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## THE NATURE OF "ALUMINUM OXIDE" HYDROSOLS

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In a previous publication, Thomas and Whitehead<sup>1</sup> suggested that the dispersed phase of hydrosols arising from the peptization of hydrous aluminum oxide by hydrochloric acid consists of olated and possibly oxolated aluminum oxychloride complexes. In the present communication certain properties of "aluminum oxide" hydrosols, particularly aluminum oxyiodide hydrosols, are described, showing the influence of the nature of the crystalloid "contra-ion," previous history of the hydrosols, etc., which are interpreted in the light of the proposed suggestion of their constitution.

Preparation of Hydrosols.—All sols were prepared by the aluminum amalgam method. A piece of pure aluminum<sup>2</sup> of about 350 g. was covered with slightly acidulated water and placed in contact with 10 g. of pure mercury. After three to four hours, the mercury had spread over the whole surface of the aluminum.<sup>3</sup> The excess of mercury was poured off and the amalgamated aluminum was rinsed with distilled water. For the preparation of the "-oxyiodide" sols it was then placed in 3 or 4 liters of distilled water and 20 to 100 cc. of 0.5 N hydriodic acid was added. The reaction was allowed to continue for eight hours at boiling temperature, or for one to three days at room temperature. At the end of the reaction, there was always a large amount of precipitate of alumina hydrate left on the bottom of the vessel.

The supernatant turbid solution was then poured into a flask and allowed to settle. After two days, it was centrifuged for one hour at a speed of 1200 r. p. m., rotating diameter being 42 cm. The supernatant portion was siphoned into and kept in "Non-Sol" glass bottles.

Some of the sols prepared in this way were dialyzed in nitrocellulose bags against distilled water at room temperature for four to fourteen days, the water being changed daily.

<sup>1</sup> Thomas and Whitehead, J. Phys. Chem., 35, 27 (1931).

<sup>2</sup> Ordinary pure aluminum which contains 99.5% of the metal has enough iron in it so that when a colloidal solution is prepared from it according to this method, iodide ion is soon oxidized to iodine, the solution becoming yellow after standing for a while. The aluminum metal which was used in this investigation was specially supplied by the Aluminum Company of America. Upon analysis it showed 99.94  $\pm$  0.03% of aluminum.

<sup>3</sup> In pure water the amalgamation process is very slow.

A summary of the conditions of preparation, composition, viscosity and  $P_{\rm H}$  values of the sols is given in Table I. The aluminum content was determined gravimetrically as oxide and the iodine content potentiometrically.<sup>4.5</sup> Qualitative tests showed no iron nor mercury present.

It is noticed in Table I that the sols prepared at room temperature were quite different from those prepared in the hot. The former had lower PH values, lower viscosities and less aluminum. The amount of aluminum in a sol was determined largely by the temperature of reaction and at a given temperature a higher concentration of acid and a longer time of reaction produced sols of a higher aluminum content. Dialysis of sols increased the PH value and decreased the iodide content. While the total aluminum concentration also diminished upon dialysis, this was due more to dilution of the solution than to diffusion of aluminum compounds through the membrane.

	Í	II	III	IV	v	VI	VII	VIII
0.5 N HI added, cc.	20	25	50		50	100		50
Total vol., liters	3	3	3		4	4	••	3
Temp. of reaction	Room	Room	Room		Boiling	Boiling		Boiling
Time of reaction	2 days	3 days	3 days		8 hrs.	8 hrs.	• •	8 hrs.
Dialysis	••	••	••	Sol I dia Sol VI dia- lyzed for lyzed for 10 days 4 days			14 days	
Aluminum content								
(millieq. per liter)	23.0	59.0	60.2	8.77	183.9	425.6	386.9	143.4
Iodide content	2.961	3.644	6.099	0.363	5.320	11.25	4.511	1.291
Ratio Al/I	7.8	16.2	9.9	24.2	34.6	37.8	85.8	111.1
Viscosity. time of outflow in seconds								
$(H_2O = 82.0)^a$	82.4	82.5	82.7	82.6	87.9	92.3	109.4	95.6
Pн value	4.20	4.21	4.31	5.77	4.88	4,98	5.05	5.63
<sup>a</sup> At 25° ≠0.1	۰.							

TABLE I PREPARATION, COMPOSITION, VISCOSITY AND PH VALUES OF THE SOLS

Neutral Salt Effect on PH of the Sols.—In studying the neutral salt effect on the hydrogen-ion activity of the sols, potassium nitrate, chloride, sulfate, acetate and oxalate were used. Since it was desired to have all

		TA	BLE II			
PH VALUES OF SALT SOLUTIONS						
Conen. normality	KNO3	KC1	$KC_2H_3O_2$	K2SO4	$K_2C_2O_4$	
0.05	6.51	5.76		6.15		
. 10	6.47	5.70	6.42	6.11	6.57	
. 25	6.37	5.63	6.44	6.06	6.58	
. 50	6.22	5.58	6.49	5.58	6.61	
1.00	••		6.63	• •	6.67	

<sup>4</sup> Hendrixson, THIS JOURNAL, **43**, 14 (1921).

<sup>8</sup> Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, New York, 1926, pp. 232-237. the salt solutions slightly acid, 0.4 cc. of normal acetic acid was added to 1950 cc. of normal potassium acetate solution and 1.0 cc. of normal oxalic acid to 1950 cc. of normal potassium oxalate solution. The *P*H values of the salt solutions used are shown in Table II.

Twenty-five cc. portions of a sol were measured into 125-cc. wide-mouthed glassstoppered bottles and to each was added an equal volume of salt solution, followed by shaking. After standing overnight, the hydrogen-ion activity of each mixture was measured by means of the quinhydrone electrode with a saturated potassium chloridecalomel cell at  $25 \pm 0.1^{\circ}$ . A constant potentiometer reading was usually obtained within five minutes if the mixture had been previously saturated with quinhydrone and allowed to come to the temperature of the thermostat before the electrode was inserted. The readings were taken to the nearest millivolt.

When the  $P_{\rm H}$  value of the mixture was near or more than 8, the hydrogen electrode was used. In this case, there being invariably complete precipitation of the sol, the mixture was filtered through a dry filter paper, rejecting the first five cc. of the filtrate. (Measurements had been tried without filtering off the precipitate, but the attainment of equilibrium was exceedingly slow, due to an accumulation of gelatinous precipitate on the platinized electrode.)



Fig. 1.—Effect of potassium sulfate on PH of sols.

Figure 1 shows that the addition of potassium sulfate produces an increase in PH value in all cases. Sols I, II and III, which had been prepared at room temperature, reacted practically alike. Sols V and VI which were prepared in the hot were more reactive, however, as were also sols IV and VII which were prepared by the room temperature dialysis of sols I and VI, respectively. The same distribution of curves was obtained upon titration

of the sols by potassium chloride, the only difference being a lower  $P_{\rm H}$  level throughout.

Figure 2 shows first that sols V and VI which had been prepared under like conditions reacted concordantly not only toward potassium chloride and potassium sulfate but also toward potassium acetate and oxalate; and second that different salts have widely different effects on the sols, potassium oxalate being most effective and potassium nitrate the least.



Fig. 2.-Effect of potassium salts on PH of sol V and sol VI.

It should be recalled that the solutions of potassium acetate and oxalate contained a small amount of added acid. Their effect upon dilute sols (I, II, III and IV) was tried and it was found that the whole effect was dominated by the buffer action.

Figure 3 shows the effect of different salts on the  $P_{\rm H}$  of sol VII. When compared with the curves for sol VI in Fig. 2, it will be noticed that for an addition of equal amounts of any salt, the effect on sol VII was greater than on sol VI. Also the order of effectiveness of anions in increasing the  $P_{\rm H}$  of a sol is shown to be the same.

It is noticed that there is a maximum in the acetate curve, which indicates that the buffer action of the acidified salt became dominant. From Table II it is clear that the resultant hydrogen-ion activity of the mixture was approaching that of the acetate solution as its concentration increased. From all the results shown in Figs. 1 to 3, the following facts are evident: (1) Salts decreased the hydrogen-ion activity of the sols and in certain cases the mixtures of sols and salt solutions became quite alkaline. (2) The order of effectiveness of the anions in increasing the  $P_{\rm H}$  of the sols was found to be: nitrate < chloride < acetate < sulfate < oxalate. (3) On addition of different salts, sols I. II and III were quite alike in reaction, as were also sols V and VI, despite the fact that they had been prepared by the reaction of different amounts of acid for different lengths of time, and that they differed considerably in their aluminum and iodide contents. Those which reacted similarly were those which had been prepared at the same temperature. (4) Sols which were prepared at high temperature and dialyzed sols were more reactive toward the salts.





stand at room temperature for one day, and centrifuged for an hour. Analytical data are given in Table III.

		Table III		
	COMPOSITION OF	BASIC ALUMIN	um Salt Sols	
	Values given	are milliequiv	. per liter	
Sols	Oxyiodide	Oxybromide	Oxychloride	Oxyacetate
Aluminum	60.9	70.9	80.2	18.01
Anion	3.27	3.50	3.54	2.53

The effects of potassium chloride and sulfate upon these sols are plotted in Figs. 4 and 5.



aluminum oxy sols.

Both Fig. 4 and Fig. 5 show that on addition of equal amounts of the same salt, the effect on the  $P_{\rm H}$  of the sols is markedly different, the order

846

from most reactive to least being aluminum oxyiodide sol > oxybromide > oxychloride > oxyacetate. It is quite interesting to compare this order with that of the effectiveness of potassium salts of these anions in increasing the  $P_{\rm H}$  values of aluminum oxychloride sols as found by Thomas and Whitehead,<sup>1</sup> namely, acetate > chloride > bromide > iodide. Hence, the anion which is more effective in increasing the  $P_{\rm H}$  of aluminum oxychloride sols makes a sol less sensitive toward the action of salts when it is part of the composition of the sol.

Effect of Aging and Heating of the Sols.—Portions of sols I, IV and V, in "Non-Sol" bottles, were stored at 90° for ten days. Then they were cooled to  $25^{\circ}$  and the *P*H values were determined immediately and at various intervals thereafter together with the *P*H values of portions of the same sols which had not been heated, as shown in Table IV.

	Change	of Phofi	HE SOLS ON	AGING AND	Heating		
Age in	Sol I		Sol	IV	Sol V		
days	heated	Heated	heated	Heated	heated	Heated	
0	4.20	3.15	5.77	4.14	4.88	4.07	
1		3.17		<b>4</b> . <b>2</b> 0	4.88	4.13	
$\overline{5}$	4.16		5.75				
10		3.28	5.67	4.42	4.80	4.26	
<b>14</b>	4.10						
20		3.31		4.48		4.28	
50	3.94	• •	5.59				
90	3.87	• •		• •	4.58		

TABLE IV

The figures in the first line of Table IV show a considerable decrease in the PH values of the sols as a result of the heating. Aging of the original sol at room temperature had the same effect although to a much less extent. Sol I became milky in appearance at the end of heating for ten days, while a partial precipitation occurred in sol V. No change in appearance was observed in sol IV.

The change in PH of the heated sols on subsequent aging at room temperature is significant. All the original unheated sols, no matter whether prepared at room temperature or at a higher temperature, decreased in PHwhile the same sols after heating increased gradually in PH while standing at room temperature.

The neutral salt effect on that portion of sol I which had been heated at  $90^{\circ}$  for ten days is given in Fig. 6.

It is evident from Fig. 6 that heating not only increased the hydrogenion activity of the sol but made it much less sensitive toward the action of salts.

Conductance Titrations of the Sols .--- If it is accepted that the order of

the effects of the anions previously described in this investigation represents their tendency to penetrate into the complex ol-compound of which the colloidal micelle is constituted, then conductivity measurements upon aluminum oxyiodide sols under titration with silver salts should show the same order.

Silver nitrate, sulfate, acetate and tartrate were used. Weighed portions of these salts were placed in 250-cc. "Non-Sol" bottles; 100-cc. portions of sol were then pipetted into these bottles. Silver nitrate and silver acetate dissolved readily while silver sulfate and tartrate required two to three days for solution even with occasional vigorous shaking. During all operations with the silver salts the usual precautions concerning exposure to actinic rays were observed.

After complete solution of the silver salt, the conductivity was measured at 25  $\pm 0.01$ ° in a cell provided with bright platinum electrodes.



Fig. 6.—Salt effect on PH of sol I (before and after heating).

The results obtained with sols V and VIII are plotted in Figs. 7 and 8. In these figures the point of intersection of the two branches of each curve corresponds to the completion of the reaction:  $Ag^+ + I^- = AgI$ . It is significant that not only do the points agree with each other but they agree also with the value of the iodide content of the sol as determined by the potentiometric method.

It is significant too that before the intersection point is reached, each curve approaches it with a different slope and that at the point where the equivalent amount of salt had been added, the conductivities of the mix-

848

tures were widely different, nitrate having the highest value and tartrate the lowest.

Although the sulfate and tartrate curves in Figs. 7 and 8 are quite close to each other, the difference in the decrease of conductivities after the addition of these silver salts was definite. The last point for silver tartrate does not fall on the curve, as is seen in both figures. This was due to some change taking place as revealed by the color of the mixture becoming quite brown after the dissolution of the salt was completed, which will be discussed later.



It should be noticed that sol VIII was prepared in the hot and then dialyzed at room temperature for two weeks. Its conductivity was about one-seventh that of sol V. The iodide content of the two sols differed widely too and this difference is considered responsible for the slight difference in the shape of the two sulfate curves.

From both figures, the following facts are evident. All the iodide in the sol was replaceable by nitrate, acetate, sulfate and tartrate ions equally

since the values of the iodine content of a sol determined by the conductance method agreed with each other as well as with the analytical result; when an amount of silver salt equivalent to the iodide content of the sol was added, the conductivity reached a minimum; and the magnitude of the decrease in conductivity was dependent upon the anion of the silver salt, the order being: nitrate < acetate < sulfate < tartrate.



Other things being equal, the conductivity of a solution depends upon the mobilities of the ions present. The mobilities of the anions are in the order: sulfate > iodide > nitrate > acetate > tartrate. In Figs. 7 and 8, the differences in the slopes of the curves before the intersection point show the difference in rates of conductivity decrease of the sols on addition of different silver salts. When silver nitrate or silver acetate is added, the decrease in conductivity may be accounted for by the fact that fast moving iodide ions outside the nucleus have been replaced by the comparatively slowly moving nitrate or acetate ions. However, with silver tartrate, the conductivity at the equivalent point was about 16% of the original value in the case of sol VIII and only 1% in the case of sol V. The difference in the mobilities of the iodide and tartrate ions alone cannot account for this drop in conductivity. A more significant point is that despite the fact that sulfate ion has a higher mobility than iodide, before the equivalent point had been reached, the conductivity of the sol was very rapidly diminished by silver sulfate. Therefore, it must be assumed that in some way most of the fast moving sulfate ions must have disappeared. This is also true for the tartrate ions and to some extent for the acetate ions. For reasons which will be explained later, it is believed that if any nitrate ion so disappeared, the amount must have been very small.

Interpretation of Results and Summary.—Based on Werner's theory as extended by Bjerrum<sup>6</sup> and Stiasny<sup>7</sup> to account for the behavior of solutions of basic chromium salts, the statements made in an earlier paper<sup>1</sup> give a consistent and satisfactory explanation for the results obtained in this investigation.

An examination of the composition of the sols (Table I) will reveal the fact that the aluminum content of each sol greatly exceeded the iodide content, especially in those sols which had been prepared in the hot. In sol VII, for example, to every mole of iodide, there were roughly 28 moles of aluminum. Accordingly these sols may be considered to consist of highly basic aluminum salt mixtures. On standing, the process of olation took place and resulted in a gradual increase of hydrogen-ion activity (Table IV). As the sol was heated, olation took place more rapidly. Oxolation to some extent was effected, too. All of these changes tended to increase the hydrogen-ion activity of the solution. The acidity of a heated sol became much higher in ten days than that of the same one, not heated, in ninety days. However, after the heated sol had been cooled, aging produced the opposite effect, that is, hydrogen-ion activity decreased, because at a lower temperature, the degree of dissociation of aquo groups in the complex decreased, on one hand, and, on the other, an excess of acid reacted with some of the ol-linkages which had been formed on heating and converted them to hydroxo groups which are supposed to be more reactive than the ol-groups. This process, which is a reverse of olation, is termed "deolation." By way of illustration, possible reactions undergone by a hypothetical compound of hepta-aquo-mono-hydroxo-dioldialumini triiodide, on heating, are pictured as follows

<sup>6</sup> Bjerrum, Z. physik. Chem., 59, 336 (1907).

<sup>7</sup> Stiasny and co-workers, *Collegium*, **657**, 190 (1925); **670**, **41** (1926); **682**, 86 (1927); **694**, 49 (1928); **694**, 72 (1928); **694**, 97 (1928).



Vol. 54



The last product may further dissociate and be olated to form still more complicated complexes as well as undergo the process of oxolation. Processes of olation and oxolation will result in the formation of less hydrated and more complex particles, *e. g.*, after heating for ten days, turbidity resulted in sol I and partial precipitation in sol V.

Sols of basic aluminum salts are regarded as formed from positively charged complex aluminum hydrates which dissociate into basic aluminum ionic micelles and hydrogen ions. It might be contended that the addition of a neutral salt would result in the so-called "negative secondary salt effect," that is, the degree of dissociation of the complex alumina hydrates would be decreased by the added salt and, consequently, the hydrogen-ion activity of the solution would decrease. However, the increase of the  $P_{\rm H}$  values of the sols on addition of neutral salts cannot be explained by this idea of change of equilibrium between basic aluminum ionic micelles and hydrogen ions, because the reaction between neutral salts and basic aluminum compounds has been demonstrated to be of a different nature. Feigl and Krauss<sup>8</sup> have shown that a solution of aluminum chloride is rendered neutral by the addition of potassium oxalate

$$AlCl_{3} + 3K_{2}C_{2}O_{4} = K_{3}[Al(C_{2}O_{4})_{3}] + 3KCl_{3}$$

while a solution of basic aluminum acetate is rendered alkaline

 $Al(OH)(C_2H_3O_2)_2 + 3K_2C_2O_4 = K_3[Al(C_2O_4)_3] + 2KC_2H_3O_2 + KOH$ and utilize these reactions in the analysis of aluminum solutions.

Passing now from such simple crystalloid solutions to gels, it may be

pointed out that when freshly precipitated alumina hydrate is treated with a neutral salt such as potassium or sodium sulfate, citrate, phosphate, etc., the solution becomes alkaline to phenolphthalein.<sup>9</sup> Furthermore, Weiser<sup>10</sup> has found that in the precipitation of aluminum oxyacetate hydrosol by salts, the anions of the added salts are removed in definite amounts from the solution by the gel.

The facts just mentioned indicate that the anions combined with the basic aluminum complex and displaced hydroxyl ions therefrom. The

<sup>8</sup> Feigl and Krauss, Ber., 58B, 398 (1925).

<sup>9</sup> Sen, J. Phys. Chem., 31, 691 (1927).

<sup>10</sup> Weiser and Middleton, *ibid.*, 24, 630 (1920).

852

amount of the latter displaced depends first of all on the penetration power of the anions added. Based on the effectiveness in increasing the  $P_{\rm H}$  values of the sols, the penetration order of the anions that were studied in this investigation is: nitrate < chloride < acetate < sulfate < oxalate.

By the amalgamated aluminum method, it was found that sols which had been prepared at the same temperature and under similar conditions reacted quite alike toward neutral salts. The probable mechanism of the formation of sols with this method can be divided into two steps: the production of alumina hydrate by the action of water upon amalgamated aluminum and the peptization of the hydrate by the acid that is present.

Neogi and Mitra<sup>11</sup> analyzed alumina hydrate that had been prepared from the aluminum-mercury combination and found it had a definite composition. They expressed the results of their analysis by the formula  $Al_2O_3 \cdot 4H_2O$ . According to the idea which is adopted in this paper, the simplest two dimensional structure of the compound corresponding to the above formula is



At the outset, in the presence of an acid, two possible reactions are expected to take place with this compound. Hydrogen ions react with the hydroxo groups (shown at the four corners in the picture above) to form aquo groups and deolation may take place to some extent. A certain number of the anions that are present in the solution may also enter the complex and displace an equivalent number of water molecules, or hydroxo groups, or both. As the reaction proceeds, the amount of free acid decreases. Finally, when an excess of freshly formed alumina hydrate is present, the solution will reach a state of approximately constant concentration of hydroxo groups in the complex aluminum ions. At a higher temperature of preparation, the solution will contain more of the hydroxo groups; because at a higher temperature the aluminum complex dissociates to a greater extent than at a lower temperature. The hydrogen ion formed as a result of this more extensive dissociation will react with the freshly produced aluminum hydroxide and, consequently, cause more aluminum to be dispersed.

The increase in the PH values of the sols upon addition of neutral salts is due primarily to the replacement of hydroxo groups by the anions of the added salts. Since sols which had been prepared at higher temperatures

11 Neogi and Mitra, J. Chem. Soc., 1222 (1927).

contained more hydroxo groups than those which had been prepared at lower temperatures, neutral salts had greater effect upon the former sols (Fig. 2 and Table I).

Dialysis removes hydrogen ion and its equivalence of anion from the sol. This is indicated by the increase in  $P_{\rm H}$  of the solution upon dialysis. Thus, the equilibrium between hydroxo groups inside of the complex and hydrogen ions outside, and that of the anions on both sides, was disturbed. Further dissociation was favored, which resulted in the formation of more hydroxo groups and removal of the anion from the inside of the complex. The sensitivity of the sol toward the action of neutral salt was thus increased (Figs. 1, 2 and 3, and Table I).

An ol-group in a complex aluminum ion is much less readily displaced by anions than an hydroxo group, and an oxo group is not displaced at all. Heat increases olation and oxolation. A heated sol, therefore, becomes much less reactive toward neutral salts than the original one (Fig. 6).

The penetration order of the halides and acetate was found to be: iodide < bromide < chloride < acetate. Since at equal concentrations, a highly penetrating ion will enter the complex to a greater extent than a less highly penetrating ion, then more hydroxo groups should be expelled from the nucleus in the former than in the latter case. When prepared under similar conditions, the micelles of aluminum oxyacetate sol should contain fewer hydroxo groups than an oxyiodide sol. On addition of equal amounts of neutral salts, oxyiodide sol consequently gave a larger increase in *P*H than oxyacetate sol, while oxychloride and oxybromide sols gave intermediate values of increase (Figs. 4 and 5).

Now, the explanation of the results of the conductivity experiments becomes evident. The cause of the decrease of conductivity upon addition of silver salts cannot be attributed alone to the fact that highly mobile iodide ions in solution were substituted by the less mobile ones, because, as has already been pointed out, sulfate ion has higher mobility than iodide, yet the decrease in conductivity on addition of silver sulfate was one of the most marked (Figs. 7 and 8). Sulfate ion is a very powerful penetrant. Before the amount equivalent to that of iodide in the sol was added, nearly all of it penetrated into the complex and, therefore, no longer affected the conductivity. The entering sulfate ions replaced aquo, iodo and hydroxo groups from the complex. The replacement of aquo groups caused a decrease in the charge of the micelles, thus resulting in a decrease in their effect upon the conductivity. The iodide ion formed by the displacement of iodo groups was precipitated as silver iodide and the hydroxyl ion from the displaced hydroxo group combined with the hydrogen ion in solution. Nitrate and acetate ions are less penetrating than sulfate ions, and consequently the slopes of their curves are not so steep.

Since the amounts of silver salts added to the sols in these conductivity

experiments were very small, no free hydroxyl ion (in excess of hydrogen ion) should be present in the solution. For example, the maximum amount of silver salt added to sol V was less than 0.007 equivalent per liter. According to Fig. 2, at such a concentration of the added anions—nitrate, acetate and sulfate—the solutions were still acid. However, oxalate ion at that concentration would displace hydroxo groups from the complex to such an extent as to bring the solution to a PH value of about 7.5. Since tartrate ion, similar to oxalate ion, is a more powerful penetrant than sulfate ion, a small amount of it would be sufficient to displace enough hydroxo groups to make the solution alkaline. In the conductivity experiments, the brown coloration observed in each of the final mixtures of silver tartrate and sols V and VIII is presumed to be due to the formation of silver hydroxide.

From the results of conductivity experiments, the penetration order of the anions studied should be: nitrate < acetate < sulfate < tartrate. The fact that nitrate ion, less penetrative than iodide, replaced all the iodide in the sol does not exclude the possibility of having a fraction of the total iodide inside of the complex in the original sol, since the mixture of the sol and silver nitrate was allowed to stand for two days. As soon as the iodide inside of the complex migrates out to restore the equilibrium and so on until all is removed from the complex.

Results of the measurements of salt effect on PH and conductivity of sols have shown the anion penetration order to be: nitrate < chloride < acetate < sulfate < oxalate, tartrate. This order is identical to that found by Thomas and Whitehead for aluminum oxychloride sols and to the anion penetration order of Stiasny for solutions of basic chromium salts, except that the positions of sulfate and acetate are interchanged.

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