

will be of importance in the decision between the older value for the atomic weight and the one here presented.

This investigation will be continued by the analysis of additional fractions of the tetrachloride from those already prepared.

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THE SOLUBILITIES OF CERTAIN METALLIC CHLORIDES IN SELENIUM OXYCHLORIDE¹

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This paper deals with the solubilities of a number of the more common chlorides in selenium oxychloride.

The observations of Lenher² have shown that when selenium oxychloride reacts with various substances its action in general is that of a chlorinating and oxidizing agent. As a part of the study of selenium oxychloride it has been deemed important to know the solubilities of the various reaction products in the reagent.

Materials

Reagent.—The selenium oxychloride used in this work was prepared by the method of Lenher.³ It was purified by distillation⁴ at reduced pressure and special precautions were taken to exclude moisture.

Metallic Chlorides.—Since selenium oxychloride is readily hydrolyzed, it is obvious that a solubility study necessitates the use of anhydrous chlorides as well as anhydrous reagent. It has been found convenient with many of the chlorides to dehydrate them by heating in a current of hydrogen chloride. Chlorides insoluble in water were prepared by the usual precipitation methods, while the volatile chlorides used were purified by sublimation or distillation. The purity of all of the chlorides used, as well as their freedom from moisture, was established by analysis.

Apparatus

All experiments were conducted in glass bottles provided with 2 well-fitting ground-glass stoppers which, in order to exclude moisture, were sealed with paraffin. These bottles containing the solvent and solute were shaken in a thermostat until equilibrium was reached. The temperature control was to within 0.05°.

¹ An abstract of a part of the thesis submitted to the Graduate School of the University of Wisconsin as a partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

² Lenher, *THIS JOURNAL*, **43**, 29 (1921); **44**, 1664 (1922).

³ Lenher, *ibid.*, **42**, 2498 (1920).

⁴ Lenher, Smith and Town, *J. Phys. Chem.*, **26**, 156 (1922).

Analysis

Since selenium oxychloride is hydrolyzed by water into selenious and hydrochloric acids, it is impracticable to determine the common metals in the mixture obtained without first removing the selenium. This procedure would in these experiments give excessive precipitates of selenium which in most cases would be cumbersome to handle.

The method used with the non-volatile chlorides consisted in evaporating the large volume of selenium oxychloride from the sample, and subsequently heating the residue in hydrogen chloride⁵ at a temperature of 250° and 100 mm. pressure.

In order to eliminate contamination by moisture in transferring a sample from the reaction bottle in the thermostat to an appropriate weighing vessel, it was necessary to filter the selenium oxychloride solution from the excess of metallic chloride after equilibrium had been reached and receive the filtered solution in a weighing bottle. To this end a suction filter and weighing bottle was devised of special construction to be moisture proof. The evaporation and all weighings were made in such a weighing bottle.

The few chloride solutions studied which contained chlorides volatile in hydrogen chloride below 250° were analyzed by standard methods after hydrolysis of the selenium oxychloride and removal of the selenium.

Procedure

About 2-4 g. of the freshly prepared anhydrous metallic chloride was introduced into the 175cc. bottle and selenium oxychloride added, precautions being taken to avoid contamination by moisture. The bottle was sealed, and maintained at about 50° for 72-96 hours with occasional shaking, after which it was placed in the thermostat and agitated until samples taken for analysis showed that equilibrium had been established.

Table I gives the solubilities of a number of the more common chlorides in selenium oxychloride at a temperature of 25°. Insoluble refers to a solubility of less than 0.1%. All solubility data recorded are the results

TABLE I
SOLUBILITIES OF THE CHLORIDES AT 25°

Chloride	Found %	Chloride	Found %	Chloride	Found %	Chloride	Found %
LiCl	3.21	AgCl	insol.	CdCl ₂	0.15	SbCl ₅	38.64
NaCl	0.57	MgCl ₂	4.96	HgCl ₂	0.89	CrCl ₃	insol.
KCl	2.89	CaCl ₂	6.11	TiCl ₄	0.75	MnCl ₂	0.16
RbCl	3.56	SrCl ₂	5.17	SnCl ₄	13.73	FeCl ₃	23.40
CsCl	3.83	BaCl ₂	3.95	PbCl ₂	insol.	NiCl ₂	0.15
CuCl ₂	insol.	ZnCl ₂	1.10	AsCl ₃	Misc. in all propor.	CoCl ₂	0.17

⁵ A modification of the method used by Lenher in determining the atomic weight of selenium. THIS JOURNAL, 20, 555 (1898).

of at least duplicate determinations which were concordant. Percentage, as used in this paper, means grams of salt in 100 g. of solution.

Experiments at a higher temperature than 25° indicated in a qualitative way that most of the chlorides are more soluble in selenium oxychloride as the temperature increases. One notable exception to this is barium chloride whose solubility at 25°, 40°, 55° and 70° was found to be 3.95, 2.35, 1.23 and 0.71%, respectively.

Effects of Small Amounts of Moisture on the Solubilities of the Various Chlorides.—While scrupulous care was taken to exclude extraneous moisture, experimentation has shown that very small quantities of water have very little effect on the solubilities. An appreciable amount of water, however, converts the selenium oxychloride into selenious and hydrochloric acids, which introduces other factors. In the case of barium chloride these products of hydrolysis actually decrease its solubility in selenium oxychloride, as is shown in Table II.

TABLE II
INFLUENCE OF WATER ON THE SOLUBILITY OF BARIUM CHLORIDE IN SELENIUM OXYCHLORIDE

Moles of H ₂ O per mole of SeOCl ₂ :	anh.	1/16	1/8	1/4	1/2	1
BaCl ₂ found, %:	3.95	3.86	3.37	2.32	1.40	0.45

Study of the Solid Phases of Various Metallic Chlorides in the Selenium Oxychloride.—Addition compounds of selenium oxychloride with stannic, titanous and antimonous chlorides have been noted by Weber.⁶ It has been thought highly desirable that more knowledge should be obtained about other chlorides.

With all the chlorides studied, an examination has been made in each case of the solid phase obtained in the solubility determinations. Many of the chlorides do not form addition products with selenium oxychloride while a number of others unite with it. The anhydrous chlorides of lithium, sodium, copper, silver, strontium, barium, zinc, cadmium, mercury, nickel and cobalt apparently do not unite with selenium oxychloride, while the chlorides of potassium, rubidium, cesium, magnesium, calcium, titanium, tin, antimony and iron form various kinds of products.

Arsenic trichloride is miscible in all proportions in the selenium oxychloride.

Titanium tetrachloride unites with selenium oxychloride to give TiCl₄.2SeOCl₂; *tin tetrachloride* forms SnCl₄.2SeOCl₂; while *antimony pentachloride* gives the compound SbCl₅.2SeOCl₂. These are white crystalline compounds.

Ferric chloride dissolves in selenium oxychloride at 25° to the extent of 23.4%. The actual rate of solution is slow and at the same time there is

⁶ Weber, *Pogg. Ann.*, **125**, 135 (1865).

a great tendency to form a supersaturated solution. Several days' shaking in the thermostat has been found necessary to attain equilibrium. In the first series of experiments in which the ferric chloride was in excess it was noted that the black ferric chloride crystals changed to ruby red. Analysis of these crystals showed that they have the composition, $\text{FeCl}_3 \cdot 2\text{SeOCl}_2$. Further experiments also showed that this new double chloride

Calc. for $\text{FeCl}_3 \cdot 2\text{SeOCl}_2$: Fe, 11.3; Se, 32.0; Cl, 50.2. Found: Fe, 11.7, 11.9; Se, 31.0, 31.0; Cl, 49.5, 49.4.

is produced when the selenium oxychloride is in excess as well as when the ferric chloride is in excess. The new compound dissolves readily in alcohol, ether, xylene, chloroform and carbon tetrachloride. Water causes hydrolysis of the compound with the production of a yellow precipitate.

Potassium chloride when brought into equilibrium with selenium oxychloride gives the solid phase, $\text{KCl} \cdot \text{SeOCl}_2$, which appears as a white crystalline compound.

Calc. for $\text{KCl} \cdot \text{SeOCl}_2$: K, 16.2; Se, 32.9; Cl, 44.2. Found: K, 16.6, 16.5; Se 31.1, 31.2; Cl, 41.4, 41.2.

This product, formed by the union of selenium oxychloride with potassium chloride, was previously prepared in this Laboratory by G. N. Quam when working with Lenher. His method of preparation was by heating a mixture of potassium chloride with selenium oxychloride in various proportions.

The compound, $\text{KCl} \cdot \text{SeOCl}_2$, is hydrolyzed by water. It is soluble in alcohol while chloroform gradually extracts the selenium oxychloride leaving potassium chloride.

Rubidium chloride forms with selenium oxychloride a solid phase of gelatinous character which obviously requires considerable time for the establishment of equilibrium to be established. When equilibrium is attained white, well-defined rectangular plates separate from the gelatinous mass together with a very small amount of a yellow powder. This compound is hydrolyzed by water and is insoluble in chloroform. Analysis of these flat rectangular plates showed them to be $\text{RbCl} \cdot \text{SeOCl}_2$.

Calc. for $\text{RbCl} \cdot \text{SeOCl}_2$: Rb, 29.8; Se, 27.6; Cl, 37.0. Found: Rb, 30.2, 30.1; Se, 26.4, 26.2; Cl, 36.3, 36.1.

Cesium chloride shows the same mechanical behavior with selenium oxychloride as is the case with rubidium chloride. A yellow gelatinous mass is produced which up to the present has not yielded a compound of sufficiently definite character to repay study.

The chlorides of calcium and magnesium yield with selenium oxychloride even more gelatinous products than is the case with the chlorides of the alkalis. Analysis of the products obtained indicate that compounds of the order of $\text{CaCl}_2 \cdot 3\text{SeOCl}_2$ and $\text{MgCl}_2 \cdot 3\text{SeOCl}_2$ exist, but from the nature of the materials and their absorptive powers other products of higher selenium oxychloride content probably are also formed. The

magnesium chloride precipitates are far more gelatinous in character than are those with calcium chloride and show apparently more absorptive properties.

The writer wishes to express his appreciation to Dr. Victor Lenher whose many valuable suggestions during the progress of this work made its early completion possible.

Summary

A method has been presented for determining the solubilities of various chlorides in selenium oxychloride.

The solubilities of 22 chlorides at 25° have been established and the solid phases investigated, showing that while a number of the chlorides do not unite with selenium oxychloride, others form characteristic double compounds.

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THE ACTION OF SOLUTIONS OF ALKALI HYDROXIDES ON COPPER OXIDE AND ON COPPER, AND THE EXISTENCE OF SALTS OF CUPRIC ACID

By H. J. M. CREIGHTON

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The majority of text-books on inorganic chemistry ignore the solution of copper hydroxide in concentrated solutions of alkali hydroxides.

Löw¹ found that copper hydroxide dissolves in a solution of sodium hydroxide and that the resulting blue solution might be diluted with 4-5 volumes of water and boiled without decomposition, but that precipitation of copper oxide took place on boiling when the blue solution was diluted with 10 volumes of water. These blue solutions were decolorized by merely shaking with copper oxide, and a bright blue powder, which decomposed into sodium oxide and cupric oxide, settled when the solution was allowed to stand for several days. According to Donath,² a blue solution is formed on treating copper oxide with a concentrated solution of potassium hydroxide. The color of this solution is intensified by the addition of alkali tartrate and destroyed by the addition of potassium cyanide.

While the formation of these blue solutions suggests the possible existence of salts of a cupric acid, analogous to the compounds formed by the interaction of alkali hydroxides and lead or tin hydroxides, Fischer³ points out that the blue color is due to a colloidal suspension of copper hydroxide, because the greater part of the hydroxide settles out and, also, because on filtering the solution the cupric oxide gel remains in the filter. Ley⁴ prepared a solution of colloidal copper hydroxide by hydrolyzing copper succinimide and dialyzing the product of hydrolysis, but the color of the colloidal solution was brown. The addition of electrolytes, such as chlorides and nitrates, to this solution precipitated

¹ Löw, *Z. anal. Chem.*, **9**, 463 (1870).

² Donath, *ibid.*, **40**, 137 (1901).

³ Fischer, *Z. anorg. Chem.*, **40**, 39 (1904).

⁴ Ley, *Ber.*, **38**, 2199 (1905).