

THE COMPLEX COMPOUND THEORY OF COLLOIDAL OXIDES

T. H. WHITEHEAD

Department of Chemistry, University of Georgia, Athens, Georgia

Received July 29, 1937

INTRODUCTION

The term "colloidal oxide" needs some explanation because it is an inexact expression. It refers to those colloidal dispersions which are produced by the hydrolysis of a metallic salt or by the peptization of the hydrous oxide of a metal. These are not truly dispersions of the oxide, because it has been shown by numerous investigators that a stable hydrosol cannot be produced without the presence of ions other than those of the metal and hydroxyl and hydrogen. Thus Thomas and Frieden (23) showed that so-called ferric oxide hydrosols always contain the anion of the ferric salt from which they were precipitated. The same thing is true for the hydrosols of aluminum, beryllium, chromium, gold, platinum, silver, and tin. Sorum (19) is unique in claiming to have prepared a colloidal dispersion of pure ferric oxide. Since the preponderance of evidence points to a complex dispersed phase in the so-called metallic oxide hydrosols, an attempt is made in this paper to present a theory concerning the structure of the micelles which is more in accord with observed facts. Although this theory may have more general applications in the field of colloid chemistry, no attempt is made here to extend the theory beyond the experimental facts upon which it is based.

Much controversy has arisen over the structure of these colloidal oxides and the cause of their stability in aqueous media. This may be due to the fact that the composition of the dispersed phase is not such that it can be represented by a simple formula. This was pointed out also for crystalloid oxides by van Bemmelen (32) as early as 1888. Furthermore, it has been shown repeatedly that the properties and composition of colloidal oxides depend upon the experimental conditions under which the oxides are prepared. The concentration of the metallic salt, the manner of preparation, the temperature of preparation, the anion of the metallic salt, and the age of the hydrosol are all important factors in determining the composition and properties of the hydrosol. These facts have led many investigators to conclude that the dispersed phase is not a true

compound, since its composition is so easily varied. Those investigators who do not think of the colloidal oxide as a compound have applied descriptive terms which are equally vague. Thus hydrosols which are readily precipitated by electrolytes are called *hydrophobic*, while those that are difficult to precipitate with electrolytes are called *hydrophilic*. This would indicate two distinct classes of colloids, but there are many colloidal oxides which are intermediate in properties between the typical *hydrophobic* and the typical *hydrophilic* colloids. These terms are used in this paper in a relative sense only, to describe rather than to classify colloids.

SOME PREVIOUS THEORIES

The first important work in this field was done by Thomas Graham (6) in 1862, when he prepared the hydrous oxides and hydrosols of aluminum, chromium, iron, molybdenum, tin, titanium, and tungsten. From this time on investigators too numerous to list have prepared colloidal oxides and studied their properties.

The early studies on these systems indicated that the behavior of colloidal oxides differed markedly from that of most crystalloid solutions. The variation in freezing point, boiling point, osmotic pressure, and viscosity with increasing concentration was so different from the behavior of true solutions that many doubted if these colloidal dispersions followed the laws of physics and chemistry. Attempts to determine the molecular weight of the dispersed phase often gave values as high as 800 for the colloidal oxides and 100,000 for hydrophilic colloids like albumins dispersed in water. This led to the belief that no formula would express the composition of the dispersed phase, and so physical principles were used to explain them, rather than chemical principles.

It is therefore logical that the first theories concerning the stability of hydrosols were almost purely physical. One of the first theories was based upon the facts of electrostatic attraction and repulsion. Thus, if the dispersed particles were postulated to be charged particles of similar sign, then mutual repulsion would prevent their coagulation and settling out. The origin of this electric charge was assumed to be due to frictional forces within the sol. The precipitation of the colloid was explained as being due to the discharge of the electric charge on the particles. This theory had the advantage of being simple, but it was shown to be untenable by the now classic papers of Smoluchowski (18) and of Porter and Hedges (15).

Another approach to an electrical theory of stability was begun by Helmholtz (8), who postulated the existence of an electrical double layer around the dispersed particles. Helmholtz derived his theory from data on electrokinetic behavior of colloidal dispersions. According to this

theory each particle of the dispersed phase carries an electrical charge on its surface, and surrounding this is a layer of solution which has an equal and opposite electric charge, similar to the relation between the plates of a charged condenser. Naturally this sets up a potential difference; according to Helmholtz this electrical potential is responsible for the stability of the dispersion, and the reduction of this potential to zero will cause precipitation of the dispersed phase. The rigid nature of the Helmholtz double layer has been modified by Gouy (5) and by Debye and Hückel (4) to agree more closely with modern ionic theories. According to their modifications the electrical layer of the solution is more diffuse and decreases in strength as the distance from the particle increases.

Still another theory based upon electrical potential and osmotic force has been advanced by John Arthur Wilson (35). Wilson assumes that a dispersed particle is a rigid sphere which may become electrically charged by attracting to itself ions from the surrounding medium. Thus a charged layer of ions surrounds each particle. Wilson further assumes that the ions bound to the particles are balanced by ions of opposite charge in the solution, producing an electrical double layer. Now, assuming that the ions on the particles are not free to move while those in the solution are free to move, Wilson invokes the Donnan equilibrium and shows that there will be more mobile ions within the double layer than outside of it when equilibrium is established. As a result of this unequal concentration of mobile ions inside and outside the double layer a potential difference and osmotic pressure will be set up. Since this will happen around each particle there will be a repulsive force between them, and this will result in a stable dispersion. The addition of other electrolytes will upset this equilibrium, reduce the potential, and cause precipitation. Although Wilson derived his theory for a hydrophobic dispersion such as a gold sol prepared by the Bredig arc method, he applies it to hydrophilic colloids such as gelatin dispersed in water.

Finally there is the very popular theory of adsorption. This theory postulates that a dispersed particle may attach to itself either positive or negative ions according to the preference which the particles have for such ions. These ions are said to be adsorbed by the dispersed particles. Ions of equal and opposite charge remain in the dispersion medium and act as balancing or contra ions, thus keeping the solution as a whole electrically neutral. This theory is most convenient, since a particle may at one time prefer positive ions and at another time negative ions. It has been given wide publicity by Bancroft (1) and others. It does not differ essentially from the previous theories in explaining the stability and precipitation of colloids, since it postulates mutual repulsion of charged particles as the cause of stability and the neutralization of these charges as the cause of precipitation.

It will be noted that all of these theories have one common element in them and all have the same inherent weakness. If these theories are correct, then three facts should be consistently found experimentally. First, oppositely charged particles should mutually precipitate when added in equivalent amounts. Second, particles of the same electric sign should stabilize each other, or at least not precipitate each other. Third, no stable dispersion should be possible unless the dispersed particles are electrically charged.

To consider the first point mentioned above, the work of Schulze (16) may be cited. Schulze studied the effect of ions in precipitating arsenious sulfide hydrosol, and since the sol was negative he placed the emphasis on cations. Schulze thought that he discovered a consistent relation between the valence of cations and their precipitating power for negative sols. This rule, which is sometimes called Schulze's valence rule, states that if a power of 1 is assigned to monovalent ions, then divalent ions will have a power of 60, and trivalent ions a power of 1650. However, this rule has been discredited by such a variety of data that it is no longer taken seriously. One of the first to discredit it was Hofmeister (9), who demonstrated that the specific nature of the ion is often more significant than its charge, since ions of the same sign and valence may have widely different precipitating powers. Thus mere neutralization of charge is secondary to the specific nature of the precipitating ion. In addition to Hofmeister's work, Loeb (11) has demonstrated that in the case of hydrophilic colloids one may reduce the electrophoretic potential difference to zero and not cause precipitation of the dispersed phase. Thus the first point, that neutralization of electric charge is sufficient to produce precipitation, is very doubtful.

Now to consider the second point. There are numerous instances reported in the literature where hydrosols of the *same* sign will mutually precipitate when mixed. Thus Odén's sulfur sol, which is negative, precipitates arsenious sulfide hydrosol, which is also negative. Likewise Odén's sulfur sol precipitates Carey Lea's silver sol, which is negative. To cite one other case, negative vanadium pentoxide hydrosol precipitates negative uranyl oxide hydrosol (22). Thus it will be seen that similarly charged particles may mutually precipitate making the second point untenable and also reflecting on the first point, since precipitation occurred without neutralization of the electric charges on the particles.

Finally there are data on the third point. Several stable sols have been reported in which the dispersed phase was not electrically charged. Stable dispersions of proteins at their isoelectric point have been reported by Loeb (11). Dispersions of β -amylose (from starch) in water media are reported by Thomas (22) to be uncharged. Soyenkoff (20) has reported

the preparation of several metallic soap dispersions in benzene in which the dispersed particles had no electric charge.

From the data cited above it should be evident that electric charge is not the whole story concerning the formation, stability, and precipitation of colloids. There is such a wealth of facts which the electrical theories cannot explain and there is so much evidence pointing to the importance of the specific nature of each ion that they seem to be no longer tenable.

THE COMPLEX COMPOUND THEORY

All of the previous theories have centered their interest around stability and precipitation of sols with little attention to the structure of the micelles. The complex compound theory puts the interest on the structure of the micelle rather than on the cause of stability. There is no adequate explanation of why cane sugar or sodium chloride remains in solution in water. If simple crystalloidal solutions are not yet explained, how much chance is there to explain the stability of such complicated systems as many colloids are?

The complex compound theory attempts to relate colloidal behavior more closely to crystalloidal behavior, to explain the more recent experimental facts, and to provide a basis for predicting the behavior of systems similar to those for which the theory was derived.

There is ample evidence for the belief that true solutions and colloidal dispersions of the same material are different in degree only. The transition in properties from a true solution to a colloidal dispersion is gradual. Loeb (11) has shown this for hydrophilic colloids in his studies on the properties of true solutions of low molecular weight amino acids as compared with colloidal dispersions of high molecular weight amino acids and proteins. Whitehead and Clay (34) have shown the same thing for the transition in properties from a true solution of aluminum chloride through the more basic aluminum chlorides to the aluminum oxychloride hydrosol. Figure 1 shows the effect of adding sodium succinate to solutions of AlCl_3 , $\text{Al}(\text{OH})\text{Cl}_2$, $\text{Al}(\text{OH})_2\text{Cl}$, and to the hydrosol. It will be noted that the change in pH value caused by addition of the salt is similar in all cases, increasing from the aluminum chloride to the hydrosol gradually. An explanation of this change will be given later in this paper. It is offered here merely to emphasize the close relation between solutions and hydrosols.

To explain how a solution of aluminum chloride can be gradually transformed into a hydrosol, the complex compound theory pictures a salt like aluminum chloride according to the Werner theory, which says that aluminum chloride is really $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ and that in solution there will be six water molecules coördinately bound to the central metallic ion

forming a complex ion, while the three chloride ions will be outside of this complex ion.

Since aluminum chloride is the salt of a strong acid and a weak base, it will hydrolyze when dissolved in water, giving an acid solution. Pfeif-

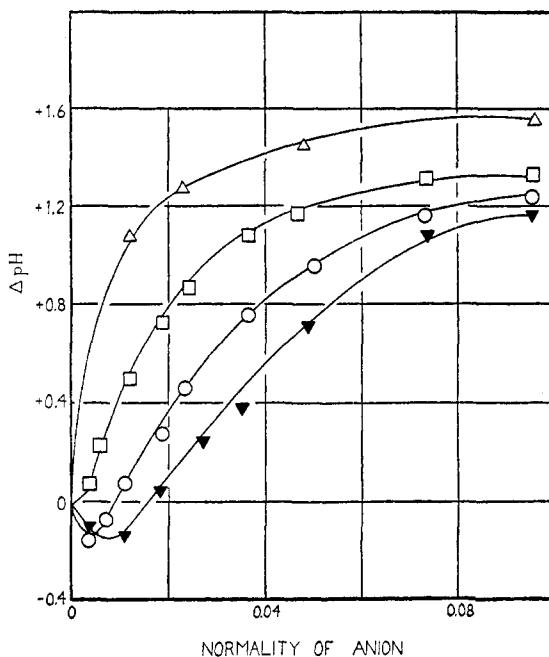
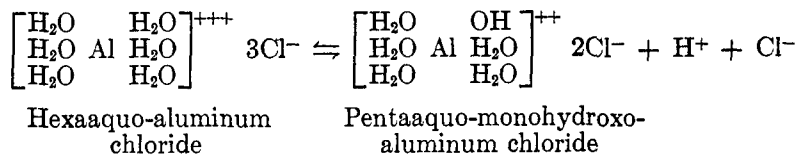


FIG. 1. Effect of sodium succinate on aluminum salts and sol. Δ , sol; \square , $\text{Al}(\text{OH})_2\text{Cl}$; \circ , $\text{Al}(\text{OH})\text{Cl}_2$; \blacktriangledown , AlCl_3 .

fer (14) proposes that this hydrolysis be pictured in terms of the Werner structure as follows:

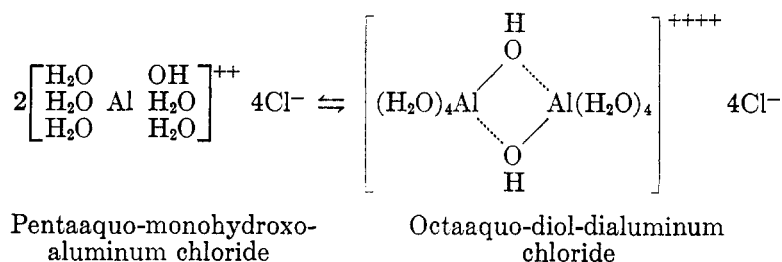


This process would produce an acid solution and a basic aluminum salt. The extent of the hydrolysis will of course be increased by a rise in temperature, as shown by Kulgren (10), by dilution, and by adding alkali to the solution. It is also dependent upon the anion of the salt, as shown by Čupr (3). However, alkali has the most pronounced effect on the

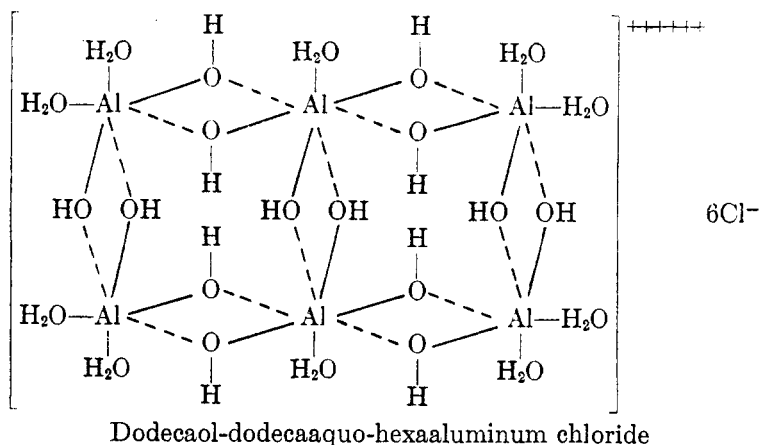
extent of hydrolysis, since it neutralizes hydrogen ion to form water and shifts the equilibrium from left to right.

If the solution should be heated and alkali added too, it would be expected that precipitation of a basic salt or a hydroxide would occur. This happens if sufficient alkali is added, but if less than the amount needed for neutralization is added while the solution is warm, polymerization occurs. Bjerrum (2), working with solutions of chromium chloride, was able to get polymers with molecular weights as high as 750. The same thing will happen with aluminum chloride, as $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were shown to be analogous by Thomas and von Wicklen (29).

Stiasny and Balanyi (21) explain this polymerization by postulating the formation of diol complexes first and then polynuclear complexes, as follows:



The formation of diol complexes was of course reported by Werner and others years before for cobalt complexes, but Stiasny extends this process and postulates that larger and larger diol complexes may be formed, such as:



Thus by a combination of hydrolysis and olation, Stiasny accounts for the formation of polynuclear complexes of high molecular weight. The

complex compound theory extends this process to include the formation of larger polynuclear complexes until colloidal dimensions are reached.

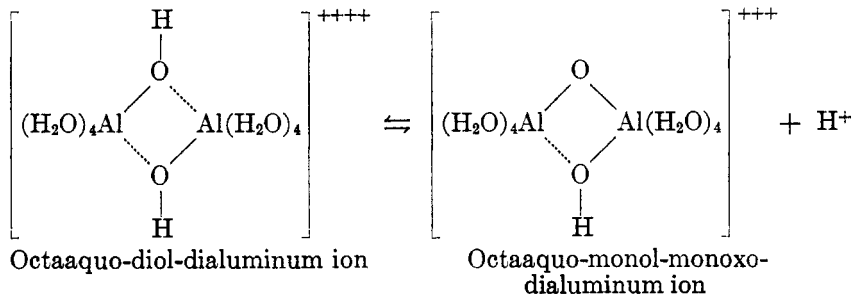
The above picture is the simplest possible one for a polynuclear complex, because anions of the salt would also be in some of the coördinate positions occupied by hydroxo or aquo groups in the above representation.

If this postulation is correct, then these polynuclear complex ions should act like other Werner complexes and there should be an equilibrium between the coördinately bound groups within the complex and the ions outside of the complex. Also, there should be an equilibrium between aquo groups within the complex and water molecules outside the complex. This would mean that any change in concentration of ions outside the complex would alter the equilibrium between complex ion and outer solution, resulting in a change of composition in the complex ion. It would also mean that a change in temperature would alter the equilibrium between aquo groups and water molecules, because increased temperatures usually cause aquo groups to move out of the complex. Finally, the composition of a complex ion formed in the solution might continually change until a stable equilibrium had been established between the complex ion and the solution outside of the complex. There is experimental evidence that all of the above conditions are fulfilled in various systems.

A. Evidence from heating

It was found by Thomas and Whitehead (30) that when an aluminum oxychloride hydrosol was obtained by peptizing hydrous alumina with hydrochloric acid at 20°C. and was then heated, the pH value of the sol decreased, i.e., it became more acidic. This might be ascribed at first thought to increased hydrolysis, because increased temperature usually increases the extent of hydrolysis, but in this case it was not a true hydrolysis because on cooling the sol back to 20°C. the pH did not return to its original value. Only after six weeks did the original pH value of the sol return.

This fact can be readily explained on the Werner-Pfeiffer basis. Assuming that the aluminum oxychloride sol was a polynuclear complex and taking the simplest complex to illustrate this point:



In the above case one of the ol groups lost a hydrogen ion to the outer solution and became an oxo group (oxygen bridge). This would increase the acidity of the outer solution and so decrease the pH value. Since the oxo group is less reactive than an ol group the equilibrium would not be restored at once upon cooling the system, but eventually the hydrogen ion would go back into the complex and change the oxo group back into an ol group. Both of these processes are indicated by the data plotted in figure 2, in which aluminum oxyiodide hydrosol is treated with potassium chloride and potassium sulfate before heating and after heating the sol. It will be noted that the two upper curves represent the effect of

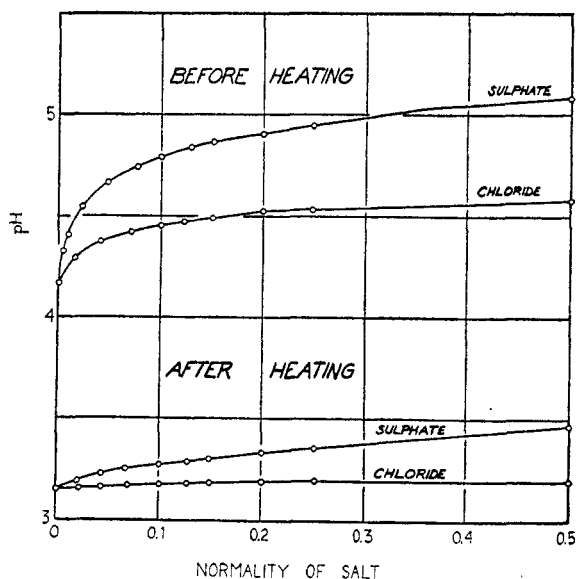


FIG. 2. Effect of potassium salts on pH of aluminum oxyiodide sols

salts upon the pH of the sol before heating. These curves begin at pH 4.17, while the lower curves representing the sol after heating begin at pH 3.15. Thus heating alone lowered the pH from 4.17 to 3.15. The explanation of this, as given above, is due to the changing of ol groups to oxo groups with a loss of one hydrogen ion per group from the inner complex to the outer solution. Thus the outer solution was made more acid. Again examining the curves, it will be noted that a given amount of salt caused a greater change in pH value in the upper curves than in the lower curves. This is interpreted as meaning that the oxo groups present in the sols represented in the lower curves were less reactive than the ol groups present in the sols represented in the upper curves. In other words,

the anions of the salts could more easily replace *ol* groups than they could *oxo* groups, and this is reflected in the relative change in pH values as plotted in this figure. The data are taken from the work of Thomas and Tai (27).

It will also be noted that oxolation decreases the charge on the complex ion, and so its speed of migration under the influence of an electric field should be decreased. This was found to be the case.

The data of Thomas and Tai given above are not isolated examples by any means. Similar results were obtained by others,—by Todd (31) for aluminum oxybromide sols, by Thomas and Whitehead (30) for aluminum oxychloride sols, by Thomas and von Wicklen (29) for chromium oxychloride sols, by Thomas and Kremer (24) for thorium oxychloride sols, and by Thomas and Miller (25) for beryllium oxychloride sols. In fact this behavior seems to be uniform for the so-called metallic oxide hydrosols, whether they are formed by hydrolysis or by peptization.

B. Evidence from aging

All of the investigators cited above found that if metallic oxysalt hydrosols are prepared at room temperatures and allowed to age at room temperatures they become more acid, but if they are heated or prepared at elevated temperatures and then allowed to age at room temperatures they become more basic. The explanation of these facts on the complex compound basis is similar to that just given for the effect of heating alone. That is, when no heat is applied hydrolysis is the principal reaction taking place, and since the equilibrium of high molecular weight complexes with their outer solutions requires considerable time for completion, the hydrogen ion concentration of the outer solution gradually increases. But if heat is applied olation occurs first, after hydrolysis, and then oxolation takes place, making the sol quite acid. Upon aging a reversal of these processes occurs and the outer solution becomes *less* acid.

C. Evidence from salt effects

It has been known for decades that when a hydrous oxide is precipitated from a solution of one of its salts by the addition of an alkali, the precipitate invariably contains more or less of the anion of the salt. Thus hydrous ferric oxide precipitated from ferric acetate or ferric chloride always contains acetate or chloride ions which are very hard to remove (23). The presence of the anions has been accounted for by some chemists as impurities which are adsorbed or occluded. However, the complex compound theory explains them in another way.

Thomas and Whitehead (30) showed that when a neutral salt is added to aluminum oxychloride hydrosols, the pH value of the system increases.

This increased basicity is too great to be accounted for by ordinary physical chemical principles such as hydration of ions, salt effect on the quinhydrone electrode used to measure pH, or increased ionic environment. However, the Werner theory offers an explanation of the facts found. Werner postulated that the composition of a complex ion was not invariable, and that ions outside the coordinated complex might displace a coordinated group and take its place in the complex ion. It is well known that in crystalloidal complexes anions can replace aquo and hydroxo groups. Therefore the complex compound theory proposes that when a neutral salt is added to a metallic oxysalt hydrosol, the anion of the salt displaces hydroxo groups from the complex ion and forces them into the outer solution and makes that solution more basic. Čupr (3) demonstrated that the dissociation of a complex ion is a function of the anion

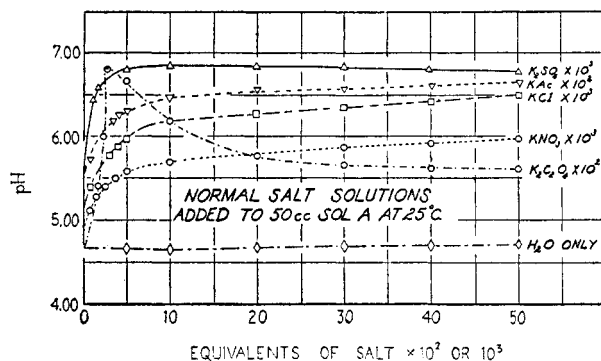


Fig. 3. Effect of salts on pH of aluminum oxychloride sol

present, and all anions are therefore not equal in their power to displace groups from the complex. This same conclusion was reached by Thomas and Whitehead (30) after studying a variety of salts. A typical set of data is plotted in figure 3. These data represent the effect of adding neutral salts to an aluminum oxychloride hydrosol. It will be noted that the effectiveness of the anions in raising the pH value of the sol was: oxalate > acetate > sulfate > chloride > nitrate. This is the same order which has been found for the stability of similar crystalloid complexes, such as cobaltamine complexes and chromic chloride complexes.

Similar results have been obtained for the hydrosols of beryllium (25), chromium (29), thorium (24), and zirconium (26).

If this complex compound theory is consistent, then there ought to be cases of hydrosols in which the cationic complex would be changed into an anionic complex just as crystalloidal complexes are. For example, it

is well known that the oxalate ion forms anionic complexes with many metal ions, a typical compound being $K_3[Co(C_2O_4)_3]$, potassium trioxalato-cobaltate. Thomas and Miller (25) treated beryllium oxychloride sols, in which the beryllium complex was a cation, with sodium or potassium oxalate and converted the beryllium complex into an anionic beryllate ion. Analysis of the new complex showed it to be a complex anion composed of beryllium ion, oxalato, aquo, and other coordinated groups. This colloidal beryllium complex thus acted exactly like crystalloidal complexes. Similar behavior was exhibited by the hydrosols of thorium (24) and zirconium (26).

Thus according to the complex compound theory the inclusion of anions in the hydrous oxide precipitate is more than a mere impurity,—the anion is part of the complex and can be removed from the complex only by replacing it. Of course washing will gradually do this by substituting aquo groups for the anion. If this concept is correct then nitrate ion should be most easily washed out, chloride next, then sulfate, and hardest of all oxalate, tartrate, or citrate. Such is the case.

D. Evidence from conductivity

The data presented by figure 3 show the effect of neutral salts upon the pH of an aluminum oxychloride sol and were interpreted as representing the displacement of hydroxo groups by the anions of the added salt. There is supporting evidence for this belief in conductivity titrations performed by Miller (25) on beryllium oxychloride sols and soluble silver salt solutions. In these cases the concentration of silver salt was so low that the anion could not displace hydroxo groups but could displace the more easily displaced groups, chloro and aquo. Figure 4 shows the effect upon the conductivity of a beryllium oxychloride sol of adding silver nitrate, acetate, and tartrate.

It will be noted that the addition of the silver salt solutions first decreased the conductivity of the system to a minimum and then increased it. The explanation, according to the complex compound theory, is that the anions of the silver salts displaced chloro groups and possibly aquo groups from the complex. If chloro groups are displaced, then they will appear as chloride ions in the outer solution and be precipitated by silver ions. This would lower the conductivity of the system. Also, if aquo groups are displaced from the complex by anions, the net positive charge on the complex ion will be decreased and this would also decrease the conductivity. Once the displacement of chloro and aquo groups has ceased, the further addition of silver salt solutions will increase the conductivity of the system. It may be argued that no account is taken of relative ionic mobilities in the above explanation, but this variable has

been considered in detail for a large number of anions by Thomas (22), and the order of conductivity lowering and the order of anion mobilities are not the same. Therefore the conductivity data cannot be explained by differences in ion mobilities alone, but, using the mechanism outlined above and admitting the influence of ion mobility, an explanation results which is in accord with the facts.

E. Evidence from peptization

If the complex compound theory is to be inclusive it must explain the formation of hydrosols by peptization as well as by hydrolysis. Thomas

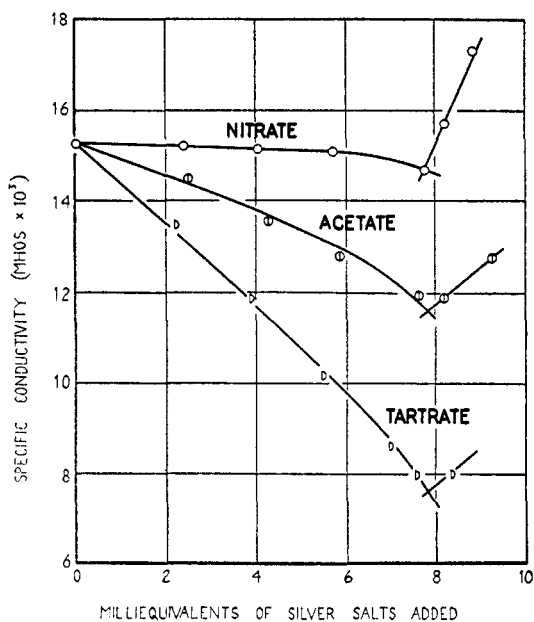


Fig. 4. Effect of silver salts on conductivity of beryllium oxychloride sol

and Vartanian (28) have studied the peptization of hydrous alumina by several acids. They found that equivalent amounts of acid were not equally effective in peptizing hydrous alumina. In fact, the effectiveness of an acid in peptizing hydrous alumina was inversely proportional to its tendency to form coördinate complexes with aluminum. Thus nitric acid is an excellent peptizing agent, while oxalic acid is very poor. It will be recalled that nitrate ion was very weak in forming complexes, as shown by its relatively small effect on the pH value of the aluminum oxychloride sols (figure 3) and in decreasing the conductivity of beryllium oxychloride sols (figure 4), while oxalate ion is very powerful in these respects. The

complex compound theory therefore explains peptization in the following way: A hydrous oxide contains many hydroxo groups and aquo groups coördinately bound to the central metallic ions; this complex is not soluble in water to any appreciable extent, but when an acid is added to it the hydrogen ions convert many hydroxo groups to aquo groups and ol groups to aquo groups, thus increasing the solubility of the complex in water. However, if the anion of the acid forms very stable coördinate complexes with the central metallic ion, then aquo and hydroxo groups will be displaced by the anion and a less soluble complex will be formed. Therefore those acids whose anions form highly dissociated complexes are best for peptization, while those acids whose anions form very slightly dissociated complexes are least effective in peptizing hydrous oxides.

This theory explains a large mass of data which are not discussed in detail in this article, but which may be found in the references and elsewhere in the literature.

One final piece of evidence has contributed considerable weight to the complex compound theory. That is the evidence presented by those who have prepared metallic hydrosols by the Bredig arc method. This method of preparation has been looked upon by many chemists as a purely mechanical process, in which extremely fine particles of metal are dispersed in an aqueous medium by means of the electric arc. S. W. Pennycuik (13), who has prepared platinum hydrosols under a variety of conditions and by several methods, has come to the conclusion that the Werner theory and its modern extensions offer the only consistent explanation for the facts observed in platinum hydrosols. Likewise Pauli (12) has adopted the Werner theory and its modern extensions to explain the behavior of gold hydrosols prepared by the Bredig arc method. Thus the Bredig arc method need no longer be looked upon as a purely physical process of dispersing fine particles of metal in water, but as a process in which definite chemical compounds are formed which, like other complex compounds, have very definite ways of behavior.

SOME APPLICATIONS

If the complex compound theory had no practical applications it would still be very interesting, but it is gratifying that important applications have been found. Two of these will be mentioned because there is considerable experimental evidence for the conclusions given.

The field of leather chemistry has always been an important and interesting one. However, the art of leather tanning got far ahead of the science until about 1924, when Stiasny in Germany and Gustavson in this country adopted the Werner theory as a working basis for explaining the process of chrome tanning. Gustavson (7) explained the tanning of leath-

ery by the chromic sulfate method as due to the formation of a sulfato-hydroxo-chromi-collagen complex compound. This theory concerning the mechanism of chrome tanning threw immediate light on other operations, such as pickling, liming, and vegetable tanning of hides. It has been a matter of practical knowledge for years that Rochelle salts will detan leather. Since tartrate ion is more powerful than sulfate ion in displacing coördinately bound groups, the stripping of the tanning agent can be explained on the same basis as other displacements from complex compounds. Gustavson (7) actually assigns a structure to the complex formed in chrome tanning as being similar to the class of compounds known as chelate compounds. This is reasonable because diamines are well known for their tendency to form chelate complex compounds with metallic ions. Therefore the complex compound theory has been most helpful in understanding the mechanism of the processes of one of our largest industries and in predicting ways to improve the quality of leathers.

There is another field which has not been so well worked out as leather tanning but is very promising. That is the field of mordant dyeing. It is well known that many dyes require a mordant to dye cotton and wool cloth successfully. These mordants are usually hydrous oxides of aluminum, chromium, or iron. Sidgwick (17) has suggested that a chelate compound may be formed between certain dyes and hydrous oxides. Since there were about one hundred and sixty dyes listed in the 1914 edition of Schultz's Farbstofftabellen as being mordanted with ions of polyvalent metals, this field offers interesting possibilities. The complex compound theory should be very useful in this field, if the dye really forms a complex with the hydrous oxide. In the closely related field of lakes used in analytical chemistry there is also a possibility of interesting research in applying the complex compound theory.

In conclusion it may be said that the complex compound theory has been found very useful for explaining the behavior of metallic oxysalt hydrosols and their mode of formation. It is a relatively young theory and there is a wide field of experimental research open for testing the validity of this theory for explaining other colloidal phenomena.

REFERENCES

- (1) BANCROFT: Applied Colloid Chemistry. The McGraw-Hill Book Co., Inc., New York (1921).
- (2) BJERRUM: Z. physik. Chem. **59**, 336 (1907).
- (3) ČUPR: Collection Czechoslov. Chem. Commun. **1**, 467 (1929); Chem. Abstracts **24**, 1013 (1930).
- (4) DEBYE AND HÜCKEL: Physik. Z. **24**, 185 (1923).
- (5) GOUY: J. phys. **9**, 457 (1910).
- (6) GRAHAM: J. Chem. Soc. **15**, 250 (1862).
- (7) GUSTAVSON: J. Am. Leather Chem. Assoc. **21**, **22**, 559 (1926).

- (8) HELMHOLTZ: *Ann. phys.* **7**, 33 (1879).
- (9) HOFMEISTER: *Arch. exptl. Path. Pharmacol.* **24**, 247 (1888).
- (10) KULGREN: *Z. physik. Chem.* **85**, 472 (1913).
- (11) LOEB: *Proteins and the Theory of Colloidal Behavior*. The McGraw-Hill Book Co., Inc., New York (1924).
- (12) PAULI: *Naturwissenschaften* **20**, 551 (1932).
- (13) PENNYCUICK: *J. Chem. Soc.* **1927**, 2600; **1928**, 551, 2108; **1929**, 618, 623; *Kolloid-Z.* **49**, 407 (1929); *Z. physik. Chem.* **A148**, 413 (1930); *J. Am. Chem. Soc.* **52**, 4621 (1930).
- (14) PFEIFFER: *Ber.* **40**, 4036 (1907).
- (15) PORTER AND HEDGES: *Phil. Mag.* **44**, 641 (1922).
- (16) SCHULZE: *J. prakt. Chem.* **25**, 431 (1882); **27**, 320 (1883); **32**, 390 (1884).
- (17) SIDGWICK: *Electronic Theory of Valence*. Oxford University Press, New York (1927).
- (18) SMOLUCHOWSKI: *Z. physik. Chem.* **92**, 129 (1917).
- (19) SORUM: *J. Am. Chem. Soc.* **50**, 1263 (1928).
- (20) SOYENKOFF: *J. Phys. Chem.* **34**, 2519 (1930).
- (21) STIASNY AND BALANYI: *Collegium* **682**, 86 (1927).
- (22) THOMAS: *Colloid Chemistry*. The McGraw-Hill Book Co., Inc., New York (1934).
- (23) THOMAS AND FRIEDEN: *J. Am. Chem. Soc.* **45**, 2522 (1923).
- (24) THOMAS AND KREMER: *J. Am. Chem. Soc.* **57**, 1821 (1935).
- (25) THOMAS AND MILLER: *J. Am. Chem. Soc.* **58**, 2526 (1936).
- (26) THOMAS AND OWENS: *J. Am. Chem. Soc.* **57**, 1825, 2131 (1935).
- (27) THOMAS AND TAI: *J. Am. Chem. Soc.* **54**, 841 (1932).
- (28) THOMAS AND VARTANIAN: *J. Am. Chem. Soc.* **57**, 4 (1935).
- (29) THOMAS AND VON WICKLEN: *J. Am. Chem. Soc.* **56**, 794 (1934).
- (30) THOMAS AND WHITEHEAD: *J. Phys. Chem.* **35**, 27 (1931).
- (31) TODD: *Dissertation*, Columbia University, 1931.
- (32) VAN BEMMELLEN: *Rec. trav. chim.* **7**, 106 (1888).
- (33) WERNER: *Ber.* **40**, 2113, 4436 (1907).
- (34) WHITEHEAD AND CLAY: *J. Am. Chem. Soc.* **56**, 1844 (1934).
- (35) WILSON: *J. Am. Chem. Soc.* **38**, 1982 (1916).