3. The smaller apparent molal volumes occupied by terminal groups in the amino acids being ascribed to electrostriction of solvent molecules, the apparent volumes of the uncharged amino and carboxyl groups have been estimated from the molal volumes of aliphatic acids, amides and amines and of hydantoic acid.

4. Apparent molal volumes yield a criterion for distinguishing between zwitterions and uncharged molecules. The measurements considered indicate that urea and hydantoic acid are not zwitterions, and that the proportion of the molecules of *m*-aminobenzoic acid that are zwitterions, is far greater than of the other aminobenzoic acids.

5. Separation of the charged groups from each other in a zwitterion increases electrostriction, which amounts to 13.3 cc. per mole when the charged amino group is in the α position and approximately 18 cc. per mole when in the ϵ position.

6. The apparent molal volumes of amino acid salts have been analyzed in terms of the volumes and electrostrictions of their constituent ions. The electrostriction due to amino acid ions appears to be slightly greater than that of the same charged groups of zwitterions even when the charged groups are separated by five carbon atoms.

7. The electrostrictions suggest the approximate dimensions of the charged groups, and the molal volumes the dimensions of amino acid and peptide molecules.

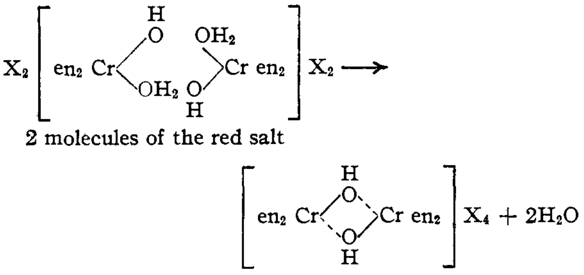
BOSTON, MASS. RECEIVED OCTOBER 21, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Nature of Chromium Oxychloride Hydrosols

BY ARTHUR W. THOMAS AND FREDERICK C. VON WICKLEN

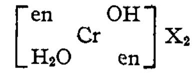
The possibility of one coördinative bond of each of two metal atoms being shared by one hydroxyl (or hydroxo) group was first suggested by Pfeiffer.[1] To compounds containing such groups Werner[2] gave the name, "ol-compounds" and described the preparation of octammino-di-ol-dicobalti sulfate from hydroxo-aquo-tetrammino-cobalti sulfate. Then Pfeiffer,[3] observing that the red colored diethylenediamine-hydroxo-aquo-chromi salts were converted to crystalline blue violet salts with the loss of one molecule of water per atom of chromium upon heating to 100–120°, proposed the formation of the di-ol compound as the most satisfactory explanation, according to the scheme



2 molecules of the red salt

1 molecule of the blue violet di-ol compound

and pointed out "Dass dieser Vorgang manche Analogie mit der Polymerisation organischer Verbindungen, z. B. der der Aldehyde zeigt, ist ohne weiteres ersichtlich."[3a] Since the flesh colored di-ethylene-diamine-hydroxo-aquo salts did not undergo this change upon heating, he ascribed to them the *trans* configuration



$$\left[\begin{matrix}\text{en} & & \text{OH}\\ & \text{Cr} & \\ \text{H}_2\text{O} & & \text{en}\end{matrix}\right]X_2$$

and to the red salt, the *cis* structure.

Bjerrum[4] found polymerization of basic chromic salts to occur upon heating of their aqueous solutions producing increases in molecular weight to as high as 750. These products were referred to by him as "latent basic" compounds.[5]

Thus from Bjerrum's discoveries concerning the extent of polymerization of his "latent basic" compounds, one might imagine that he had in solution, among other complexes, dodecaol-dodecaaquohexachromi chloride[6] of molecular weight 732.

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[1] P. Pfeiffer, *Z. anorg. Chem.*, **29**, 107 (1902).

[2] A. Werner, *Ber.*, **40**, 2113, 4436 (1907).

[3] P. Pfeiffer, *Z. anorg. Chem.*, **56**, 261 (1908).

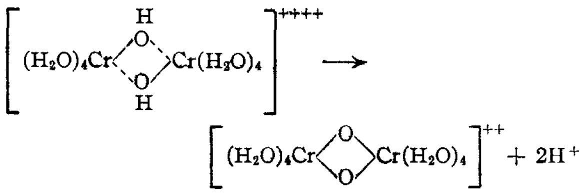
[3a] "That this reaction shows many analogies to the polymerization of organic compounds, for example of the aldehydes, is quite obvious."

[4] N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907); **73**, 724 (1910); "Studier over Basike Kromiforbindelser," Kopenhagen, 1908.

[5] It should be recalled that T. W. Richards and F. Bonnet, *Z. physik. Chem.*, **47**, 29 (1904), had reported the existence of a variety of basic chromic sulfate solutions containing particles of high molecular weight.

[6] (a) E. Stiasny and O. Grimm, *Collegium*, **691**, 505 (1927); (b) E. Stiasny and D. Balanyi, *ibid.*, **682**, 86 (1927).

About twenty years later, Stiasny,[6b] finding that "ol" or "latent basic" compounds split off hydrogen ion when their solutions were heated, proposed the following mechanism by way of explanation



the hydrogen ions coming from the conversion of the "ol" bridges to oxygen bridges, producing, in his terminology, "oxo" compounds. While ol compounds readily change to oxo compounds upon heating their solutions, the reversal of the process has been found to be exceedingly slow upon temperature drop. Also while ol compounds can be depolymerized without much difficulty (they are more resistant to acid than hydroxo compounds) finally to the normal salts upon addition of hydrogen ion, oxo compounds as would be expected from the preceding statement, are very resistant to the action of hydrogen ion.

It is the purpose of this paper to present evidence in favor of the consideration of "chromic oxide," or more accurately speaking chromic oxy salt hydrosols as poly-olated complexes which may also be more or less oxolated.

Preparation of Hydrosols

Starting with E. de Haën A. G. reagent grade chromic acid anhydride, dark green crystals of chromic chloride hexahydrate were prepared according to the method of Recoura:[7] 0.5 or 1 normal solutions were treated with sodium hydroxide solutions of the same normality in the proportion of 85 volumes of sodium hydroxide solution to 100 volumes of chromic chloride solution. After twenty-four hours these mixtures were dialyzed at room temperature against distilled water running through nitrocellulose tubes, these having been prepared from an alcohol-ether solution of du Pont "Parlodion." The dried membranes were soaked in alcohol of about 85% by volume for twenty-four hours and then perfused with distilled water for twenty-four hours prior to use in order to increase their permeability. When this continuous dialysis process had operated for a time deemed sufficient, the sols were centrifuged to remove the slight sediment and bottled in resistance glass ("Non-Sol"). The sols were green both by reflected and transmitted light and possessed a slightly turbid appearance. When subjected to the action of an electric field, the chromic micelles migrated to the cathode in all cases.

Six hydrosols were studied in this investigation, three of which are discussed in this paper inasmuch as they are typical. Fundamental properties are given in Table I.

Titration with Neutral Salts

It has been shown previously[8,9] that the *P*H values of aluminum oxyhalide hydrosols are increased upon addition of neutral salts, the effect varying markedly according to the nature of the anion of the salt. In this investigation the influence of potassium salts upon the chromic oxychloride sols was measured, using a technique previously described.[9]

TABLE I

DESCRIPTION OF HYDROSOLS

Sol No.	8	12	13
Normality $CrCl_3$ used	1.0	0.5	0.5
Dialysis, hours	120	120	192
Cr, m. e.[a]/liter	156.0	144.9	75.88
Cl, m. e./liter	17.93	15.74	5.14
Ratio Cr:Cl	8.7	9.2	14.8
*P*H at end of dialysis (25°)	3.88	3.75	4.30

[a] m. e. = milliequivalents.

TABLE II

*P*H VALUES OF 0.1 NORMAL POTASSIUM SALT SOLUTIONS

Nitrate	5.3	Sulfate	5.4
Chloride	5.4	Tartrate	6.5
Thiocyanate	5.7	Citrate	6.8
Acetate	6.7	Oxalate	6.4

The *P*H values of the pure salt solutions are recorded in Table II.

The *P*H values of the hydrosols measured after sixteen hours of standing at room temperature subsequent to the addition of the salt solutions are plotted in Figs. 1 and 2. It is seen that the effects vary according to the nature of the anion, the *P*H values being raised in each case, and to an alkaline reaction in the cases of citrate and oxalate. The order of effectiveness of the salts is seen to be oxalate ≧ citrate > acetate ≧ tartrate > sulfate > thiocyanate > chloride > nitrate. Thus chromic oxychloride hydrosols behave in this respect substantially like aluminum oxyhalide sols.[8,9]

It may be well to refer to crystalloidal chromic salt solutions in this connection. First, it is known that oxalate, acetate, tartrate and sulfate ions readily react with chromic chloride, displacing coördinatively bound aquo groups or chlorido groups and, if at a sufficient concentration actually convert the chromic cation to an anion resulting in the formation of chromiates.[10] Nitrate and chloride are much less powerful in

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[7] A. Recoura, *Compt. rend.*, **102**, 515 (1886).

[8] A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, **35**, 27 (1931).

[9] A. W. Thomas and A. P. Tai, THIS JOURNAL, **54**, 841 (1932).

[10] E. Stiasny, "Gerbereichemie (Chromgerbung)," Theodor Steinkopff, Leipzig, 1931. Chap. 14–17.

this respect and do not produce chlorido or nitrato chromiates although the triaquo-trichlorido chromium has been recognized. Second, it has been shown that low concentrations of sodium chloride decrease the hydrogen ion activity of chromic chloride solution[11] and it is known that sodium sulfate is more potent in this respect.[10]

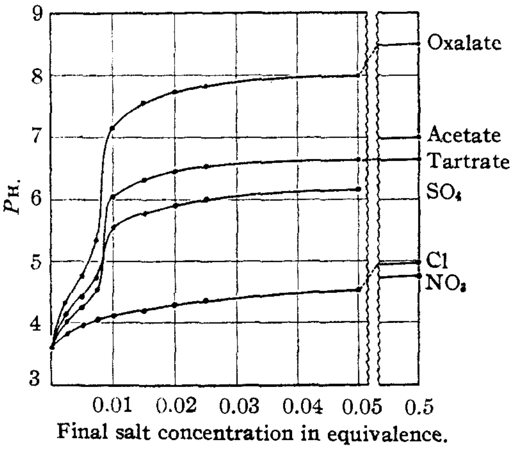

Fig. 1.—Titration of sol No. 8 with neutral salt solutions.

Although it has been denied[12] that hydroxo groups can be replaced by neutral salt anions from crystalloid and semi-colloid chromic complex ions, the data given in Figs. 1 and 2 give

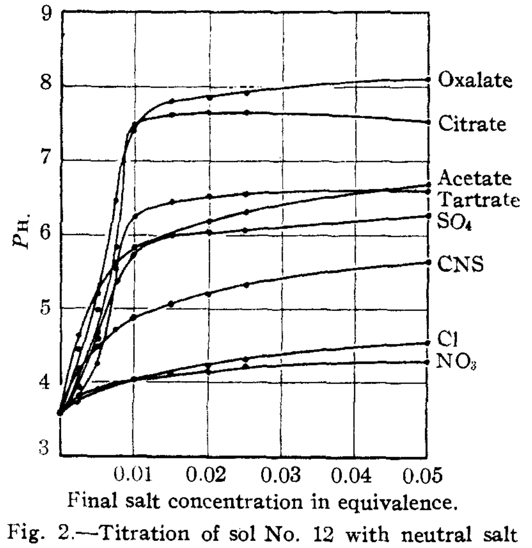

Fig. 2.—Titration of sol No. 12 with neutral salt solutions.

strong indication that either hydroxo or ol (or both) groups have been replaced from the chromic micelles by the added neutral salt anions. The steep rise noted in the polyvalent anion curves just under 0.01 normal concentration of added salt would indicate that at concentrations below about 0.05 normal the aquo and chlorido groups are being replaced to a much greater extent than hydroxo groups are. This is reasonable in view of the fact that hydroxo groups are known to be about the most strongly coördinatively bound groups in low molecular weight chromium complexes.[13]

Experiments on attainment of equilibrium in the decrease of hydrogen ion activity as a result of neutral salt additions are shown in Fig. 3. It is evident that the *P*H values approached equilibrium sooner in the case of added potassium chloride than with either the sulfate or oxalate. Precipitation started within the first hour when the latter two salts were added while none was produced by the chloride at any time interval.

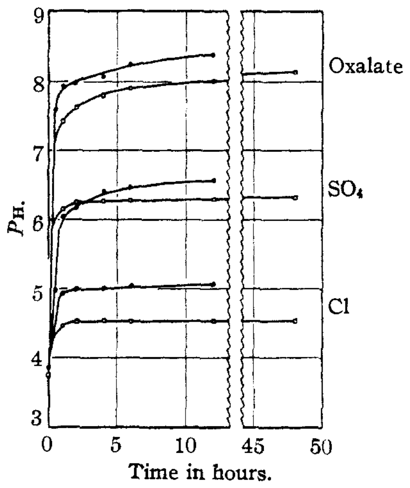

Fig. 3.—Rate of change in *P*H: dots, sol No. 8 at salt concentration of 1 *N*; circles, sol No. 12 at salt concentration of 0.1 *N*.

Influence of Age and of Elevated Temperature

The *P*H values of five different chromic oxychloride hydrosols stored in resistance glass bottles at 25° and measured from time to time demonstrated that the hydrogen-ion activity steadily increased as the sols aged at room temperature. Representative results are presented in Table III. Formation of ol compounds ("olation") and/or the conversion of ol bridges to oxo bridges ("oxolation") account for this effect. Since olation removes primary hydrolytic products, the hydroxo compounds, the equilibrium is thereby disturbed resulting in further hydrolysis of the

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[11] K. H. Gustavson, *Ind. Eng. Chem.*, **17**, 945 (1925).

[12] Ref. 10, p. 361.

[13] Ref. 10, p. 339.

chromic oxychloride complexes producing more hydroxo compounds and hydrogen ion. The increase in acidity resulting from oxolation of ol groups is illustrated by the type reaction given in one of the opening paragraphs of this paper.

These hydrosols were also heated at 90° in tightly stoppered resistance glass bottles for ten days, when they were cooled to 25°. The *P*H measurements made thereupon immediately and after certain intervals of standing at 25° are recorded in Table III. The results for "zero age"[14] strikingly show the expected indication of olation and/or oxolation which are favored by elevation of temperature. The increase in *P*H values of the heat treated sols upon subsequent standing at 25° shows slow reversal of the process; more likely de-olation than de-oxolation.

TABLE III

EFFECT OF AGE AND OF ELEVATED TEMPERATURE

Age in days	Original sol not heated Sol 8	 Sol 12	Sol after heating Sol 8	 Sol 12
0	3.88	3.75	2.71	2.93
7	3.86	3.75	2.73	2.95
14	3.81	3.73	2.75	2.97
21	3.79	3.73	2.80	2.98
28	3.73	3.71	2.83	3.00
45	..	3.70	..	3.04

The results of neutral salt titrations of sol 12 before and after heating are plotted in Fig. 4. It is obvious that the sol is much less responsive to the action of chloride and sulfate after the elevated temperature "aging" than before. This result is just what one would expect if the heat treatment converted ol groups to oxo bridges. However, one cannot ascribe it to this alone. If olated –OH groups are not so easily displaced by other anions as coördinatively bound hydroxo groups, the behavior may also be interpreted as a result of olation produced by the heating. Inasmuch as Bjerrum's "latent basic" chromic complexes (ol complexes) were found to be more resistant to the action of acids than the simple basic salts (hydroxo compounds), the latter statement is reasonable.

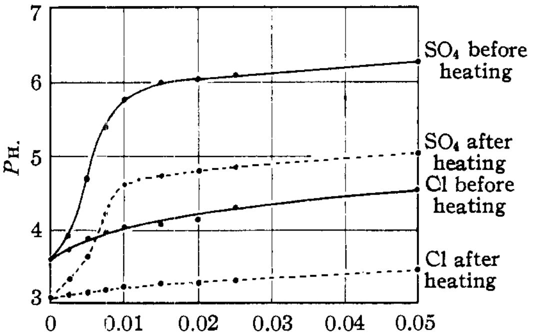

Fig. 4.—Effect of neutral salts on *P*H of sol No. 12 before and after having been heated.

The above described behavior of chromic oxychloride hydrosols is substantially like that previously found for aluminum oxyhalide hydrosols.[8,9]

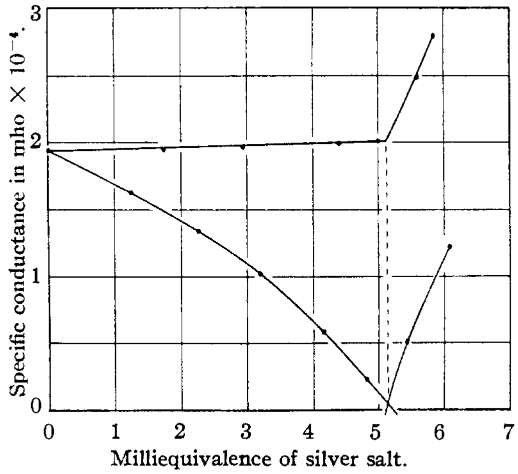

Fig. 5.—Conductance titration of sol No. 13 with silver salts. Upper curve, silver nitrate; lower curve, silver sulfate.

Conductance Titrations

By means of a technique previously described,[9] conductance titrations with silver nitrate and sulfate were performed and the measurements upon sol 13 are shown in Fig. 5. The vertical dotted line in the figure marks the total chlorine content of the hydrosol.

Figure 5 shows that added amounts of silver nitrate caused an increase in conductivity in the first part of the curve, while the reverse was found true for the sulfate. These facts may be explained by assuming an equilibrium between the free chloride ion and the coördinatively bound chlorido atoms. When silver ion is added to the sol, the chloride ion is removed and coördinatively bound chlorine moves out of the complex. Since the nitrate ion shows a very slight tendency toward complex formation, one may assume that aquo groups enter the complex to satisfy the coordination number of the chromium. As shown

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[14] "Age in days" in the case of the unheated sols commenced with cessation of the dialysis whereas in the heated sols it commenced with conclusion of the ten-day heating period.

by Werner,[15] replacing of a negatively charged group, such as chlorido, by an uncharged group, such as aquo, in the complex, causes an increase in both the positive charge on the cationic complex and the conductivity.

The decrease in conductivity on addition of silver sulfate can be explained in a similar manner. Silver ion removes chloride ion, and coördinatively bound chlorido groups move out to take its place. However, instead of aquo groups entering the complex, we can assume here that sulfate ion, a powerful "penetrator," goes into the complex becoming a coördinatively bound sulfato group. If all the sulfate ion added to the sol finds its way into the complex, and since there was more added than equivalent to that part of the chlorine which is complex bound, aquo groups must be replaced along with the chlorine.[16] The effect here is just the opposite from that noted above in the case of the nitrate. Uncharged aquo groups are replaced by negatively charged sulfato groups, resulting in a lowering of the positive charge on the complex and a decrease in conductivity. In both curves after the point was reached where all the chlorine was precipitated, the conductivity curve rose steeply as the added silver salt increased the total number of ions in solution.

While this chromic oxychloride sol behaved similarly to two aluminum oxyiodide sols[9] upon treatment with silver sulfate, it reacted differently to silver nitrate. Silver nitrate produced a lowering of the conductivity of the previously reported[9] aluminum oxyiodide sols, which is interpreted as showing that the nitrate anion has a greater tendency to be coördinatively bound to the metallic atoms in aluminum than in chromium oxy salt micelles.

Argument

The known tendency for basic chromic salts to polymerize in aqueous solution or, in the language of Werner and Pfeiffer, for simple hydroxochromi ions to form ol compounds, has been extended to include the so-called "chromic oxide" or, more accurately, the chromic oxychloride, hydrosols. When these sols are regarded as dispersions of poly-olated chromic complexes, the cationic micelle containing some aquo, some chlorido groups, perhaps some hydroxo groups, and, if heated, some oxo groups, their behavior becomes readily understood by application of the knowledge pertaining to the crystalloidal basic salts, their simple polymerization products and their reactions with diverse neutral salt anions. This point of view also allows for the existence of a vast number of chromic oxychlorides, an even greater number of chromic oxy salt hydrosols and illustrates why no two "identical" colloidal solutions of this kind are quantitatively identical in behavior although their ultimate analyses for chromium and salt anion[17] are the same.

Inasmuch as the experimental data submitted in this paper show chromic oxychloride sols to act substantially like aluminum oxyhalide sols previously reported from this Laboratory, the suggested point of view is not restricted to "chromic oxide" hydrosols.

NEW YORK, N. Y.

RECEIVED OCTOBER 23, 1933

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[15] A. Werner and P. Pfeiffer, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Vieweg und Sohn, Braunschweig, 1923, 225 ff.

[16] It is to be recalled that higher concentrations of added sulfate will replace coördinatively bound –OH groups.

[17] In the colloid literature, this anion is called the anion of the "peptizer."