The use of hydrazine hydrochloride or sulfate in the citric or oxalic acid method invariably gives selenium contaminated by tellurium with correspondingly low tellurium results.

Conclusions

It is possible to separate selenium and tellurium in hydrochloric, tartaric or citric acid solution by means of hydroxylamine hydrochloride. The sulfate of hydroxylamine proved to be less satisfactory. The procedure of separation is very simple and is susceptible of wide variations in the details of technique.

Both hydrazine hydrochloride and the sulfate tend to cause precipitation of tellurium with the selenium; this can be avoided in the method of Pellini by proper control of temperature.

By use of oxalic acid, it is possible by means of hydroxylamine hydrochloride to separate selenium from tellurium, but the technique is so highly complicated by minor factors that it is not as satisfactory as the tartaric or citric acid methods.

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A GENERAL THEORY OF SOLVENT SYSTEMS

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Our theory of solution has developed largely, if not entirely, from a study of water solutions. Water is remarkable as being the parent substance of a large number of acids, the ordinary oxygen or aquo-acids, of bases, the metallic oxides and hydroxides, and of salts, the oxy or aquo salts, besides acting as solvent for a long list of non-related acids and salts, such as the hydro-halides and other non-oxygen acids and their salts. Parallel with this behavior of water is the behavior of liquid ammonia, which has been shown by Franklin to be the parent substance of a series of acids, the ammono acids, of bases, the metallic nitrides, imides and amides, and of salts, the ammono salts;[1] like water, ammonia readily acts as solvent for a great many non-related acids and salts, and in addition acts as solvent for many metals and intermetallic salts.[2] Many solvents have been studied with a view to determining the solubility of the well-known acids, bases and salts, their reactivity with one another and with the solvent, and the conductivity of their solutions.[3] But few, aside from water and ammonia, have been considered from the standpoint of the

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[1] Franklin, THIS JOURNAL, **46**, 2137 (1924).

[2] Kraus, *ibid.*, **44**, 1216 (1922).

[3] See, for example, the publications of Walden, Kahlenberg, Naumann, and of Archibald, MacIntosh and Steele.

existence of a system of *typical* acids, bases and salts; among these few are hydrogen sulfide, hydrogen cyanide, hydrogen fluoride, hydrogen chloride and methane.[1] Considered as ionizing solvents, all of those studied up to the present time yield hydrogen ion as cation, which is, therefore, characteristic of all typical acids, but the negative ion changes from one solvent to another, so that bases typical of the different solvent systems yield different anions, depending on the negative ion of the solvent.

From a purely theoretical standpoint, there is no more justification for the restriction of the idea "acid" to a hydrogen compound, as sulfuric or nitric acid, than there is for the restriction of the idea "base" to oxides or hydroxides of metals; at least one group of bases not conforming to this formula ought to be familiar to every chemist, namely the ammono bases, of which potassium amide, KNH_2, is typical.[1] The actual discovery of a solvent, carbonyl chloride, commonly known as phosgene, which conforms to the general requirements of the parent substance of a system of acids, bases and salts, but which contains no hydrogen,[4] makes it necessary to adjust our conception of an acid to include the new case, and to generalize our definitions relating to solvent systems.

Reactions in Water Solution

Sulfuric acid may be taken as a typical aquo acid; it is formed whenever sulfur trioxide is dissolved in water, one of the hydrates formed, the monohydrate, being designated sulfuric acid. At least four other hydrates are known: $SO_3.\frac{1}{2}H_2O$, $SO_3.2H_2O$, $SO_3.3H_2O$ and $SO_3.5H_2O$, which are designated consecutively pyrosulfuric acid and the mono-, di- and tetrahydrate of sulfuric acid.

Calcium oxide may be taken as a typical aquo base; it is formed by the union of calcium with oxygen, or by the action of water on calcium. By the latter method the base first formed, calcium oxide, reacts with water by what may be termed a hydrolytic reaction to produce calcium hydroxide. Calcium oxide is water in which all the hydrogen has been replaced by metal; calcium hydroxide is more nearly related to water, in that only half of the hydrogen has been replaced by metal; thus there may be two different forms of the aquo base of the same metal; with solvents containing more hydrogen, such as ammonia, there may be three—the nitride, the imide and the amide; of these, the one containing the least metal will be most nearly like the solvent and, other things being equal, the most soluble, while the one containing the most metal will be least soluble. Thus, among water compounds, oxides are generally insoluble, while hydroxides are more or less soluble. On the other hand, with such solvents as hydrogen chloride, there will exist only one base corresponding to a given metal, and this may be insoluble in the parent solvent.

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[4] Germann, *Science*, **61**, 71 (1925).

Calcium sulfate may be regarded as a typical aquo salt, and may be formed by the action of sulfuric acid on metallic calcium, or by the action of the acid on calcium oxide or hydroxide. The salt crystallizes from solution with two molecules of water of crystallization.

Solutions of the acid, base and salt conduct the electric current, hydrogen or calcium is set free at the cathode, calcium reacting with the solvent to give secondary products; at the anode the anion is discharged and reacts with the solvent, setting free oxygen; virtually, therefore, what happens when a dilute solution of a typical acid, base or salt is electrolyzed is the decomposition of water, except when the metal of the base or salt is stable in contact with water. In liquid-ammonia solution the electrolysis of a typical acid, such as ammonocarbonic acid (cyanamide), H_2CN_2, or of a typical base, such as potassium amide, KNH_2, or of a typical salt, such as potassium ammonocarbonate, K_2CN_2, would result similarly in the decomposition of the solvent, ammonia, setting free hydrogen at the cathode, and nitrogen at the anode.

Discussion of reactions in a given solvent system will be limited, in this paper, to acids, bases and salts that are typical of the given solvent; thus, for example, the discussion of solutions of the hydro-halogens and the metallic halides in water will be omitted, since these acids and salts are not typical water compounds; similarly, the discussion of solutions of nitrates, sulfates, halides, phosphates, etc., in liquid ammonia will not be included, since these compounds are not typical ammono compounds. In this connection it may be well to formulate definitions to cover these terms.

Definitions

Parent Solvent.—A parent solvent, $A_\beta B_\alpha$, is an ionizing solvent, the parent substance of a system of acids, bases and salts which are therefore typical of the solvent, and may be called solvo acids, solvo bases and solvo salts. Its ionization into $\beta A^{\alpha+}$ and $\alpha B^{\beta-}$ is so slight that it is classed as a non-conductor, but it yields conducting solutions of acids, bases and salts. When $\beta > \alpha$, there may be more than one variety of negative ion, as $B^{\beta-}$, $(A_{\beta-1}\, B_\alpha)^{\alpha-}$, $(A_{\beta-2}\, B_\alpha)^{2\alpha-}, \ldots\ldots (AB_\alpha)^{\alpha(\beta-1)-}$. The solubility of polar substances in an ionizing solvent is probably related to its dielectric constant and to its degree of ionization.

Solvo Acid.—A solvo acid, $A_{\beta x}N_{\beta y}B_{\alpha x + \nu y}$, is the addition compound formed between x molecules of a parent solvent, $A_\beta B_\alpha$, and y molecules of one of its slightly polar derivatives, $N_\beta B_\nu$; the solvo acid is usually separable from the solution as a crystalline solvate, that is, with one or more molecules of solvent of crystallization. The solution of the solvo acid conducts the electric current, the solvent being decomposed in the process; at the cathode, A is set free as a primary product of electrolysis, and at the anode, B is set free as a secondary product. The solvo acid neutralizes related solvo bases with the formation of the related solvo salt and the parent solvent, and it reacts with metals more electropositive than A with the formation of solvo salts and the evolution of A; it may also react with non-related solvo bases. The solvo acid ionizes as follows: $A_{\beta x}N_{\beta y}B_{\alpha x + \nu y} \rightleftarrows \beta x A^{\alpha +} + (N_{\beta y}B_{\alpha x + \nu y})^{\alpha\beta x -}$.

Solvo Base.—A primary solvo base, $M_{\beta}B_{\mu}$, is a metallic derivative of a parent solvent formed by the replacement of A by the metal, or by direct combination of the metal with B; with solvents for which $\beta > \alpha$, solvolysis may occur on contact with the solvent, with formation of secondary or tertiary solvo bases, $M_{\alpha(\beta-1)}(B_{\alpha}A)_{\mu}, \ldots . M_{\alpha}(B_{\alpha}A_{\beta-1})_{\mu}$, according to the general equations, $\mu A_{\beta}B_{\alpha} + \alpha(\beta - 1)M_{\beta}B_{\mu} \longrightarrow \beta M_{\alpha(\beta-1)}(B_{\alpha}A)_{\mu}$, and $(\beta - 1)\mu A_{\beta}B_{\alpha} + \alpha M_{\beta}B_{\mu} \longrightarrow \beta M_{\alpha}(B_{\alpha}A_{\beta-1})_{\mu}$. These solvolytic products will in general be more soluble than the primary solvo bases. The solution of a solvo base conducts the electric current, the metal M (which may react with the solvent) being deposited on the cathode, and B being set free at the anode. The solvo-base ionizes as follows:

$$M_{\alpha}(B_{\alpha}A_{\beta-1})_{\mu} \rightleftarrows \alpha M^{\mu +} + \mu(B_{\alpha}A_{\beta-1})^{\alpha -}$$

Solvo Salt.—A solvo salt is the product of the interaction of a solvo acid with a solvo base, and is identical with the product formed by the action of the solvo acid on the metal itself or other compound of the metal. $\mu A_{\beta x}N_{\beta y}B_{\alpha x + \nu y} + \alpha x M_{\beta}B_{\mu} \longrightarrow M_{\alpha\beta x}(N_{\beta y}B_{\alpha x + \nu y})_{\mu} + \mu x A_{\beta}B_{\alpha}$; $\mu A_{\beta x}N_{\beta y}B_{\alpha x + \nu y} + \alpha\beta x M \longrightarrow M_{\alpha\beta x}(N_{\beta y}B_{\alpha x + \nu y})_{\mu} + \mu\beta x A$. In the first case the by-product is the parent solvent, while in the second case the by-product is A. The solution of a solvo salt conducts the electric current with decomposition of the solvent if the metal first deposited at the cathode reacts with the solvent; since most solvo acids are weak, the solution of the solvo salt will usually conduct better than the solution of the solvo-acid from which it was derived. The solvo salt, when crystallized from the parent solvent, may separate as a crystalline solvate. Solutions of solvo salts may be expected to exhibit the well-known type reactions, such as metathesis, solvolysis, etc. The solvo salt ionizes as follows: $M_{\alpha\beta x}(N_{\beta y}B_{\alpha x + \nu y})_{\mu} \rightleftarrows \alpha\beta x M^{\mu +} + \mu(N_{\beta y}N_{\alpha x + \nu y})^{\alpha\beta x +}$.

These definitions might be expressed more briefly as follows.

A parent solvent is the substance from which a system of solvo acids, solvo bases and solvo salts is derived.

A solvo acid is any electrolyte which, in a given solvent, yields cations identical with the cations of the parent solvent, and anions containing, in addition to the atom characteristic of the individual solvo acid, atoms characteristic of the anion of the parent solvent.

A solvo base is any electrolyte which, in a given parent solvent, yields simple metal cations, and anions identical with the anions of the parent solvent.

A solvo salt is the electrolyte produced when a solvo acid reacts with a metal, or with a solvo base derived from the same or other parent solvent.

For the purpose of this discussion, then, hydrobromic acid, hydrochloric acid, hydrosulfuric acid, hydrocyanic acid, etc., would not be solvo acids in any solvent; fluosilicic acid would be a solvo acid in hydrogen fluoride solution; chloro-cuprous acid, $HCuCl_2$, in hydrogen chloride solution; cyanoplatinous acid, $H_2Pt(CN)_4$, in hydrogen cyanide solution; cyanamide, H_2CN_2, in ammonia solution; thio-ortho-arsenious acid, H_3AsS_3, in hydrogen sulfide solution, etc. Metallic salts of hydrochloric acid, hydrobromic acid, hydrogen sulfide, hydrocyanic acid, etc., would not be solvo salts in any solvent, but sodium chloride would be classified as a solvo base in hydrogen chloride, potassium fluoride and potassium acid fluoride solvo bases in hydrogen fluoride, calcium bromide a solvo base in hydrogen bromide, sodium cyanide a solvo base in hydrogen cyanide, cupric oxide and hydroxide solvo bases in water solution, potassium sulfide and acid sulfide solvo bases in hydrogen sulfide solution, and cupric nitride, Cu_3N_2, lead imide, PbNH, and potassium amide, KNH_2, solvo bases in ammonia solution. Solvo salts would be metallic derivatives of solvo acids, such as those mentioned above.

The Phosgene System of Acids, Bases and Salts

If we turn now to the reactions in phosgene solution which have been found to parallel the well-known reactions in water solution, as outlined above, the following observations stand out prominently: anhydrous aluminum chloride, a slightly polar compound (fused aluminum chloride is a non-conductor),[5] is soluble in phosgene, and Baud[6] has reported the following addition compounds or phosgenates: $4AlCl_3.COCl2$, $2AlCl_3.3COCl_2$, $2AlCl_3.5COCl_2$. The specific conductivity of liquid phosgene is no more than 0.007×10^{-6}, but the solutions of aluminum chloride conduct up to approximately 100,000 times as well. Electrolysis of the solution results in the decomposition of the solvent, carbon monoxide being liberated at the cathode, and chlorine at the anode.[7] The solution dissolves metals such as magnesium, calcium, potassium, cadmium, zinc, etc., with concomitant evolution of carbon monoxide, and formation of salts crystallizing with phosgene of crystallization.[8] Metallic chlorides, such as magnesium chloride, silver chloride, barium chloride, calcium chloride, sodium chloride, strontium chloride, etc., react with phosgene solutions of aluminum chloride to yield salts identical with those formed by action on the metal. Phosgene solutions of these salts, as has been shown by C. R. Timpany[8a] in the case of the calcium salt, are much better conductors of the electric current than the solution of aluminum chloride itself; in the case mentioned, metallic calcium is deposited at the cathode, but later dissolves, while chlorine is evolved at the anode. When a solution of the cadmium salt in an excess of the aluminum chloride solution is added to an excess of pure phosgene, an amorphous precipitate of cadmium chloride forms.

If we try to interpret these phenomena, which closely parallel the be-

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[5] Biltz and Voigt, *Z. anorg. Chem.*, **126,** 39 (1923).

[6] Baud, *Compt. rend.*, **140,** 1688 (1905).

[7] Ref. 4, p. 70.

[8] Germann and Gagos, *J. Phys. Chem.*, **28,** 965 (1924).

[8a] Stanford University, *Thesis*, **1925.**

havior of sulfur trioxide in water solution with metals and metallic oxides, in the light of the ionic theory, we must suppose the existence of a solvo (phosgeno) acid in phosgene solution. As indicated by the conductivity of its solution as compared with that of its calcium salt, this phosgeno acid is evidently a weak solvo acid; it reacts with metals and with phosgeno bases (metallic chlorides) to form phosgeno salts. As we have seen, both sulfur trioxide and aluminum chloride form several crystalline solvates with their respective parent solvents. When the solution of sulfur trioxide hydrate in water is neutralized with calcium oxide, only two hydrogen atoms are displaced, and the resultant salt has the formula $SO_3.CaO.2H_2O$, which we may consider as derived from the hydrate $SO_3.3H_2O$. Analogously, when the phosgene solution of aluminum chloride phosgenate is neutralized with calcium chloride, the salt formed has the formula $2AlCl_3.CaCl_2.2COCl_2$, which we may consider as derived from the phosgenate $2AlCl_3.3COCl_2$ by displacement of one carbonyl group. Just as, by a study of the reaction of sulfuric acid with other bases, the displacement of two hydrogen atoms for each sulfur trioxide group has been found to be typical, leading to the accepted formula, H_2SO_4, for sulfuric acid, so a study of the reaction of this phosgeno acid with other bases has shown that the displacement of one carbonyl group for each aluminum chloride (Al_2Cl_6) group is typical, leading to the formula $COAl_2Cl_8$ for phosgeno aluminic acid.

We may then write the following parallel reactions: $SO_3 + H_2O \longrightarrow H_2SO_4$; $2AlCl_3 + COCl_2 \longrightarrow COAl_2Cl_8$; $H_2SO_4 \rightleftarrows 2H^+ + SO_4^{--}$; $COAl_2Cl_8 \rightleftarrows CO^{++} + Al_2Cl_8^{--}$; $H_2SO_4 + Ca \longrightarrow CaSO_4 + H_2$; $COAl_2Cl_8 + Ca \longrightarrow CaAl_2Cl_8 + CO$; $CaSO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O$; $CaAl_2Cl_8 + 2COCl_2 \longrightarrow CaAl_2Cl_8.2COCl_2$; $H_2SO_4 + CaO \longrightarrow CaSO_4 + H_2O$; $COAl_2Cl_8 + CaCl_2 \longrightarrow CaAl_2Cl_8 + COCl_2$; $CuSO_4 + H_2O \rightleftarrows H_2SO_4 + CuO$; $CdAl_2Cl_8 + COCl_2 \rightleftarrows COAl_2Cl_8 + CdCl_2$.

Other slightly polar chlorides that might yield solutions having acid properties when dissolved in phosgene are iodine trichloride, arsenic trichloride, the chlorides of antimony and the chlorides of sulfur, to mention only those found to be soluble by Beckmann and Junker.[9] Chlorine itself is very soluble in phosgene, and forms addition compounds with it,[10] which are excellent oxidizing and chlorinating agents; bromine and iodine are also soluble, and probably also form addition compounds, which should have valuable properties in synthetic reactions. Boron trifluoride is soluble in phosgene, forming addition compounds with it,[11] which suggests that boron trichloride would also be soluble, to yield a possible phosgeno boric acid; carbon dioxide also forms an addition compound with phosgene,

[9] Beckmann and Junker, *Z. anorg. Chem.*, **55**, 371 (1907).

[10] Germann and Jersey, *Science*, **53**, 582 (1921).

[11] Ref. 10, p. 145.

which may prove to be a mixed aquo-phosgeno acid. Schützenberger's carbonyl-chloroplatinum compounds[12] may be found to fit into the group of phosgeno acids, although this does not seem probable.

Other Solvents

Sulfuryl chloride, SO_2Cl_2, whose dielectric constant is 10, would seem to offer interesting possibilities as a parent solvent, as it is known from Walden's work[13] to be an ionizing solvent. Aluminum chloride is soluble in this solvent, and probably forms addition compounds with it; this solution should conduct electricity, with the evolution of sulfur dioxide and chlorine. It should react with metals with evolution of sulfur dioxide and formation of salts crystallizing with sulfuryl chloride of crystallization, and should react with metallic chlorides to yield salts and sulfuryl chloride (neutralization). This possibility is now being investigated.

Selenium oxychloride has been found by Wildish[14] to have a rather high dielectric constant, namely 45, and its properties have been rather fully investigated by Lenher and his co-workers. Wise has investigated the solubility of a number of anhydrous chlorides in selenium oxychloride;[15] he found all of those investigated somewhat soluble, with some of them showing a very high solubility; in many cases the formation of addition compounds with the solvent was observed; Julien[16] investigated the conductivity of selenium oxychloride solutions. The possibility that selenium oxychloride may prove to be a parent solvent is especially interesting in connection with the long disputed question as to the existence of Berzelius' selenium monoxide. Selenium oxychloride might be expected to ionize as follows: $SeOCl_2 \rightleftarrows SeO^{++} + 2Cl^-$. Electrolysis of solutions of typical acids might be expected to yield selenium monoxide, SeO, at the cathode, if this disputed compound is at all capable of existence. Ray has investigated the action of selenium oxychloride on certain metals,[17] and has observed the separation of selenium dioxide; it would thus seem probable that the ionic reaction will be more complex than indicated in the above equation. But we may as well recall that the existence of tellurium monoxide seems to be well authenticated;[18] sulfur monoxide may be capable of independent existence;[19] it would not be surprising, then, if selenium monoxide should eventually be added to our list of authentic compounds.

[12] Schützenberger, *Ann. chim. phys.*, [4] **21**, 350 (1872). See also Pullinger, *J. Chem. Soc.*, **59**, 598 (1891).

[13] Walden, *Z. anorg. Chem.*, **25**, 209 (1900).

[14] Wildish, THIS JOURNAL, **42**, 2607 (1920).

[15] Wise, *ibid.*, **45**, 1233 (1923).

[16] Julien, *ibid.*, **47**, 1799 (1925).

[17] Ray, *ibid.*, **45**, 2090 (1923).

[18] Doolan and Partington, *J. Chem. Soc.*, **125**, 1402 (1924).

[19] Riesenfeld and Feld, *Z. anorg. Chem.*, **119**, 225 (1921).

What has been said of selenium oxychloride applies equally well to thionyl chloride, whose dielectric constant is 9.05,[20] and which is known to yield conducting solutions.[13] The conclusions of Riesenfeld and Feld[19] concerning the action of hydrogen sulfide on sulfur dioxide in water solution are that sulfur monoxide is the primary product, and that this polymerizes to yield (with water) polythionic acids. It is entirely possible that sulfur monoxide, produced in a water-free environment, such as in the electrolysis of a hypothetical thiono-acid in thionyl chloride solution, might be capable of independent existence.

Many more solvents suggest themselves as worthy of study. Whatever the results of investigation might be, they cannot fail to throw new and important light on the theory of electrolytic dissociation, and advance our knowledge of the theory of solution.

Summary

Based on a study of the analogy between reactions in water and in phosgene solution, a general theory of acids, bases and salts as related to a parent solvent has been outlined, and applications to other solvents have been suggested.

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AVERAGE CROSS-SECTIONAL AREAS OF MOLECULES BY GASEOUS DIFFUSION METHODS

BY EDWARD MACK, JR.

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During the past few years our ideas regarding the sizes and shapes of typical organic and inorganic molecules have been greatly clarified by several interesting lines of work. The Hardy-Langmuir-Harkins treatment of oriented molecules in oil films has developed for us, especially in the hands of Langmuir,[1] and in the extension of his general method by Adam,[2] fairly definite ideas about the length and cross-section of long, slender molecules. Also, the inferences drawn by W. H. Bragg[3] about the sizes and shapes of molecules like naphthalene and anthracene from the X-ray examination of the crystals, and the deductions of W. L. Bragg[4] and Davey[5] regarding the distances separating the centers of atoms in

[20] Schlundt, *J. Phys. Chem.*, **5**, 513 (1901).

[1] Langmuir, *Proc. Nat. Acad. Sci.*, **3**, 251 (1917); THIS JOURNAL, **39**, 1848 (1917), and other papers.

[2] Adam, *Proc. Roy. Soc.*, **103A**, 676, 687 (1923), and other papers.

[3] W. H. Bragg, *Proc. Phys. Soc.*, **34**, 33 (1921); **35**, 167 (1923); and W. H. and W. L. Bragg, "X-Ray Analysis and Crystal Structure," G. Bell and Sons, **1924**.

[4] W. L. Bragg, *Phil. Mag.*, **40**, 169 (1920).

[5] Davey, *Phys. Rev.*, **18**, 102 (1921); **22**, 211 (1923).