

ISOTOPE EXCHANGE REACTIONS
IN SELENIUM OXYCHLORIDE

by

DELMAN ROBERT ASHER

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1955

APPROVED:

Redacted for Privacy

Professor of Chemistry

In Charge of Major

Redacted for Privacy

Chairman of Department of Chemistry

Redacted for Privacy

Chairman of School Graduate Committee

Redacted for Privacy

Dean of Graduate School

Date thesis is presented 8-15-54

Typed by Evelyn Kanzelmeyer

ACKNOWLEDGMENT

The author is greatly indebted to Professor T. H. Norris, who, as major professor, gave invaluable assistance and guidance during the course of this research.

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. EXPERIMENTAL PROCEDURES	9
A. Counting Techniques	9
B. Materials Handling Techniques	10
C. Preparation of Materials	12
III. RUN PROCEDURES	17
A. Potassium Chloride-Selenium Oxychloride Experiments	17
B. Ferric Chloride-Selenium Oxychloride Experiments	21
IV. RESULTS AND DISCUSSION	29
A. Potassium Chloride-Selenium Oxychloride Experiments	29
B. Ferric Chloride-Selenium Oxychloride Experiments	31
V. BIBLIOGRAPHY	35

LIST OF TABLES

	<u>Page</u>
I. Solubilities of Chlorides in Selenium Oxychloride.	5
II. Results of acid Treatment of Active Mercurous Chloride Samples.	27
III. Results of Exchanges Between Potassium Chloride and Selenium Oxychloride	29
IV. Results of Exchanges Between Ferric Chloride and Selenium Oxychloride	31

LIST OF FIGURES

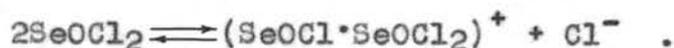
I. Bombs Used in KCl Exchanges	18
II. Bombs Used in FeCl ₃ Exchanges	22

ISOTOPE EXCHANGE REACTIONS IN SELENIUM OXYCHLORIDE

I. INTRODUCTION

Much interest has been shown during the last few years in the general field of non-aqueous ionizing solvents. Both theoretical interest and the possibility of practical applications have led investigators to study a variety of solvents, among them phosgene, sulfuric acid, liquid sulfur dioxide, liquid ammonia, glacial acetic acid, liquid hydrogen fluoride, selenium oxychloride, liquid iodine, bromine trifluoride, various alcohols, amines, glycols, esters, and ketones. Recently efforts have been made to show specifically how such solvents could be used to effect various chemical reactions and syntheses, some of which are difficult or impossible to effect in water (1,p.245).

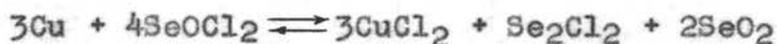
Among the foregoing solvents, the material selenium oxychloride has received considerable attention. Investigations have been carried out on this as a parent solvent of a system of compounds, and on the products of its reaction with water and with certain electron pair donors. It was postulated by Smith (13,p.167), in interpretation of his observations, that selenium oxychloride undergoes the following self-ionization:



Selenium oxychloride has a dielectric constant which approaches that of water and accordingly is one of the more

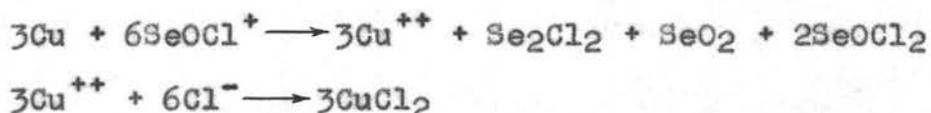
water-like of the non-protonic solvents which have been investigated to any extent. Its high specific conductance, 2×10^{-5} ohms⁻¹ (8,p.1803), indicates that the ion concentration of the pure liquid is very high. This value is of the same order as that of liquid hydrogen fluoride; like sulfuric acid in this respect; furthermore, it is expected and found to be a powerful solvolyzing agent. Selenium oxychloride's wide liquid range (8.5° to 179.4°C) would indicate its extensive usefulness as a solvent medium for chemical reactions. However, its reactivity, especially towards water, and its oxidizing ability at higher temperatures tend to limit its usefulness.

The action of selenium oxychloride on several metals, namely copper, lead, cobalt, iron, tin and silver, has been studied (12,pp.2091-4) and found to give the chlorides of the metals, selenium dioxide, and selenium monochloride. As a result the reaction has been formulated as follows:



Saturated solutions of potassium and stannic chloride in selenium oxychloride were electrolyzed and it was found (13,p.168) that chlorine was liberated at the anode and that selenium dioxide was precipitated at the cathode, with the solution around the cathode becoming reddish-brown, indicating the formation of selenium monochloride.

Conductance of pure selenium oxychloride is sufficiently low so that electrolysis is not convenient; however, chlorine is liberated at the anode and the solution around the cathode becomes reddish-brown. As a result of these observations Smith (13,p.168) explained the action of selenium oxychloride on metals as follows:



This indicates the powerful oxidizing ability of the so-called selenium oxychloro ion and accounts in part at least for the reactivity of selenium oxychloride.

The following broad definition of the terms acid and base was suggested by Smith (13,p.166): a solute is an acid when it is an electron-pair acceptor toward the solvent, and a solute is a base when it is an electron-pair donor toward the solvent. Thus, chlorides of non-metals or of amphoteric elements are to be regarded as acids, while first and second group metallic chlorides would be bases. The action of selenium oxychloride and of a twenty per cent solution of stannic chloride in selenium oxychloride on the several metals (13,p.169), magnesium, calcium, lead, mercury, copper, zinc, and sodium, were compared. In general it was observed that the metals were more reactive and soluble in the stannic chloride solution. Stannic chloride thus experimentally shows acid behavior in the selenium

oxychloro system. Experimentation (13,p.169) also has shown that the solubilities of barium chloride, calcium chloride, and potassium chloride were greater in solutions of stannic chloride in selenium oxychloride than in selenium oxychloride alone.

The solubilities of a number of the more common metallic chlorides in selenium oxychloride have been quantitatively determined (14,pp.1234-7). With due precaution to exclude moisture, although subsequent investigation showed a small amount of water had little effect on solubility, the solubilities at 25°C of some twenty-two chlorides were established. The solid phases of the solvates were investigated when they occurred. It was found that the anhydrous chlorides of lithium, sodium, copper, silver, strontium, barium, zinc, cadmium, mercury, nickel, and cobalt apparently do not solvate with selenium oxychloride. The chlorides of potassium, rubidium, cesium, magnesium, calcium, titanium, tin, antimony, and iron do form various solvates with selenium oxychloride. There are few organic compounds which will dissolve in selenium oxychloride without reaction, even carbon tetrachloride being slowly attacked. Saturated hydrocarbons are immiscible with the solvent whereas carbon tetrachloride, chloroform and benzene are miscible in all proportions. Table I gives a sampling of some of the chloride solubility

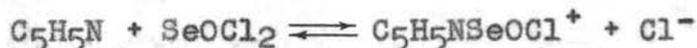
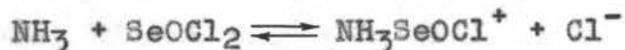
data (14,p.1234).

TABLE I
SOLUBILITIES OF CHLORIDES IN
SELENIUM OXYCHLORIDE

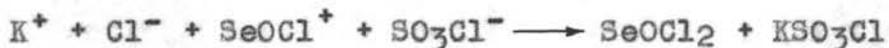
Metal	Solubility, g./100g. solution	Solvates formed
Li	3.21	
Na	0.57	
K	2.89	KCl·SeOCl ₂
Rb	3.56	RbCl·SeOCl ₂
Ca	6.11	CaCl ₂ ·3SeOCl ₂
Zn	1.10	
Cd	0.15	
Sn(IV)	13.73	SnCl ₄ ·2SeOCl ₂
As(III)	miscible in all proportions	
Sb(V)	38.64	SbCl ₅ ·2SeOCl ₂
Cr(III)	insoluble	
Fe(III)	23.40	FeCl ₃ ·2SeOCl ₂

As may be seen from Table I, several chlorides which are soluble in selenium oxychloride separate from super-saturated solutions as solvates, such as KCl·SeOCl₂, CaCl₂·3SeOCl₂, SnCl₄·2SeOCl₂, and FeCl₃·2SeOCl₂. Furthermore, it is apparent that solvate formation usually accompanies high solubilities. The formation of these solvates seems consistent with the postulation regarding the self-ionization of the parent solvent selenium oxychloride. Thus Smith (13,p.169) suggests that the analytical formulas for such compounds as SnCl₄·2SeOCl₂ and FeCl₃·2SeOCl₂ be written in rational formulas of the form $(\text{SeOCl})_2^{++} \text{SnCl}_6^{--}$ and $(\text{SeOCl})_2^{++} \text{FeCl}_5^{--}$.

As a result of Smith's definition of acids and bases, such things as ammonia, pyridine and quinoline are considered bases. Typical ionization reactions are as follows (13,p.172):



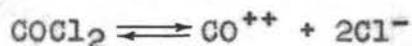
Neutralization of an acid in selenium oxychloride, such as stannic chloride, by titration potentiometrically or conductimetrically, with a base, such as pyridine, in selenium oxychloride, have been accomplished (13,pp.175-182; 11,pp.2403-6). Definite breaks in the titration curves indicate that chemical reactions or changes do occur. Selenium oxychloride solutions of sulfur trioxide were used extensively as the acid titrant (11,p.2405), in which cases the reaction with potassium chloride solution was believed to be as follows:



Suggestive of this pathway was the observation that the precipitate formed was the solvated potassium chlorosulfate, containing potassium and sulfur in a 1:1 ratio. The relative strengths of acid and bases, as determined by titrations (11,p.2406), were, in decreasing order: bases - isoquinoline, quinoline, pyridine, and potassium chloride; acids - sulfur trioxide, iron(III) chloride, and tin(IV) chloride.

It is evident that the foregoing treatment of selenium oxychloride chemistry lays heavy stress on ionic mechanisms. The same is true of discussions of chemistry in other non-aqueous solvents which have appeared. The viewpoint reflected in such discussions has led to the so-called solvent systems formulation of acid-base behavior. This formulation, which differs somewhat from that of Smith given above, specifies that an acid is a solute capable of increasing the concentration of the cation characteristic of the solvent, while a base is defined as a solute capable of increasing the concentration of the characteristic anion (2, pp.1425-8).

One of the first experiments which extended the solvent systems theory to non-protonic solvents was the work done with acid-base reactions in phosgene (5, pp.879-87). It was postulated that the self-ionization of phosgene would take place as follows:



and that it would react with an acid chloride in the following manner:



The active agent in an aluminium chloride solution is then the CO^{++} ion which is capable of such reactions as:



Radioisotopes offer a valuable tool for testing the validity of reactions and equilibria such as those which have been discussed. Thus if the equations in the last paragraph are realistic, one should be able to observe a rapid radiochlorine exchange between solvent phosgene and dissolved, labeled aluminium chloride. Such experiments have recently been carried out by Huston¹ and it is found that the exchange is quite slow. Huston's interpretation is that, in fact, the solvent systems theory is not applicable to phosgene, but rather that this material should be thought of as an "inert" solvent towards materials dissolved in it.

In view of the results with phosgene, the present parallel study of isotopic exchange behavior in selenium oxychloride, already underway, took on new interest. It was felt that, just as with phosgene, tracer experiments would be of value in giving further indications as to the acceptability of the general picture of selenium oxychloride chemistry, which has been outlined above. This thesis presents the results of a radiochlorine exchange investigation of two solutes: an acid, ferric chloride, and a base, potassium chloride.

¹ Huston, John L. A tracer study of liquid phosgene as an acid-base solvent. Paper presented before the Kansas City Meeting of the American Chemical Society. Kansas City, Missouri, March, 1953.

II. EXPERIMENTAL PROCEDURES

A. COUNTING TECHNIQUES. All tracer work in this investigation involved the use of chlorine-36, from a pile-produced potassium chloride sample obtained from the Oak Ridge National Laboratory of the U. S. Atomic Energy Commission. Chlorine-36 is a beta emitter with a maximum energy of 0.66 Mev., and a half-life of 2×10^6 years (4, p.305). The specific activity of the original potassium chloride sample was determined to be of the order of 40 cpm./mg. counted as mercurous chloride.

All counting was accomplished with the chlorine in the form of mercurous chloride, plated from an acetone slurry onto stainless steel cupped planchets. The thickness of the counting samples varied from 4-40 mg./cm.², and, as a result of this variation, it was necessary to establish an empirical self-absorption curve. The use of heavier plates was prompted by the desire to increase the total activity of the sample on a given planchet.

The determination of the activities was made with a Tracerlab end window counter tube, type TGC-2, having a window thickness of about 1.5 mg./cm.². The pulses from this tube were scaled on a time-preset decimal counter with a capacity of more than 3×10^4 counts per second and a dead time of less than ten microseconds. No counting was done which required any correction for coincidence. A

standard mercurous chloride sample with an activity of about 32,000 raw counts per minute was used to check the constancy of the counter sensitivity for each series of counts.

B. MATERIALS HANDLING TECHNIQUES. Due to the reactivity of selenium oxychloride with water, it was necessary to handle the solvent in all cases either in a vacuum system or in a phosphorus pentoxide-dried glove box. It had been originally intended that all transfers of the solvent would be done in a vacuum system, using liquid nitrogen to facilitate the transfer from storage flask to reaction bomb. However, it was found that because of its low volatility (b.p. 179.4°C), selenium oxychloride distilled only very slowly. It would scarcely distill at all through constrictions, stopcocks, or over very large vertical or horizontal distances, even when liquid nitrogen was used to cool the receiver. Consequently the reaction bombs were filled with solvent and salt in the dry box; after removal, they were then evacuated and sealed.

To facilitate weighing out salt to be used in a run, the dry box contained a balance with the front door removed. The technique used led to a weighing accuracy of within four per cent, sufficient for the present purposes.

The solvent was handled with a pipette made of 4 mm. Pyrex tubing inserted in a rubber bulb pipette control

attachment. The volume delivered from a file mark on the pipette was determined by weighing an equal volume of mercury delivered by the pipette.

The vacuum system consisted of a single stage mercury diffusion pump backed by a Cenco Hyvac mechanical fore-pump. The pressure was read with both a mercury manometer and with a mercury-filled McLeod gauge. The system was cold trapped with liquid nitrogen to protect the pumps. All stopcocks and ground glass fittings were lubricated with Apiezon "N" stopcock grease. The system was built entirely of Pyrex glass tubing which was degassed by heating and pumping before use. It was found that a pressure of 10^{-5} mm. of mercury could be obtained and held overnight.

The phosphorus pentoxide-dried glove box was an airtight wooden box, with a top consisting of a plexi-glass window in a wooden frame, held in place by a series of spring clamps. A flow of air, dried by successive passage through calcium chloride, magnesium perchlorate, and phosphorus pentoxide was swept through the box; the resultant positive pressure gave assurance that any possible leaks would result only in an outflow of air. The box contained a blower which circulated the air over two phosphorus pentoxide-filled dishes. A minimum of three hours was allowed for the absorption of moisture before the box was used.

Manipulation of materials was accomplished by use of a pair of arm length rubber gloves inserted and sealed into the front of the box.

C. PREPARATION OF MATERIALS. 1. Selenium Oxychloride. The selenium oxychloride was Baker's technical quality. The original material, dark red in color, was purified before use. A distillation was accomplished using the apparatus described by Herber (6,p.40), which consisted of a distillation flask, a condenser, and a fraction-collection head. The latter, built between two lengths of tubing, was permitted to rotate by use of a standard taper ground glass joint on one end and a ball and socket joint on the other. The distillation flask was fitted with a thin capillary to allow a slow current of calcium chloride-dried air to enter the solvent below its surface for the sake of preventing bumping during the distillation. To the collection head two all-glass storage flasks were attached; this allowed a first fraction of ca. 20% to be discarded, and a second fraction of ca. 60% to be sealed off and saved for future use; about 20% then remained finally in the distillation flask. The whole apparatus was attached to the vacuum line by use of Pyrex tubing. The distillation was run at about 5 mm. of mercury and the fraction retained distilled at a temperature of 65-68°C. This is to be compared with an expected boiling point of

about 64°C. at 5 mm. pressure (10,p.160). The fraction collected for use was almost colorless and had a density of 2.43 at a temperature of 21.8°C. to be compared to an expected value of 2.44 g./cm.² at 22°C. (9,p.264). An approximate chloride analysis, performed incidently in connection with working out the run procedures, showed the chloride content to agree with the anticipated value within at least two percent.

2. Potassium Chloride. The material in this case was prepared by purification of active potassium chloride which had been received from the Oak Ridge National Laboratory about one and a half years earlier. This substance had been activated by neutron bombardment according to the reaction $_{17}\text{Cl}^{35}(\text{n},\gamma)_{17}\text{Cl}^{36}$. However at the time of commencement of the research, the sample was still somewhat contaminated with sulfur-35 (88 day half-life), produced via the reaction $_{17}\text{Cl}^{35}(\text{n},\text{p})_{16}\text{S}^{35}$.

Purification was achieved by the addition of concentrated sulfuric acid with the resultant liberation of the chloride as hydrogen chloride, the evolved gas being absorbed in a potassium hydroxide solution. The apparatus used was of all glass construction, consisting of a reaction bulb to which three female ground glass joints were attached. The first served to allow a flow of dry nitrogen gas to sweep out the hydrogen chloride after the reaction

was complete; the second permitted the introduction of a separatory funnel which contained the concentrated sulfuric acid; the third led to a series of absorption towers, which were constructed with frittered glass gas absorption tubes and contained the potassium hydroxide solution. The resultant slightly acid solution was titrated with sufficient potassium hydroxide to give a final pH of 5.3. The solution was left slightly acid and taken to dryness on the steam bath, after which it was dried in the oven at 130°C. for eight hours. The weight of product compared to that of starting material indicated a recovery of ninety-seven percent. The activity of the original sample, of the order of 40 cpm./mg. counted as mercurous chloride, presumably included some radiosulfur contamination. This activity was reduced to 31.5 cpm./mg., as mercurous chloride, in the purified material.

3. Ferric Chloride. Baker's Analyzed C.P. ferric chloride was further purified by vacuum sublimation. The apparatus used was of all glass construction and consisted of three legs attached to a manifold: a distillation leg and two receiving legs each about 10 centimeters apart, the whole being constructed of 16 mm. Pyrex tubing. The ferric chloride was introduced into the distillation leg in the dry box, after which the whole apparatus was evacuated and sealed off. The vaporization of ferric chloride was

accomplished by means of a hand gas torch. It was necessary to "chase" the condensed ferric chloride down the connecting tubing and in and out of the first receiving leg by means of the hand torch. The procedure consisted of an initial sublimation into the first receiving leg and a subsequent sublimation of a portion of this material into the second leg; the amount collected amounted to about half the starting material. The almost black product was composed of very small crystals. The apparatus was opened in the dry box, and the ferric chloride transferred to a ground glass stoppered storage bottle, which was kept in a calcium chloride-dried dessicator. All the material retained had been vaporized and condensed several times in its passage down the distillation apparatus to the second receiving leg, and should therefore have been substantially increased in purity.

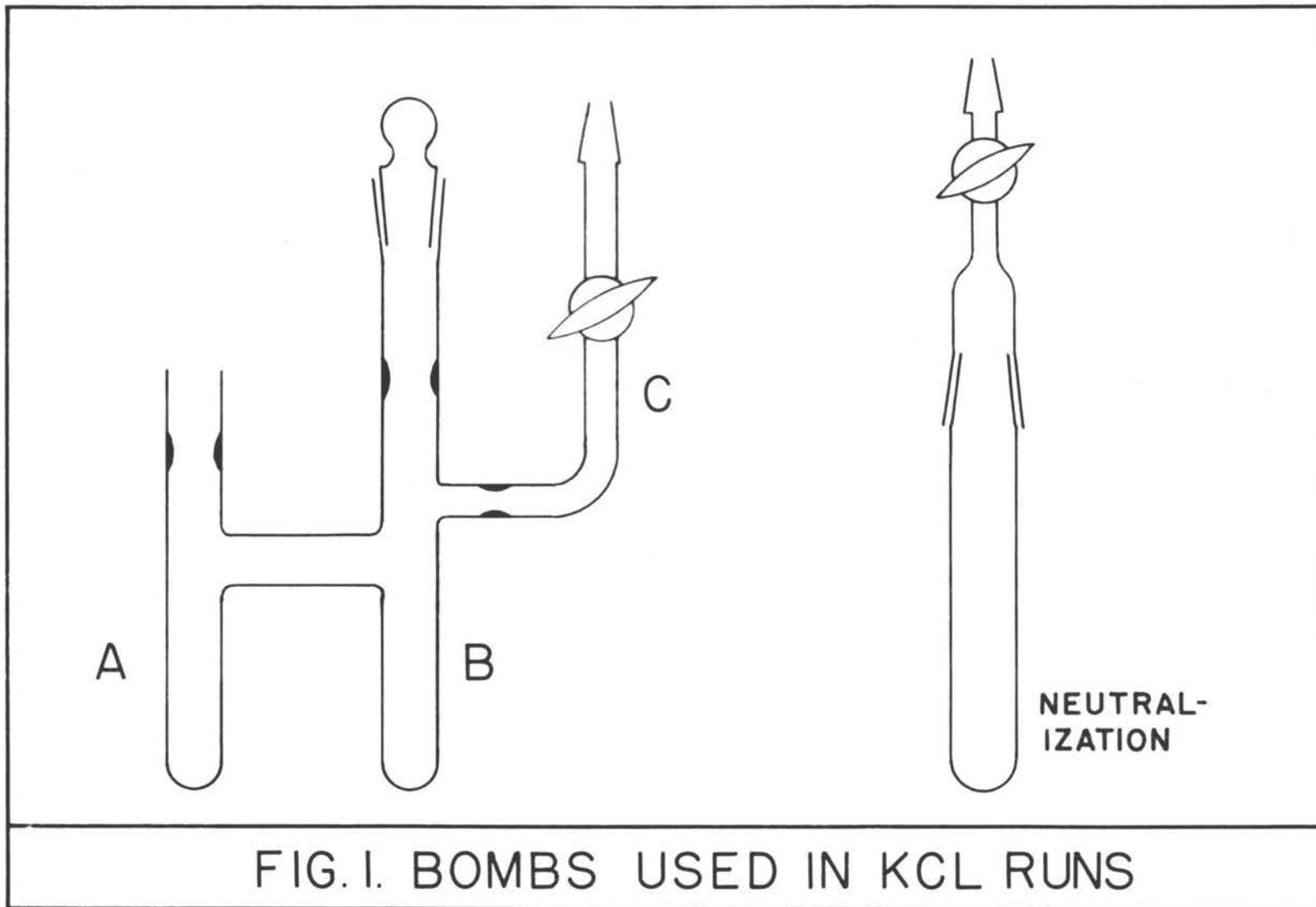
4. Labeled Selenium Oxychloride. Due to the anticipated difficulty in preparing an active ferric chloride sample, it was deemed advisable to activate the solvent in the second series of exchange experiments. This was accomplished by carrying out a complete exchange of the solvent with labeled potassium chloride, this exchange having been found to be rapid in the first set of experiments. As a result of the limited solubility of potassium chloride in selenium oxychloride, however, this process yielded only a

low specific activity, and so a two-step activation was carried out. The active potassium chloride (150 mg., 31.5 cpm./mg.) was placed in the salt leg (A) of a reaction bomb (Figure I) and the selenium oxychloride (3 ml.) was pipetted into the solvent leg (B) in the dry box. The distillation was carried out as described below in connection with the potassium chloride-selenium oxychloride exchange experiments. Then the activated solvent from the first distillation served as the solvent which was introduced into a second identical reaction bomb for further activation. The final solvent leg was broken open in the dry box and the contents stored in a ground glass stoppered storage bottle, which was left in a calcium chloride-dried dessicator.

III. RUN PROCEDURES

A. POTASSIUM CHLORIDE-SELENIUM OXYCHLORIDE EXPERIMENTS. The exchanges were carried out in all glass reaction bombs of the form shown in Figure I. These were constructed of 12 mm. Pyrex tubing, with the evacuation outlet (C) being of 7 mm. tubing. Constrictions were included in the bomb's construction, where shown, to simplify sealing it off after complete evacuation. The amount of solvent used in both active runs was 1.04 ml. (15.2 mM.), which theoretically would dissolve up to 75.4 mg. (1.01 mM.) of potassium chloride.

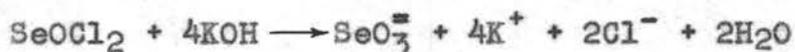
The active potassium chloride was dried in an oven for an extended period of time before use, after which the forty milligrams used per run was weighed out and placed in the salt leg (A) of the reaction bomb; the top of the salt leg was then sealed off. All the necessary materials and equipment were placed in the dry box, which was allowed a minimum of three hours drying time. The correct volume of solvent was then pipetted into the solvent leg (B), and the leg was stoppered. After closing the stopcock, the bomb was removed from the dry box, and partially evacuated via the vacuum system. The top of the solvent leg was next sealed off at the constriction provided for that purpose. During this partial evacuation and sealing, and during the subsequent complete evacuation, the solvent leg was kept



immersed in liquid nitrogen. When a pressure of 10^{-5} mm. of mercury was attained, the evacuation outlet (C) was sealed off at the constriction. The solvent was then allowed to liquefy and was poured over into the salt leg which was frozen to complete the transfer of solvent from its leg. The solvent and salt were then allowed to come to the temperature at which the run was to be made. When all the potassium chloride was in solution, the distillation was begun by immersion of the solvent leg (B) in liquid nitrogen, the salt leg (A) being in a water bath at the prescribed temperature. As a result of the salt's being the labeled material, it was not necessary to distill off more than sufficient solvent for counting requirements. In this case roughly one-fourth of the solvent was distilled from the solution. The solvent and salt legs were then both frozen and separated by sealing off the connecting tube.

Two neutralization bombs (Figure I), which contained excess of the required amount of potassium hydroxide solution, were placed in the dry box with the solution frozen through the use of liquid nitrogen. The two reaction bomb legs were broken open and dropped into the frozen potassium hydroxide solutions. The neutralization bombs were then greased and closed, and after removal from the dry box, were partially evacuated to minimize the danger of

pressure development during neutralization. The bombs were then set aside and the contents allowed to liquefy and react slowly, according to the following reaction:



The solutions from the two neutralization bombs were then quantitatively transferred to beakers, and made slightly acid to Universal indicator paper by the addition of 4 N nitric acid. The solutions were then warmed prior to precipitation of the chloride with 0.2 N mercurous nitrate solution. Care was taken not to precipitate the chloride present completely, in order to avoid co-precipitation of mercurous selenite. Experiments showed that where only about 10-20% of the chloride is precipitated, co-precipitation of the selenium compound is not significant, whereas if one attempts complete precipitation of chloride, extensive co-precipitation occurs. This problem is further discussed below, following the material on the second series of exchange experiments. The precipitate of mercurous chloride was filtered, using a sintered glass filter of medium porosity, and subsequently washed several times with water and then acetone. Sufficient acetone was then added to allow the formation of a slurry, which was transferred to previously weighed stainless steel cupped planchets. The planchets were then dried under an infra-red lamp, weighed, and counted.

B. FERRIC CHLORIDE-SELENIUM OXYCHLORIDE EXPERIMENTS. The exchange runs with ferric chloride in selenium oxychloride were carried out in reaction bombs of the type shown in Figure II. These bombs were constructed of 12 mm. Pyrex tubing except for the evacuation outlet, which was formed from 7 mm. tubing. The angle between legs (A) and (B) was approximately ninety degrees, giving the solution in the horizontal leg (A) a larger surface area for the sake of giving a decreased distillation time, while leg (B) remained in the vertical position required for immersion in liquid nitrogen.

Unlike potassium chloride, the anhydrous ferric chloride could not be handled other than in the dry box. As a result, the two procedures differ in several respects.

The required amount of ferric chloride, which was kept in a dessicator in the dry box, was weighed out on the balance in the dry box, mentioned above. As an aid to the introduction of the ferric chloride into only leg (A) of the bomb, a funnel with a stem longer than the bomb leg was constructed of as large tubing as possible. The funnel was inserted into the bomb leg and the weighed amount of ferric chloride was poured through it. The funnel was then withdrawn and the correct amount of selenium oxychloride was pipetted into the same leg. The bomb was removed from the dry box after it had been stoppered and the stopcock

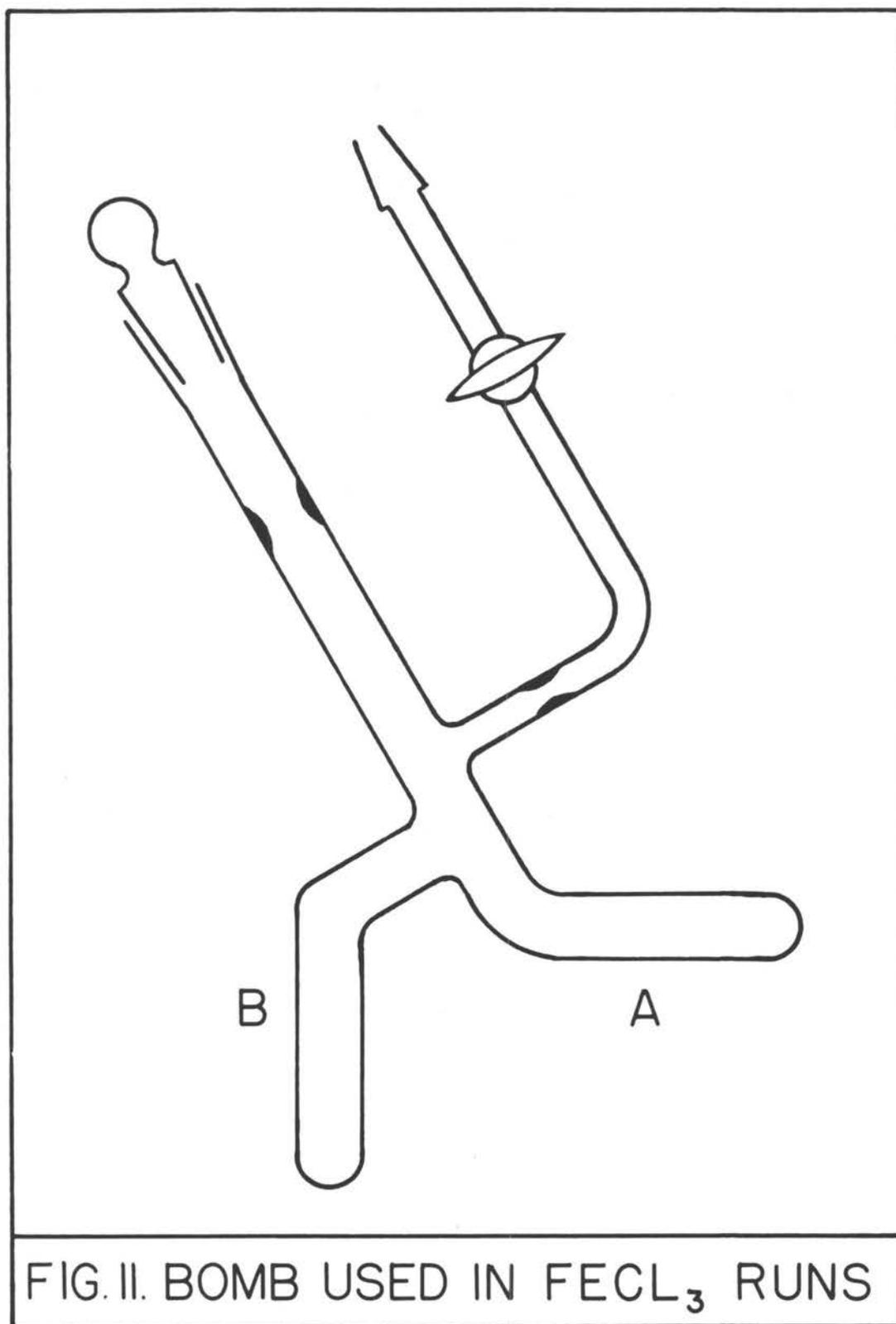


FIG. II. BOMB USED IN FeCl_3 RUNS

closed. The bomb leg containing the solvent and salt was frozen and partially evacuated. The constriction just below the stopper was sealed off and the bomb subsequently completely evacuated (10^{-5} mm. mercury) and finally sealed off at the second constriction. The salt and solvent were then allowed to thaw and form a solution, which was a dark red color and of a viscous nature.

The distillation was begun by cooling the solvent leg (B) in liquid nitrogen and setting a heating element under the salt leg (A), which was maintained at a temperature of 40°C . as measured by a thermometer whose bulb was in contact with the leg. Since exchange was to be looked for by counting the solute, ferric chloride, the solvent being labeled in these experiments, it was necessary to distill all of the latter out of the salt leg. In consequence the distillation required a matter of hours. In this connection it may be mentioned that there usually appeared a slight cream-colored precipitate in the distillate when this was thawed for the sake of examination. The nature of this precipitate was never elucidated, though it doubtless resulted from some slight decomposition of the reactants.

When the distillation was complete, the solvent leg was completely frozen. A file mark was quickly made and the solvent leg broken off and dropped into the

neutralization bomb, described above, which contained an excess of frozen potassium hydroxide solution. The neutralization bomb was partially evacuated, closed, set aside and allowed to thaw. Meanwhile, the bottom end of the salt leg (A), containing the ferric chloride, was broken off and dropped into a 250 ml. beaker containing 40-50 ml. of distilled water. The ferric chloride went into solution quickly, and the bomb leg segment was removed after careful washing.

The neutralized selenium oxychloride solution was quantitatively transferred into a second 250 ml. beaker. It had been found in preliminary experiments, that the presence of ferric ion tended to discolor the final mercurous chloride precipitate. The ferric chloride solutions were therefore made basic and the resulting ferric hydroxide filtered off.

Both solutions, made slightly acid to indicator paper with the addition of 4 N nitric acid, were warmed slightly, and the chloride precipitated by the addition of 0.2 N mercurous nitrate. The precipitated mercurous chloride was filtered through a sintered glass filter of medium porosity, washed with water and acetone and slurried with acetone. The mercurous chloride slurry was transferred to weighed stainless steel cupped planchets, and subsequently dried, reweighed, and counted.

It has been stated above that ferric chloride forms the disolvate $\text{FeCl}_3 \cdot 2\text{SeOCl}_2$ in selenium oxychloride. The question naturally arises as to whether the distillation procedure, as carried out in this work, sufficed to decompose such a material completely. In blank runs, chloride determinations were made, by titration with standard silver nitrate solution, on both the distillate and the apparently dry residual salt. Although the latter had the same general appearance as the original material, the analysis showed selenium oxychloride to have been retained in the ratio of about two-thirds of a mole per mole of salt. The presence of this residue would naturally lead to the observance of an apparent partial exchange, even though none had really taken place. This effect, however, would have been much smaller than the exchange values which were actually observed, and so is not significant in the present instance.

The finding of a retention of solvent by the ferric chloride suggested an explanation for some inconsistencies which had been found in the analysis of the results of these experiments. In order to decrease the total exchange time, a minimum quantity of ferric chloride, 25 mg., had been used, with the expected substantial decrease in distillation time. However, in order to obtain sufficient material for counting, it had been necessary to approach

quantitative precipitation of the chloride from the salt; it was in connection with this situation that the inconsistencies mentioned appeared. It was soon found that the problem consisted in a co-precipitation of mercurous selenite along with the chloride. Experiments with solutions of selenous acid and of chlorides showed that, as mentioned in connection with the potassium chloride experiments, so long as no attempt was made to precipitate more than 10-20% of the chloride, co-precipitation was not a problem. However, it became a very real problem if precipitation of most of the chloride was attempted.

It was found that the mercurous chloride precipitates could be freed of the selenite by treatment with 71% perchloric acid, which dissolved the latter but not the former. Consequently, several of the counting samples which had given the anomalous results were subjected to such a treatment. The mercurous chloride plates were scraped into centrifuge tubes and approximately 20 ml. of 71% perchloric acid added. The tubes were warmed slightly and stirred for several minutes, after which the solutions were centrifuged and the acid poured off. The precipitates were washed with water and acetone several times and slurries made in the centrifuge tubes, with the addition of small amounts of acetone. New planchets were used and the plates remade, dried and counted. The results of the

treatments, as shown by the increase in the activity of the mercurous chloride may be seen in Table II. The figures given represent averages for two planchets each for Runs 4-6 (cf. Results and Discussion).

TABLE II
RESULTS OF ACID TREATMENT OF
ACTIVE MERCUROUS CHLORIDE SAMPLES

	Run No.	Original Activity	Activity after treatment
Solvent:	4	1.81 cpm./mg.	1.87 cpm./mg.
	5	1.74	2.01
	6	1.82	1.94
Salt:	4	1.53	1.73
	5	1.12	1.66
	6	1.16	1.68

It is evident that the perchloric acid treatment had its greatest effect on the salt activities for Runs 5 and 6, these being the cases where the small amount of ferric chloride had been used. For Run 4, the increase in activity was much smaller and for the salt was comparable to that observed for the solvent samples. Consequently it did not seem necessary to extend the acid treatment to the counting samples used in other runs. Run 3 had been comparable to Run 4 in quantity of salt used; in Runs 1 and 2 both "salt" and "solvent" samples had been precipitated

from comparable solutions, consisting primarily of solvent, with, in the former case, a small amount of dissolved salt.

IV. RESULTS AND DISCUSSION

A. POTASSIUM CHLORIDE-SELENIUM OXYCHLORIDE EXPERIMENTS. The results of the two experiments are summarized in Table III.

TABLE III
RESULTS OF EXCHANGES BETWEEN
POTASSIUM CHLORIDE AND SELENIUM OXYCHLORIDE

Run No.	Millimoles		Temp °C	Time min	Sp Act's, c/m/mg		% Exch
	SeOCl ₂	KCl			SeOCl ₂	SeOCl ₂ -KCl	
1	15.2	0.546	48	31	0.76	0.77	99
2	15.2	0.534	21	47	0.84	0.80	103

Both because of the low activity of the original potassium chloride and because of the relatively small solubility of the salt, the measured specific activities of the samples, as indicated in the table, were rather low. In consequence long counting times were necessary; in no case, however, did the probable error of a measurement exceed 3%. It is evident that these low activities are responsible for the obvious lack of precision in the recorded percentage exchange values.

In these experiments the percent exchange has been calculated on the basis of the conventional expression

$$F = \frac{S_a}{S_{a00}}$$

where percent exchange equals 100F and S_a represents the solvent distillate (about one-quarter of the original) specific activity at the end of a run. The value of the infinite time specific activity of the solvent is obtained from the expression

$$S_a = \frac{S_a (a) + S_b (b)}{(a + b)}$$

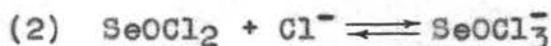
Here S_b represents the specific activity of the residue from the distillation, i.e., about three-quarters of the original solvent plus all the salt. The millimole quantities of distillate and residue are given, respectively by a and b.

The times given in Table III refer to the total contact time between solvent and salt, from the time the solvent was allowed to liquefy in the presence of the salt, until both reaction bomb legs were frozen, after about one-fourth of the solvent had been removed by distillation. Since this distillation proceeded steadily and since no exchange could have occurred involving distilled material, it would seem that the exchange might actually have been complete within somewhat shorter times than those recorded.

It is evident that rapid, complete exchange occurred in both the experiments. Such a finding was not entirely surprising in view of similar results reported for other solvents, as discussed below, where in several cases rapid

exchange of basic solutes with the solvent has been observed.

The rapidity of the exchange appears to lend support to the concept of a rapid reversible ionization equilibrium for this solvent involving chloride ions and leading to exchange. However, it seems clear that there are two possible mechanisms by which this could occur:



Of these two, the former seems the more likely on the basis of the results obtained in the second series of exchanges, involving an "acid" solute, which are discussed in the next section.

B. FERRIC CHLORIDE-SELENIUM OXYCHLORIDE EXPERIMENTS. The results of the ferric chloride exchange experiments with labeled selenium oxychloride are recorded in Table IV.

TABLE IV

RESULTS OF EXCHANGES BETWEEN
FERRIC CHLORIDE AND SELENIUM OXYCHLORIDE

Run No.	Millimoles SeOCl ₂	Millimoles FeCl ₃	Temp °C	Time hrs	Sp Act's, SeOCl ₂	c/m/mg FeCl ₃	% Exch
3	7.4	0.308	45	12.2	2.06	1.97	96.1
4	7.4	0.308	40	4.4	1.87	1.73	92.4
5	3.6	0.154	40	2.5	2.01	1.66	82.5
6	3.6	0.154	40	88.5	1.94	1.68	86.8

It is seen that a certain amount of uncertainty exists as to the true value of the percent exchange. The low values of Runs 5 and 6, can probably be explained in terms of a lack of complete correction for dilution of the active counting sample of ferric chloride by co-precipitation, a problem which has been discussed in the section on Run Procedures. The fact that the shortest and longest runs, in terms of contact time, give approximately the same percent exchange values would suggest that total exchange occurred in less time than the 2.5 hours of Run 5. Added to this the fact that higher values for the percent exchange were found in Runs 3 and 4, where no acute problem of co-precipitation existed, leads one to make the assumption that the exchange was complete and that the lower values found are the result of the experimental procedure used.

Actually, one can probably assume that, as with potassium chloride, the time for complete exchange is considerably less than even the figure of two and one-half hours, since this time again has reference to a steady distillation. Taking this shorter time arbitrarily as that corresponding to distillation of one-fourth of the solvent, an estimate of a time for complete exchange of less than forty minutes seems not unreasonable.

In view of the interest attached to these results, it would seem pertinent to attempt to do experiments of shorter duration, in order to obtain more explicit data on the possibility of finding a measurably slow exchange rate. To this end the use of labeled ferric chloride of moderately high activity is suggested. In such a case, the contact time between solvent and salt could be reduced considerably, since it would then be necessary to distill off only just enough solvent to count, as was done in the potassium chloride experiments above.

These results give a basis for selection, as to which of the two ionization equilibria suggested in the previous section might be correct. Since acceptance of a chloride ion by ferric chloride, rather than ionization to give one, is more probable, it seems to be suggested that selenium oxychloride ionizes to give a chloride ion and the SeOCl^+ ion. The present exchange would thus proceed as follows:



The equivalence of the chlorines in the FeCl_4^- would lead quickly to a randomization of the chlorine-36 present.

The finding of a rapid exchange involving the basic solute potassium chloride is consistent with the observations of others; whether a rapid exchange would occur with the acid solute ferric chloride was more open to question.

Thus Johnson and co-workers (7, pp. 3052-5), using radiosulfur, found a rapid exchange with the solvent, liquid sulfur dioxide, of the basic solute, tetramethylammonium sulfite, and no significant exchange rate at all for the acid solute, thionyl chloride. Similarly, Evans and co-workers (3, pp. 4985-91) observed a rapid exchange of carbon-14-labeled acetate ions (basic) with the solvent acetic acid; with acetic anhydride solvent, the acid solute acetyl chloride gave only a slow exchange. Most interesting in this regard is the recent research with liquid phosgene by Huston discussed in the Introduction. Here only a slow exchange was observed between the acid aluminum chloride (labeled with chlorine-36) and the solvent, in direct contradiction with the predictions of the solvent systems picture as applied to this solvent.

It is apparent that, insofar as the present experiments go, they tend to lend support to the solvent systems picture as applied to selenium oxychloride, both in its behavior towards acid and towards basic solutes. Thus, in contrast to Huston's conclusion concerning liquid phosgene, one must conclude that selenium oxychloride is not an inert solvent, but does in fact enter into ionization equilibria.

V. BIBLIOGRAPHY

1. Audrieth, Ludwig F. and Jacob Kleinberg. Non-aqueous solvents. New York, Wiley, 1953. 284p.
2. Cady, H. P. and H. M. Elsey. A general definition of acids, bases, and salts. Journal of chemical education 5:1425-8. 1928.
3. Evans, Ersel A., J. L. Huston and T. H. Norris. Isotopic exchange reactions in acetic acid and acetic anhydride. Journal of the American chemical society 74:4985-91. 1952.
4. Friedlander, Gerhart and Joseph W. Kennedy. Introduction to radiochemistry. New York, Wiley, 1949. 412p.
5. Germann, Albert F. O. Reactions in phosgene solution. Journal of physical chemistry 28:879-87. 1924.
6. Herber, Rolfe H. Isotopic exchange reactions in liquid sulfur dioxide. Ph.D. thesis. Corvallis, Oregon State College, 1952. 144 numb. leaves.
7. Johnson, Rowland E., T. H. Norris and J. L. Huston. Acid-base exchange reactions in liquid sulfur dioxide. Journal of the American chemical society 73:3052-5. 1951.
8. Julien, A. P. The electrical conductance of selenium oxychloride solutions. Journal of the American chemical society 47:1799-1807. 1925.
9. Lange, Norbert Adolph (ed.). Handbook of chemistry. 7th ed. Sandusky, Ohio, Handbook Publishers, 1949. 1920p.
10. Lenher, Victor, G. B. L. Smith and G. G. Town. Vapor pressure of selenium oxychloride. Journal of physical chemistry 26:156-60. 1922.
11. Peterson, W. S., C. J. Heimerzheim and G. B. L. Smith. Neutralization reactions in selenium oxychloride. Journal of the American chemical society 65:2403-06. 1943.

12. Ray, Ward L. The action of selenium oxychloride on various metals and metallic chlorides. *Journal of the American chemical society* 45:2090-94. 1923.
13. Smith, G. B. L. Selenium oxychloride as a solvent. *Chemical reviews* 23:165-85. 1938.
14. Wise, Clarence R. The solubilities of certain metallic chlorides in selenium oxychloride. *Journal of the American chemical society* 45:1233-1237. 1923.