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A Study of the Co-Gelation of Silica and Titania

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A STUDY
of
THE CO-GELATION OF SILICA AND TITANIA

Theodore Male '43

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This thesis is presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry, by

Thistou Male

Approved by

Charles B. Hurd

April 14, 1943
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INTRODUCTION

Silica gels have been the object of extensive research. Titania gels have been the object of limited research, but they have been reported as made successfully. The most commonly used silicate solutions are basic and the titanium solutions are acidic. Acids are used to control the gelation of silica, and bases are used to control the gelation of titania. The imagination is taxed only slightly in assuming as plausible the use of the acid titanate solution to control the gelation of silica and the basic silicate solution to control the gelation of titania, and thereby produce a mixed gel. If the pH regions of gelation overlay, the above theory should be true in practice. The goal of this research was to make a gel containing both silica and titania, and, if possible, study some of its properties and characteristics.
The mixing of a solution of sodium silicate and an acid solution to form a gel has been the object of considerable study. Silica gels have been known for over a century. During that time, numerous investigators have continued the studies and broadened the field.

The formation of the gel takes a finite time, and the relation of setting time with variable factors has been studied. The variable factors include pH, temperature, concentration of silica, presence and concentration of other salts, other foreign substances, and the acid used to contribute the hydrogen ion. Other related experiments include the migration of ions through the gels and the effect of setting upon electrical conductivity.

The present and most accepted theory of gel formation and structure is the "fibrillar" or "brush-heap" concept of Zsigmondy (1) which presupposes a condensation of ortho-silicic acid molecules and the consequent splitting-out of water molecules. The condensation forms long threads or fibrils which intermesh and form a semi-rigid mass containing the water split out during the process.
The rate of set can be controlled by the hydrogen ion concentration, and it has been shown by Hurd and Letteron (2) that the most rapid setting, with other variables fixed, occurs in the region of pH 7. However, gels can be made in the basic regions, as well as in the very acid regions. Hurd and Letteron have shown that increase of temperature decreases the time of set. Hallstrom (3) has shown that the addition of salts, with the exception of sodium di-acid phosphate, accelerates the gel-formation in acid mixtures. The salts Hallstrom used include sodium chloride, potassium chloride, lithium chloride, sodium nitrate, sodium sulphate, potassium nitrate and potassium sulphate, and all of the salts accelerated the gel-formation with only slight changes of pH. Sodium di-acid phosphate, di-sodium acid phosphate and sodium oxalate, however, cause large pH changes. Clum (4) has shown that silicic acid gels have high elasticity, but low tensile strength. Hurd (5) has worked out a relation between the logarithm of the time of set and the reciprocal absolute temperature, and found an "energy of activation" of 16,600 calories.

The above citations show the extent of the work upon silicic acid gels. In contrast, let us look at the work upon titania gels.
Titania gels have been known since 1823, when Rose (6) prepared a gel by treating a fusion of titania and sodium carbonate with hydrochloric acid, filtering, and allowing the filtrate to stand. The result was a soft titania "jelly". A few other workers have experimented with titania, the work of Klosky and Marzano (7) being well recognized. They prepared a sodium titanate by the thorough fusion of sodium carbonate and titania in the ratio of mole for mole. A fine sandy substance was obtained by pouring the fusion into cold water. Their method was almost identical to that of Rose. They treated the resulting product with concentrated hydrochloric acid, forming a lemon-canary colored solution. They found that the above procedure has to be carried out in the cold because titania has two modifications, the alpha or ortho and the beta or meta forms. The ortho form changes spontaneously with time to the meta, and the change is rapid when heated. The two forms are chemically the same. Physically, the beta form is insoluble in water and in most acids except sulphuric, whereas the alpha form is soluble in dilute acids. To bring about the correct conditions for gelation, the pH must be raised from its very acid state. They tried adding ammonium hydroxide, sodium hydroxide, potassium carbonate, sodium carbonate and ammonium carbonate.
The best results were obtained with the carbonates, the potassium carbonate forming the clearest gels. Considerable difficulty was experienced with precipitation of ortho-titanic acid upon addition of hydroxide or carbonate. The neutralizing agent was added drop by drop and shaken to peptize any precipitate. They reported the formation of firm titania gels.

Recently, work has been carried out by Hurd, Jacober, and Godfrey (8) concerning the effect of temperature on the time of set. The method of Klosky and Marzano was used in their experiments. The conclusion drawn was that increase of temperature decreased the time of set, the same as silica. Increase of pH of the acidic mixtures also decreased the time of set, as well as with increase of titania content. The energy of activation was found to be approximately 22,000 calories. The gels of titania are, for comparative concentrations, much softer than silica gels, and the titania gels have a surface skin that is tougher than the gel interior. The formation of the skin during setting interferes with the accurate determination of the time of set. Silica gels fail to show a skin effect, and, if present, the skin does not alter measurably the time of set. Titania gels break down, after being allowed to stand after setting, to a granular precipitate and liquid.
The precipitate is considered to be the meta modification of the ortho-titanic acid.

The above is almost a complete picture of the limited work upon titanic-acid or titania gels. As far as is known, the co-gelation of silica and titania has never been tried.
THEORETICAL

Titanium is an element in the fourth group of the periodic table and has a common valence of plus four, although compounds are readily made in which titanium has a valence of plus two or three. It forms the well known simple compounds, like the dioxide, tetrachloride, sulphate, acetate, oxychloride, and titanates. It has properties similar to silicon, and its hydrous oxides react with alkalis or acids to give salts. The hydroxide, therefore, is amphoteric, as is to be expected. Titanium salts in acid solution frequently form hydro-sols, and if made alkaline, form hydrogels.

Silicon is also an element in the fourth group of the periodic table, with a common valence of plus four. The metal forms the dioxide, tetrachlorides, nitrides, and silicates, as well as many lesser important compounds. The property of silicon, pertinent to this research, is that alkaline silicate sols will gel if made acidic.

Titania gels are formed by mixing a basic solution and an acid titanium solution. The common titanium solutions used are sodium titanate dissolved in concentrated hydrochloric acid which essentially reacts to form titanium oxychloride, and the solutions of titanium tetra-
chloride, titanium acetate, and possibly titanium sulphate. The sulphate solution is quite unstable, due to the sulphate ion. The basic solutions that are usually added to increase the pH are carbonates; other solutions, yet untried, may be equally as effective. The hydroxides of sodium, potassium and ammonium have shown tendencies toward precipitating the hydrous titanium oxide. The most favorable pH for gelation has been shown to be slightly above 2.75.

Silica gels are formed by mixing a silicate solution and an acid. Sodium silicate (water-glass) solution has shown extremely good results, and the acids used include acetic, hydrochloric, and sulphuric acids. Gelation of silica occurs over the wide pH range of 1 to 10. A favorable concentration of silicate solution has been one which is about 1.5 normal in sodium hydroxide equivalent when the soda to silica ratio is about 1 to 3.25.

In choosing a solution of titanium and a solution of silicate that can be mixed to produce a co-gel, several factors must be considered. The pH regions of gelation must overlap so that it is possible for each solution to gel as though each were independent of the other. The concentrations of each must be favorable for gelation. Lastly, the effect of the ions present
on gelation must be ascertained. That is; will the ions from the silicate solution interfere with or aid the gelation of titania, and will those of titania influence the gelation of silica?

The effects of the chloride, acetate and sulphate ions on the gelation of silica from sodium silicate solutions have been found to be favorable toward gelation and have caused only slight pH changes. Therefore sodium silicate is the logical compound to contribute the silica. Also, the sodium and silicate ions are the only two ions in the sodium silicate solution.

The logical choice of a titanium solution might seem to be the sodium titanate dissolved in concentrated hydrochloric acid. The sodium titanate reacts to form titanyl chloride. However, the solution contains other sodium ions and excess chloride ions, in addition to the titanium and oxychloride ions. With excess chloride ion in the solution, it would be impossible to determine whether the gelation of silica is influenced by the excess acid or by the titanium compound. It is better to forgo the use of the better known sodium titanate solution for a solution containing only the ions of the titanium compound.

Gels from titanium tetrachloride solutions have been produced and it is the next best solution to se-
lect, since it readily dissolves in water to give titanium and chloride ions. The compound was not available because of war time restrictions, and attempts to make it resulted in failure.

Titanium acetate was unavailable.

The poorest choice is normal titanium sulphate, because the sulphate ion contributes toward instability of the titanium solution. However, the sulphate ion is favorable toward gelation of silica, and it is the only anion present in the titanium sulphate solution. The effect of the sodium and silicate ions on the gelation of titania is one of the unsettled questions because experiments have not been tried. The sodium ion shows least effect on the titania gelation, shown by the favorable mixing of titanium solutions with sodium carbonate and the unfavorable mixing with sodium hydroxide. The concentration of titanium sulphate is also an undetermined variable factor.

The object of this research is to mix the sodium silicate solution and titanium sulphate solutions to produce an mixed gel (co-gel). The titania gels and silica gels have similar, yet decidedly different physical appearances, and the assumption could be made that the co-gel would result with the individual appearances modified. Titania gels are much softer than
silica gels, and titania gels have a surface skin that is not apparent with silica gels. The physical appearance is one indication of the mixture of the two gels and may be a good check, but a more reliable method for determining the presence of both gels simultaneously should be used.

To prove the presence of both gels in the mixed gel, gels of each should be made separately, with conditions as though both were present. This means that dual experiments should be performed, one with the sodium silicate and titanium sulphate mixture, and a similar one with an acid replacing the sulphate solution. Similarly, dual experiments should be made replacing the silicate solution with a base.

The hydrolysis of titanium sulphate to titanium dioxide and sulphuric acid, as is indicated by the charring of paper in contact with the compound, shows its the similarity of titanium sulphate to sulphuric acid. Thus, the logical acid to substitute for the titanium sulphate solution in the dual experiments is sulphuric acid. This is purely theoretical and has not yet been proven valid.

The sodium silicate solution is essentially a solution of soda and silica. Therefore, the sodium hydroxide is the logical base to use in the substitution of
sodium silicate solution in the dual experiment. The concentrations of sodium hydroxide and sodium silicate, in sodium hydroxide equivalent, should be the same. Similarly, the titanium sulphate and sulphuric acid solutions should be equivalent in hydrogen ion concentration.

If gels form with titanium and silicate solutions mixed, and gels also form with the respective acid and base substitutions, it can safely be assumed that the gel is a mixture of hydrated silica and hydrated titan- ia. Confirmatory tests should be made by close examination of the gel as to structure, rigidity, elasticity, and the scattering of light through the gel, the latter being perhaps the least known and studied, although offering a unique analysis.
EXPERIMENTAL

Titanium sulphate cake, produced by the Titanium Alloy Manufacturing Company of Niagara Falls, was used throughout the experiments as the initial titanium compound. It was not analyzed for purity, but appeared to contain water, probably by adsorption.

A preliminary run was performed by dissolving varying amounts of titanium sulphate in water, and then adding potassium carbonate solution to each sample with resulting precipitation of insoluble titanium dioxide. The solutions were allowed to stand and evaporate. The clear portion of the solution, containing 5 grams of sulphate per 50 milliliters of water, gelled after standing about a week, and became firm but non-vibrant. A cube of one centimeter dimensions was analyzed for titania by weighing, igniting, washing out the salts and igniting to titanium dioxide, whence the gel was calculated to contain the equivalent of 290 grams of titanium sulphate per liter of the original solution. The titanium sulphate solution was then made by arbitrarily dissolving 150 grams of the cake per liter of water, and filtering from the finely divided white residue. The filtrate, when analyzed by precipitation of the titanium hydroxide and heating to the dioxide, proved to be 0.367 molar or
1.467 normal with respect to the hydrogen ion concentration.

The silicate solution was made with "B" brand sodium silicate, produced by the Philadelphia Quartz Company. Two liters of the concentrated silicate were dissolved in fourteen liters of distilled water. The analysis by titrating the alkaline silicate with sulphuric acid, using modified methyl orange as indicator, showed a normality of 0.578 in sodium hydroxide equivalent, which is approximately 0.939 molar in silica.

The solutions were pipetted into 100 milliliter beakers and mixed by pouring back and forth twice. The mixtures of high silica content gelled rapidly, while those of high titania content took longer. (Table 1.) The pH tests of all mixtures, using the quinhydrone potentiometer, showed an acid range that was below a pH of 1. The gels with higher titania content were clearer, softer, less-vibrant than the high-silica-content gels, and a surface skin, characteristic of titania gels, appeared with the gels of highest titania content, and also with those gels which were diluted with water. Throughout this experiment the beakers remained uncovered and the gels were allowed to evaporate.

An experiment concerning the effect of evaporation on setting was conducted by studying the same mixtures,
and noting the time of set and gel characteristics when uncovered, covered with a watchglass, and when enclosed in a desiccator filled with water to maintain a saturated atmosphere. Solutions (1) and (6) of Table 1. were used, and the uncovered gels confirmed the results of Table 1., forming clearly, firmly, and non-vibrant. The gels (Table 2.) containing the higher silica content all gelled before the others under correspondingly similar conditions, but the gels covered by the watchglass and in the desiccator filled with water took considerably longer to form. In the two latter cases, the gels were vastly different from the first, being softer, glossy white, opaque, and "similar to firm egg white". The similarity of the gels covered by the watchglass and in the desiccator confirmed the practicability of using the convenient watchglass method of preventing evaporation.

The first two series of experiments revealed one weakness; the solutions were too acid for rapid gelation of either titania or silica, since the normality of the titanium sulphate was almost three times the normality of the silicate. The ratio of silica equivalent in the soda-silica solution to the titania equivalent in the titanium sulphate solution was about 2 to 1.

The normality of the silicate was then increased to 1.278. A solution of 1.278 normal sodium hydroxide was
then made as the substitute referred to in the theoretical and a 1.467 normal H$_2$SO$_4$ solution was also made as substitute for the titanium sulphate. The results of Table 3. show general silica gel characteristics of firmness and opalescence. The pH control was slightly better than previous, but the silica content far exceeded the titania content in the ratio (gel 4) of 6 to 1.

Similar experiments were performed substituting the sodium hydroxide for the sodium silicate, but the results were discouraging. A precipitate settled out in each case. In this and the following series of experiments, the quantities of the solutions used were measured in a quantitative way with graduated cylinders, and the pH tests were made with universal indicator. Table 4. shows the results of the sodium hydroxide substitution.

A solution of sodium silicate was then made by adding sodium hydroxide to the sodium silicate solution until the ratio of soda to silica was about 1 to 1. The normality was about three times that of the titanium sulphate, and the silica content was about six times that of the titania. The silicate solution was diluted to three times its original volume to make the normalities approximately equal.

In all cases, the base was added to the acid and
the precipitate of titanic acid formed was dissolved by motor stirring. The reverse, addition of acid to base, always resulted in precipitation of insoluble titanium dioxide. The results are shown in Table 5.

Attempts to make pure titania gels by adding potassium carbonate to the titanium sulphate were futile, and always ended with a precipitate. Sen (9) suggests the addition of dextrose to the solutions, which is intended to act as a peptizing agent. Identical tests with and without dextrose contradicted his alleged results. However, these tests were not exhaustive.

An attempt to make a pure titania gel with titanium tetrachloride solution also failed. The tetrachloride was made by precipitating titanium hydroxide from the sulphate solution by adding ammonium hydroxide. The precipitate was filtered, washed with very dilute ammonia water to dissolve and separate adsorbed sulphate ions, and the precipitate then dissolved with concentrated hydrochloric acid. Dilute hydrochloric acid would not dissolve the hydroxide, which could mean that the ortho form of the hydrous oxide was changing to the meta form.
CONCLUSIONS

The problem of the co-gelation of silica and titania remains unsolved. The experiments of this limited research confirm the results of other workers concerning the instability of titanium sulphate solutions. It is possible but difficult to form a gel from titanium sulphate solutions, and the difficulty is increased when uncontrollable factors are introduced, such as the presence of another gel system.

A comparison of the results of similar mixtures of sodium silicate with titanium sulphate and sodium hydroxide with titanium sulphate shows that the gel formed must be a silica gel, since none forms in the latter mixture. The gel characteristics also seem to be those of silica. The formation of a surface skin on some gels offers the one disturbing note in the following conclusion. The obvious conclusion is that the sodium silicate solution is a good choice to contribute silica, since the results appear positive toward silica. The negative results of titania do not necessarily mean that the sulphate solution will not work; the concentration of the sulphate solution may have been incorrect for gelation.

The precipitation difficulties with titanium sulphate solutions are barriers perhaps not insurmountable,
but certainly not meriting the time of further research when other titanium compounds offer greater possibilities. Further research toward the making of a co-gel of titania and silica should be conducted using titanium tetrachloride and sodium silicate or titanium acetate and sodium silicate. Either of the above compounds of titanium has shown good gelation characteristics.

The formation of a surface skin, characteristic of titania gels, with some of the mixtures in this research, confirms, in this author's mind, the possibility of forming a co-gel of silica and titania.
<table>
<thead>
<tr>
<th>Gel No.</th>
<th>Sodium Silicate (cc)</th>
<th>Titanium Sulphate (cc)</th>
<th>Water (cc)</th>
<th>pH</th>
<th>Gel Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>25</td>
<td>0</td>
<td>&gt;1</td>
<td>non-vibrant, firm clear</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>20</td>
<td>0</td>
<td>&gt;1</td>
<td>slightly vibrant, spongy-firm, opalescent</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>15</td>
<td>0</td>
<td>1.8</td>
<td>slightly vibrant, firm, opalescent</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>10</td>
<td>0</td>
<td></td>
<td>vibrant, firm opalescent</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>30</td>
<td>0</td>
<td>&gt;1</td>
<td>slightly vibrant, spongy-firm, opalescent</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>35</td>
<td>0</td>
<td>&gt;1</td>
<td>soft, very spongy, surface skin, clear</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>40</td>
<td>0</td>
<td>&gt;1</td>
<td>liquid</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>20</td>
<td>5</td>
<td>&gt;1</td>
<td>very soft, opalescent</td>
</tr>
<tr>
<td>9</td>
<td>25</td>
<td>15</td>
<td>10</td>
<td>&gt;1</td>
<td>slightly vibrant, slightly soft, surface skin, opalescent</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>25</td>
<td>5</td>
<td>&gt;1</td>
<td>surface skin, slightly soft, clear</td>
</tr>
</tbody>
</table>
TABLE 2

<table>
<thead>
<tr>
<th></th>
<th>Open</th>
<th>Covered with watchglass</th>
<th>Desiccator containing water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel No.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Sodium silicate (cc.)</td>
<td>25</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>Titanium sulphate (cc.)</td>
<td>25</td>
<td>35</td>
<td>25</td>
</tr>
<tr>
<td>Time of set (days)</td>
<td>7</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>Percent loss by weight</td>
<td>49</td>
<td>61</td>
<td>11</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear, non-vibrant, firm</td>
<td>Glossy white vibrant, firm</td>
<td>&quot;like egg white&quot;</td>
</tr>
</tbody>
</table>
**TABLE 3**

<table>
<thead>
<tr>
<th>Gel No.</th>
<th>Sodium Silicate</th>
<th>Titanium Sulphate</th>
<th>Approximate time of set</th>
<th>pH</th>
<th>Gel Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 cc.</td>
<td>40 cc.</td>
<td>-</td>
<td>&gt;1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>35</td>
<td>-</td>
<td>&gt;1</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>30</td>
<td>-</td>
<td>&gt;1</td>
<td>after 4 hrs.; solution slightly cloudy</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>25</td>
<td>4 hrs</td>
<td>-</td>
<td>white, opaque, non-vibrant, soft with slightly firm surface</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>20</td>
<td>immediate</td>
<td>-</td>
<td>non-vibrant, firm white, opaque</td>
</tr>
<tr>
<td>6</td>
<td>35</td>
<td>15</td>
<td>immediate</td>
<td>-</td>
<td>non-vibrant, firm white, opaque</td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>10</td>
<td>1 hr.</td>
<td>basic</td>
<td>white, opaque slightly soft very vibrant</td>
</tr>
</tbody>
</table>

Sodium silicate - 1.278 normal in sodium hydroxide equivalent

Titanium sulphate - 1.467 normal in hydrogen ion concentration
<table>
<thead>
<tr>
<th>Gel No.</th>
<th>Titanium Sulphate</th>
<th>Sodium Hydroxide</th>
<th>Water</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>30 cc.</td>
<td>2 cc.</td>
<td>18 cc.</td>
<td>precipitate formed</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>0</td>
<td>30</td>
<td>precipitate formed</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>5</td>
<td>55</td>
<td>precipitate formed</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>20</td>
<td>0</td>
<td>precipitate formed</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>60</td>
<td>precipitate formed</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>2.5</td>
<td>37.5</td>
<td>precipitate formed</td>
</tr>
</tbody>
</table>

Gel No 6, dilution of the titanium sulphate with water, shows vividly the instability of the titanium sulphate solution.
### TABLE 5

<table>
<thead>
<tr>
<th>Gel No.</th>
<th>Titanium Sulphate</th>
<th>Sodium Silicate</th>
<th>Water</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30 cc.</td>
<td>10 cc.</td>
<td>20 cc.</td>
<td>precipitate (acid) formed</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>10</td>
<td>0</td>
<td>gel</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>10</td>
<td>20</td>
<td>mushy precipitate (basic solution)</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>10</td>
<td>20</td>
<td>gel (acid solution)</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>10</td>
<td>20</td>
<td>very soft gel with a tough skin formed after weeks of setting (acid solution)</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY

1. Hurd
   Chem. Reviews, 22: 403-22 (1938)

2. Hurd & Letteron
   J. Phys. Chem., 36 (part 1)
   604-15 (1932)

3. Hallstrom
   Thesis, Union College (1936)

4. Glum
   Thesis, Union College (1940)

5. Rose
   Gilbert's Ann., 73: 76 (1823)

6. Hurd
   Chem. Reviews, 22: 403-22 (1938)

7. Klosky & Marzano

8. Hurd, Jacober & Godfrey
   (1941)

9. Sen
   Schreibtschrift fur Anorganische
   und Allgemeine Chemie, 174: 61-74
   (1928)

GENERAL REFERENCES

Thornton
   Titanium - Monograph Series (1927)

Weiser
   Inorganic Colloid Chemistry - Vol. 2
   (1935)

Weiser & Milligan

Rose
   Liebig's Ann., 53: 267 (1845)

Melor
   A Comprehensive Treatise on Inorganic
   and Theoretical Chemistry - Vol. 7
   (1927)

Fraser
   Thesis, Union College (1937)

Jacober
   Thesis, Union College (1938)

Godfrey
   Thesis, Union College (1939)

Caven
   Text-Book on Inorganic Chemistry - Vol. 5
   Edited by J. Newton Friend (1921)