

SOME PROPERTIES OF SELENIUM OXYCHLORIDE.

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As a part of the studies on selenium and tellurium which have been conducted in this laboratory, preliminary experiments showed that the oxychloride of selenium, SeOCl_2 , possesses properties which deserve further study. A few papers have been published by Weber,¹ Michaelis² and Clausnizer,³ who have given certain methods for its formation, a few of its physical properties, and a few of the chemical reactions.

Physical Properties.

Selenium oxychloride is a liquid which is slightly yellow as ordinarily prepared. Purification by distillation under diminished pressure, and recrystallization by freezing, give a product which is nearly colorless. The boiling point of the material thus purified is 176.4° at 726 mm. Weber gives 220° , Michaelis 179.5° , and Clausnizer, between 175° and 176° at 735 mm. Its melting point is 8.5° .⁴ Its refractive index at 20° is 1.6516.⁵ Preliminary experiments have shown that its electrical conductivity is low, its specific conductivity obtained with carbon electrodes being approximately 9.6×10^{-4} at 28° . Selenium oxychloride, while slightly yellow, is transparent to visual light but is so opaque to ultra-violet light that it makes a practically perfect screen for all wave lengths below 4050.

Selenium oxychloride is miscible in all proportions with carbon tetrachloride, chloroform, carbon disulfide, and benzol. The solutions formed with these solvents are physical mixtures rather than chemical compounds, since they can be separated by fractional distillation or by treatment with water, in which latter case the selenium oxychloride is hydrolyzed.

With the saturated aliphatic hydrocarbons, at the ordinary temperature, there is apparently no chemical action, or if any, very slight. Indeed such pure hydrocarbons as pentane, hexane, heptane, nonane and decane are immiscible with the reagent. The lighter hydrocarbons float on the heavier liquid, selenium oxychloride, and when the 2 immiscible liquids are shaken thoroughly, the lighter hydrocarbon immediately rises to the surface and forms a transparent layer. When the hydrocarbon of a higher carbon content such as paraffin, or vaseline, are mixed with selenium oxychloride, the hydrocarbons float on the heavier liquid. When paraffin or vaseline is heated with selenium oxychloride to about 150-

¹ Weber, *Pogg. Ann.*, 108, 615 (1859); 125, 325 (1865).

² Michaelis, *Z. Chem.*, [2] 6, 460 (1870); *Jena Z.*, 6, 79 (1871).

³ Clausnizer, *Ann.*, 196, 265 (1879).

⁴ A. J. Snyder. This laboratory.

⁵ J. H. Mathews. This laboratory.

160°, the 2 liquids become perfectly miscible. On cooling, the 2 layers separate, as is the case in the system phenol and water.

Chemical Properties.

Action on Non-Metals.—Members of the sulfur family, sulfur, selenium, and tellurium, dissolve with ease in large quantities in the cold in selenium oxychloride. Their deportment towards the reagent when heated is somewhat complicated. Decomposition of the reagent takes place in the case of sulfur, with the formation of selenium monochloride, while at the same time sulfur dioxide and sulfur monochloride are also produced. Tellurium yields its tetrachloride.

Red phosphorus reacts with selenium oxychloride in the cold with the evolution of light and heat, while the reaction with white phosphorus is explosive.

Bromine and iodine are dissolved by the reagent. Bromine forms a red-brown solution, while iodine forms a purple colored solution. Both of these solutions are very active. Boron, silicon, and all of the various forms of carbon, whether graphite, charcoal, activated carbon, or diamond, are not attacked in the cold by selenium oxychloride.

Action on Metals.—Most of the metals react with selenium oxychloride forming the chloride of the metal and red-brown selenium monochloride, Se_2Cl_2 . This, subsequently treated with water, gives hydrochloric acid, selenious acid, and the red precipitated variety of selenium. The alkali metals, sodium and potassium, present a curious deportment towards the reagent. Sodium, when introduced into the liquid, is not acted on. Indeed selenium oxychloride can be distilled in the presence of metallic sodium and no action is apparent, even at a temperature of 176.4°, the boiling point of selenium oxychloride. Sodium, when dropped on selenium oxychloride, floats, and if a few drops of water be carefully added, the water will float on the heavier selenium oxychloride. The sodium will float on top of this water, and gives off hydrogen in its usual manner without any violence. Metallic potassium, on the other hand, when brought in contact with selenium oxychloride, in the cold, explodes with great violence.

Metallic aluminum, zinc, bismuth, and tin are readily attacked by the reagent, while calcium, copper, magnesium, chromium, lead, nickel, arsenic, cadmium, cobalt, gold and platinum are slowly attacked. Powdered antimony takes fire when introduced into the liquid. Iron slowly reacts in the cold, but the action is accelerated on heating. Metallic titanium is not attacked in the cold by selenium oxychloride, but is, at a very high temperature.

Metallic tungsten is not acted on at the ordinary temperature by selenium oxychloride.

Action on Oxides.—Selenium oxychloride dissolves selenium dioxide to a limited extent. It also dissolves arsenic trioxide, vanadium pentoxide, and molybdenum trioxide, all of which are acted on chemically by the reagent. When molybdenum trioxide has been freshly ignited, it dissolves only slightly in selenium oxychloride, but when slightly hydrated, it dissolves readily in the reagent. The solution of molybdenum trioxide in selenium oxychloride, when exposed to sunlight or to strong artificial light, as for example, from an electric arc, shows a striking reversible photochemical reaction. The solution in a strong light becomes indigo-blue in a few minutes, and when brought into subdued light, this color fades in a few hours to the pale yellow of the original solution. This discharge of color can also be accomplished by heating the blue solution to a moderate temperature.

The oxides of aluminum, thorium, the rare earths, titanium, zirconium, columbium, and tantalum are not appreciably attacked in the cold by selenium oxychloride. Uranium oxide is slowly attacked by the reagent.

Tellurium dioxide is dissolved and on evaporation of the solvent, is recovered as such. On the other hand, when tellurium dioxide and selenium tetrachloride are brought together in molecular proportions, and heat is applied, reaction takes place between the two. Quite a high temperature is necessary to start the reaction, but when once begun, it proceeds readily. Selenium oxychloride first distils at its boiling point, and, on raising the temperature to a little below 400°, tellurium tetrachloride distils, while tellurium dioxide remains as a non-volatile residue. The reaction probably proceeds as follows,



Tellurium trioxide is not acted on by selenium oxychloride.

Sulfur trioxide dissolves in selenium oxychloride to form a thick, heavy solution, which is a powerful solvent. This solution will dissolve the oxides of aluminum, chromium, the rare earths, titanium, columbium, molybdenum, vanadium, and uranium, but will not dissolve the oxides of zirconium or of tungsten, and dissolves the oxide of tantalum only very slightly. It is probable that by the use of this solution certain separations can be effected which to-day are very troublesome for the chemist.

Carbonates.—The anhydrous carbonates of sodium and potassium, as well as the bicarbonates of these metals, react with this anhydrous acid chloride with the liberation of carbon dioxide.

Calcium carbonate slowly becomes encrusted with a white coating of selenite of calcium. Strontium carbonate dissolves with ease, with the evolution of carbon dioxide, the other products of the reaction being completely soluble in the reagent. Barium carbonate effervesces with selenium oxychloride, to form an insoluble gel. Inasmuch as a small amount of the

barium salts dissolves in selenium oxychloride this difference of behavior of the alkaline earth carbonates towards selenium oxychloride will not afford a quantitative separation.

Zinc carbonate dissolves at once in the cold in selenium oxychloride.

The carbonates of lead, copper, nickel, and cobalt are only slightly attacked in the cold by selenium oxychloride.

The reaction of the pink carbonate of cobalt with selenium oxychloride makes a beautiful lecture experiment. When the pink carbonate of cobalt is treated with selenium oxychloride, it instantly turns blue without showing effervescence. If water be added, the selenium oxychloride is at once hydrolyzed and the acid set free reacts energetically on the carbonate, causing effervescence and the formation of a blue cobalt solution which with further addition of water transforms to the beautiful rose color, characteristic of dilute cobalt solutions.

Magnesium carbonate is peptized by selenium oxychloride to a gel. When the 2 are brought together, magnesium carbonate goes at once into the colloidal form, which state is even more accentuated when the 2 are boiled together. When a little water is added to the suspended gel, hydrolysis of the selenium oxychloride is effected, and brisk effervescence at once takes place.

Sulfides.—The sulfides of arsenic, antimony, and cadmium react in the cold with selenium oxychloride liberating heat. Pyrite, marcasite, and arsenopyrite are slowly acted on in the cold by selenium oxychloride, but when heated the reaction is more energetic. Sulfur dioxide is evolved and selenium monochloride is formed at the same time.

Calcium hydride and selenium oxychloride do not react even when boiled together. When water is added to the mixture, decomposition at once begins and red selenium is precipitated.

Calcium carbide does not react with selenium oxychloride in the cold, but slowly reacts with it on boiling.

Calcium phosphide and selenium oxychloride do not react in the cold, but do react slowly at the boiling temperature.

Barium Sulfate.—Contact of selenium oxychloride with finely divided barium sulfate peptizes the latter at once. Its physical appearance is changed from the finely divided condition to that of a gel much resembling freshly precipitated aluminum hydroxide. This gelatinous form of barium sulfate can also be produced when a solution of selenium oxychloride containing dissolved barium chloride is treated with a solution of selenium oxychloride containing sulfuric acid. When these 2 solutions are brought together, barium sulfate is precipitated in a gelatinous form. This colloidal form of barium sulfate immediately changes to the ordinary form when treated with water.

Oxidizing Agents.—Chromium trioxide or potassium dichromate

dissolves in selenium oxychloride to form a beautiful red colored solution. On heating, heavy fumes of chromyl chloride are evolved.

With potassium permanganate, on first contact there is no action, or at most only a superficial action, and it is only after many hours of contact that there is any appreciable reaction between the two.

Potassium chlorate dissolves in selenium oxychloride, and on warming the solution, evolves chlorine.

Potassium perchlorate does not react with selenium oxychloride.

Hydrocarbons.—The saturated paraffin hydrocarbons are slowly attacked by selenium oxychloride at a high temperature.

The unsaturated hydrocarbons of the aliphatic series unite with selenium oxychloride directly, frequently with the manifestation of great energy. For example, amylene reacts with selenium oxychloride with great violence.

With such hydrocarbons as turpentine the reaction is as violent as is that of the halogens on turpentine.

The aromatic hydrocarbons, such as benzene and toluene, form physical mixtures which can be separated by purely physical means, such as fractional distillation. The complete recovery of the hydrocarbon can also be accomplished by hydrolysis of the selenium oxychloride with water.

Separation of the Hydrocarbon Series by Selenium Oxychloride.—It is thus possible to separate such unsaturated aliphatic hydrocarbons as amylene from heptane, a saturated hydrocarbon, by simple contact with this solvent. Similarly, when a mixture of heptane and benzene is treated with selenium oxychloride the benzene forms a solution with the selenium oxychloride, while the lighter heptane rises to the top and forms an immiscible layer.

Carbohydrates and Proteins.—Selenium oxychloride dissolves protein containing material such as hair, bristles, silk, and leather in the cold. The reactions are in all cases much accelerated on heating.

Cellulose is not appreciably acted on by selenium oxychloride. A piece of filter paper, sealed up in a tube with selenium oxychloride, showed practically no action after being allowed to stand for 6 months. It has frequently been found convenient to filter selenium oxychloride solutions through ordinary filter paper during our laboratory experiments. Starch and cane sugar are not appreciably acted on by selenium oxychloride in the cold, but when slightly warm, decomposition begins. The action of selenium oxychloride with hydrocellulose is very sluggish, even when the 2 are boiled together.

Vegetable and Fish Oils.—The behavior of selenium oxychloride toward vegetable and fish oils is in many respects similar to that of sulfur monochloride on the oils. With linseed oil, selenium oxychloride forms a rubber-like mass similar in many respects to that formed by sulfur

monochloride. Menhaden oil reacts with selenium oxychloride to form a water-proof rubber-like mass.

Rubber.—Pure rubber, vulcanized rubber, and vulcanite react chemically with selenium oxychloride in the cold. The reaction is much accelerated by heating. The chemical character of the rubber is changed by the reaction. The solution obtained when hydrolyzed by water gives in addition to hydrochloric acid, selenious acid, and red elementary selenium, a white insoluble product of gelatinous character which contains selenium and chlorine in addition to carbonaceous matter.

The insoluble phenolic condensation products, redmanol, bakelite and condensite, dissolve with ease in selenium oxychloride. The reaction is accelerated by heating. Chemical change takes place.

Gums, resins, dried paints, shellac, dried varnish, lacquer, agar, celluloid, gelatin, glue, including the insoluble casein glues are all dissolved readily in the cold by selenium oxychloride.

The natural asphalts, and resins, bitumens dissolve with ease in selenium oxychloride in the cold when they are of unsaturated character. Such a natural product as ozocerite, which consists essentially of saturated hydrocarbons, behaves towards selenium oxychloride much like paraffin. It is scarcely acted on in the cold, but when the two are heated together it forms a homogeneous liquid phase, which, in cooling, separates into the solid phase of hydrocarbons and the liquid phase of selenium oxychloride.

Coals and Carbons.—When natural coals are brought in contact with selenium oxychloride, it reacts with the bituminous and resinic materials, extracting at least a part of these materials, leaving behind a carbonaceous residue.

Thoroughly ignited coke loses nothing when treated with selenium oxychloride; partially coked soft coal does. Anthracite coal containing practically no volatile combustible matter shows little action. Semi-anthracite coals lose a considerable amount of extractive matter with selenium oxychloride, while such coals as the Illinois, Ohio, cannel, and the bituminous coals from Pennsylvania and Virginia, lose a large amount of extractive matter. Preliminary experiments made in this laboratory by W. T. Schrenk on Illinois coal containing 40% of volatile, combustible matter show on extraction with selenium oxychloride a total loss in weight of 20%. The insoluble material was found to contain selenium and chlorine in considerable quantities.

When the soft coals are powdered, selenium oxychloride reacts with them, evolving considerable heat.

Lampblack, when treated with selenium oxychloride, loses its hydrocarbon content, leaving behind carbon.

Carbon from Iron and Steel.—The carbonaceous material separated from either iron or steel by the copper chloride treatment consists of

graphite, together with the material which E. D. Campbell considers unsaturated hydrocarbons. Such material when treated with selenium oxychloride gives a black extract, showing that at least part of the material has been acted on. It is possible that a further study of this reaction may throw some light on the constitution of iron and steel.

The same care is used in the laboratory in handling selenium oxychloride as with any other highly corrosive liquid. Its vapors have shown no other physiological action than that of the hydrochloric acid produced by its hydrolysis with the mucous membranes.

MADISON, WIS.

THE ORIENTATION OF MOLECULES IN SURFACES. VI. COHESION, ADHESION, TENSILE STRENGTH, TENSILE ENERGY, NEGATIVE SURFACE ENERGY, INTERFACIAL TENSION, AND MOLECULAR ATTRACTION.

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Introduction.

This paper presents data which were obtained in order to exhibit the relation between the chemical properties of organic liquids and the total amount of energy which is used in separating them from water or from themselves. It includes somewhat complete data, the first of the sort to be obtained, on the surface and interfacial energy relations of 12 organic liquids.

Work of Adhesion.

The equation developed by Dupré in 1869¹ gives the *adhesion work* (W_A) involved in the approach of 2 unlike surfaces, which is equal to the decrease of free energy during their approach:

$$W_A = -\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{1,2},$$

where γ_1 and γ_2 give the free energy (numerically equal to the surface tension) of the 2 unlike surfaces before their approach, and $\gamma_{1,2}$ is the free energy of the interface (numerically equal to the interfacial tension). A recent paper from this laboratory² gives values for the work of adhesion toward water of 70 organic liquids at 20°.

Fig. 1 plots the adhesion work toward water for 11 organic liquids at temperatures between 0° and 50°, and presents for comparison the values at 20° for 28 other liquids. It may be noted that the temperature coefficient has specially low negative values (about -0.178) for the 2 halogen compounds, carbon tetrachloride and ethylene bromide, and

¹ Dupré, "Theorie Mécanique de la Chaleur," Paris, 1869, p. 69; Lord Rayleigh, London, *Phil. Mag.*, [5] 30, 461 (1890); Hardy, London, *Proc. Roy. Soc.*, 86B, 634 (1911).

² Harkins, Clark and Roberts, *THIS JOURNAL*, 42, 700-12 (1920).