on the P–T curve at 374° is the critical pressure of water. More work is needed on $Na_4P_2O_7$. The experimental results for $K_4P_2O_7$ do not fall on a single smooth curve, and the P–T curve has arbitrarily been drawn as if there were a change in the solid phase in the neighborhood of 600°. Morey, Boyd, England and Chen[10] did not observe an inversion in this region, but from analogy with $Na_4P_2O_7$[11] polymorphic forms would be expected.

Experiments were made with $Na_2B_4O_7$, but the solutions obtained were so viscous they would not run out of the perforated crucible. On cooling the pasty hydrous glasses usually contained freshly crystallized $Na_2B_4O_7 \cdot 5H_2O$.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OREGON STATE COLLEGE]

Radiochlorine Exchange Reactions in Acid Chloride Solvents and in Liquid Sulfur Dioxide[1]

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Radiochlorine exchange reactions of both acid and basic chloride solutes have been studied in three non-aqueous solvents: thionyl chloride, selenium oxychloride and phosphorus oxychloride. Exchange appears to be reasonably rapid and complete in every case in support of self-ionization schemes which have been advanced for these solvents. The exchange between thionyl chloride and tetramethylammonium chloride dissolved together in liquid sulfur dioxide is also found to be very fast, rendering plausible the slight ionization of the former, in this solvent, to $SOCl^+$ and Cl^- ions.

Isotopic exchange experiments have shown that, despite its merits, the solvent systems interpretation of non-aqueous solvent phenomena cannot be uniformly applied with confidence. Thus neither liquid sulfur dioxide[3–5] nor liquid phosgene[6] show the anticipated ready exchangeability with the respective "acids" thionyl chloride (or bromide) and aluminum chloride. In contrast, nitrosyl chloride does exchange rapidly with chloride solutes[7] ("bases"), its assumed self-ionization to nitrosyl and chloride ions thus being apparently confirmed.

We have now examined the chloride exchange behavior toward solutes of three additional acid chloride solvents[8]: thionyl chloride, selenium oxychloride and phosphorus oxychloride, both acid and basic solutes being used. Self-ionizations which have been assumed for each solvent, yielding chloride ions (solvated or otherwise), *e.g.*, equation 1 below, should lead to rapid isotopic exchanges in every case.

A problem related to its self-ionization is the nature of the ionic species (if any) which thionyl chloride may yield in liquid sulfur dioxide solution. The absence of isotopic exchange with the solvent[3–5] excludes the once assumed[9] thionyl ions, SO^{++}. On the other hand, it would be plausible and consistent with their general chemical nature[10,11] for these feebly conducting[12] solutions to ionize slightly to the intrinsically more reasonable species[13] $SOCl^+$ (*cf.* equation 1). To test for this possibility we have studied the radiochlorine exchange between thionyl chloride and tetramethylammonium chloride, dissolved together in liquid sulfur dioxide. Such an ionization equilibrium would, naturally, lead to a rapid exchange.

Results and Discussion

Exchanges in Acid Chloride Solvents.—Given in Table I are percentage exchanges calculated generally from the measured final specific activities of separated solvent and solute (or solute-enriched solvent) fractions. Exchange is substantially complete in all but the ferric chloride–selenium oxychloride case. Here, however, the apparent incompleteness is probably illusory, resulting from inadequate removal of coprecipitated material from the solute-derived counting sample precipitates (see Experimental section). Such an effect, which naturally dwarfs the recorded counting uncertainties, is further indicated by the long-time run (5300 minutes), which fails to show exchange approaching completion, giving figures within the same range as three short-time runs. One concludes, therefore, that in every instance exchange is probably complete within the shortest recorded time.

The foregoing calculated percentages, together with the indicated uncertainty estimates, have been used to obtain the recorded approximate upper limits for exchange half-times. All are relatively

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[2] Taken from the Ph.D. thesis of B. J. Masters and the M.S theses of N. D. Potter and D. R. Asher, at Oregon State College, June, 1954.

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[8] For investigations of chemical phenomena in these solvents see, for example: H. Spandau and E. Brunneck, *Z. anorg. allgem. Chem.*, **278**, 197 (1955) ($SOCl_2$); G. B. L. Smith, *Chem. Revs.*, **23**, 165 (1938) ($SeOCl_2$); V. Gutmann, *Z. anorg. allgem. Chem.*, **270**, 179 (1952) ($POCl_3$).

[9] G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, p. 210.

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[11] B. J. Masters and T. H. Norris, THIS JOURNAL, **77**, 1346 (1955).

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[13] L. C. Bateman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 243 (1944).

TABLE I

EXCHANGES IN ACID CHLORIDE SOLVENTS

Temp., °C.	Solute, mole fraction	Time,^{a} min.	Exch., %	Max. $t_{1/2}$,^{b} min.
		Me_4NCl^* in $SOCl_2$		
25	0.023	60	99^c	~ 8
25	.0127	50	100^c	
25	.0176	40	100^c	
0	.0181	90	100^c	~13
0	.0184	80	100^c	
		$SbCl_3$ in $SOCl_2^*$		
0	0.0124	40	96^d	~11
0	.0089	40	98^d	
		Me_4NCl^* in $POCl_3$		
35	9.5×10^{-4}	85	100^c	~13
25	9.0×10^{-4}	120	96^c	~23
25	8.4×10^{-4}	105	99^c	
		KCl^* in $SeOCl_2$		
48	0.035	30	99^d	~7
21	.034	50	104^d	~8
		$FeCl_3$ in $SeOCl_2^*$		
45	0.041	730	93^d	(~240)
40	.080	260	88^d	(~ 96)
40	.040	150	71^d	
40	.040	5300^e	78^d	

^{a} The recorded figures represent normally the approximate total time for dissolving the solute and distilling the requisite amount of solvent. ^{b} Upper limits based on the estimated minimum exchange (*cf.* footnotes *c* and *d*). ^{c} Estimated uncertainty, ±1%. ^{d} Estimated uncertainty, ±5%. These errors are based on reasonable estimates of the experimental accuracy of the specific activities involved. ^{e} The solution stood for *ca.* 5100 minutes at room temperature and then was distilled at 40° over a period of *ca.* 200 minutes.

short except for the last exchange, where the values seem artificially high, resulting from the illusory incompleteness just discussed. Thus reasonably rapid exchange is indicated for all cases.[14]

The rapidity of the exchanges seems to align these solvents more with nitrosyl chloride[7] than with phosgene, although the differentiation from the latter is admittedly not distinct, especially for selenium oxychloride.[15] Thus some type of ionic equilibrium is probably plausible for all three. This may, but does *not necessarily* imply the occurrence of significant self-dissociation of the solvents since two distinct types of ionic processes would give the observed rapid activity randomization: (1) self-ionization equilibria suggested by previous investigators, giving solvent cations and chloride ions (possibly solvated) which would readily exchange with solute chloride ions, *e.g*

$$SOCl_2 \rightleftarrows SOCl^+ + Cl^- \quad (1)$$

(2) simple addition equilibria of solute chloride ions adding to un-ionized solvent molecules, *e.g.*

$$SOCl_2 + Cl^- \rightleftarrows SOCl_3^- \quad (2)$$

Lewis and Wilkins[7] conclude that in nitrosyl chloride self-ionization is, in fact, involved, arguing that a type (2) process is unlikely, both NOCl and Cl^- being electron pair donors. Our present results, while not excluding the possible simultaneous occurrence of a type (2) process, seem to imply self-ionization here also, at least in two of the solvents ($SOCl_2$ and $SeOCl_2$), where exchange is rapid with acidic as well as basic chlorides. Although the argument is admittedly not conclusive, it seems more attractive to think of antimony trichloride and ferric chloride achieving exchange as acceptors of chloride ions from a type (1) dissociation, rather than as chloride donors in a type (2) equilibrium.

The present results and those for nitrosyl chloride provide an interesting comparison with the slower exchange of aluminum chloride in phosgene. Apparently for acid–base processes in its solutions phosgene serves as a more nearly inert medium than do these other acid chloride solvents. Presumably, the difference can be related to the fact that, of all five solvents, phosgene has the lowest dielectric constant (4.34 at 22°[16]). It might be fruitful to explore the exchange behavior of the other solvents further with a greater variety of solutes and under conditions more favorable to yielding measurable rates (*e.g.*, lower temperatures and shorter run times[14]), to find how consistently rapid exchange occurs. Conceivably thionyl chloride, with the next lowest dielectric constant (9.25 at 20° [17]), might give lower rates than the remaining three solvents. Conceivably also it might exchange more slowly than it does (see next section) as a solute in liquid sulfur dioxide, where the dielectric constant is 14.1 at 20°.[18]

Chloride Exchanges of Thionyl Chloride in Liquid Sulfur Dioxide.—Table II gives the results for the radiochlorine exchange between tetramethylammonium chloride and thionyl chloride dissolved in liquid sulfur dioxide. Again the ex-

TABLE II

Me_4NCl-$SOCl_2$ EXCHANGE IN SO_2^a

Temp., °C.	Time,^{b} min.	Exch.,^{c} %	Max. $t_{1/2}$,^{d} min.
25	1500	100	. .
25	20	102	~3
−18	60	101	. .
−20	60	101	. .
−20	5	101	~1

^{a} Mole fractions: $SOCl_2$, 0.095; Me_4NCl (labeled), 0.032. ^{b} Total contact time of reactants, including distillation time. ^{c} Estimated uncertainty, ±1%, based on reasonable estimates of the experimental accuracy of the specific activities involved. ^{d} Upper limits based on estimated minimum exchange values (*cf.* footnote *c*).

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[14] A further factor inflating the half-time estimates in the last exchange was the long time needed to distil the relatively non-volatile solvent completely away from the solute; the various tabulated times represent in general the minimum required to combine and separate the exchange components. Refinement of technique which might well significantly shorten the experiment times would include the use of higher specific activities and solute-labeling exclusively, so that only a little solvent need be distilled off. Higher specific activities would also permit lower temperature experiments where in some cases solubilities are limiting.

[15] In the $COCl_2$–$AlCl_3$ exchange half-times of 12 to 62 hours at 0° were reported.[6] However, in nearly saturated solutions at 25°, values of about 15 minutes are found (J. L. Huston, private communication).

[16] H. Schlundt and A. F. O. Germann, *J. Phys. Chem.*, **29**, 353 (1925).

[17] M. Beyaert and F. Govaert, *Natuurw. Tijdschr.*, **20**, 119 (1938).

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change is very rapid. Despite dilution in a solvent, lower temperatures and shorter time experiments than those described above, complete exchange occurred in every case.

These results suggest that, while thionyl chloride certainly gives no thionyl ion, SO^{++}, in sulfur dioxide solution, it may well engage in *some* ionic process involving chloride ion. The same points discussed above are pertinent here, namely, the possibility of either a chloride ion *dissociation* or *association* equilibrium. Pending evidence to the contrary, it seems reasonable to assume that the solute dissociates slightly but significantly to yield the ion $SOCl^+$ in accordance with equation 1.

Experimental

Materials.—**Sulfur dioxide** (Ohio Chemical) and **thionyl chloride** (Matheson, Coleman and Bell, b.p. 75–76°) were purified and handled as previously described.[11]

Selenium oxychloride (J. T. Baker, Technical) was fractionated *in vacuo*. A middle cut, about one-quarter of the original, boiling range 65–68° at ~5 mm. (expected b.p. 64°[19]), was collected and stored in a sealed tube.

Anal. reptd. for $SeOCl_2$: $d^{22}{}_4$, 2.424.[20] Found: $d^{22}{}_4$, 2.43.

Phosphorus oxychloride (Mallinckrodt, Reagent) was taken from a fresh bottle, opened in the dry box, and used without further purification.

Antimony trichloride (J. T. Baker, Reagent) and **ferric chloride** (Coleman and Bell, Reagent, anhydrous, sublimed) were twice distilled (sublimed) *in vacuo*, the products being transferred in the dry box to a closed container.

Radiochlorine.—Chlorine-36 was obtained from the Oak Ridge National Laboratory as neutron-irradiated potassium chloride. Except for some old samples where it had already decayed, most of a substantial sulfur-35 contamination was precipitated as barium sulfate (carrier added), the salt (plus some barium chloride) being recovered by crystallization on the steam-bath.

Labeled potassium chloride was prepared from the above active potassium chloride. Hydrogen chloride, generated by addition of concentrated sulfuric acid, was absorbed in either water or a slight stoichiometric deficiency of potassium hydroxide. After neutralization of the resulting solution with potassium hydroxide, the product was recovered by crystallization on the steam-bath and dried at 130°. The specific activity of the material used in the selenium oxychloride experiments was *ca.* 40 c.p.m./mg. (as mercurous chloride).

Labeled tetramethylammonium chloride was prepared as previously described[11] for the inactive salt, *via* a heterogeneous metathesis between tetramethylammonium bromide solution and freshly precipitated active silver chloride (from the purified radiochloride solutions described above). Colorless, odorless crystals were obtained with a specific activity of *ca.* 450 c.p.m./mg. (as mercurous chloride). After drying, the highly hygroscopic material was stored in an opaque desiccator.

Anal. Calcd. for Me_4NCl: Cl, 32.40. Found: Cl, 32.43.

Labeled thionyl chloride was obtained *via* the rapid exchange found to occur between thionyl chloride and tetramethylammonium chloride. About 150 mg. of active salt was dissolved in *ca.* 7 ml. of solvent, which was then immediately distilled off. Repetition of the process with the same solvent and a like amount of fresh salt gave a product with specific activity 5.3 c.p.m./mg. which was stored in a sealed container.

Labeled selenium oxychloride was similarly prepared by the rapid exchange with the solvent of labeled potassium chloride. The procedure resembled that for thionyl chloride, 3 ml. being activated in two stages, with 150 mg. of salt dissolved at each stage. The product, stored sealed in darkness, had a specific activity of *ca.* 2 c.p.m./mg.

Counting.—Samples were counted as mercurous chloride, plated from acetone slurries onto stainless steel planchets, using a thin end-window Geiger tube. Minor self-absorption corrections were calculated where necessary from an empirically prepared curve. All counts were long enough to minimize statistical factors compared to other error sources, such as separation imperfection or sample mounting irreproducibility.

Run Procedures.—These involved mostly standard high vacuum techniques similar to those previously used.[11] Distillations were effected by cooling receivers with liquid nitrogen, heat being applied only when needed to obtain reasonable rates. A dry box was used for some operations not conveniently done *in vacuo*.

Typically a weighed amount of solute, well dried if exposed to air (KCl and Me_4NCl), was dissolved in a measured quantity of solvent in a sealed, evacuated, usually two-legged reaction bomb. Sulfur dioxide and thionyl chloride were dosed out in the vacuum system. Selenium and phosphorus oxychlorides were quantitatively pipetted in the dry box. Separation was by distillation of solvent (plus thionyl chloride in the sulfur dioxide experiments) to the bomb's second leg. The recorded times (Tables I and II) include dissolving plus distillation, the latter having normally been started immediately upon completion of solution.

Substantially all volatile material was usually distilled off. Selenium oxychloride distilled slowly, requiring some hours. In the $SeOCl_2$–KCl^* exchange, the solvent being initially inactive, time was saved by distilling only a portion for activity assay. In the three $SOCl_2$-salt exchanges, the solutes ($SbCl_3$ and Me_4NCl) showed no solvent retention, a qualitative check indicating the absence of sulfur, and chloride analyses closely checking the expected composition.[21] In the $SeOCl_2^*$–$FeCl_3$ exchange, however, although the residue apparently resembled the original material, analysis showed solvent retention in a 1:1 mole ratio with solute.[22] The observed specific activity was accordingly corrected, assuming retained solvent to have the same specific activity as the bulk of the solvent.

Runs were at room temperature, or in various baths at approximately the indicated temperature. The two separated fractions were dissolved in base (or water, if appropriate); addition of mercurous nitrate to the resulting solutions, made slightly acid with nitric acid, precipitated mercurous chloride, which was filtered and counted. Percentage exchange, $100F$, was normally calculated from the expression $F = S/S_\infty$, S being the final specific activity of the initially inactive component. Infinite time specific activity, S_∞, was calculated, assuming complete activity randomization, from the measured activities, and known amounts of each of the two fractions.

In the selenium oxychloride experiment, complete precipitation of chloride was generally avoided so as to minimize selenite coprecipitation. This appeared insignificant when only 10–20% was precipitated. With ferric chloride, however, the small amount of solute necessitated more complete recovery from this fraction (ferric ion first precipitated as hydroxide), and selenite coprecipitation substantially lowered the resulting apparent specific activity. This effect was mostly corrected for by extraction of the various precipitates with 71% perchloric acid. However, this extraction raised the solute fraction's specific activity significantly more than the solvent fraction's, so any incompleteness of the treatment would lead to relatively low specific activities for the former. It is to such an incompleteness that we are inclined to attribute the apparent exchange incompleteness with ferric chloride (Table I).

Before precipitation of chloride from sulfur(IV)-containing fractions, the latter was oxidized with 30% hydrogen peroxide, excess being destroyed by boiling. In some cases sulfur was also removed as barium sulfate before the chloride. In the antimony trichloride experiment, 4 *N* HNO_3 was used to dissolve the recovered solute, this solution then

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(19) V. Lenher, G. B. L. Smith and G. G. Town, *J. Phys. Chem.*, **26**, 156 (1922).

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(21) This result contrasts with the previously observed non-recovery of pure salt on evaporating sulfur dioxide solutions of tetramethylammonium bromide plus thionyl bromide, the latter apparently being significantly retained: R. H. Herber, T. H. Norris and J. L. Huston, THIS JOURNAL, **76**, 2015 (1954).

(22) Solid ferric chloride in equilibrium with selenium oxychloride solution forms the solvate $FeCl_3 \cdot 2SeOCl_2$: C. R. Wise, THIS JOURNAL, **45**, 1233 (1923).

being diluted tenfold and saturated with hydrogen sulfide to eliminate antimony before chloride precipitation.

In the phosphorus oxychloride experiment, the low salt solubility led to low final measured activities. A reasonable calculation of exchange percentage was made, however, on the basis of the salt's final specific activity compared to its initial activity, its expected final activity being computed from the known reactant amounts.

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[CONTRIBUTION FROM THE DEPARTMENT OF MEDICINE, THE JOHNS HOPKINS SCHOOL OF MEDICINE]

Low Pressure Reduction of Carbon^{14}-Labeled Barium Carbonate to Cyanide

BY SUSANNE VON SCHUCHING[1] AND THEODORE ENNS

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The conditions of reduction of carbon^{14}-labeled barium carbonate to carbon^{14}-labeled cyanide with zinc were investigated. A low pressure steel reaction vessel which allowed control of all variables was constructed and gave reproducible high yields of cyanide.

A number of syntheses of $NaC^{14}N$ from $BaC^{14}O_3$ have been described since 1941.[2-12] Initial attempts at synthesis followed the procedure of Jeanes,[11] according to which a boat containing a mixture of barium carbonate, sodium and zinc is placed in a Vycor train partially filled with iron wire and a stream of dry ammonia is passed through the tube for 4 hours at 650°. About twenty runs were carried out in this fashion; they showed a random distribution from 38 to 100% of the cyanide yields. After six or eight runs the Vycor tube usually cracked. It was therefore decided to devise a more reproducible procedure.

A systematic study of the influence of temperature on the yield of cyanide was first carried out. Since the end-product, zinc cyanide, is stable,[13] it was thought that the temperature at which the reduction occurs might be critical. The temperature reading was taken inside the Vycor train, directly above the boat containing the reactants. An iron–constantan couple was used, its insulation being replaced by narrow Vycor tubing. The control of the temperature was indeed the governing factor for a high conversion yield of cyanide from carbonate. A temperature change of 7% results in a 30% difference of yield. At a temperature of 640–650°, the yield of cyanide was 70%; at 655–670°, 90%; and at 670–680°, quantitative.

In order to control the temperature better and facilitate the carrying out of the final synthesis of C^{14}-labeled cyanide, a stainless steel vessel was constructed. The following procedure was arrived at after test runs with inactive barium carbonate: barium carbonate, an excess of zinc, and a catalytic amount of reduced iron powder[14] were mixed in a 12 × 80 mm. test-tube and the test-tube introduced into the reactor. Instead of gaseous ammonia, sodamide was used. The air was removed by flushing with a stream of dry ammonia and the vessel sealed and heated for 2 hours in a furnace to 680°. Six runs with inactive barium carbonate showed a 82–88% yield of cyanide. No cyanamide was formed. A blank run showed that no cyanide is formed in the absence of barium carbonate. Two runs with $BaC^{14}O_3$ were converted to silver cyanide. The specific activity was equal to that of the starting material.

Experimental

The reaction vessel had a volume of 20 ml. and accommodated a 12 × 80 mm. test-tube. The chamber was constructed to withstand a pressure of 140 atmospheres. The pressure during the reaction did not exceed 60 atmospheres. The outer dimensions were such that the bomb fitted into a Fisher Heavy-Duty combustion furnace. The oven was calibrated before the run to operate at exactly 680°. Power was supplied to the oven and series rheostat from a variable transformer for fine adjustment through a time switch for on and off regulation.

For each run about 0.75–1 mmole of barium carbonate was mixed in a small test-tube with 0.5–1 g. of zinc and about 10 mg. of iron powder reduced by hydrogen. The test-tube was transferred to the reactor which was then flushed with dry ammonia to replace the air and 15 mmoles of commercial sodamide was added. The head of the reactor was fastened tightly and the assembly placed in the cold oven and heated for 2 hours to 680°. After cooling the contents were washed out with water and the zinc powder removed by filtration. A few drops of $Ba(OH)_2$ were added for the precipitation of any unreacted carbonate which can be recovered by filtration. The volume of the solution did not exceed 25 ml. The hydrogen cyanide formed on acidification with 50% sulfuric acid was steam distilled in a micro-Kjeldahl apparatus. The yield of cyanide determined by argentimetric method was 82–88%. Two radioactive runs made with barium carbonate having a reported activity of 0.77 mc.[15] per millimole were analyzed. Found: (1) 124 mg. of $BaCO_3$ gave 69.2 mg. of AgCN (82% yield), with an activity of 0.76 mc. per mmole. (2) 148 mg. of $BaCO_3$ gave 88.5 mg. of AgCN (88% yield), with an activity of 0.78 mc. per mmole. Between runs the stainless steel vessel was cleaned with dilute nitric acid and dried. All traces of rust were removed with steel wool.

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