A GENERAL CONCEPTION OF ACIDS AND BASES

By

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Approved by:

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At this place the writer wishes to record his appreciation of the manner in which Dr. H, P. Cady has directed this work and in which Dr. H. M. Elsey has aided in the preparation of apparatus; and to acknowledge his indebtedness to both Dr. Cady and Dr. Elsey for many helpful ideas and suggestions.

C O N T E N T S

A GENERAL CONCEPTION OF ACIDS AND BASES

Acids and bases are commonly defined with aqueous solutions alone in view. Thus a widely used textbook on physical chemistry states that "any electrolyte which gives hydrogen-ion (H^+) as one of the direct products of its ionization is called an acid", and that " any electrolyte which gives hydroxyl-ion as one of the direct products of its ionization is called a base".[1] Yet more than twenty years ago Franklin[2] observed that certain substances when dissolved in liquid ammonia possessed properties which were strictly analogous to those manifested by acids or bases in aqueous solutions, and that reactions took place between members of these two classes of substances which were essentially the same as neutralization reactions between acids and bases in water solutions. Thus sodium and potassium amides behave as bases when in solution in liquid ammonia, and acetamide and benzamide act as acids. The reactions between these substances may be represented by the equations

$$Na^+ + NH_2^- + CH_3CONH^- + H^{+*} = CH_3CONHNa + NH_3$$

$$K^+ + NH_2^- + C_6H_5CONH^- + H^+ = C_6H_5CONHK + NH_3 \; .$$

[1] E.W. Washburn; An Introduction to the Principles of Physical Chemistry; Second Edition. See pp. 361-2.

[2] Franklin and Kraus; Electrical Conductivity of Liquid Ammonia Solutions; American Chemical Journal, 23 , 277-313.

* This ion is no doubt solvated and representable by $(H \cdot NH_3)^+$.

These reactions are clearly analogous to the following ones in aqueous solutions

$$Na^+ + OH^- + CH_3COO^- + H^+ = CH_3COONa + H_2O$$

$$K^+ + OH^- + C_6H_5COO^- + H^+ = C_6H_5COOK + H_2O$$

General definitions which not only cover each of these cases equally well but also are entirely free from specifications as to the composition of electrolyte or solvent were set forth in a paper read at the Birmingham meeting of the American Chemical Society in the spring of 1922,* which contained the following statment: " An acid for any system involving an ionizing solvent is a substance which forms by its direct ionization a cation identical with the positive ion of the solvent, and a base is one which furnishes an anion which is the same as the negative ion of the solvent. If, then, there were brought together in such a solvent two substances, one giving the same cation as that of the solvent (the acid), and the other yielding the same anion as the solvent (the base), neutralization would take place with the formation of more of the solvent and a solution of a new salt."

Because of the great similarity between water and ammonia (their positive ions are identical and their negative ions have the element hydrogen in common), the study of these two systems cannot conclusively substantiate such

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* H.P.Cady and H.M.Elsey, A General Conception of Acids, Bases, and Salts.

a general conception of acids and bases. For this purpose the study of solutions in solvents which contain no hydrogen is obviously the most satisfactory.

Of all solvents containing no hydrogen, liquid sulfur dioxide appeared to be the most promising as a dissociative[1,2,3] medium in addition to being readily available and fairly convenient of manipulation. Consequently it was selected as the first solvent to be used in an effort to test out experimentally the above conception of acids and bases.

Ionization of sulfur dioxide may be considered to take place in one or more of the following ways:[1]

$$SO_2 = S^{++++} + 2\,O^{--}$$
$$3SO_2 = S^{++++} + 2\,SO_3^{--}$$
$$SO_2 = SO^{++} + O^{--}$$
$$2SO_2 = SO^{++} + SO_3^{--}$$

The last manner of ionization seems the most probable, at least as far as the primary dissociation is concerned; but according to either of the last two views thionyl chloride (assuming the dissociation $SOCl_2 = SO^{++} + 2Cl^-$) should act as an acid when dissolved in sulfur dioxide, while the sulfites (assuming the ionization $M_2SO_3 = 2M^+ + SO_3^{--}$ in the latter case and the dissociation $M_2SO_3 = 2M^+ + O^{--} + SO_2$ in the former)

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1. Walden and Centnerszwer; Flüssiges Schwefeldioxyd als Lösungsmittel; Zeitschrift f. phys. Chemie; 39 , 513-596.

2. Walden; Ueber ein neues, anorganisches, ionisirendes Lösungsmittel; Berichte; 32 , 2862-2871.

3. Walden; Uber abnorme Elektrolyte; Zeit. f. phys. Chemie; 43, 385-464.

should act as bases. While thionyl chloride was used as the hypothetical acid throughout the work on sulfur dioxide solutions, a number of sulfites were utilized in the basic rôle. The first of the latter was methyl ammonium sulfite, $(CH_3NH_2)_2SO_3$. This was prepared as follows: A measured volume of a strong aqueous solution of methyl amine was saturated with SO_2 gas and an equal volume of the untreated amine solution was then added; the liquid was evaporated to dryness over an electric lamp at a temperature of about 40° C.

A two-legged Pyrex tube of the type used by Franklin* in his work on chemical reactions in liquid ammonia was prepared and provided with a stopcock. About two grams of dry methylammonium sulfite were introduced into one leg and the end was sealed off. About one cubic centimeter of thionyl chloride was then poured into the other leg, and the end of this was likewise sealed off. A slow stream of SO_2 gas was allowed to pass through the apparatus during the introduction of materials and sealing. This was done not only to protect the materials from atmospheric moisture but also to sweep out the air so that sulfur dioxide could later be readily distilled into the tube. This addition of SO_2 by distillation was accomplished simply by placing the leg of the tube containing the sulfite in a freezing mixture of ice and salt and connecting the tube with a cylinder of commercial sulfur dioxide. When about fifteen cc. of SO_2

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* Franklin and Stafford; Reactions between Acid and Basic Amides in Liquid Ammonia; Amer. Chem. Jour.; 28, 83-107.

had distilled in the stopcock was turned and wired in place, and the connection with the cylinder was broken. The tube was removed from the freezing mixture, the SO_2 was warmed to approximately room temperature, and the liquid above the sulfite was poured over into the leg containing thionyl chloride. The sulfur dioxide was then distilled back into the sulfite compartment by placing that leg in the freezing mixture and the other in tepid water. The solvent was next warmed as before and poured off from the sulfite back into the thionyl chloride chamber. This process of alternate pouring and distillation of the SO_2 was continued until all the sulfite had dissolved and been poured over into the thionyl chloride. A white solid separated out in the $SOCl_2$ compartment, and this was purified by pouring off the supernatant liquid into the other leg. The SO_2 was distilled back as described above, and this washing with the solvent was repeated about six times. With all the washings collected in the original sulfite leg, the stopcock was turned and the sulfur dioxide allowed to evaporate. To make the removal of absorbed solvent as complete as possible, the tube was kept evacuated with a filter pump for at least fifteen hours. The leg containing the white solid was cut off from the rest of the apparatus, and the product was poured out into a weighing bottle and subjected to analysis.

The material was readily soluble in water. The absence of chlorides was shown by the failure of the aqueous solution, made slightly acid with nitric acid, to give a precipitate upon the addition of a solution of silver nitrate. A determination of nitrogen by the Kjeldahl method gave the following results:

Trial I

Weight of bottle & sample	10.9158 grams
" " "	10.7307 "
" " "	0.1851 "

Volume of 0.5 normal HCl placed in absorption flask: 45.00 cc.

Volume of 0.5 normal NaOH required for neutralization: 41.40 cc.

$$\frac{0.01401}{2}(45.00 - 41.40) = 0.0252 \text{ gm. of nitrogen}$$

(as ammonia) collected.

$$\frac{0.0252}{0.1851}100 = \underline{\underline{13.61}}\ \% \text{ of nitrogen in sample.}$$

Trial II

Weight of bottle & sample	10.7310 grams
Weight " "	10.5385 "
" " "	0.1925 "

Volume of 0.5 normal HCl: 45.00 cc.

" " " " NaOH: 41.27 "

$$\frac{0.01401}{2}(45.00 - 41.27) = 0.0261 \text{ gm. of nitrogen}$$

$$\frac{0.0261}{0.1925}(100) = \underline{13.53\ \%} \text{ of nitrogen.}$$

It is interesting to note that the percentage of nitrogen in a solvated substance of the constitution $(CH_3NH_3)_2SO_3 \cdot SO_2$ would be 13.45 %, which agrees fairly well with that found in the above product. The idea that this product was a solvated sulfite is supported by the observation that, while it gave tests for sulfites and primary amines just as did the original sulfite, the latter was appreciably soluble in sulfur dioxide whereas the product formed was practically insoluble in that liquid.

The failure of the reaction $(CH_3NH_3)_2SO_3 + SOCl_2 = CH_3NH_3Cl + 2\ SO_2$ to take place in liquid SO_2 made it seem advisable to work with the sulfite of a stronger base than methyl ammonium hydroxide. The caesium salt was chosen because of the unequaled basicity of that element.

Silver sulfite was prepared by the addition of a solution of silver nitrate to a solution of sodium sulfite. After thorough washing the precipitate was added in excess to a solution of caesium chloride (Merck). The silver chloride and excess silver sulfite were filtered off and the solution of caesium sulfite was evaporated to dryness by very gentle heating in a flask kept evacuated by a filter pump. The caesium sulfite was given an opportunity to react with thionyl chloride in a sulfur dioxide solution just as was methyl ammonium sulfite in the procedure described above. The Cs_2SO_3 was only slightly soluble in liquid SO_2, but by transferring repeated saturated portions of the solvent to the thionyl chloride compartment a white crystalline product virtually insoluble in SO_2 was obtained. After this solid was purified by repeated washing with sulfur dioxide, the solvent was removed as before and the product taken from the apparatus. This substance proved to be very easily soluble in water, and qualitative tests showed chlorides to be present in very considerable quantities and sulfites and sulfates to a smaller extent. A determination of chlorides by the Gooch crucible method gave the following result:

Weight of bottle and sample	13.7901 grams
" " "	13.1927 "
" " "	0.5974 "
Weight of crucible & AgCl	14.6920 grams
" " "	14.3333 "
" " " "	0.3587 "

$\frac{Cl}{AgCl}$ (0.3587) = 0.0886 gm. of chlorine

$\frac{0.0886}{0.5974}$ (100) = 14.84 % of chlorine. $\left(\frac{Cl}{CsCl} = 21.07\ \%\right)$

$\frac{Cl}{CsCl}$ = 0.2107. $\frac{0.0886}{0.2107}$ = 0.4200 gm. of CsCl to which the chlorine actually found would correspond.

$\frac{0.4200}{0.5974}$ (100) = 70.35 %, portion of sample which may have been caesium chloride.

An attempt was made to purify the above product by dissolving out the CsCl with liquid ammonia and recovering it by evaporation of the solvent; but none of the constituents of the sample appeared to be appreciably soluble in ammonia at its boiling point (-33.5°).

An analysis of the CsCl used in the preparation of the caesium sulfite used above gave this result:

Weight of bottle & sample	24.7360 grams
" " "	24.1792 "
" " "	0.5568 "
Weight of crucible & AgCl	15.1935 grams
" " "	14.7208 "
" " "	0.4727 "

$\frac{Cl}{AgCl}$ (0.4727) = 0.1169 gm. of chlorine

$\frac{0.1169}{0.5568}$ (100) = 20.99 % of chlorine.

In order to make an effort to secure more conclusive evidence of the reaction $Cs_2SO_3 + 2\,SOCl = 2\,CsCl + 2\,SO_2$, it seemed wise to use a sample of caesium sulfite prepared by a more satisfactory method than that involving the rather unstable silver sulfite. Since no caesium salts were available which could be readily converted into the sulfite it was decide to start with the mineral pollucite, $H_2Al_2Cs_2Si_5O_{15}$. Instead of making the extraction of caesinm by the expensive and tedious hydrofluoric acid treatment devised by Chabrie*, the following method was used:

A sample of pollucite said to contain 28 % Cs_2O was

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* Contributions à l'Étude du Caesium; Comptes Rendus; 133, 295-297.

was ground so as to pass through a "150 mesh". A kilogram of the powder was digested for about fifteen hours with 400 grams of concentrated sulfuric acid and about 100 grams of water. (This was the minimum quantity of water required to thoroughly wet the entire mass after the addition of the acid). The digested material was heated with about one and one-half liters of water for an hour or more — until the liquid was practically saturated with caesium alum. The solution was filtered by suction through a Buchner funnel while hot, and the residue was treated with another portion of water. This process was repeated until the filtrate, upon concentration and cooling, gave no appreciable yield of alum crystals. The caesium alum which separated from various portions of the filtrate was purified by three recrystallizations from water. The crystals finally obtained when dissolved in hot water gave no flame test for sodium, no spectroscopic test for any alkali metals (other than sodium and caesium) or alkaline earths, and no test for iron with potassium ferrocyanide or potassium sulfocyanate. While the solubility of the alum in hot water is not great, the solubility in cold water is so much less* (at 20° is probably not more than one-twentieth as great as at 100°) that crystallization from water never-

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* Carl Setterberg; Ueber die Darstellung von Rubidium- und Caesiumverbindungen; Annalen der Chemie; 211 , 100-116.

theless furnishes a good method for the formation and purification of the compound.

One hundred grams of the purified caesium alum were dissolved in hot water, and 120 grams of $Ba(OH)_2 \cdot 8H_2O$ were then added . The primary reaction taking place under these conditions is, of course, the following:

$$CsAl(SO_4)_2 + 2\ Ba(OH)_2 = 2\ BaSO_4 + CsOH + Al(OH)_3$$

The precipitated barium sulfate was filtered off, but the aluminum hydroxide could not be thus removed because of its solubility in CsOH:

$$CsOH + Al(OH)_3 = CsAlO_2 + 2\ H_2O$$

Consequently a stream of carbon dioxide was passed into the filtrate until it no longer gave a reaction alkaline to phenolphthalein, due to the conversion of the carbonates first formed into hydrogen carbonates:

$$2\ CsAlO_2 + 3\ H_2O + CO_2 = Cs_2CO_3 + 2\ Al(OH)_3;$$

$$Cs_2CO_3 + H_2O + CO_2 = 2\ CsHCO_3.$$

The excess barium hydroxide added above was, of course, affected as follows:

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$$

$$BaCO_3 + H_2O + CO_2 = Ba(HCO_3)_2$$

The precipitate was filtered off and the filtrate heated to boiling in order to decompose the hydrogen carbonates and make complete the precipitation of the excess barium.

$$2\ CsHCO_3 = Cs_2CO_3 + H_2O + CO_2$$

$$Ba(HCO_3)_2 = BaCO_3 + H_2O + CO_2.$$

The precipitate was removed by filtration, and the filtrate was evaporated to a volume of about fifteen cc. On cooling and standing long white crystals of caesium carbonate were very slowly formed. The flame spectrum of the product contained no visible lines except that of sodium (asbestos was used to hold the solution being tested) and the two bright blue lines of caesimm. The flame coloration obtained by heating a clean platinum wire that had been dipped into the solution was a beautiful blue, showing that sodium was not present in essential quantities.

The following method* was used in preparing anhydrous caesium sulfite from the carbonate. To five grams of Cs_2CO_3 there were added 250 cc. of absolute alcohol and eight cc. of water. As the mixture was heated the carbonate melted under the liquid before dissolving. The solution was divided into two equal parts, and one portion was heated to boiling under a reflux condenser and treated with a stream of sulfur dioxide until it was thoroughly saturated, thus forming the hydrogen sulfite:

$$Cs_2CO_3 + 2\ SO_2 + H_2O \quad = \quad 2\ CsHSO_3 + CO_2$$

To the solution of the acid sulfite the second portion of caesium carbonate in alcohol was added. The mixture was heated gently to evaporate off the the alcohol and complete the reaction $2\ CsHSO_3 + Cs_2CO_3 = Cs_2SO_3 + H_2O + CO_2$.

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* Chabrie; Contribution à l'Étude du Caesium; Comptes Rendus; 133 , 295-297.

The sulfite was dried over sulfuric acid in a vacuum. About a gram of the dry product was placed in one leg of a bent tube of the type described above, and thionyl chloride was poured into the other leg it was intended to use a safe excess of $SOCl_2$ but delay in sealing off one end of the tube permitted volatilization to an unknown extent. About fifteen cc. of liquid SO_2 was distilled into the sulfite leg, allowed to become saturated with the sulfite, poured over into the thionyl chloride compartment, and then distilled back. This process was repeated until practically all of the sulfite had been transferred to the $SOCl_2$ leg. The white solid which separated out in the latter compartment was finally washed with SO_2 by reversing the direction of distillation. The product was removed from the tube, dried over H_2SO_4 in a vacuum, heated to 110° for at least an hour, and a portion of it was dissolved in water and analyzed for chlorine content by the Gooch crucible method for soluble chlorides.

Weight of bottle & sample	10.6612 grams
" " "	10.5370 "
" " "	0.1242 "
Weight of crucible & AgCl	14.3429 grams
" " "	14.2501 "
" " "	0.0928 "

$\frac{Cl}{AgCl}$ (0.0928) = 0.02295 gm. of chlorine

$\frac{0.02295}{0.1242}$ (100) = 18.48 % of chlorine.

Trial II

Weight of bottle & sample	10.5363 grams
" " "	10.4131 "
" " "	0.1232 "
Weight of crucible & AgCl	14.4349 grams
" " "	14.3429 "
" " "	0.0920 "

$\frac{Cl}{AgCl}$ (0.0920) = 0.02275 gm. of chlorine

$\frac{0.02275}{0.1232}$ (100) = 18.47 % of chlorine. ($\frac{Cl}{CsCl}$ = 21.07 %)

Qualitative tests showed some sulfite to be present in the product; consequently it seemed reasonable to suppose that thionyl chloride had not actually been present in excess and to expect that a product higher in chlorine content would be obtained in case of such an excess.

Another quantity of caesium sulfite was prepared by the method outlined above. A solution of this compound in liquid sulfur dioxide was added to an excess of thionyl chloride in the same manner as in previous trials. The white crystalline solid which separated out in the $SOCl_2$ was washed with repeated portions of SO_2, removed from the tube, dried over sulfuric acid in a vacuum, heated to about 110° for more than an hour, and subjected to analysis.

Trial I

Weight of bottle and sample	13.1194 grams
" " "	12.9837 "
" " "	0.1357 "

Weight of crucible & AgCl 14.5482 grams

" " " 14.4349 "

" " " 0.1133 "

$\frac{Cl}{AgCl}$ (0.1133) = 0.02802 gm. of chlorine

$\frac{0.02802}{0.1357}$ (100) = 20.66 % of chlorine.

Trial II

Weight of bottle and sample 12.9824 grams

" " " 12.8364" "

" " " 0.1218 "

Weight of crucible & AgCl 14.6699 grams

" " " 14.5481 "

" " " 0.1218 "

$\frac{Cl}{AgCl}$ (0.1218) = 0.0301 gm. of chlorine

$\frac{0.0301}{0.1460}$ (100) = 20.63 % of chlorine. $\left(\frac{Cl}{CsCl} = 21.07\ \%\right)$

An analysis of the solid material left in the sulfite compartment after the washing of the product in the other leg and evaporation of the solvent resulted as follows:

Weight of bottle & sample 13.8472 grams

" " " 13.6156 "

" " " 0.2316 "

Weight of crucible & AgCl 14.8342 grams

" " " 14.6697 "

" " " 0.1645 "

$\frac{Cl}{AgCl}$ (0.01645) = 0.0406 gm. of chlorine

$\frac{0.0406}{0.2316}(100) = \underline{17.53}$ % of chlorine.

Qualitative tests on the product from the thionyl chloride compartment failed to show the presence of anioms other than the chloride or of cations other than caesium. Moreover it was observed that the substance readily absorbed moisture. Consequently it seemed proable that a higher and more nearly correct value for the chlorine content would be obtained after more thorough drying of the product. After being heated at 140-150° for about five hours a sample gave this analysis:

Weight of bottle & sample	12.0395 grams
" " "	11.8318 "
" " "	0.2077 "
Weight of crucible & AgCl	15.0482 grams
" " "	14.8720 "
" " "	0.1762 "

$\frac{Cl}{AgCl}(0.1762) = 0.04357$ gm. of chlorine

$\frac{0.04357}{0.2077}(100) = 20.99$ % of chlorine.

Trial II

Weight of bottle and sample	11.8318 grams
" " "	11.6873 "
" " "	0.1445 "
Weight of crucible and AgCl	15.1698 grams
" " "	15.0473 "
" " "	0.1225 "

$$\frac{Cl}{AgCl}(0.1225) = 0.03028 \text{ gm. of chlorine}$$

$$\frac{0.03028}{0.1445}(100) = 20.97\ \% \text{ of chlorine.} \left(\frac{Cl}{CsCl} = 21.07\%\right)$$

The results of the last determination seem to establish in a satisfactory manner that the reaction

$$SOCl_2 + Cs_2SO_3 = 2\ CsCl + 2\ SO_2$$

does take place in liquid sulfur dioxide and that in the presence of an excess of thionyl chloride it goes from left to right practically completely. There is clearly an analogy between this reaction, represented ionically, and the one by which caesium chloride is formed from caesium hydroxide and hydrogen chloride in the water system. $H^+ + Cl^- + Cs^+ + OH^- = Cs^+ + Cl^- + H_2O$

$$SO^{++} + 2\ Cl^- + 2\ Cs^+ + SO_3^{--} = 2\ Cs^+ + 2\ Cl^- + 2\ SO_2$$

It was decided to repeat the above procedure using silver sulfite in the place of caesium sulfite. A stream of SO_2 gas was passed into a strong aqueous solution of silver nitrate until precipitation was complete. The white crystalline product was washed repeatedly with water by decantation until the excess* SO_2 was completely removed . As much water as possible was eliminated by filtering and pressing the precipitate between layers of dry filter paper. The remainder of the moisture was removed by drying to constant weight over sulfuric acid, much of the

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* Gmelin Kraut's Handbuch der anorganische Chemie, Band II, Abteilung I; 46.

time under reduced pressure. All of the work of preparation was done by artifical light, and the sulfite was not exposed to daylight until dry;and not to direct sunlight then. When sulfur dioxide was distilled in upon some of the sulfite placed in one leg of a bent tube, the solid failed to dissolve to an appreciable extent. The SO_2 was repeatedly warmed with the sulfite, poured over into the thionyl chloride compartment and distilled back; but not only did the sulfite in the first compartment fail to undergo visible diminution, but also nothing separated out in the $SOCl_2$ leg. To make the trial with silver sulfite still more unsatisfactory this compound underwent gradual decomposition, and in the course of a few days became quite dark in color.

An attempt was next made to bring about a reactinn between potassium sulfite and thionyl chloride in sulfur dioxide. The anhydrous sulfite was prepared as follows:* About fifty grams of stick potassium hydroxide were dissolved in the minimum quantity of water at room temperature, and the dissolved oxygen was removed from the solution by passing a stream of natural gas through it for more than two hours. The solution was divided into two equal parts; one of them was saturated with sulfur dioxide, thus forming the acid sulfite; then the other portion of

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* Gmelin Kraut's Handbuch der anorganischen Chemie, Band II, Abteilung I; 46.

the hydroxide solution was added to form normal potassium sulfite. The resulting solution was evaporated to dryness at a temperature of about 80° in a flask kept evacuated by a good filter pump. After making sure that the sulfite was dried to constant weight some of it was placed in a bent tube with sulfur dioxide and thionyl chloride as before. The potassium sulfite did not appear to be as soluble as caesium sulfite in liquid SO_2, but by saturating repeated portions of the solvent with the sulfite and pouring them over into the thionyl chloride compartment the quantity of K_2SO_3 in its leg was made to appreciably diminish and a white crystalline solid separated out in the $SOCl_2$ compartment. After this product was washed with SO_2, removed from the tube, and heated at 140-150° for about five hours to remove all volatile impurities, a determination of the chlorides present was made.

Trial I

Weight of bottle & sample	13.5003 grams
" " "	13.2986 "
" " "	0.2017 "
Weight of crucible & AgCl	15.8937 grams
	15.5090 "
	0.4557 "

$$\frac{Cl}{AgCl}(0.3847) = 0.09517 \text{ gm. of chlorine}$$

$$\frac{0.09517}{0.2017}(100) = 47.18\ \%\text{ of chlorine}$$

Trial II

Weight of bottle & sample	13.2986 grams
" " "	13.0600 "
" " "	0.2386 "
Weight of crucible & AgCl	16.3494 grams
" " "	15.8937 "
" " "	0.4557 "

$\frac{Cl}{AgCl}$ (0.4557) = 0.1127 gm of chlorine

$\frac{0.1127}{0.2386}$ (100) = 47.25 % of chlorine. $\left(\frac{Cl}{KCl} = 47.558\%\right)$

The material which remained in the sulfite compartment after completing the washing of the other product and evaporating off the solvent was removed from the tube, heated at about 140° for over three hours and analyzed for chlorine content.

Trial I

Weight of bottle & sample	12.6035 grams
" " "	12.3857 "
" " "	0.2178 "
Weight of crucible & AgCl	16.7121 grams
" " "	16.3493 "
" " "	0.3628 "

$\frac{Cl}{AgCl}$ (0.3628) = 0.0897 gm. of chlorine

$\frac{0.0897}{0.2178}$ (100) = 41.20 % of chlorine.

Trial II

Weight of bottle & sample	12.3857	grams
" " "	12.1263	"
" " "	0.2594	"
Weight of crucible & AgCl	17.1457	grams
" " "	16.7121	"
" " "	0.4336	"

$\frac{Cl}{AgCl}(0.4336) = 0.1072$ gm. of chlorine

$\frac{0.1072}{0.2594}(100) = \underline{41.28\ \%}$ of chlorine.

The product (from the thionyl chloride compartment) was found to contain a trace of sulfate, and a similar trace proved to be present in the potassium sulfite used in the experiment. Consequently, although the chlorine percentage found above was more than 0.3 % below the value for potassium chloride (47.558 %), it is highly probable that virtually all the sulfite present reacted with thionyl chloride — in the presence of an excess of the latter — according to the equation:

$$2\ K^{+} + SO_3^{--} + SO^{++} + 2\ Cl^{-} = 2\ KCl + 2\ SO_2.$$

It was hoped to supplement the results obtained in the case of sulfur dioxide solutions with work on another solvent containing no hydrogen. The work of Lenher[*] with selenium oxybromide made it seem possible that the following reactions might be made to take place in that solvent:

$$SeOBr_2 \quad K_2CO_3 = CO_2 \quad K_2SeO_2Br_2$$

$$K_2SeO_2Br_2 \quad SeBr_4 = 2\ KBr \quad 2\ SeOBr_2.$$

Some selenium in the form of a powder was dried at 150° and then ignited in a stream of oxygen dried by passage through P_2O_5. An 800cc. Kjeldahl flask was used as ignition chamber. The product had a marked pinkish tint, due no doubt to the presence of some of the unburned element in the oxide. Fifty grams of the dried and powdered element were added to seventy grams of the oxide in the reaction chamber; then 200 grams of bromine (dried and purified by distillation over P_2O_5 and KBr) were slowly run in from a dropping funnel. The flask was cooled while the first and more vigorous reaction was taking place: $Br_2 + 2\ Se = Se_2Br_2$. After the completion of the addition of bromine and the formation of $SeBr_4$ ($Se_2Br_2 = 3\ Br_2 + 2\ SeBr_4$), the flask was heated gently (below 100°) in order to melt together the SeO_2 and $SeBr_4$ and so bring about the reaction $SeO_2 + SeBr_4 = 2\ SeOBr_2$. For some reason free bromine proved to be present in the selenium oxybromide thus prepared. Due to this difficulty and to the inconvenience of working with a solvent which is a solid at temperatures below 43°, the work with this compound was abandoned in favor of phosphorus oxychloride.

With potassium carbonate and phosphorus oxychloride it seemed possible that the following reactions might be made to take place.

$$POCl_3 + K_2CO_3 = CO_2 + K_2PO_2Cl_3$$

$$K_2PO_2Cl_3 + PCl_5 = 2\ POCl_3 + 2\ KCl.$$

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* Selenium Oxybromide; Jour. of Am. Chem. Soc.; 44, 1668.

When some stock $POCl_3$ was added to K_2CO_3 which had been dried at 140-150° for about two hours, a rather vigorous reaction took place and carbon dioxide was given off together with fumes of the oxychloride. Some of the oxychloride* was dried by allowing it to stand over P_2O_5 for several hours and then distilling it from the same drying agent, collecting the fraction which came over at 107-108°. When this dried $POCl_3$ was brought in contact with K_2CO_3 there was no apparent reaction whatever. The carbonate was not appreciably soluble in the oxychloride. The reaction first obtained was no doubt due to the presence of water in the $POCl_3$:

$$3\ H_2O + POCl_3 = 3\ HCl + H_3PO_4.$$

$$2\ HCl + K_2CO_3 = 2\ KCl + CO_2 + H_2O.$$

Sodium peroxide was next tried out with phosphorus oxychloride, the hypothetical reactions in this case being

$$2\ POCl_3 + 2\ Na_2O_2 = O_2 + 2\ Na_2PO_2Cl_3.$$

$$Na_2PO_2Cl_3 + PCl_5 = 2\ POCl_3 + 2\ NaCl.$$

When a little stock sodium peroxide (J.T.Baker) was added to some of the dried oxychloride a very vigorous reaction took place and oxygen was evolved. The heat liberated was so great that the containing test tube was cracked in some of the trials. A white solid remained in the tube under the excess oxychloride. The liquid was heated to boiling for several minutes, and then, although the

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* Walden; Einige Molekulargrossen in Phosphoroxychlorid als kryoskopischen Solvens; Zeit. f. anorg. Chem. 68, 307.

solid appeared to be practically insoluble in the oxychloride, the hot liquid was poured off into another test tube and phosphorus pentachloride was added. Upon further heating all the pentachloride dissolved, and upon cooling the liquid a small quantity of a rather finely divided white solid separated out. This product was removed from the tube, heated for about three hours at 130-150°, and subjected to a chloride determination.

Weight of bottle & sample	13.3949 grams
" " "	13.3654 "
" " "	0.0295 "
Weight of crucible & AgCl	15.1408 grams
" " "	15.0926 "
" " "	0.0482 "

$$\frac{Cl}{AgCl}(0.0482) = 0.01193 \text{ gm. of chlorine}$$

$$\frac{0.01193}{0.0295}(100) = 40.45\ \% \text{ of chlorine.}$$

$$\left(\frac{Cl}{NaCl} = 0.6065\right)$$

Some of the original product of the reaction of $POCl_3$ with Na_2O_2 was heated for several hours at 130-150° to remove all traces of the oxychloride. The material proved to be rather slowly but quite extensively soluble in water. The solution was very faintly acid to litmus . A typical silver chloride precipitate was formed when silver nitrate was added to some of the solution made acid with nitric acid. A light white precipitate appeared when a solution of calcium chloride was added, but upon adding two or three drops of potassium hydroxide solution a heavy white precipitate came down. A determination was made for chlorides by the Gooch crucible method, and one of phosphates by precipitation with "magnesia mixture" and ignition to magnesium pyrophosphate. Also an estimation of the sodium content was made by adding an excess of barium hydroxide, filtering off the precipitate, passing in carbon dioxide to throw down the excess barium, filtering again, adding an excess of HCl, evaporating to dryness, and finally weighing the residue as sodium chloride.

Weight of bottle & sample	14.4829 grams
" " "	14.1224 "
" " "	0.3605 "
Weight of crucible & AgCl	15.5090 grams
" " "	15.1410 "
" " "	0.3680 "

$$\frac{Cl}{AgCl}(0.3680) = 0.0910 \text{ gm. of chlorine}$$

$$\frac{0.0910}{0.3605}(100) = 25.22\ \% \text{ of chlorine.}$$

$$\left(\frac{3\ Cl}{Na_2PO_2CL_3} = 0.4938 \right)$$

Weight of bottle & sample	14.1228 grams
" " "	13.9713 "
" " "	0.1515 "
Weight of crucible & $Mg_2P_2O_7$	8.4372 grams
" " "	8.3958 "
" " "	0.0414 "

$$\frac{2\ P}{Mg_2P_2O_7}\ (0.0414) \quad = \quad 0.0115 \text{ gm of phosphorus}$$

$$\frac{0.0115}{0.1515}\ (100) \quad = \quad \underline{7.61}\ \% \quad \text{of phosphorus.}$$

$$\left(\frac{P}{Na_2PO_2Cl_3} \quad = \quad 0.1442 \right)$$

Weight of bottle and sample	13.9713 grams
" " "	13.4331 "
" " "	0.5382 "
Weight of dish & NaCl	10.3945 grams
	10.0020 "
	0.3925 "

$$\frac{Na}{NaCl}\ (0.3925) \quad = \quad 0.1548 \text{ gm. of sodium}$$

$$\frac{0.1548}{0.5382}\ (100) \quad = \quad 28.75\ \% \quad \text{of sodium.}$$

$$\left(\frac{2\ Na}{Na_2PO_2Cl_3} \quad = \quad 0.2137 \right)$$

The above results clearly do not check with the calculated values for the anticipated compound. Moreover the results do not correspond to any simple or reasonable formula. The material analyzed was no doubt a mixture, complicated perhaps by the presence of impurities in the sodium peroxide used.

S U M M A R Y

1, A general definition of acids and bases applicable to solutions in any dissociating solvent is enunciated.

2. This conception is given experimental support by a study of the reactions between thionyl chloride and the sulfites of caesium and potassium in liquid sulfur dioxide.

3. It is found that methyl ammonium sulfite fails to react with thionyl chloride in liquid sulfur dioxide, and that the reaction of silver sulfite under the same conditions cannot readily be determined because of its insolubility and instability.

4. Some work is done with selenium oxybromide and phosphorus oxychloride, but no results of apparent significance are obtained.

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