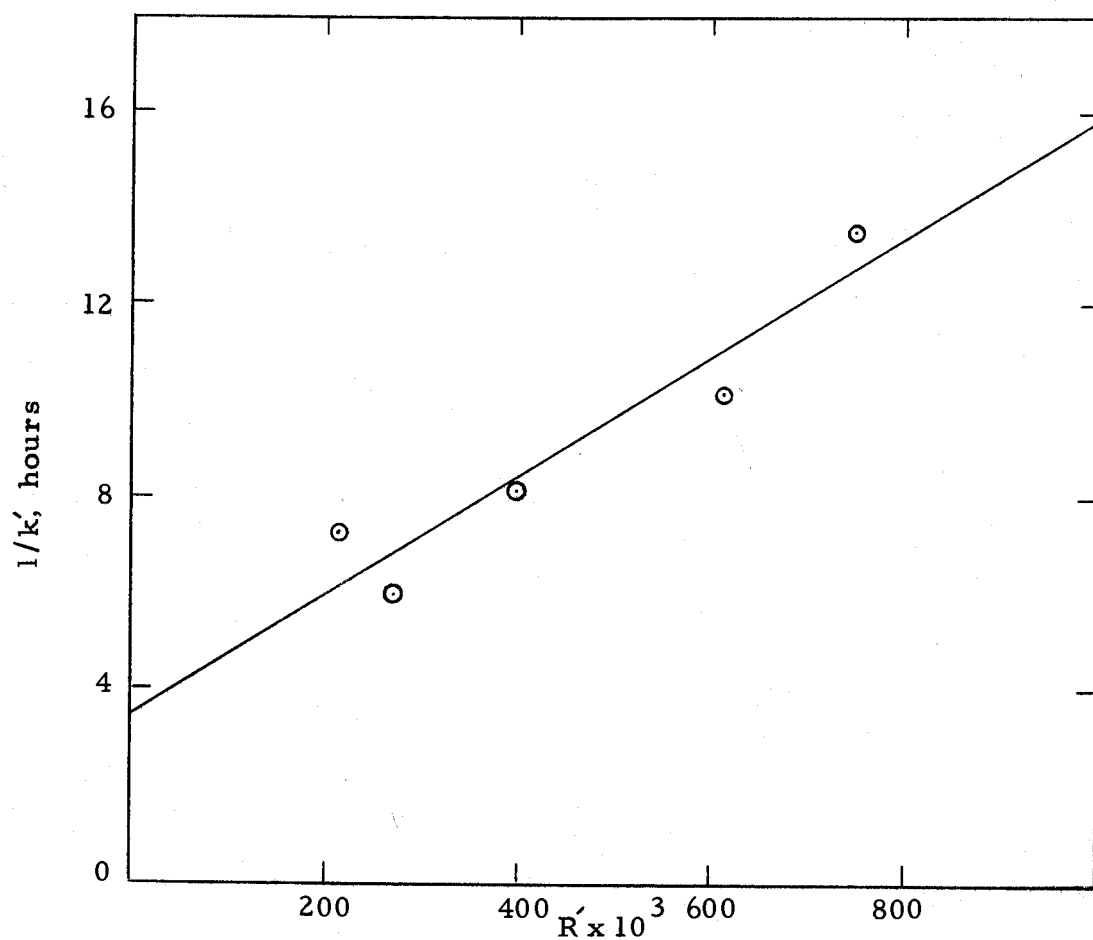


Figure 12. Rate-bomb volume dependency, 100% H_2SO_4 at 194.4° C (Batch VI).

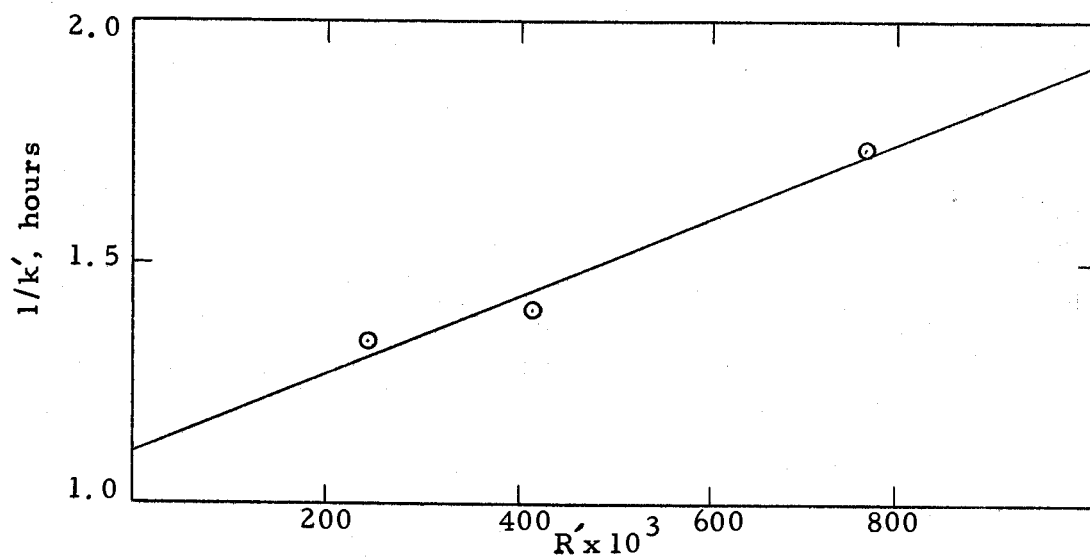


Figure 13. Rate-bomb volume dependency, 100% H_2SO_4 at 225.3° C (Batch VII)

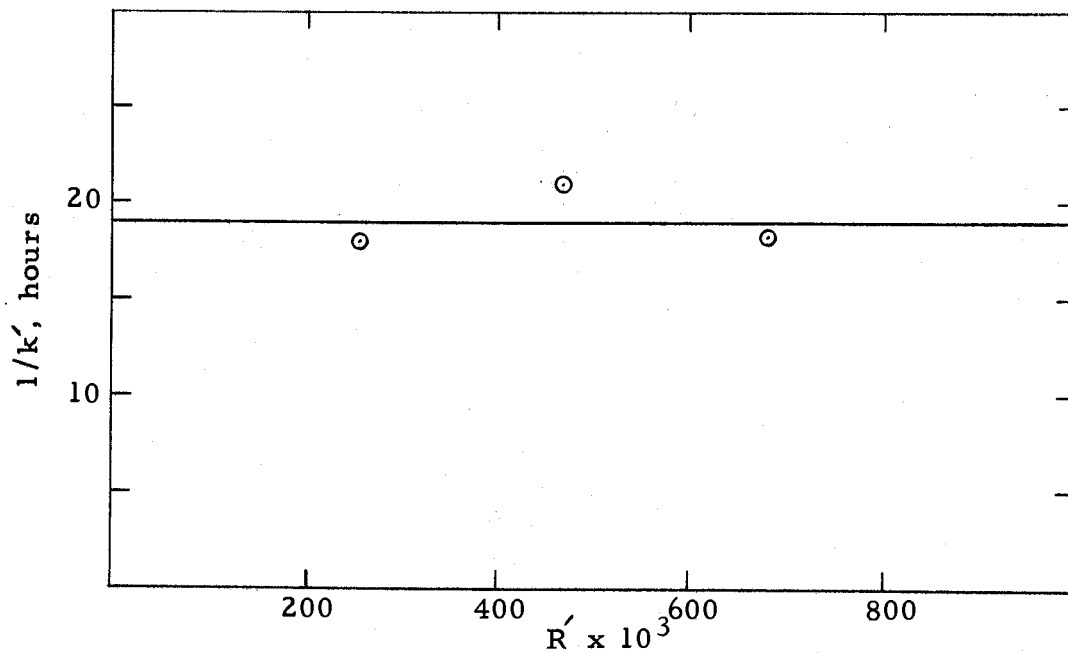


Figure 14. Rate-bomb volume dependency, 1:1 NH_4HSO_4 - 84.5% H_2SO_4 mixtures at 167.5°C (Batch VIII).

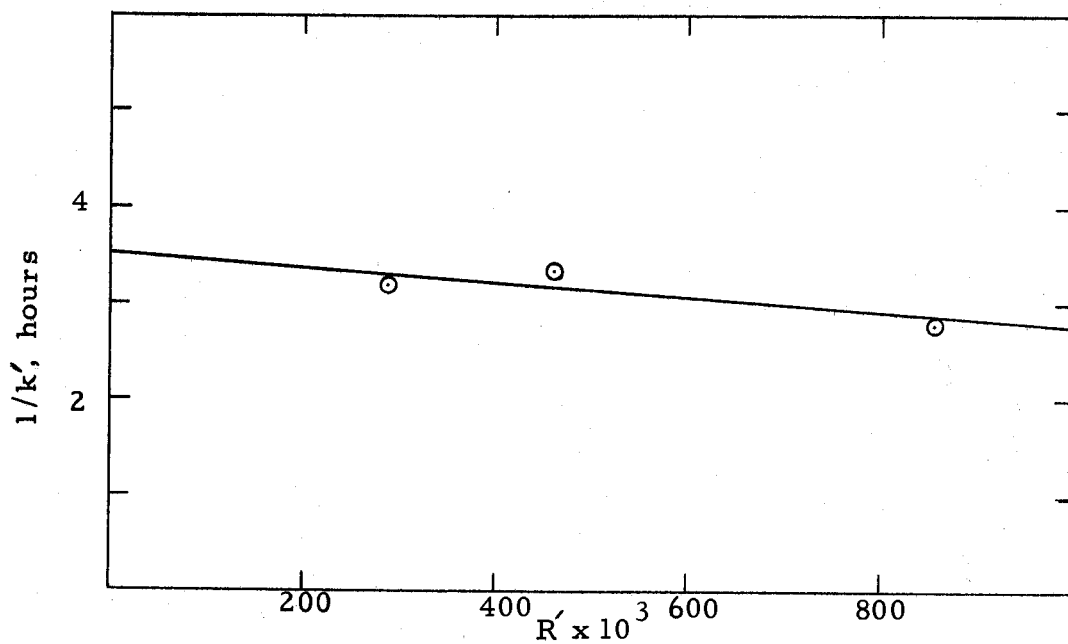


Figure 15. Rate-bomb volume dependency, 1:1 NH_4HSO_4 - 84.5% H_2SO_4 mixtures at 194.4°C (Batch IX).

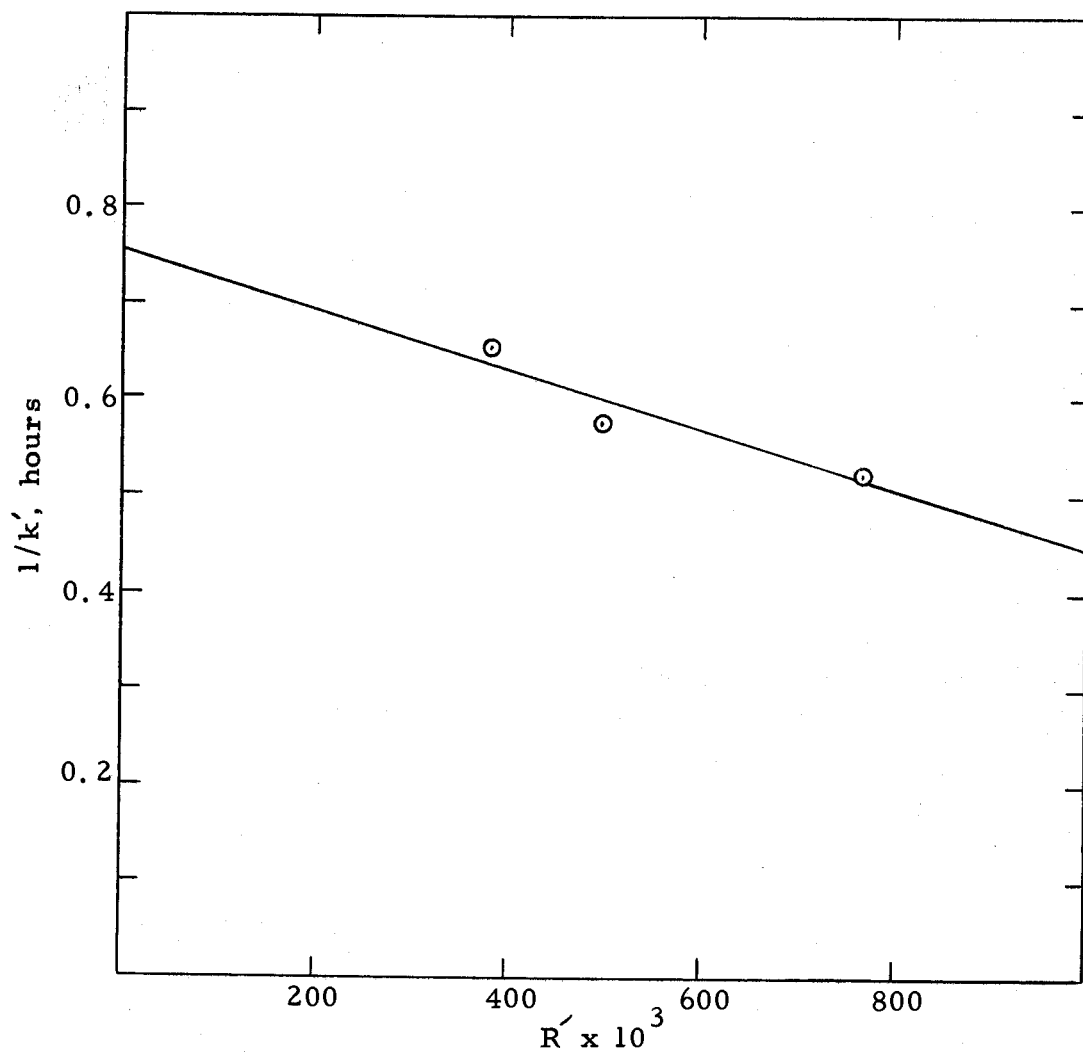


Figure 16. Rate-bomb volume dependency, 1:1 NH_4HSO_4 - 84.5% H_2SO_4 mixtures at 225.3° C (Batch X).

to $1/kc$. The ratio of the intercepts of the straight line obtained in plots of this type yields the distribution coefficient, c . The k values obtained are summarized in Table V and the c values are summarized in Table VI.

In Table III A, the results of two groups of exchange experiments between sulfur dioxide and pure ammonium bisulfate at 169.5°C are summarized. The purpose of running these experiments was to supplement the previous work by the author (1, p. 28) for this system, and specifically to allow a better estimation of the slope of the $1/k'$ versus R' plot previously given. A new plot of $1/k'$ versus R' , based on both the previous and the present work, is given in Figure 6.

Study of Temperature Effect on Exchange Rates

The Arrhenius equation (5, p. 1)

$$k = A e^{-E_a/RT} \quad (1)$$

where A is a constant

E_a is the activation energy

R is the gas constant

T is the absolute temperature

may be written in the alternative form

TABLE V. Rate Constants.

Batch Number	Sulfur(VI) Reactant	Temp., °C	Temp., °K	$\frac{1}{T} \times 10^3$ °K ⁻¹	1/k, hrs	k, hr ⁻¹
I	NH ₄ H [*] SO ₄	169.5	442.7	2.26	140.3	7.13 × 10 ⁻³
II	NH ₄ H [*] SO ₄	225.3	498.5	2.01	14.24	7.02 × 10 ⁻²
III	2.05:1 NH ₄ H [*] SO ₄ and 100% H ₂ SO ₄	194.4	467.6	2.14	12.65	7.91 × 10 ⁻²
IV	1:4 NH ₄ H [*] SO ₄ and 100% H ₂ SO ₄	194.4	467.6	2.14	2.78	0.360
V	100% H ₂ SO ₄ [*]	167.5	440.7	2.27	83.1	1.203 × 10 ⁻²
VI	100% H ₂ SO ₄ [*]	194.4	467.6	2.14	15.90	6.29 × 10 ⁻²
VII	100% H ₂ SO ₄ [*]	225.3	498.5	2.01	1.915	0.522
VIII	1:1 NH ₄ H [*] SO ₄ and 84.5% H ₂ SO ₄	167.5	440.7	2.27	19.09	5.24 × 10 ⁻²
IX	1:1 NH ₄ H [*] SO ₄ and 84.5% H ₂ SO ₄	194.4	467.6	2.14	2.74	0.365
X	1:1 NH ₄ H [*] SO ₄ and 84.5% H ₂ SO ₄	225.3	498.5	2.01	0.442	2.26

TABLE VI. Summary of c Values.

Batch Number	Sulfur (VI) Reactant	Temp., °C	1/k, hrs	1/kc, hrs	c
I	$\text{NH}_4\text{HSO}_4^*$	169.5	140.3	7.09	19.79
II	$\text{NH}_4\text{HSO}_4^*$	225.3	14.24	1.412	10.08
III	2.05:1 $\text{NH}_4\text{HSO}_4^*$ and 100% H_2SO_4	194.4	12.65	4.76	2.66
IV	1:4 $\text{NH}_4\text{HSO}_4^*$ and 100% H_2SO_4	194.4	2.78	2.50	1.112
V	100% H_2SO_4^*	167.5	83.1	28.0	2.97
VI	100% H_2SO_4^*	194.4	15.90	3.45	4.61
VII	100% H_2SO_4^*	225.3	1.915	1.117	1.714
VIII	1:1 $\text{NH}_4\text{HSO}_4^*$ and 84.5% H_2SO_4	167.5	19.09	19.02	1.004
IX	1:1 $\text{NH}_4\text{HSO}_4^*$ and 84.5% H_2SO_4	194.4	2.74	3.53	0.776
X	1:1 $\text{NH}_4\text{HSO}_4^*$ and 84.5% H_2SO_4	225.3	0.442	0.750	0.589

$$\ln k = \ln A - E_a / RT$$

$$\log k = \log A - E_a / 2.303 RT \quad (2)$$

Thus, as seen from equation (2), a plot of $\log k$ against $1/T$, should yield a straight line of slope = $-E_a / 2.303R$, from which the value of the activation energy, E_a , may be obtained. From the Arrhenius equation and the activation energy thus obtained, it is also possible then to calculate a value for the frequency factor, A .

From the same data, the entropy of activation, ΔS^\ddagger , can be calculated from equation 3 (5, p. 199)

$$k = (e) \left(\frac{k''T}{h} \right) e^{-E_a/RT} e^{\Delta S^\ddagger/R} \quad (3)$$

where k'' represents the Boltzmann constant, and h , Planck's constant. T is the absolute temperature and R , the gas constant.

The exchange reaction between sulfur dioxide and pure ammonium bisulfate was studied at 169.5°C and 225.3°C with values of k equal to $7.13 \times 10^{-3} \text{ hr}^{-1}$ and $7.02 \times 10^{-2} \text{ hr}^{-1}$ (see Table V). A batch of experiments was also done by the author (1, p. 30) in which the same exchange was studied at 194.8°C with k equal $3.04 \times 10^{-2} \text{ hr}^{-1}$. In Figure 17, k values are plotted against $1/T$. The value of E_a derived from the straight line plotted is 18.07 kcal/mole. By substitution of E_a with its derived value in equation (2), together with the observed k values, computing the frequency factor

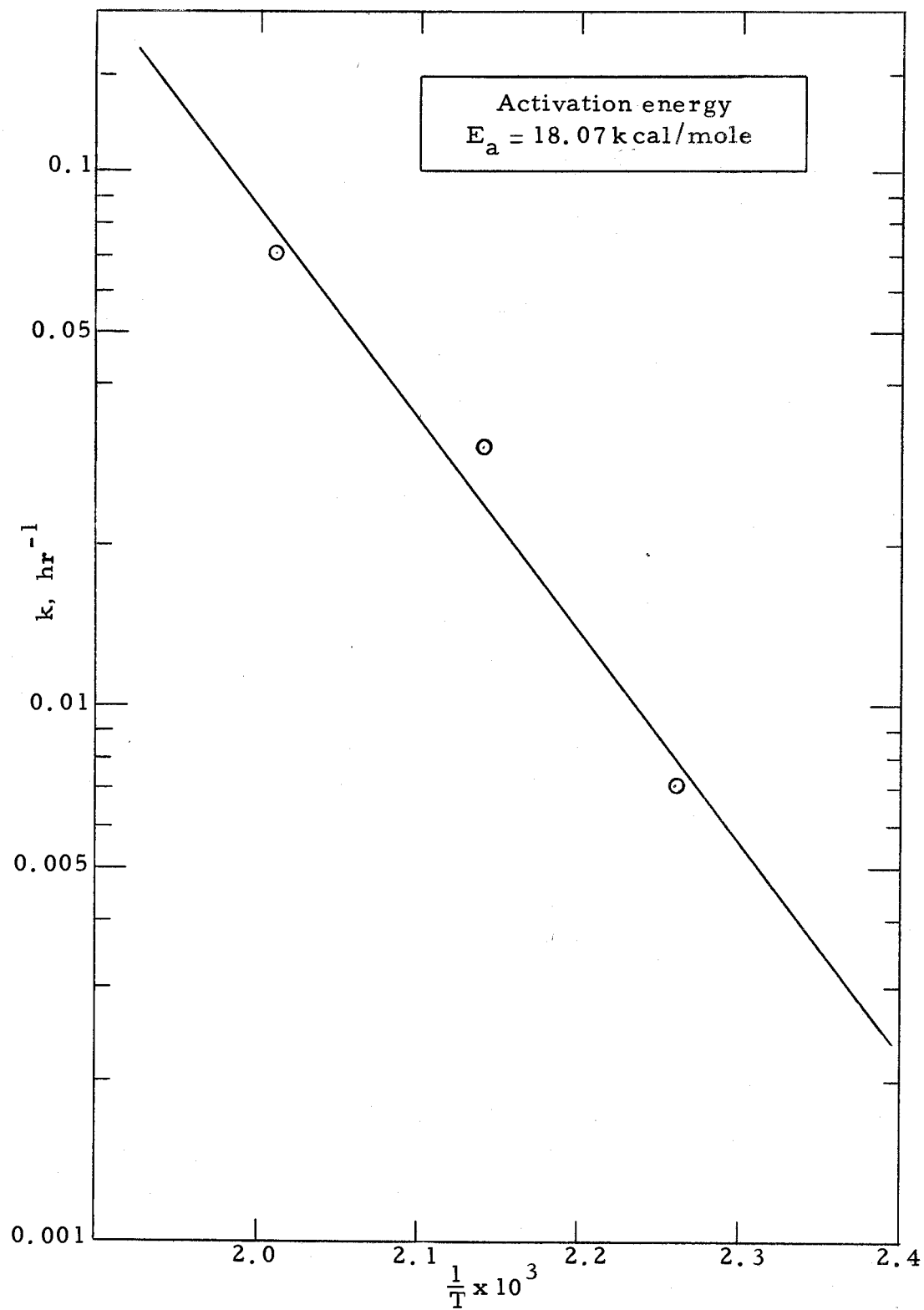


Figure 17. $\text{Log } k \text{ vs. } \frac{1}{T} \text{ } ^\circ\text{K}^{-1}$, pure NH_4HSO_4 .

A at the three temperatures under consideration and taking the average, the value of A was found to be $1.892 \times 10^3 \text{ sec}^{-1}$. Further, from equation (3), on the basis of the same data, the average value of entropy of activation, ΔS^\ddagger , was found to be -46.5 e. u.

The exchange reaction between sulfur dioxide and 100% sulfuric acid was studied at 167.5°C , 194.4°C and 225.3°C with values of k equal to $1.203 \times 10^{-2} \text{ hr}^{-1}$, $6.29 \times 10^{-2} \text{ hr}^{-1}$ and 0.522 hr^{-1} (see Table V). A group of experiments was also done by McDonald (13, p. 35) in which he studied the same exchange at 174.0°C with k equal to $1.377 \times 10^{-2} \text{ hr}^{-1}$. A summary of his data is listed in Table VII. In Figure 18, k values are plotted against $1/T$ and it may be seen that the points fall reasonably satisfactorily along a straight line. The value of E_a derived from the plot is 29.6 kcal/mole . By substituting E_a with its calculated value in equation (2) and computing the frequency factor A at the three temperatures under consideration and taking the average, the value of A was found to be $1.344 \times 10^9 \text{ sec}^{-1}$. From equation (3), the average value of the entropy of activation, ΔS^\ddagger , was found to be -19.66 e. u.

The exchange reaction of sulfur dioxide with the mixture of 1:1 ammonium bisulfate and 84.5% sulfuric acid was studied at 167.5°C , 194.4°C , and 225.3°C with values of k equal to $5.24 \times 10^{-2} \text{ hr}^{-1}$, 0.365 hr^{-1} , and 2.26 hr^{-1} (see Table V). Figure 19 shows a plot of $\log k$ against $1/T$. The value of E_a derived from

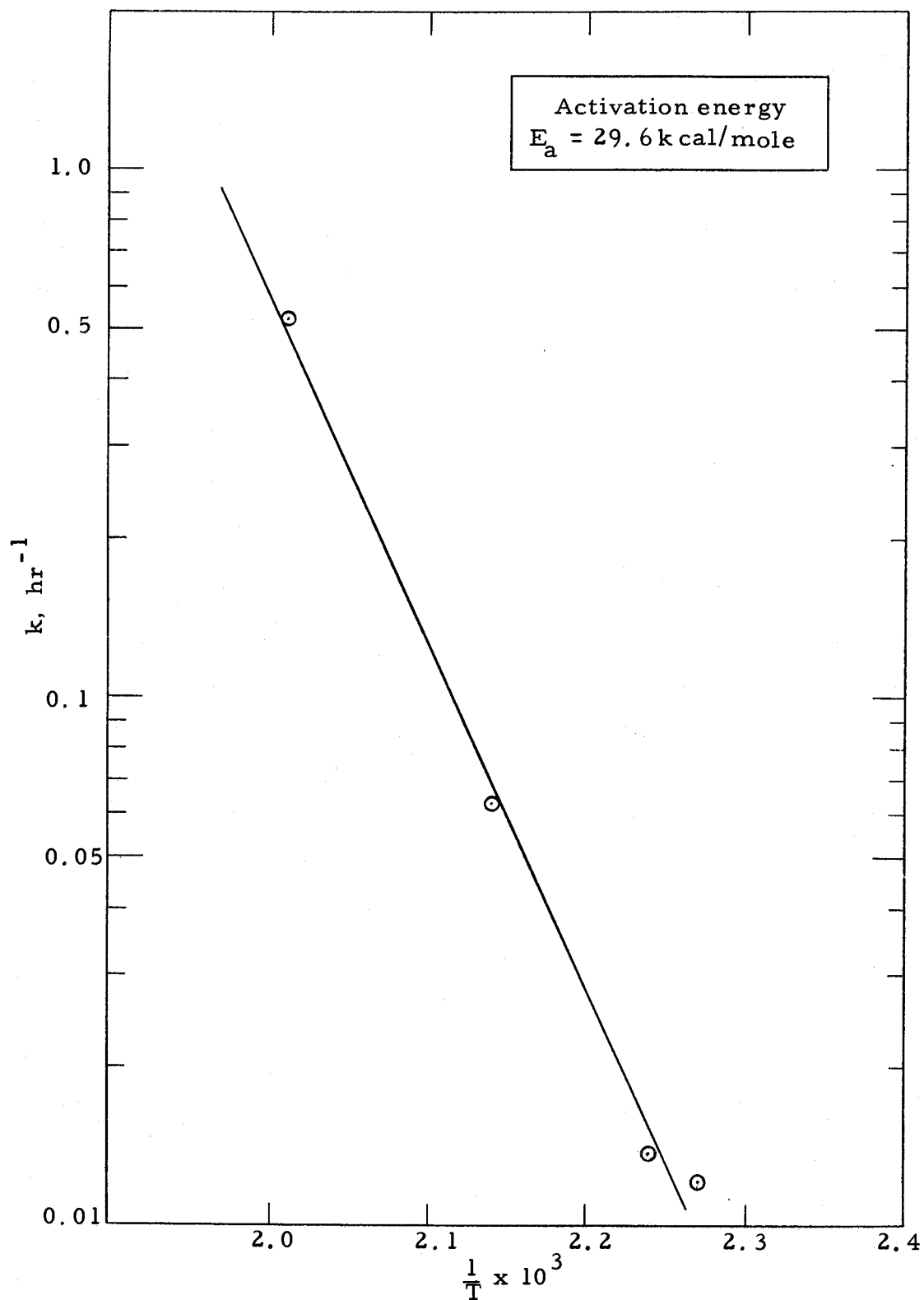


Figure 18. $\text{Log } k$ vs. $\frac{1}{T} \text{ } ^{\circ}\text{K}^{-1}$, 100% H_2SO_4 .

TABLE VII. Radiosulfur Exchange Experiments between SO_2 and 100% H_2SO_4 , Previous Results^(a)

(Gas vol^(b) < 0.1 ml; liq. vol.^(b) = 0.885 ml. Temp. = 174.0 ± 0.1°C)
 $k = 1.377 \times 10^{-2} \text{ hr}^{-1}$ (c)

Expt.	H_2SO_4 (%)	H_2SO_4^* (b) (mols/l)	H_2O (b) (mols/l)	SO_2 (mmols)	Exch. time (hours)	A_{SO_2} (cpm/mg)	$A_{\text{H}_2\text{SO}_4}$ (cpm/mg)	F
39 ^a	100	17.1	0	0.746	23.2	88.1	304	0.300
39 ^b	100	17.1	0	0.746	50.1	151.4	286	0.541
39 ^c	100	17.1	0	0.746	85.6	193.0	270	0.725

(a) Data taken from McDonald (13, p. 35).

(b) Calculated at the exchange temperature.

(c) The same methods described previously (see Section III) were applied in the calculation of k . A plot of $\log(1-F)$ against time gave the half-time value, $t_{1/2}$, as 48.0 hours. Knowing the half-time and the concentrations of both sulfuric acid and sulfur dioxide, the rate of the re-reaction was calculated according to equation (3), Section III and found to be 1.072×10^{-2} mmoles hr^{-1} . By applying equation (8), Section III, noting that $R' = 1$ for this group of experiments so that $k' = k$, the value of k was computed as $1.377 \times 10^{-2} \text{ hr}^{-1}$, as shown.

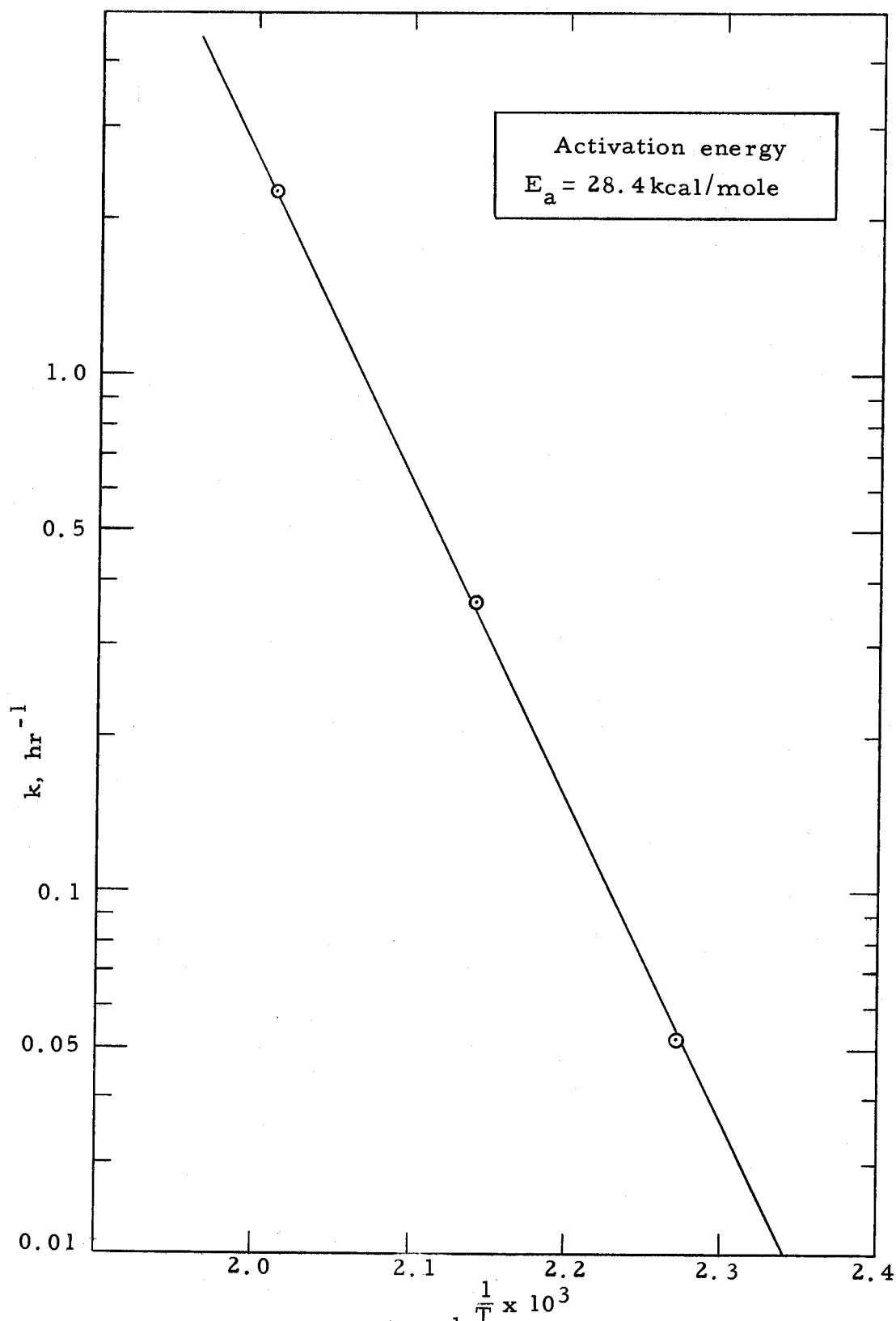


Figure 19. $\text{Log } k \text{ vs. } \frac{1}{T} \text{ } ^\circ\text{K}^{-1}$, 1:1 NH_4HSO_4 -84.5% H_2SO_4 .

the plot is 28.4 k cal/mole. By substituting E_a with its calculated value in equation (2), together with the observed k values, computing the frequency factor A at the three temperatures under consideration, and taking the average, the value of A is found to be $1.837 \times 10^9 \text{ sec}^{-1}$. Further, from equation (3), using the same data, the average value of the entropy of activation ΔS^\ddagger is found to be -19.05 e. u.

V. DISCUSSION

The exchange reaction between sulfur dioxide and sulfuric acid in aqueous medium was studied extensively by McDonald (13, p. 1-138). For this reaction he offered a self-consistent interpretation of the results, leading to the rate law

$$\text{Rate} = k_1(\text{SO}_2)(\text{HSO}_4^-) + k_2(\text{SO}_2)(\text{H}_2\text{SO}_4) \quad (1)$$

which describes the exchange throughout the entire sulfuric acid range 2.3 - 100% acid. Following McDonald's work, a study of the exchange reaction between sulfur dioxide and fused ammonium bisulfate was carried out at two temperatures by the author (1, p. 1-50). The latter system was of particular interest because its study could be considered as the first phase of a study of the exchange reaction between sulfur dioxide and sulfuric acid in liquid ammonia solution. It represented, for the liquid ammonia system, the equivalent of the aqueous system involving a one-to-one mole ratio mixture of water and sulfuric acid, i. e. 84.5% sulfuric acid.

In order to compare the rates observed with those found by McDonald, it was assumed that the fused salt was completely ionized as ammonium and bisulfate ions. Thus one may compare the observed exchange rate to the first, k_1 , term of McDonald's rate law.

$$\text{Rate} = k(\text{SO}_2)_t F' = k(\text{SO}_2) = k_1(\text{SO}_2)(\text{HSO}_4^-) \quad (2)$$

where $(\text{SO}_2)_t$ is the total amount of sulfur dioxide put into the reaction tubes, F' is the fraction of the sulfur dioxide dissolved and (SO_2) represents the actual dissolved sulfur dioxide concentration. (For computational convenience, SO_2 millimole amounts per bomb, rather than molar concentrations were actually employed in the author's work, both previous and present, Rate values being obtained in corresponding units. Since the units of (SO_2) and Rate cancel, however, this procedure does not affect the resulting calculated k values). (HSO_4^-) represents bisulfate ion concentration.

From equation (2) one obtains a relationship between k , the rate constant actually observed in the fused ammonium bisulfate work, and k_1 , the computed rate constant to be compared with the rate constant given by McDonald.

$$k_1 = \frac{k}{(\text{HSO}_4^-)} \quad (3)$$

From values of k , k_1 values for each of the experimental temperatures and then, by interpolation, the value of k_1 corresponding to the temperature at which McDonald's value was quoted were computed. The value of $k_1(174.0^\circ\text{C})$ was found as: $1.073 \times 10^{-5} \text{ l mole}^{-1} \text{ min}^{-1}$, to be compared to $1.06 \times 10^{-4} \text{ l mole}^{-1} \text{ min}^{-1}$, McDonald's k_1 value. Thus the reaction in the ammonium bisulfate is apparently about ten times slower than the reaction of sulfur dioxide with

bisulfate ion in sulfuric acid.

The main purpose of the present study was to extend further the comparison of exchange rates between sulfur dioxide and sulfur (VI) in ammonia-containing systems with those observed in aqueous acid systems and to try to obtain, if possible, a better understanding of the basis for the apparent difference in the rates observed in the two systems.

In order to proceed with the comparison, values of k (the first order rate constant actually observed, as defined by equation (2)), as well as c (the distribution coefficient) obtained from previous studies and the present work are listed in Tables VIII through XVII. In Table VIII, the values of k and c from Doherty's data are listed. Values of k are taken from the graphs illustrated in Figures 1 through 5 in his thesis (2, p. 20-24) and c values (slightly corrected in two cases) from his Table IV (2, p. 25). In Table XI, values of k and c for McDonald's data involving concentrated sulfuric acid are listed. Values of k , the observed rate constants were calculated from the values of the rates listed in Table 16 of his thesis (13, p. 65), on the basis of the equation, $\text{Rate} = k(\text{SO}_2)F'$. The rates are given in his thesis in terms of moles $\ell^{-1} \text{min}^{-1}$ and since $R' = 1$ (and therefore $F' = 1$) for all the experiments under consideration, the values of k are equal (in min^{-1}) to the values of the rates, $R(\text{moles } \ell^{-1} \text{min}^{-1})$, divided by

TABLE VIII. Rate Constants and c Values
for Doherty's Data

Temp., °C	% Acid	$k \times 10^2$, hr^{-1}	c
167.5	98.0	1.889	2.60
167.5	90.8	3.03	2.06
194.4	98.0	8.93	2.83
194.4	97.0	11.17	2.39
194.4	96.0	12.50	2.35
194.4	94.9	14.6	2.04
194.4	93.1	15.4	1.97
194.4	90.8	18.0	1.71
194.4	85.2	21.75	1.67
225.3	98.0	74.1	1.69
225.3	90.8	111.7	1.60

the recorded concentrations of SO_2 used (in moles ℓ^{-1}).

As for values of c , McDonald did not determine these, and the pertinent data are not available in the literature. Hence it was necessary to make estimates of these values from data at other temperatures. In order to estimate c values for these sulfuric acid solutions at 174.0°C , an attempt was made to approximate a plot of $\log c$ vs. $\% \text{H}_2\text{SO}_4$ for this temperature. For this purpose, plots were made of $\log c$ vs. $1/T$ for 85.2, 90.8, 93.1, 94.9, 96, 97, 98 and 100% acid, points being used from the present work, Doherty's (2, p. 25) results, and data given by Miles and Carson (15). For this latter purpose it was necessary to calculate c values from values of grams of sulfur dioxide dissolved (at one atmosphere pressure) per 100 grams of sulfuric acid solution, this being the way the solubility data were reported by Miles and Carson. To this end, a functional relationship between the two solubility functions, c and $g/100g$ acid, was computed, use being made of the ideal gas law and acid density values for 20°C , 40°C and 60°C from the literature (4, p. 56-57). A summary of these values appears in Table IX. A typical plot of $\log c$ vs $1/T$ for 90.8% H_2SO_4 is illustrated in Figure 20. From these $\log c$ vs $1/T$ plots, then, values of c at various acid concentrations and temperatures were read off, these values being recorded in Table X. Finally, on the basis both of the data in Table IX and those in Table X, it was possible to draw the plots

TABLE IX. Variation of c Values with $1/T$
for Various Acid Concentrations

Temp., °C	Gas Sol'ty, g/100g	Acid Density	c	$\frac{1}{T} \times 10^3$	Data Source (a)
85.0% Acid					
20	2.85	1.779	19.0	3.41	M
40	1.50	1.758	10.59	3.19	M
60	0.90	1.736	6.67	3.00	M
194.4	--	---	1.670	2.14	D
87.0% Acid					
20	2.90	1.795	19.52	3.41	M
40	1.55	1.774	11.03	3.19	M
60	0.90	1.753	6.72	3.00	M
89.0% Acid					
20	2.95	1.809	20.0	3.41	M
40	1.65	1.787	11.83	3.19	M
60	0.95	1.767	7.16	3.00	M
90.8% Acid					
20	3.15	1.818	21.5	3.41	M
40	1.75	1.798	12.60	3.20	M
60	1.00	1.778	7.60	3.00	M
167.5	--	---	2.06	3.27	D
194.4	--	---	1.71	3.14	D
225.3	--	---	1.60	3.01	D
93.1% Acid					
20	3.25	1.828	22.3	3.41	M
40	1.81	1.807	13.11	3.19	M
60	1.08	1.788	8.22	3.00	M
194.4	--	---	1.97	2.14	D
94.9% Acid					
20	3.55	1.834	24.4	3.41	M
40	1.90	1.814	13.83	3.19	M
60	1.18	1.794	9.02	3.00	M
194.4	--	---	2.04	2.14	D

TABLE IX. Continued

Temp., °C	Gas Sol'ty, g/100g	Acid Density	c	$\frac{1}{T} \times 10^3$	Data Source (a)
96.0% Acid					
20	3.80	1.836	26.2	3.41	M
40	1.950	1.816	14.21	3.19	M
60	1.25	1.797	9.60	3.00	M
194.4	--	---	2.35	2.14	D
97.0% Acid					
20	3.88	1.836	26.7	3.41	M
40	2.00	1.817	14.58	3.19	M
60	1.30	1.798	9.97	3.00	M
194.4	--	---	2.39	2.14	D
98.0% Acid					
20	3.98	1.836	27.4	3.41	M
40	2.03	1.816	14.8	3.20	M
60	1.40	1.798	10.7	3.00	M
167.5	--	---	2.60	2.27	D
194.4	--	---	2.83	2.14	D
225.3	--	---	1.69	2.01	D
100% Acid					
20	3.88	1.8305	26.7	3.41	M
40	2.16	1.8107	15.68	3.20	M
60	1.48	1.792	11.31	3.00	M
167.5	--	---	2.97	2.27	HB
194.4	--	---	4.61	2.14	HB
225.3	--	---	1.714	2.01	HB

(a) The letter M stands for Miles and Carson, the letter D for Doherty and the letters HB for the present author's work.

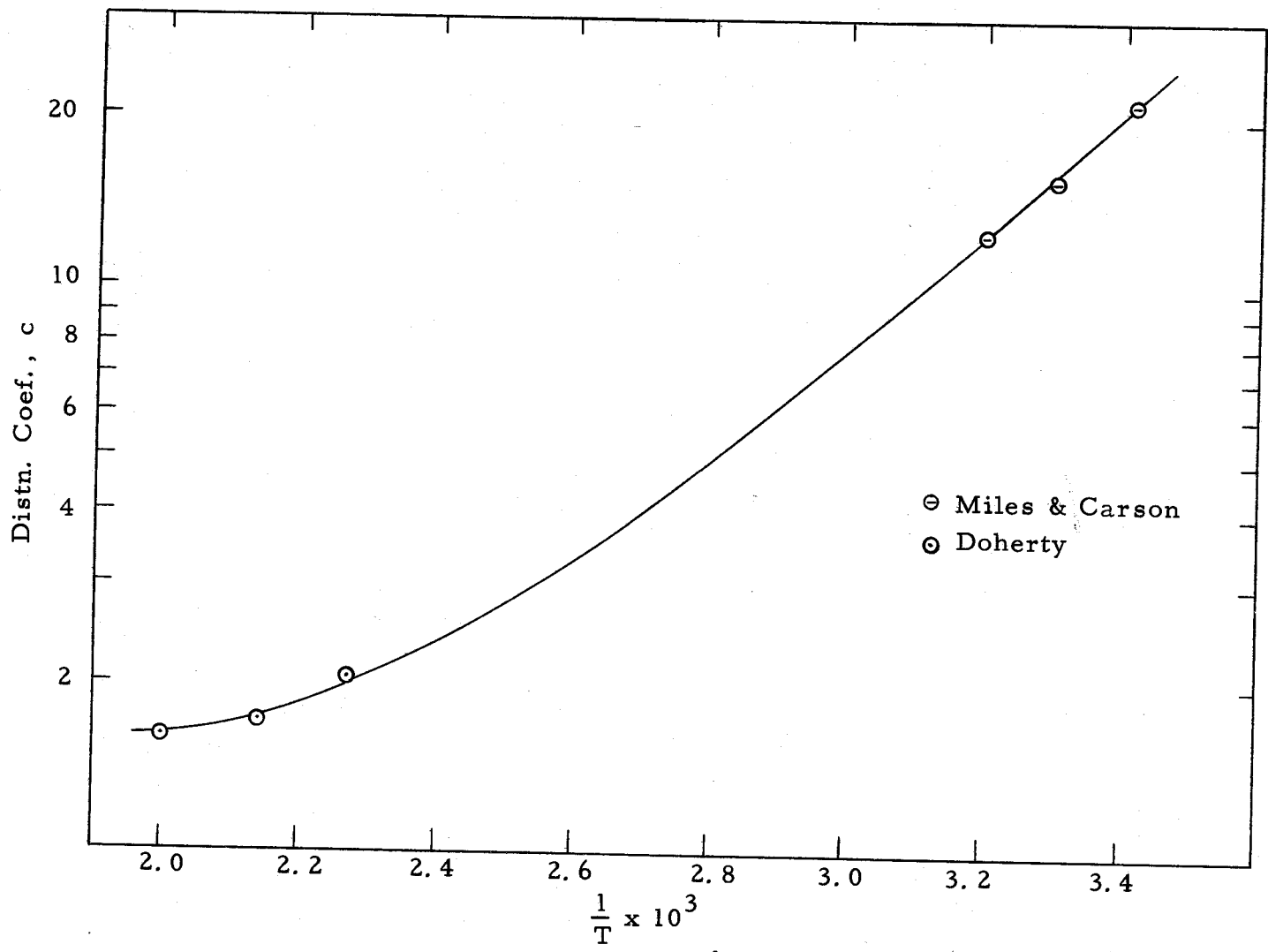


Figure 20. Typical plot of $\log c$ vs. $\frac{1}{T}$, 90.8% H_2SO_4 (see Table IX).

TABLE X. Estimated^(a) c Values

Temp., °C	c	$\frac{1}{T} \times 10^3$	Temp., °C	c	$\frac{1}{T} \times 10^3$
85.0% Acid			96.0% Acid		
167.5	1.90	2.27	167.5	2.77	2.27
174.0	1.86	2.24	174.0	2.68	2.24
225.3	1.47	2.01	225.3	2.10	2.01
90.8% Acid			97.0% Acid		
174.0	1.96	2.24	167.5	2.75	2.27
			174.0	2.65	2.24
93.1% Acid			98.0% Acid		
167.5	2.25	2.27			
174.0	2.18	2.24	174.0	2.57	2.24
94.9% Acid			100% Acid		
167.5	2.40	2.27	174.0	2.75	2.24
174.0	2.30	2.24			
225.3	1.77	2.01			

(a) The given c values have been estimated by interpolation or extrapolation from observed c values on plots of log c vs. 1/T.

TABLE XI. Rate Constants and c Values for McDonald's Data

Temp., °C	% Acid	$k \times 10^4$, min ⁻¹	$k \times 10^2$, hr ⁻¹	c
174.0	100	2.43	1.458	2.75
174.0	99.2	3.25	1.950	2.66
174.0	95.3	6.21	3.73	2.42
174.0	88.2	11.16	6.70	1.88
174.0	84.6	11.04	6.62	1.84

appearing in Figure 21 for $\log c$ vs. acid concentration at different temperatures, namely 60°C , 167.5°C , 174.0°C , 194.4°C and 225.3°C . Values of c , read directly from the 174.0°C plot in Figure 21 for the sulfuric acid concentrations at which McDonald (13, p. 1-138) worked are listed, along with the related k values from his results, in Table XI.

A study of the exchange reaction between sulfur dioxide and concentrated sulfuric acid (73.1 - 98.0% H_2SO_4) was also carried out by Masters and Norris (12). Values of k , the observed rate constants, and c , the distribution coefficients, from this study are listed in Table XII.

TABLE XII. Rate Constants and c Values
for Data of Masters and Norris

Temp., $^\circ\text{C}$	% Acid	$k \times 10^2$, hr^{-1}	c
194.4	98.0	9.57	2.77
194.4	96.2	13.05	2.30
194.4	90.9	21.47	1.77
194.4	80.3	19.63	1.55
194.4	73.1	17.38	1.56

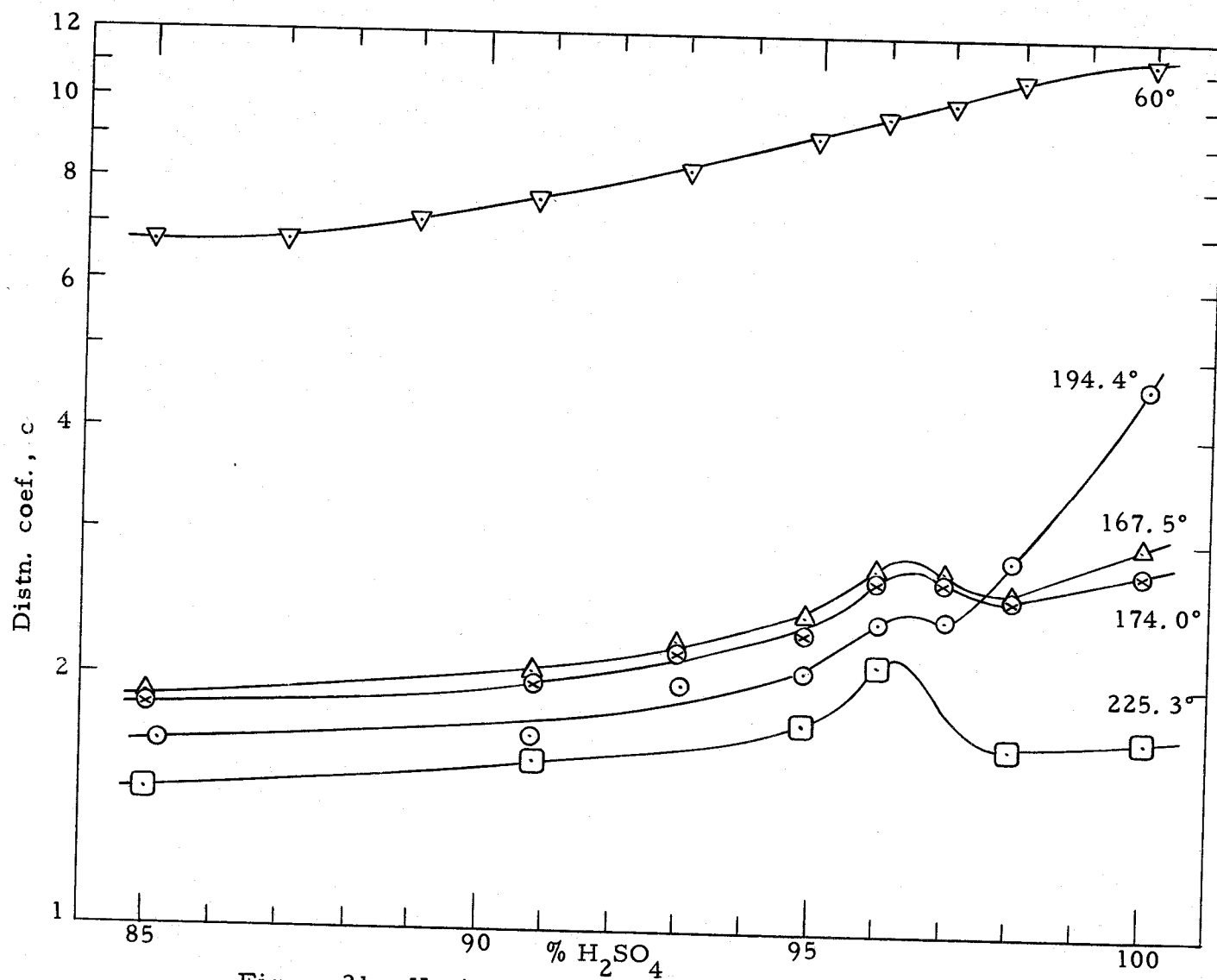


Figure 21. Variation of c values with acid concentration.

TABLE XIII. Rate Constants and c Values
for Present and Previous Work

Temp., °C	Sulfur (VI) Reactant	$k \times 10^2$, hr ⁻¹	c	Data Source (a)
Temperature = 167.5 - 169.5°C				
167.5	100% H ₂ SO ₄	1.203	2.97	HB
167.5	98% H ₂ SO ₄	1.889	2.60	D
167.5	90.8% H ₂ SO ₄	3.03	2.06	D
169.5	pure NH ₄ HSO ₄	0.713	19.79	HB
167.5	1:1 NH ₄ HSO ₄ and 84.5% H ₂ SO ₄	5.24	1.004	HB
Temperature = 174.0°C				
174.0	100% H ₂ SO ₄	1.458	2.75	McD
174.0	99.2% H ₂ SO ₄	1.950	2.66	McD
174.0	95.3% H ₂ SO ₄	3.73	2.42	McD
174.0	88.2% H ₂ SO ₄	6.70	1.84	McD
174.0	84.6% H ₂ SO ₄	6.62	1.88	McD
Temperature = 194.4 - 194.8°C				
194.4	100% H ₂ SO ₄	6.29	4.61	HB
194.4	98.0% H ₂ SO ₄	8.93	2.83	D
194.4	98.0% H ₂ SO ₄	9.57	2.77	MN
194.4	97.0% H ₂ SO ₄	11.17	2.39	D
194.4	96.2% H ₂ SO ₄	13.05	2.30	MN
194.4	96.0% H ₂ SO ₄	12.50	2.35	D
194.4	94.9% H ₂ SO ₄	14.6	2.04	D
194.4	93.1% H ₂ SO ₄	15.4	1.97	D
194.4	90.9% H ₂ SO ₄	21.47	1.77	MN
194.4	90.8% H ₂ SO ₄	18.0	1.71	D
194.4	85.2% H ₂ SO ₄	21.75	1.67	D

TABLE XIII. Continued

Temp., °C	Sulfur (VI) Reactant	$k \times 10^2$, hr^{-1}	c	Data Source (a)
194.4	80.3% H_2SO_4	19.63	1.55	MN
194.4	73.1% H_2SO_4	17.38	1.56	MN
194.4	1:4 NH_4HSO_4 and 100% H_2SO_4	36.0	1.112	HB
194.4	2.05:1 NH_4HSO_4 and 100% H_2SO_4	7.91	2.66	HB
194.8	NH_4HSO_4	3.04	10.61	HB
194.4	1:1 NH_4HSO_4 and 84.5% H_2SO_4	36.5	0.776	HB
Temperature = 225.3°C				
225.3	100% H_2SO_4	52.2	1.714	HB
225.3	98% H_2SO_4	74.1	1.69	D
225.3	90.8% H_2SO_4	111.7	1.60	D
225.3	NH_4HSO_4	7.02	10.08	HB
225.3	1:1 NH_4HSO_4 and 84.5% H_2SO_4	226	0.589	HB

(a) Sources of data were as follows: HB represents the present author's results; D represents Doherty's results; McD represents McDonald's data; and MN represents the data of Masters and Norris.

For the sake of making the comparison between the previous work and the present easier, all the data have been rearranged anew and listed in Table XIII. At each reaction temperature, the k 's are listed along with the corresponding values of c for all the various types of solutions examined.

Apart from the intrinsic worth of the solubility data represented in the preceding table, these data are also useful in leading to values for the activity coefficients of sulfur dioxide in the solutions here involved. The availability of such values, it materializes, is of particular importance in that it appears that taking them into account may possibly lead to a more adequate interpretation of the exchange rate data. Thus, if we assume the exchange rate to be proportional to the activity of dissolved sulfur dioxide rather than its concentration, it is of interest to see whether we can obtain a better reconciliation of the aqueous acid and the fused ammonium bisulfate rate data. The possible validity of this point of view is illustrated by the material presented in Tables XIV through XVII.

In order to proceed with the comparison of rate constants based on activities, the indicated activity coefficients, γ , were first calculated from the previously recorded c values, and from these, then, the revised activity rate constants were calculated. Details are recorded in Tables XIV through XVII.

The activity coefficients of SO_2 were computed from the

equation

$$\gamma = \frac{P}{P'} \quad (4)$$

where P is the actual partial pressure of the solute SO_2 over the solution at the composition of interest and P' is the calculated ideal solution (Raoult's Law) partial pressure at the same solution composition. Since it has been established that Henry's Law applies to the solutions here involved, it is apparent that γ will be a constant for a particular type of solution, independent of SO_2 concentration (though varying, of course, with the other components of the solution). Hence for any particular type of solution, any convenient sulfur dioxide solution concentration may be taken as a basis for the following calculations. In the succeeding tables a solution 0.1M in SO_2 was taken as the basis for all the calculations.

In order to calculate the ideal solution SO_2 partial pressures for the various solutions examined (values of P' in equation (1)), one would normally employ the known vapor pressures of the pure liquid solute, P° , together with its mole fraction concentration in the solution. However a difficulty exists here relative to such a procedure in that we are dealing with a gas at a temperature in excess of its critical temperature (157.2°C). In order to handle this situation, the same procedure has been followed as that used by Hildebrand and Scott (8, p. 241) in their treatment of gaseous solutions at temperatures above the critical point. The procedure

consisted in extrapolating a plot of $\log P^\circ$ vs. $1/T$, a plot which is essentially linear up to the critical point. Such a plot for sulfur dioxide, based on data given by Kang, et al. (10), is shown in Figure 22. Values of P° at the temperatures of interest were read directly from this graph and have been listed in column 12, Part 1 of Tables XIV, XVI and XVII and in column 10, Part 1 of Table XV.

In order to calculate the mole fraction of SO_2 in the solutions, it was necessary to compute the total number of moles in the solutions. The latter was arbitrarily calculated on the basis of the assumption that each of the solution components H_2O , NH_3 , H_2SO_4 and SO_2 exists independently in the solution, no interaction whatsoever among these species being assumed. Density values used for this calculation are listed in column 3 (Part 1 of the Tables). The solution densities listed were determined experimentally (see Tables I and II), except for those related to McDonald's data at 174.0°C where the density values given are his estimated values obtained by him by extrapolation from lower temperatures (13, p. 59). Density values for sulfuric acid solutions with which Masters and Norris (12) worked were experimentally determined values for densities, when available (see Table II) or were values estimated by extrapolation by these workers. The calculated values of molar concentration for each reactant in the solution (other than SO_2 , assumed 0.1M) are listed in columns 7, 8 and 9 (Part 1 of Tables

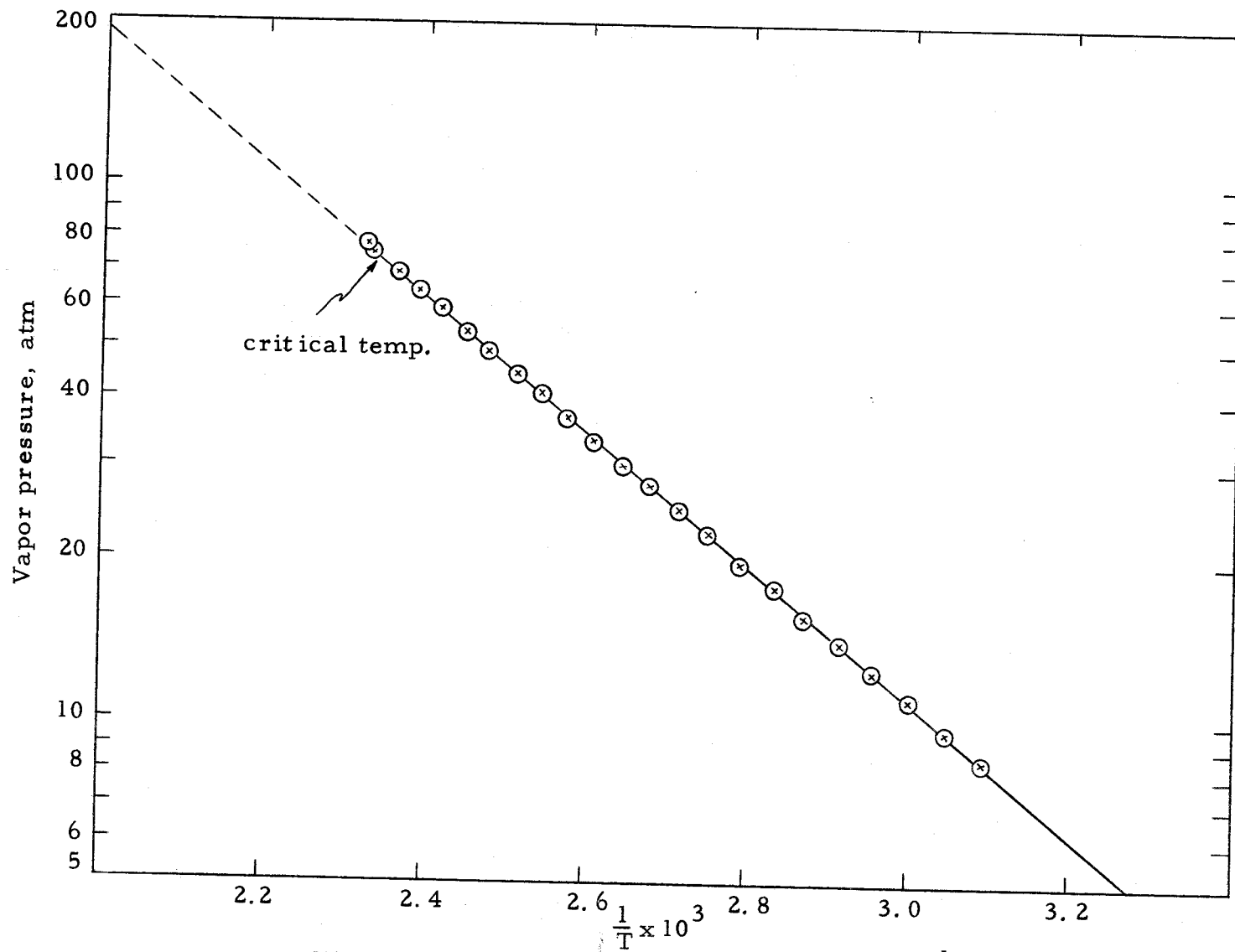


Figure 22. Vapor pressure of liquid SO₂ vs. $\frac{1}{T}$.

XIV, XVI and XVII and column 6 and 7 (Part 1 of Table XV). It should be noted here that ammonium bisulfate salt was considered in the calculations as a 1:1 (in molar ratio) mixture of ammonia and sulfuric acid. In column 10 (Part 1 of Tables XIV, XVI and XVII) and column 9 (Part 1 of Table XV) are listed the total number of moles (apart from SO_2), namely moles of H_2SO_4 , NH_3 and H_2O , present in one liter of solution. From these values, then, the mole fraction of SO_2 (for the assumed 0.1M SO_2 solutions) were directly calculated. The resulting figures are tabulated in column 11 (Part 1 of Tables XIV, XVI and XVII) and column 9 (Part 1 of Table XV).

On the basis of the calculated mole fraction values of SO_2 in the solution, together with the estimated P° values for SO_2 at the temperatures under consideration, P' values (equation 1) were finally calculated by applying Raoult's law:

$$P'_{\text{SO}_2} = (P^\circ_{\text{SO}_2}) (MF_{\text{SO}_2}) \quad (2)$$

The values of P'_{SO_2} so calculated are listed in column 2 (Part 2 of Tables XIV through XVII).

Values of P in equation (1) were calculated directly from c values listed in column 3 (Part 2 of the Tables). The quantity c represents the distribution coefficient of the sulfur dioxide between liquid and gas phases, i. e. the equilibrium molar concentration in solution divided by that in the gas, a figure thus giving the solubility

of this substance. Directly from this definition of c , account being taken of the fact that the solution was assumed 0.1 molar in SO_2 , the concentration of SO_2 in the gas phase was computed. From this figure, then, the gas phase pressure of SO_2 was calculated by applying the ideal gas law. These two latter quantities are listed in columns 4 and 5 (Part 2 of Tables XIV through XVII).

At this point, having P and P' values available, values of γ were calculated (see equation 1) and these computed values are listed in column 6 (Part 2 of Table XIV through XVII).

In the seventh column (Part 2 of Tables XIV through XVII) are listed the observed first order rate constants for the reaction, k , calculated from the expression $\text{Rate} = k (\text{SO}_2)$, where (SO_2) represents sulfur dioxide concentration in the solution. The eighth column (Part 2 of the Tables) gives the first order rate constant, k_a , corrected in terms of this activity coefficient, i. e. calculated in terms of the expression $\text{Rate} = k_a \gamma (\text{SO}_2)$. This last rate equation represents an expression of the dependence of the rate on the activity of sulfur dioxide rather than its concentration, since $\text{Activity}_{\text{SO}_2} = \gamma (\text{SO}_2)$. It may be noted here that any difference between activity coefficients calculated on the basis of solute mole fractions as opposed to solute molar concentrations is of negligible consequence for the low concentrations here involved.

TABLE XIV - Part 1. Computation of $\frac{k}{\gamma}$ at 167.5 - 169.5 °C. (a)

Temp., °C	Solution	Sol. Density, g/ml	Concentrations, g/l			Concentrations, mole/l.				Mol. Frac. ^(a) SO ₂	p ^(b) SO ₂ , atm
			H ₂ O	H ₂ SO ₄	NH ₃	H ₂ O	H ₂ SO ₄	NH ₃	Total		
167.5	100% H ₂ SO ₄	1.722	0	1722	0	0	17.56	0	17.56	0.00566	89.5
167.5	98.0% H ₂ SO ₄	1.697	33.94	1663	0	1.883	16.96	0	18.84	0.00531	89.5
167.5	90.8% H ₂ SO ₄	1.676	154.2	1522	0	8.56	15.52	0	24.08	0.00414	89.5
169.5	NH ₄ HSO ₄	1.695	-	-	-	0	14.73	14.73	29.46	0.00338	92.0
167.5	1:1 NH ₄ HSO ₄ and 84.5% H ₂ SO ₄	1.662	-	-	-	7.02	14.04	7.02	28.08	0.00355	89.5

TABLE XIV Part 2.

Solution	P _{SO₂} ^(c) atm.	c	SO ₂ in Vapor Phase		γ	k x 10 ² hr ⁻¹	k _a x 10 ^{2(e)} hr ⁻¹	k _a x 10 ² /2H ₂ SO ₄ 1 mol ⁻¹ hr ⁻¹
			Conc., mol/l	P _{SO₂} , atm (d)				
100% H ₂ SO ₄	0.507	2.97	0.0337	1.219	2.40	1.203	0.501	0.0285
98% H ₂ SO ₄	0.475	2.60	0.0385	1.392	2.93	1.889	0.645	0.0380
90.8% H ₂ SO ₄	0.371	2.06	0.0485	1.754	4.73	3.03	0.641	0.0413
NH ₄ HSO ₄	0.311	19.79	0.00505	0.1827	0.587	0.713	1.215	0.0825
1:1 NH ₄ HSO ₄ and 84.5% H ₂ SO ₄	0.318	1.004	0.0996	3.60	11.32	5.24	0.463	0.0330

(a) A 0.1M SO₂ Solution is assumed as the basis of computation.

(b) Extrapolated liquid sulfur dioxide vapor pressure.

(c) Sulfur dioxide partial pressure calculated on basis of Raoult's law, P_{SO₂}' = (P^o_{SO₂}) (MF_{SO₂}).

(d) Actual sulfur dioxide partial pressure over assumed 0.1M SO₂ solution.

(e) k_a = k/γ.

TABLE XV - Part 1. Computation of $\frac{k}{\gamma}$ at 174.0°C. (a)

Temp., °C.	Solution	Sol. Density, g/ml	Concentrations, g/l		Concentrations, mole/l			Mol. Frac. (a) SO ₂	P ^o SO ₂ , atm (b)
			H ₂ O	H ₂ SO ₄	H ₂ O	H ₂ SO ₄	Total		
174.0	100% H ₂ SO ₄	1.684	0	1684	0	17.17	17.17	0.00579	97.0
174.0	99.2% H ₂ SO ₄	1.688	13.50	1674	0.749	17.07	17.82	0.00558	97.0
174.0	95.3% H ₂ SO ₄	1.688	79.3	1609	4.40	16.40	20.80	0.00478	97.0
174.0	88.2% H ₂ SO ₄	1.650	194.7	1455	10.80	14.83	25.63	0.00389	97.0
174.0	84.6% H ₂ SO ₄	1.623	250	1373	13.87	14.00	27.87	0.00358	97.0

TABLE XV - Part 2.

Solution	P ['] SO ₂ , atm (c)	c	SO ₂ in Vapor Phase		γ	k x 10 ² hr ⁻¹	k _a x 10 ² hr ⁻¹ (e)	k _a x 10 ² / Σ H ₂ SO ₄ 1 mole ⁻¹ hr ⁻¹
			Conc., mol/l	P _{SO₂} , atm (d)				
100% H ₂ SO ₄	0.562	2.75	0.0364	1.336	2.38	1.458	0.613	0.0357
99.2% H ₂ SO ₄	0.541	2.66	0.0376	1.379	2.55	1.950	0.765	0.0448
95.3% H ₂ SO ₄	0.464	2.42	0.0413	1.515	3.27	3.73	1.141	0.0696
88.2% H ₂ SO ₄	0.377	1.88	0.0532	1.952	5.18	6.70	1.293	0.0872
84.6% H ₂ SO ₄	0.347	1.84	0.0543	1.992	5.74	6.62	1.153	0.0824

(a) A 0.1M SO₂ solution is assumed as the basis of computation.

(b) Extrapolated liquid sulfur dioxide vapor pressure.

(c) Sulfur dioxide partial pressure calculated on basis of Raoult's law, $P'_{SO_2} = (P^o_{SO_2})(MF_{SO_2})$.

(d) Actual sulfur dioxide partial pressure over assumed 0.1M SO₂ solution.

(e) $k_a = k/\gamma$.

TABLE XVI - Part 1. Computation of k/γ at 194.4 - 194.8°C. (a)

Temp., °C	Solution	Sol. Density, g/ml	Concentrations, g/l			Concentrations, mole/l				Mol. Frac. ^(a) SO ₂	P _{SO₂} ^(b) atm
			H ₂ O	H ₂ SO ₄	NH ₃	H ₂ O	H ₂ SO ₄	NH ₃	Total		
194.4	100% H ₂ SO ₄	1.651	0	1651	0	0	16.83	0	16.83	0.00591	130
194.4	98.0% H ₂ SO ₄	1.674	33.48	1640	0	1.858	16.72	0	18.58	0.00535	130
194.4(f)	98.0% H ₂ SO ₄	1.674	33.48	1640	0	1.858	16.72	0	18.58	0.00535	130
194.4	97.0% H ₂ SO ₄	1.684	50.5	1633	0	2.80	16.65	0	19.45	0.00512	130
194.4(f)	96.2% H ₂ SO ₄	1.673	63.6	1609	0	3.53	16.40	0	19.93	0.00499	130
194.4	96.0% H ₂ SO ₄	1.675	67.0	1608	0	3.72	16.39	0	20.11	0.00495	130
194.4	94.9% H ₂ SO ₄	1.669	85.1	1584	0	4.72	16.15	0	20.87	0.00477	130
194.4	93.1% H ₂ SO ₄	1.663	114.8	1548	0	6.37	15.78	0	22.15	0.00449	130
194.4(f)	90.9% H ₂ SO ₄	1.658	150.9	1507	0	8.37	15.37	0	23.74	0.00419	130
194.4	90.8% H ₂ SO ₄	1.650	150.2	1498	0	8.34	15.27	0	23.61	0.00422	130
194.4	85.2% H ₂ SO ₄	1.612	239	1373	0	13.26	14.00	0	27.26	0.00365	130
194.4(f)	80.3% H ₂ SO ₄	1.577	311	1266	0	17.26	12.91	0	30.17	0.00330	130
194.4(f)	73.1% H ₂ SO ₄	1.501	404	1097	0	22.40	11.18	0	33.58	0.00297	130
194.4	1:4NH ₄ HSO ₄ and 100%H ₂ SO ₄	1.721	-	-	-	0	16.95	3.39	20.34	0.00489	130
194.4	2.05:1NH ₄ HSO ₄ and 100%H ₂ SO ₄	1.704	-	-	-	0	15.56	10.45	26.01	0.00383	130
194.8	NH ₄ HSO ₄	1.651	-	-	-	0	14.34	14.34	28.68	0.00347	132
194.4	1:1NH ₄ HSO ₄ and 84.5%H ₂ SO ₄	1.615	-	-	-	6.98	13.96	6.98	27.92	0.00357	130

TABLE XVI - Part 2

Solution	$P_{\text{SO}_2}^{\circ}$, atm	c	SO ₂ in Vapor Phase			$k \times 10^2$ hr ⁻¹	$k_a \times 10^{2(e)}$ hr ⁻¹	$k_a \times 10^2 / \Delta H_{\text{H}_2\text{SO}_4}$ 1 mol ⁻¹ hr ⁻¹
			Conc., mol/l	P_{SO_2} , atm (d)	γ			
100% H ₂ SO ₄	0.768	4.61	0.0217	0.833	1.085	6.29	5.80	0.345
98% H ₂ SO ₄	0.696	2.83	0.0353	1.356	1.948	8.93	4.58	0.274
98% H ₂ SO ₄ (f)	0.696	2.77	0.0361	1.386	1.991	9.57	4.81	0.288
97% H ₂ SO ₄	0.666	2.39	0.0418	1.605	2.41	11.17	4.63	0.278
96.2% H ₂ SO ₄ (f)	0.649	2.30	0.0435	1.670	2.57	13.05	5.08	0.310
96.0% H ₂ SO ₄	0.644	2.35	0.0426	1.636	2.54	12.5	4.92	0.300
94.9% H ₂ SO ₄	0.620	2.04	0.0490	1.882	3.04	14.6	4.80	0.297
93.1% H ₂ SO ₄	0.584	1.97	0.0508	1.951	3.34	15.4	4.61	0.292
90.9% H ₂ SO ₄	0.545	1.77	0.0565	2.170	3.98	21.47	5.39	0.351
90.8% H ₂ SO ₄	0.549	1.71	0.0585	2.25	4.1	18.0	4.39	0.287
85.2% H ₂ SO ₄	0.475	1.67	0.0599	2.30	4.84	21.75	4.49	0.321
80.3% H ₂ SO ₄ (f)	0.429	1.55	0.0645	2.48	5.78	19.63	3.40	0.263
73.1% H ₂ SO ₄ (f)	0.386	1.56	0.0641	2.46	6.37	17.38	2.73	0.244
1:4NH ₄ HSO ₄ and 100% H ₂ SO ₄	0.636	1.112	0.0899	3.45	5.42	36.0	6.64	0.392
2.05:1 NH ₄ HSO ₄ and 100% H ₂ SO ₄	0.498	2.66	0.0376	1.444	2.90	7.91	2.73	0.1754
NH ₄ HSO ₄	0.458	10.61	0.00943	0.362	0.790	3.04	3.85	0.268
1:1 NH ₄ HSO ₄ and 84.5% H ₂ SO ₄	0.464	0.776	0.1289	4.95	10.67	36.5	3.42	0.245

(a) A 0.1M SO₂ solution is assumed as the basis of computation.

(b) Extrapolated liquid sulfur dioxide vapor pressure.

(c) Sulfur dioxide partial pressure calculated on basis of Raoult's law, $P_{\text{SO}_2} = (P_{\text{SO}_2}^{\circ}) (M_{\text{SO}_2})$.

(d) Actual sulfur dioxide partial pressure over assumed 0.1M SO₂ solution.

(e) $k_a = k/\gamma$.

(f) Data are from Masters and Norris' work (8).

TABLE XVII - Part 1. Computation of k/γ at 225.3°C. (a)

Temp., °C	Solution	Sol. Density, g/ml	Concentrations, g/l			Concentrations, mole/l				Mol. Frac. (a) SO ₂	p ^(b) SO ₂ , atm
			H ₂ O	H ₂ SO ₄	NH ₃	H ₂ O	H ₂ SO ₄	NH ₃	Total		
225.3	100% H ₂ SO ₄	1.650	0	1650	0	0	16.82	0	16.82	0.00591	189
225.3	98% H ₂ SO ₄	1.650	33.0	1617	0	1.831	16.49	0	18.32	0.00543	189
225.3	90.8% H ₂ SO ₄	1.611	148.2	1463	0	8.22	14.92	0	23.14	0.00430	189
225.3	NH ₄ HSO ₄	1.617	-	-	-	0	14.05	14.05	28.1	0.00355	189
225.3	1:1NH ₄ HSO ₄ and 84.5% H ₂ SO ₄	1.567	-	-	-	6.78	13.56	6.78	27.12	0.00367	189

TABLE XVII - Part 2.

Solution	P' _{SO₂} ^(c) atm.	c	SO ₂ in Vapor Phase			kx10 ² hr ⁻¹	k _a x10 ² ^(e) hr ⁻¹	k _a x10 ² /ΣH ₂ SO ₄ l mole ⁻¹ hr ⁻¹
			Conc., mol/l	P _{SO₂} ^(d) , atm	γ			
100% H ₂ SO ₄	1.117	1.714	0.0583	2.38	2.13	52.2	24.5	1.457
98.0% H ₂ SO ₄	1.026	1.69	0.0592	2.42	2.36	74.1	31.4	1.904
90.8% H ₂ SO ₄	0.813	1.60	0.0625	2.56	3.15	111.7	35.5	2.38
NH ₄ HSO ₄	0.671	10.08	0.00992	0.406	0.605	7.02	11.60	0.826
1:1 NH ₄ HSO ₄ and 84.5% H ₂ SO ₄	0.694	0.589	0.1698	6.94	10.0	226	22.6	1.667

- (a) A 0.1M SO₂ solution is assumed as the basis of computation.
- (b) Extrapolated liquid sulfur dioxide vapor pressure.
- (c) Sulfur dioxide partial pressure calculated on basis of Raoult's law, $P'_{SO_2} = (P^{\circ}_{SO_2})(MF_{SO_2})$.
- (d) Actual sulfur dioxide partial pressure over assumed 0.1 M SO₂ solution.
- (e) $k_a = k/\gamma$.

The rate constants listed respectively in columns 7 and 8, Part 2 of Tables XIV - XVII provide a basis for making the desired assessment of the relative merits of the two types of rate constants, namely those based on sulfur dioxide concentrations and those based on sulfur dioxide activities. For the sake of facilitating this comparison, the values for these constants have been reproduced together in one table for various key types of solution (Table XVIII). Examination of the data both in Tables XIV - XVII and XVIII reveals a striking comparison between the two types of rate constants. It is readily seen that the concentration rate constants, k , vary drastically from one solution to another at a particular temperature. A particularly marked comparison, for example, is provided by the k value for the 1:1 mixture of ammonium bisulfate with 84.5% sulfuric acid at 225.3°C ($k=226 \times 10^{-2} \text{ hr}^{-1}$) as compared to the corresponding value for pure ammonium bisulfate ($k=7.02 \times 10^{-2} \text{ hr}^{-1}$). Here the constants differ by a factor of 32. In sharp contrast with this large variability in k , one finds the activity rate constants, k_a , to vary among themselves to only a modest degree. The data at 194.4 - 194.8°C, in particular, provide a remarkable display of constancy with varying solvent composition, the greatest deviation amounting to only a factor of 2.5. The two constants above referred to, (at 225.3°C), which differed by a factor of 32, now, on correction to k_a (activity) constants differ only by a factor of two. On examination of the data

TABLE XVIII. Comparison of Rate Constants

Solution	$k \times 10^2, \text{hr}^{-1}$			$k_a \times 10^2, \text{hr}^{-1}$		
	167.5	194.4	225.3°C	167.5	194.4	225.3°C
	-169.5°C	-194.8°C		-169.5°C	-194.8°C	
100% H_2SO_4	1.203	6.29	52.2	0.501	5.80	24.5
98.0% H_2SO_4	1.889	8.93	74.1	0.645	4.58	31.4
90.8% H_2SO_4	3.03	18.00	111.7	0.641	4.39	35.5
85.2% H_2SO_4	--	21.75	--	--	4.49	--
1:1 NH_4HSO_4						
-84.5% H_2SO_4	5.24	36.5	226	0.463	3.42	22.6
NH_4HSO_4	0.713	3.04	7.02	1.215	3.85	11.60

as a whole, one finds the greatest spread exhibited between maximum and minimum k_a values to amount only to a factor of 3. 1.

On the basis of the observations cited in the preceding paragraph, one may clearly reach the conclusion that the exchange rate appears to depend on the activity of the dissolved sulfur dioxide rather than its concentration. Thus the apparently slower rate in fused ammonium bisulfate as compared to 84.5% sulfuric acid is illusory, the lower concentration rate constant in the former case being compensated for by a much greater sulfur dioxide solubility. The cause for this large variation in sulfur dioxide solubility between the two solutions, of course, poses another question inviting examination, for which we have here no immediate explanation. Such an uncertainty, does not, however, affect the cited conclusion concerning rate dependency on sulfur dioxide activity. The exploration of the possible occurrence of such a dependency represented one of the major objects of this research and it is most gratifying to have been able to demonstrate this occurrence. This demonstration probably represents one of the principle accomplishments of the present work.

The foregoing discussion has ignored a significant fact, namely that the solutions examined display a large variation in the ratio of bisulfate ion concentration to unionized sulfuric acid concentrations. Thus, while the unionized molecular species is clearly the primary

solution component in 100% acid, bisulfate ions representing only a modest percentage of the total sulfur (VI) present, just the opposite situation prevails in either fused ammonium bisulfate, 84.5% acid or mixtures of the two, where bisulfate ion must clearly predominate. Hence the data presented reveal an additional interesting feature, namely that the corrected, activity rate constants, k_a , vary but little with the relative $(\text{HSO}_4^-) - (\text{H}_2\text{SO}_4)$ concentration. Thus we see that, at any particular temperature, the k_a value is approximately independent of the type of solution, whether sulfuric acid of varying concentration, fused ammonium bisulfate, or acid-salt mixtures.

The total sulfate concentration varies but little in these solutions, so that we do not, therefore, have here a test of the exchange rate dependence on this quantity. McDonald's results (13, p. 1-138), however, have clearly shown, at least in aqueous solution, that there is a first order dependence of exchange rate on bisulfate ion concentration. Hence, if we make the reasonable assumption that the same dependency applies in the concentrated acid solutions, we are led to the conclusion that, while a two term rate law probably applies, as McDonald proposed (cf. equation (1)), the two terms apparently contribute equally effectively to the rate. In other words, we conclude that sulfur dioxide molecules react about equally as well with bisulfate ion as with unionized H_2SO_4 . Such a deduction

is of real interest and is clearly at variance with the previous conclusion of a greater reactivity for bisulfate ions. The last column of Tables XIV to XVII (Parts 2) gives values for the second order rate constant obtained by dividing the previously deduced first order activity-based constant, k_a , by total sulfur (VI) concentration. Scrutiny of the data shows that the new constant still displays but little variation from one solution to another. Such a feature, however, provides no real new information, since, as already indicated, the total sulfur (VI) concentration in the solutions examined varies but little from one case to the next.

It now appears quite possible that the exchange rate may be at least approximately represented, for all the various types of solutions examined, by a rate law of the form

$$\text{Rate} = k_2 \gamma_{\text{SO}_2} (\text{SO}_2) [(\text{HSO}_4^-) + (\text{H}_2\text{SO}_4)] \quad (5)$$

A natural question arises as to why, if the rate is a function of sulfur dioxide activity, it is not also a function of sulfur (VI) species activity rather than concentration. The answer to this problem is that, of course, it is a function of this latter activity, but that an additional factor must be taken into account, namely the activity coefficient of the activated complex. Thus for the activation step involving bisulfate ion, for example, one may write the equation



For this process the equilibrium constant would be

$$K = \frac{(\text{SO}_2 \cdot \text{HSO}_4^{-\ddagger})}{(\text{SO}_2)(\text{HSO}_4^{-})} \cdot \frac{\gamma^{\ddagger}}{\gamma_{\text{SO}_2} \gamma_{\text{HSO}_4^{-}}} \quad (7)$$

Here the quantities in parentheses represent molar concentrations and the gammas represent the related activity coefficients. Assuming the exchange rate to be proportional to the concentration of the activated complex, $(\text{SO}_2 \cdot \text{HSO}_4^{-\ddagger})$, one obtains for the (HSO_4^{-}) rate step the expression

$$\text{Rate}_{\text{HSO}_4^{-}} = kK \frac{\gamma_{\text{SO}_2} \gamma_{\text{HSO}_4^{-}}}{\gamma^{\ddagger}} (\text{SO}_2)(\text{HSO}_4^{-}) \quad (8)$$

For lack of better information, one may make the assumption that, at least to a first approximation, $\gamma_{\text{HSO}_4^{-}}$ and γ^{\ddagger} will be roughly equal, both species being singly charged negative ions. Hence these two gammas cancel. Thus equation (8) becomes

$$\text{Rate}_{\text{HSO}_4^{-}} = kK \gamma_{\text{SO}_2} (\text{SO}_2)(\text{HSO}_4^{-}) \quad (9)$$

For the exchange step involving interaction between sulfur dioxide and unionized H_2SO_4 , one may similarly assume an approximate cancellation of the activity coefficients γ^{\ddagger} and $\gamma_{\text{H}_2\text{SO}_4}$. Thus one obtains the rate law

$$\text{Rate} = kK \gamma_{\text{SO}_2} (\text{SO}_2)(\text{HSO}_4^{-}) + k'K'\gamma_{\text{SO}_2} (\text{SO}_2)(\text{H}_2\text{SO}_4) \quad (10)$$

This last equation is identical with the proposed experimental one,

equation (5), if one makes the final assumption that $kK = k'K' = k_2$. Thus the lack of appearance of sulfur (VI) activity coefficients in the rate law would appear plausible.

It is of interest at this point to study the temperature effect on the exchange rate through the revised exchange rate constants. The data available may be treated using equations (2) and (3) on page 71. For the exchange reaction between sulfur dioxide and pure ammonium bisulfate, values of k_a were $1.215 \times 10^{-2} \text{ hr}^{-1}$, $3.85 \times 10^{-2} \text{ hr}^{-1}$, and 0.1160 hr^{-1} at the temperatures 169.5°C , 194.8°C and 225.3°C , respectively. In Figure 23 is given a semi-log plot of k_a values plotted against $1/T$, the best straight line having been drawn by the least squares method. The value of the activation energy, E_a , derived from the straight line plotted is 17.93 kcal/mole . The average value of the frequency factor, A , is $2.38 \times 10^3 \text{ sec}^{-1}$. The average value of the entropy of activation, ΔS^\ddagger , is -46.0 e. u. These values are to be compared with their parallels based on the concentration rate constant, k , namely 18.07 kcal/mole for activation energy, $1.892 \times 10^3 \text{ sec}^{-1}$ for frequency factor and -46.5 e. u. for entropy of activation.

In the case of the study of the exchange reaction between sulfur dioxide and 100% H_2SO_4 , values of k_a were $5.01 \times 10^{-3} \text{ hr}^{-1}$, $6.13 \times 10^{-3} \text{ hr}^{-1}$, $5.80 \times 10^{-2} \text{ hr}^{-1}$ and 0.245 hr^{-1} at the temperatures 167.5°C , 174.0°C , 194.4°C and 225.3°C . In Figure 24, is

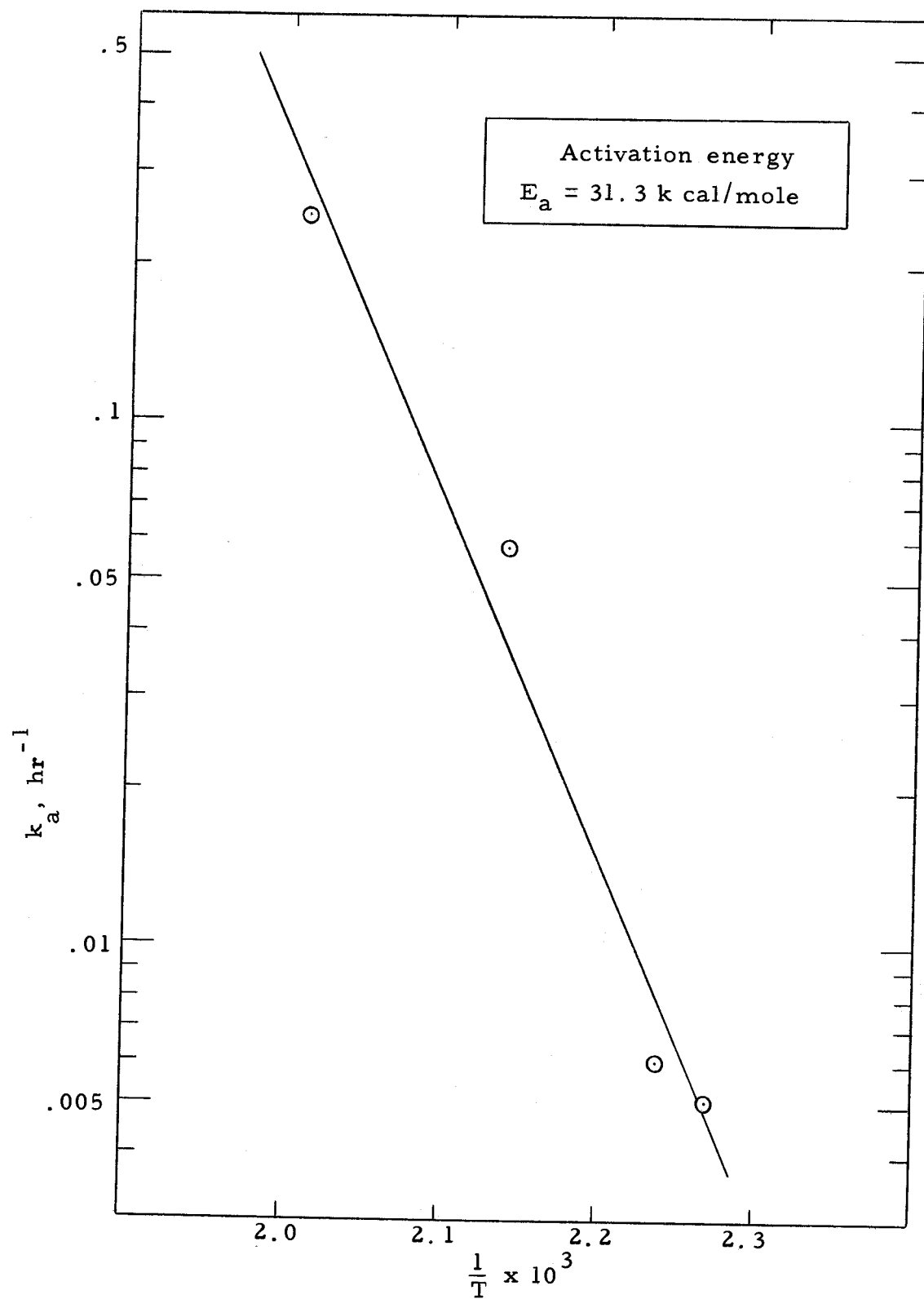


Figure 24. $\text{Log } k_a$ vs. $\frac{1}{T}$, 100% H_2SO_4 .

given a semi-log plot of k_a values, plotted against $1/T$, the least squares method again having been used. The value of the activation energy, E_a , derived from the straight line plotted is 31.3 kcal/mole. The average value of the frequency factor, A , is $4.66 \times 10^9 \text{ sec}^{-1}$. The average value of the entropy of activation is $\Delta S^\ddagger = -17.25 \text{ e. u.}$ The values of E_a , A and ΔS^\ddagger computed from the concentration rate constants k are 29.6 kcal/mole, $1.344 \times 10^9 \text{ sec}^{-1}$ and -19.66 e. u.

In the case of the study of the exchange reaction between sulfur dioxide and a mixture of 1:1 NH_4HSO_4 and 84.5% H_2SO_4 , values of k_a were $4.63 \times 10^{-3} \text{ hr}^{-1}$, $3.42 \times 10^{-2} \text{ hr}^{-1}$ and 0.226 hr^{-1} at the temperatures 167.5°C, 194.4°C and 225.3°C, respectively. In Figure 25, k_a values are again plotted against $1/T$, the least squares method having been used. The value of the activation energy, E_a , derived from the straight line plotted is 29.4 kcal/mole. The average value of the frequency factor, A , is $5.44 \times 10^8 \text{ sec}^{-1}$. The average value of entropy of activation is $\Delta S^\ddagger = -21.6 \text{ e. u.}$ The values of E_a , A and ΔS^\ddagger computed from the concentration rate constants k are 28.5 kcal/mole, $1.837 \times 10^9 \text{ sec}^{-1}$ and -19.05 e. u.

The foregoing calculated values of E_a , A and ΔS^\ddagger have been collected for the sake of comparison in Table XIX. It is immediately apparent that use of k_a values in place of k values has not led to any great modification in the values of these three kinetic parameters. Thus, despite the fact that treatment of the data in terms

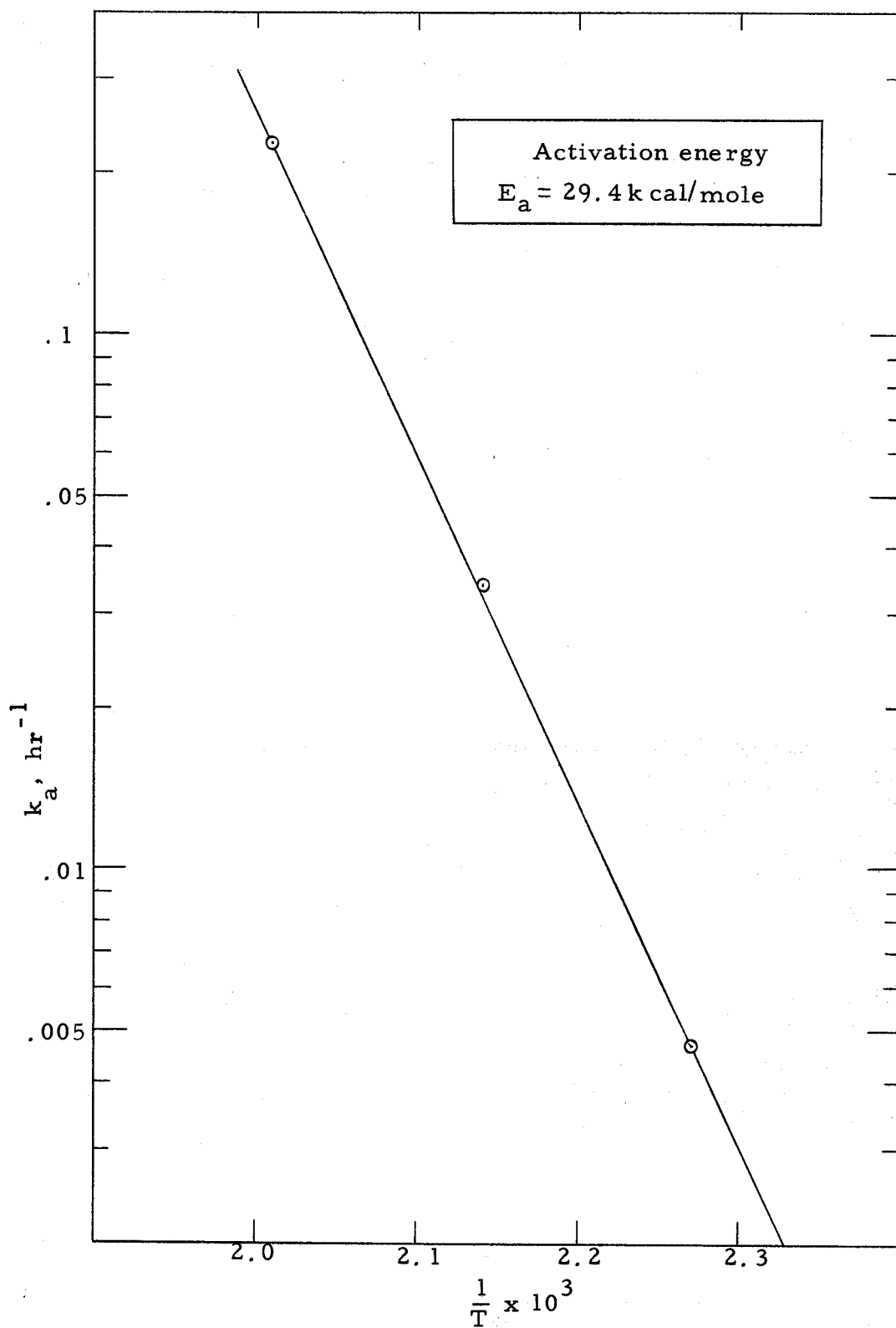


Figure 25. $\text{Log } k_a$ vs. $\frac{1}{T}$, 1:1 NH_4HSO_4 and 84.5% H_2SO_4 .

of activities in place of concentrations of sulfur dioxide has resulted in a greater concord among the rate constants themselves for the various solutions, it has not led to a corresponding accord among these three parameters. The values of E_a and A for ammonium bisulfate, for example, both previously much smaller than the corresponding quantities for 100% H_2SO_4 or the 1:1 mixture, still remain much smaller, even though calculated on the basis of k_a . Similarly, ΔS^\ddagger , previously much more negative, remains so.

TABLE XIX. Comparison of Kinetic Parameters

Solution	Values based on k			Values based on k_a		
	E_a kcal/mole	A , sec ⁻¹	ΔS^\ddagger e. u.	E_a , kcal/mole	A , sec ⁻¹	ΔS^\ddagger e. u.
100% H_2SO_4	29.6	1.344×10^9	-19.66	31.3	4.66×10^9	-17.25
1:1 NH_4HSO_4 -84.5% H_2SO_4	28.5	1.837×10^9	-19.05	29.4	5.44×10^8	-21.6
NH_4HSO_4	18.07	1.892×10^3	-46.5	17.93	2.38×10^3	-46.0

In view of the above comparison, the question immediately arises as to whether, in fact, the comparison of the rates on the basis of activities rather than concentrations really has any particular merit, since it does not lead to a complete reconciliation of all kinetic factors. While admittedly an altogether unequivocal answer to this question cannot be given for the present, it does seem reasonable to believe the activity treatment to have merit,

simply on the basis of the behavior of the rate constants themselves, without regard to the other parameters. With regard to the pronounced variation among these other three parameters, however, it seems possible that another factor may be involved. Specifically, it must be remembered that we have assumed above that the activity coefficient ratios $\gamma_{\text{HSO}_4^-}/\gamma^{\ddagger}$ and $\gamma_{\text{H}_2\text{SO}_4}/\gamma^{\ddagger}$ are both essentially unity. Such an assumption clearly represents only an approximation, and it seems possible that the degree of validity of this approximation may vary both with solution type and with temperature. Hence one wonders whether the large apparent variation in values of E_a , A and ΔS^{\ddagger} may not have its basis actually in a variation in values of the indicated activity coefficient ratios. Pending further study, we take this to be a plausible possibility.

This research has been of interest in displaying the pattern of exchange behavior in a variety of solutions, ranging from fused ammonium bisulfate, through mixtures of this material with sulfuric acid, up to 100% sulfuric acid. As previously indicated, the work's principal contribution would appear to be the demonstration that exchange rate constants based on sulfur dioxide activities rather than concentrations show a quite reasonably good concordance among themselves irrespective of solution type. A rather large question mark has been raised by the fact that it has not been possible to show a similar accord among the calculated values of activation

energies, frequency factors, and activation entropies, but it has been possible to postulate a plausible basis for this difficulty. Nevertheless, the question remains, and further work would certainly be desirable for the sake of resolving it. Such work might well take a number of directions. Experiments at higher and lower temperatures than those here studied would be helpful. Experiments in acid solutions more concentrated than 100% H_2SO_4 (i. e. fuming sulfuric acid) would be desirable. Further useful research might include experiments in other fused salt systems, such as fused potassium bisulfate (m. p. 210°C). By means of experiments along such lines it might be hoped that the exchange picture in this interesting system might be significantly further clarified.

VI. SUMMARY

1. The present study has served to provide a comparison of isotopic exchange rates between sulfur dioxide and sulfur (VI) in a variety of ammonia-containing systems with those previously observed in aqueous acid systems.
2. The exchange systems studied included: (1) sulfur dioxide and fused ammonium bisulfate at 169.5°C and 225.3°C; (2) sulfur dioxide and a 2.05:1 mole ratio mixture of ammonium bisulfate and 100% H_2SO_4 at 194.4°C; (3) sulfur dioxide and a 1:4 mixture of ammonium bisulfate and 100% H_2SO_4 at 194.4°C; (4) sulfur dioxide and 100% H_2SO_4 at 167.5°C, 194.4°C and 225.3°C; (5) sulfur dioxide and a 1:1 mixture of ammonium bisulfate and 84.5% H_2SO_4 at 167.5°C, 194.4°C and at 225.3°C. The rates of the exchange reactions were conveniently measurable at all the temperatures investigated.
3. Data from previous research were re-examined along with the present results. In particular the data were used to examine the question as to whether the exchange rates in the different types of systems might show a better accord among themselves if interpreted as depending on sulfur dioxide activity rather than concentration.
4. For the purpose of making the activity versus concentration

dependency comparison, rate constants k and k_a were calculated, corresponding to the two rate laws

$$\text{Rate} = k (\text{SO}_2) \quad (1)$$

$$\text{Rate} = k_a \gamma (\text{SO}_2) \quad (2)$$

Here (SO_2) represents the sulfur dioxide concentration in the solution.

5. The activity coefficients of SO_2 were computed by means of the equation

$$\gamma = P/P' \quad (3)$$

where P is the actual partial pressure of solute SO_2 over the solution at the composition of interest and P' is the calculated ideal solution (Raoult's law) partial pressure at the same solution composition. Values of P were computed directly from the solubility values of sulfur dioxide in the solutions, determined in terms of the distribution coefficient, c

$$c = \frac{(\text{SO}_2)_l}{(\text{SO}_2)_g}$$

where $(\text{SO}_2)_l$ refers to the molar concentration of sulfur dioxide in the liquid, and $(\text{SO}_2)_g$ the molar concentration in the gas phase.

6. Comparison between the two types of rate constants, k and k_a , showed that the rate constants, k , vary drastically from one solution to another, at a particular temperature, while the

activity rate constants, k_a , vary among themselves to only a quite moderate degree. This striking feature clearly suggests the merit of considering the rate to be a function of the activity rather than the concentration of sulfur dioxide.

7. Apparent activation energies, frequency factors and entropies of activation, for both k and k_a values, were calculated for the exchange reactions between sulfur dioxide and ammonium bisulfate, sulfur dioxide and 100% sulfuric acid and that between sulfur dioxide and a 1:1 mixture of ammonium bisulfate and 84.5% H_2SO_4 . It was found that use of k_a values in place of k values did not lead to any great modification in the values of these three kinetic parameters. The kinetic parameters based on k values showed a considerable variation between the different types of solutions, and this variation remained for the parameters based on k_a values, even though the k_a values themselves, in contrast to k values, were, at any particular temperature, relatively similar from one solution to another. It seems possible that an explanation for this lack of accord among the kinetic parameters is to be found in differing variation, in the various solutions, of the activity coefficients of the sulfur (VI) species and of the activated complex.

8. The fact that approximately the same activity rate constant, k_a , was obtained in all the solutions implies a lack of dependence of rate on the ratio of bisulfate ion concentration to the

concentration of unionized H_2SO_4 . The sulfur (VI) species in 100% H_2SO_4 is almost exclusively the latter, for example, while in fused ammonium bisulfate the former dominates. Since the total sulfur (VI) concentration in the various solutions examined varied but little from one case to the next, the present work did not provide a test of rate dependency on this factor. Previous work in aqueous solution, however, has shown the rate to be first order in bisulfate ion. Hence, if one makes the reasonable assumption that the same rate dependency exists in the solutions here examined, one deduces that the rate is first order both in bisulfate ion and in the concentration of unionized H_2SO_4 , and that the specific rate constants for both exchange pathways are approximately the same. Therefore it is tentatively proposed that, at least approximately, the exchange rate may be appropriately described, for all the various types of solutions studied, by a rate law of the form

$$\text{Rate} = k_2 \gamma (\text{SO}_2) [(\text{HSO}_4^-) + (\text{H}_2\text{SO}_4)]$$

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