A GENERAL CONCEPTION OF
ACIDS AND BASES

By

Dale H. Puffett

Submitted to the Department of Chemistry and to the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Master's degree.

Approved by:

[Signature]
Department of Chemistry

May 25, 1923
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.
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Statement of Conception</td>
<td>2</td>
</tr>
<tr>
<td>Methyl Ammonium Sulfite</td>
<td>4</td>
</tr>
<tr>
<td>Caesium Sulfite I</td>
<td>7</td>
</tr>
<tr>
<td>Pollucite</td>
<td>9</td>
</tr>
<tr>
<td>Caesium Sulfite II</td>
<td>12</td>
</tr>
<tr>
<td>Caesium Sulfite III</td>
<td>14</td>
</tr>
<tr>
<td>Silver Sulfite</td>
<td>17</td>
</tr>
<tr>
<td>Potassium Sulfite</td>
<td>18</td>
</tr>
<tr>
<td>Selenium Oxybromide</td>
<td>22</td>
</tr>
<tr>
<td>Phosphorus Oxychloride</td>
<td>23</td>
</tr>
<tr>
<td>Summary</td>
<td>27</td>
</tr>
<tr>
<td>Bibliography</td>
<td>28</td>
</tr>
</tbody>
</table>
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

\[
\begin{align*}
\text{Na}^+ + \text{NH}_2^- + \text{CH}_3\text{CONH}^- + H^+ & = \text{CH}_3\text{CONHNa} + \text{NH}_3 \\
\text{K}^+ + \text{NH}_2^- + \text{C}_6\text{H}_5\text{CONH}^- + H^+ & = \text{C}_6\text{H}_5\text{CONHK} + \text{NH}_3
\end{align*}
\]


\(^2\) Franklin and Kraus; Electrical Conductivity of Liquid Ammonia Solutions; American Chemical Journal, 23, 277-313.

\(^*\) This ion is no doubt solvated and representable by \((H\cdot\text{NH}_3)^+\).
These reactions are clearly analogous to the following ones in aqueous solutions

$$\text{Na}^+ + \text{OH}^- + \text{CH}_3\text{COO}^- + \text{H}^+ = \text{CH}_3\text{COONa} + \text{H}_2\text{O}$$

$$\text{K}^+ + \text{OH}^- + \text{C}_6\text{H}_5\text{COO}^- + \text{H}^+ = \text{C}_6\text{H}_5\text{COOK} + \text{H}_2\text{O}$$

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 statement: "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

*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 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:

\[
\begin{align*}
S_2O_2 &= S^{++} + O^{--} + 2O^- \\
3SO_2 &= S^{+++} + 2SO_3^- \\
SO_2 &= SO^{++} + O^{--} \\
2SO_2 &= SO^{++} + SO_3^{--}
\end{align*}
\]

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 \( M_2SO_3 = 2M^+ + 2O^- + SO_2 \) in the former)


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

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 sulfate, \((\text{CH}_3\text{NH}_2)_2\text{SO}_3\). This was prepared as follows: A measured volume of a strong aqueous solution of methyl amine was saturated with \(\text{SO}_2\) 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 sulfate 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 \(\text{SO}_2\) 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 \(\text{SO}_2\) 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 \(\text{SO}_2\)

* 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 \( \text{SO}_2 \) 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 \( \text{SO}_2 \) was continued until all the sulfite had dissolved and been poured over into the thionyl chloride. A white solid separated out in the \( \text{SOCl}_2 \) compartment, and this was purified by pouring off the supernatant liquid into the other leg. The \( \text{SO}_2 \) 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**

<table>
<thead>
<tr>
<th>Weight of bottle &amp; sample</th>
<th>10.9158 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10.7307 &quot;</td>
</tr>
<tr>
<td></td>
<td>0.1851 &quot;</td>
</tr>
</tbody>
</table>

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.

\[
\frac{0.0252}{0.1851} \times 100 = 13.61 \% \text{ of nitrogen in sample.}
\]

**Trial II**

<table>
<thead>
<tr>
<th>Weight of bottle &amp; sample</th>
<th>10.7310 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10.5385 &quot;</td>
</tr>
<tr>
<td></td>
<td>0.1925 &quot;</td>
</tr>
</tbody>
</table>

Volume of 0.5 normal HCl: 45.00 cc.

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

\[
\frac{0.0261}{0.1925} \times 100 = 13.53 \% \text{ of nitrogen.}
\]
It is interesting to note that the percentage of nitrogen in a solvated substance of the constitution \((\text{CH}_3\text{NH}_3)_2\text{SO}_3\cdot\text{SO}_2\) 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 \((\text{CH}_3\text{NH}_3)_2\text{SO}_3 + \text{SOCl}_2 = \text{CH}_3\text{NH}_3\text{Cl} + 2\text{SO}_2\) to take place in liquid \(\text{SO}_2\) 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 \(\text{Cs}_2\text{SO}_3\) was only slightly soluble in liquid \(\text{SO}_2\), but by transferring repeated saturated portions of the sol-
vent to the thionyl chloride compartment a white crystalline product virtually insoluble in $\text{SO}_2$ 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

\[
\begin{array}{c|c}
& 13.7901 \text{ grams} \\ 
\hline
\text{bottle} & 13.1927 \\ 
\text{sample} & 0.5974 \\
\end{array}
\]

Weight of crucible & AgCl

\[
\begin{array}{c|c}
& 14.6920 \text{ grams} \\ 
\hline
\text{crucible} & 14.3333 \\ 
\text{AgCl} & 0.3587 \\
\end{array}
\]

\[
\frac{\text{Cl}}{\text{AgCl}} = \frac{0.3587}{0.5974} = 0.0886 \text{ gm. of chlorine}
\]

\[
\frac{0.0886}{0.5974} \times 100 = 14.84\% \text{ of chlorine.} \quad \left( \frac{\text{Cl}}{\text{CsCl}} = 21.07\% \right)
\]

\[
\left( \frac{\text{Cl}}{\text{CsCl}} = 0.2107, \quad \frac{0.0886}{0.2107} = 0.4200 \text{ gm. of} \right)
\]

\[
\left( \frac{\text{CsCl}}{0.5974} \right) \text{ to which the chlorine actually found would correspond.}
\]

\[
\left( \frac{0.4200}{0.5974} \times 100 = 70.35\%, \text{ portion of sample} \right)
\]

\[
\left( \frac{0.5974}{0.4200} \right) \text{ which may have been caesium chloride.}
\]

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:

<table>
<thead>
<tr>
<th>Description</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of bottle &amp; sample</td>
<td>24.7360 grams</td>
</tr>
<tr>
<td>&quot;</td>
<td>24.1792 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.5568 &quot;</td>
</tr>
<tr>
<td>Weight of crucible &amp; AgCl</td>
<td>15.1935 grams</td>
</tr>
<tr>
<td>&quot;</td>
<td>14.7208 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.4727 &quot;</td>
</tr>
</tbody>
</table>

\[
\frac{Cl}{AgCl} = \frac{0.4727}{0.5568} = 0.1169 \text{ gm. of chlorine}
\]

\[
\frac{0.1169 \times 100}{0.5568} = 20.99\% \text{ of chlorine.}
\]

In order to make an effort to secure more conclusive evidence of the reaction \( \text{Cs}_2\text{SO}_3 + \text{SOCl} = 2 \text{CsCl} + 2 \text{SO}_2 \), 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, \( \text{H}_2\text{Al}_2\text{Cs}_2\text{Si}_5\text{O}_{15} \).

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% \( \text{Cs}_2\text{O} \) was

---

* 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-

* 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)\(_2\)·8H\(_2\)O were then added. The primary reaction taking place under these conditions is, of course, the following:

\[ \text{CsAl(SO}_4\text{)}\text{2} + 2 \text{Ba(OH)}\text{2} = 2 \text{BaSO}_4 + \text{CsOH} + \text{Al(OH)}\text{3} \]

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

\[ \text{CsOH} + \text{Al(OH)}\text{3} = \text{CsAlO}_2 + 2 \text{H}_2\text{O} \]

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:

\[ 2 \text{CsAlO}_2 + 3 \text{H}_2\text{O} + \text{CO}_2 = \text{Cs}_2\text{CO}_3 + 2 \text{Al(OH)}\text{3} ; \]
\[ \text{Cs}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 = 2 \text{CsHCO}_3 . \]

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

\[ \text{Ba(OH)}\text{2} + \text{CO}_2 = \text{BaCO}_3 + \text{H}_2\text{O} \]
\[ \text{BaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 = \text{Ba(HCO}_3\text{)}\text{2} \]

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.

\[ 2 \text{CsHCO}_3 = \text{Cs}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]
\[ \text{Ba(HCO}_3\text{)}\text{2} = \text{BaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 . \]
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 caesium. 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 Cs₂CO₃ 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:

$$\text{Cs}_2\text{CO}_3 + 2 \text{SO}_2 + \text{H}_2\text{O} = 2 \text{CsHSO}_3 + \text{CO}_2$$

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

$$2 \text{CsHSO}_3 + \text{Cs}_2\text{CO}_3 = \text{Cs}_2\text{SO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

* 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 SOCl₂ but delay in sealing off one end of the tube permitted volatilization to an unknown extent. About fifteen cc. of liquid SO₂ 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 SOCl₂ leg. The white solid which separated out in the latter compartment was finally washed with SO₂ by reversing the direction of distillation. The product was removed from the tube, dried over H₂SO₄ 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.

<table>
<thead>
<tr>
<th>Weight of bottle &amp; sample</th>
<th>10.6618 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot; &quot;</td>
<td>10.5370 &quot;</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.1242 &quot;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight of crucible &amp; AgCl</th>
<th>14.3429 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot; &quot;</td>
<td>14.2501 &quot;</td>
</tr>
<tr>
<td>&quot; &quot;</td>
<td>0.0928 &quot;</td>
</tr>
</tbody>
</table>

\[
\frac{\text{Cl}}{\text{AgCl}} = \frac{0.0928}{0.02235} = \text{18.45% of chlorine}
\]
Trial II

Weight of bottle & sample 10.5363 grams
  "        "  10.4131 "
  "        "  0.1232 "

Weight of crucible & AgCl 14.4349 grams
  "        "  14.3429 "
  "        "  0.0920 "

\[ \frac{Cl}{AgCl} = \frac{0.0920}{0.1232} = 0.02275 \text{ gm. of chlorine} \]

\[ \frac{0.02275 (100)}{0.1232} = 18.47\% \text{ 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 "

Trial II

Weight of bottle & sample 10.5363 grams
  "        "  10.4131 "
  "        "  0.1232 "

Weight of crucible & AgCl 14.4349 grams
  "        "  14.3429 "
  "        "  0.0920 "

\[ \frac{Cl}{AgCl} = \frac{0.0920}{0.1232} = 0.02275 \text{ gm. of chlorine} \]

\[ \frac{0.02275 (100)}{0.1232} = 18.47\% \text{ of chlorine. ( } \frac{Cl}{CsCl} = 21.07\% \) \]
Weight of crucible & AgCl 14.5482 grams
" " " 14.4349 "
" " " 0.1133 "

\[
\frac{Cl}{AgCl} (0.1133) = 0.02802 \text{ gm. of chlorine}
\]

\[
0.02802 (100) = 20.66\% \text{ of chlorine.}
\]

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 "

\[
\frac{Cl}{AgCl} (0.1218) = 0.0301 \text{ gm. of chlorine}
\]

\[
0.0301 (100) = 20.63\% \text{ of chlorine. (} \frac{Cl}{CsCl} = 21.07\% \text{)}
\]

An analysis of the solid material left in the sulfite compartment after the washing of the product in the pH meter 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 "

\[
\frac{Cl}{AgCl} (0.01645) = 0.0406 \text{ gm. of chlorine}
\]
$$0.0406 \ (100) = \frac{17.53 \% \ of \ chlorine}{0.2316}$$

Qualitative tests on the product from the thionyl chloride compartment failed to show the presence of anions other than the chloride or of cations other than caesium. Moreover it was observed that the substance readily absorbed moisture. Consequently it seemed probable 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:

<table>
<thead>
<tr>
<th>Weight of bottle &amp; sample</th>
<th>12.0395 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11.8318</td>
</tr>
<tr>
<td></td>
<td>0.2077</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Weight of crucible &amp; AgCl</th>
<th>15.0482 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14.8720</td>
</tr>
<tr>
<td></td>
<td>0.1762</td>
</tr>
</tbody>
</table>

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

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

**Trial II**

<table>
<thead>
<tr>
<th>Weight of bottle and sample</th>
<th>11.8318 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11.6873</td>
</tr>
<tr>
<td></td>
<td>0.1445</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight of crucible and AgCl</th>
<th>15.1698 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15.0473</td>
</tr>
<tr>
<td></td>
<td>0.1225</td>
</tr>
</tbody>
</table>
\[
\frac{Cl (0.1225)}{AgCl} = 0.03028 \text{ gm. of chlorine}
\]

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

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

\[
SOCl_2 + Cs_2SO_3 = 2 \text{CsCl} + 2 \text{SO}_2
\]

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.

\[
H^+ + Cl^- + Cs^+ + OH^- = Cs^+ + Cl^- + H_2O
\]

\[
SO^{2+} + 2 \text{Cl}^- + 2 \text{Cs}^+ + SO_3^- = 2 \text{Cs}^+ + 2 \text{Cl}^- + 2 \text{SO}_2
\]

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

\* 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 artificial 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 $\mathrm{SO}_2$ 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 $\mathrm{SOCl}_2$ 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 reaction 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

* 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**

<table>
<thead>
<tr>
<th>Description</th>
<th>Weight (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of bottle &amp; sample</td>
<td>13.5003</td>
</tr>
<tr>
<td>&quot;</td>
<td>13.2986</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.2017</td>
</tr>
<tr>
<td>Weight of crucible &amp; AgCl</td>
<td>15.8937</td>
</tr>
<tr>
<td>&quot;</td>
<td>15.5090</td>
</tr>
<tr>
<td>&quot;</td>
<td>0.4557</td>
</tr>
</tbody>
</table>

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

$\frac{0.09517 \times 100}{0.2017} = 47.18 \% \text{ of chlorine}$
Trial II

Weight of bottle & sample 13.2986 grams
  "  "  "  13.0600  "
  "  "  "  0.2386  "

Weight of crucible & AgCl 16.3494 grams
  "  "  "  15.8937  "
  "  "  "  0.4557  "

\[ \frac{\text{Cl} (0.4557)}{\text{AgCl}} = 0.1127 \text{ gm of chlorine} \]
\[ \frac{0.1127 (100)}{0.2386} = 47.25\% \text{ of chlorine.} \left( \frac{\text{Cl}}{\text{KCl}} = 47.558\% \right) \]

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  "

\[ \frac{\text{Cl} (0.3628)}{\text{AgCl}} = 0.0897 \text{ gm. of chlorine} \]
\[ \frac{0.0897 (100)}{0.2178} = 41.20\% \text{ of chlorine.} \]
Trial II

Weight of bottle & sample 12.3857 grams
  "  "  "  12.1263 "
  "  "  "  0.2594 "

Weight of crucible & AgCl 17.1457 grams
  "  "  "  16.7121 "
  "  "  "  0.4336 "

\[
\frac{\text{Cl}}{\text{AgCl}} = \frac{0.4336}{0.2594} = 0.1072 \text{ gm. of chlorine}
\]

\[
\frac{0.1072 (100)}{0.2594} = 41.28\% \text{ of chlorine.}
\]

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:

\[
2 K^+ + SO_3^- + SO_4^{2-} + 2 \text{Cl}^- = 2 \text{KCl} + 2 \text{SO}_2
\]

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\textsuperscript{*} with selenium oxybromide made it seem possible that the following reactions might be made to take place in that solvent:

\[
\text{SeOBr}_2 + K_2CO_3 = CO_2 + K_2\text{SeO}_2\text{Br}_2
\]

\[
K_2\text{SeO}_2\text{Br}_2 + \text{SeBr}_4 = 2 \text{KBr} + 2 \text{SeOBr}_2
\]
Some selenium in the form of a powder was dried at 150° and then ignited in a stream of oxygen dried by passage through $\text{P}_2\text{O}_5$. 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 $\text{P}_2\text{O}_5$ and $\text{KBr}$) were slowly run in from a dropping funnel. The flask was cooled while the first and more vigorous reaction was taking place: $\text{Br}_2 + 2 \text{Se} = \text{Se}_2\text{Br}_2$. After the completion of the addition of bromine and the formation of $\text{SeBr}_4$ ($\text{Se}_2\text{Br}_2 = 3 \text{Br}_2 + 2 \text{SeBr}_4$), the flask was heated gently (below 100°) in order to melt together the $\text{SeO}_2$ and $\text{SeBr}_4$ and so bring about the reaction $\text{SeO}_2 + \text{SeBr}_4 = 2 \text{SeOBr}_2$.

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.

$$\text{POCl}_3 + \text{K}_2\text{CO}_3 = \text{CO}_2 + \text{K}_2\text{PO}_2\text{Cl}_3$$

$$\text{K}_2\text{PO}_2\text{Cl}_3 + \text{PCl}_5 = 2 \text{POCl}_3 + 2 \text{KCl}.$$
When some stock \( \text{POCl}_3 \) was added to \( \text{K}_2\text{CO}_3 \) 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 \( \text{P}_2\text{O}_5 \) for several hours and then distilling it from the same drying agent, collecting the fraction which came over at 107-108°. When this dried \( \text{POCl}_3 \) was brought in contact with \( \text{K}_2\text{CO}_3 \) 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 \( \text{POCl}_3 \):

\[
3 \text{H}_2\text{O} + \text{POCl}_3 = 3 \text{HCl} + \text{H}_3\text{PO}_4.
\]

\[
2 \text{HCl} + \text{K}_2\text{CO}_3 = 2 \text{KCl} + \text{CO}_2 + \text{H}_2\text{O}.
\]

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

\[
2 \text{POCl}_3 + 2 \text{Na}_2\text{O}_2 = \text{O}_2 + 2 \text{Na}_2\text{PO}_2\text{Cl}_3.
\]

\[
\text{Na}_2\text{PO}_2\text{Cl}_3 + \text{PCl}_5 = 2 \text{POCl}_3 + 2 \text{NaCl}.
\]

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

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 "

\[
\frac{\text{Cl}}{\text{AgCl}} (0.0482) = 0.01193 \text{ gm. of chlorine} \\
\frac{0.01193 (100)}{0.0295} = 40.45 \% \text{ of chlorine.}
\]

\[
\left\{ \begin{array}{c}
\frac{\text{Cl}}{\text{NaCl}} = 0.6065 \\
\end{array} \right\}
\]

Some of the original product of the reaction of POC\textsubscript{3}\text{Cl} with Na\textsubscript{2}O\textsubscript{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.

<table>
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<th>Weight of bottle &amp; sample</th>
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<tr>
<td>&quot; &quot; &quot;</td>
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<tr>
<td>&quot; &quot; &quot;</td>
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<table>
<thead>
<tr>
<th>Weight of crucible &amp; AgCl</th>
<th>15.5090 grams</th>
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<tr>
<td>&quot; &quot; &quot;</td>
<td>15.1410 &quot;</td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>0.3680 &quot;</td>
</tr>
</tbody>
</table>

\[
\frac{\text{Cl} (0.3680)}{\text{AgCl}} = \frac{0.0910 \text{ gm. of chlorine}}{0.3605}
\]

\[
0.0910 (100) = 25.22 \% \text{ of chlorine.}
\]

\[
\left( \frac{3 \text{ Cl}}{\text{Na}_2\text{P}_2\text{Cl}_3} \right) = 0.4938
\]

<table>
<thead>
<tr>
<th>Weight of bottle &amp; sample</th>
<th>14.1228 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot; &quot; &quot;</td>
<td>13.9713 &quot;</td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>0.1515 &quot;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight of crucible &amp; Mg\text{2P}_2\text{O}_7</th>
<th>8.4372 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot; &quot; &quot;</td>
<td>8.3958 &quot;</td>
</tr>
<tr>
<td>&quot; &quot; &quot;</td>
<td>0.0414 &quot;</td>
</tr>
</tbody>
</table>
\[
\frac{2 \text{ P}}{\text{Mg}_2\text{P}_2\text{O}_7} (0.0414) = 0.0115 \text{ gm of phosphorus}
\]

\[
\frac{0.0115}{0.1515} (100) = 7.61\% \text{ of phosphorus.}
\]

\[
\left( \frac{\text{P}}{\text{Na}_2\text{P}_2\text{O}_2\text{Cl}_3} = 0.1442 \right)
\]

Weight of bottle and sample 13.9713 grams

Weight of dish & NaCl 10.3945 grams

Na (0.3925) = 0.1548 gm. of sodium

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

\[
\left( \frac{2 \text{Na}}{\text{Na}_2\text{P}_2\text{O}_2\text{Cl}_3} = 0.2137 \right)
\]

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.
SUMMARY

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.
BIBLIOGRAPHY

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

Walden und Centnerschwer, Flüssiges Schwefeldioxyd als Lösungsmittel; Zeitschrift für physikalische Chemie; 39, 513-596.


Franklin, Electrical Conductivity of Liquid Sulfur Dioxide Solutions; Journal of Physical Chemistry; 15, 675-697.


Cady, Electrolysis and Electrolytic Conductivity of Certain Substances Dissolved in Liquid Ammonia; Jour. of Phys. Chem.; 1, 707-713.

Franklin and Kraus, Liquid Ammonia as a Solvent; Amer. Chem. Jour.; 20, 820-836.


Franklin and Kraus, Properties of Liquid Ammonia; Amer. Chem. Jour.; 21, 8-14.
Franklin and Kraus, Electrical Conductivity of Liquid Ammonia Solutions; Amer. Chem. Jour.; 23, 277-313.


Franklin, Reactions in Liquid Ammonia; Jour. of Amer. Chem. Society; 27, 820-851.


Chabrié, Contribution à l'Étude du Caesium; Comptes Rendus; 132, 295-297.

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


Walden, Einige Molekulargrossen in Phosphoroxychlorid als kryoskopischen Solvens; Zeit. f. anorganische Chemie; 68, 307.