52. *Chromium Phosphates. Part II.*[1] *Phase Diagram at 70° and Further Ion-exchange Studies in the System Chromium*(III)*–Phosphoric Acid.*

By J. P. Redfern and J. E. Salmon.

A phase-diagram study of the system Cr_2O_3–P_2O_5–H_2O at 70°, where both solutions and solid materials were green, showed that no one solid phase occurred in the range 1—20% of phosphoric oxide. The system gave a series of parallel or slightly diverging tie-lines which are interpreted as indicating that the solid phases possess ion-exchange properties. Preliminary experiments indicate that the material in fact exhibits cation-exchange properties. Batch ion-exchange experiments carried out with solutions aged at 70° indicated the presence of polynuclear cationic complexes. Chromatographic separations employing a gradient elution technique indicated the presence of polynuclear ions having the probable structures $[H_2PO_4\text{–}(Cr\text{–}HPO_4)_n\text{–}Cr\text{–}H_2PO_4]^{x+}$ where $n = 0, 1, 2, 3,$ or 6.

In Part I[1] it was shown that at 0° in freshly prepared solutions of the purple tertiary chromium(III) phosphate dissolved in phosphoric acid over a range of 1—25% of phosphoric oxide there was no evidence for complex formation involving the phosphate ion; that is, the ions in such solutions were $[Cr(H_2O)_6]^{3+}$ together with H_3O^+, $H_2PO_4^-$, and HPO_4^{2-}. However, if such solutions were aged at 40° they became green. Ion-exchange and pH studies by Holroyd and Salmon[2] indicated complex formation. Study by Jameson and Salmon[1] of saturated solutions aged at 40° indicated the presence of the following complexes: $[Cr(PO_4)_2]^{3-}$, $[CrHPO_4]^+$, and less probably $[CrH_2PO_4]^{2+}$. It is clear from the difficulty experienced by these workers in achieving a full saturation of the resin that other larger complexes were probably also present: the temperature of 40° was selected as one at which the conversion of the purple-red uncomplexed solution into the green complexed form took place at a reasonable rate. These workers also reported that a radical change seemed to take place in solutions kept above this temperature for any length of time; this was in accord with an observation by Vauquelin.[3] The work has been extended to determine the solubility isotherm of the system at 70° and also the nature of the solid phases and the solution phase at this temperature.

Experimental

Apparatus.—The ageing of solutions at 70° was carried out in an air thermostat. The samples for the phase studies were treated as described in Part I.[1] The solutions for use in the ion-exchange studies were aged in glass bottles closed with Polythene stoppers.

Preparation of Solutions.—Solutions were prepared by dissolving the purple tertiary salt[1] in phosphoric acid solutions and ageing them at 70°. The time required for equilibration was found by an ion-exchange method. At suitable periods an aliquot part of the ageing solution was transferred to a dry, conical flask into which had been introduced ½ g. of the cation-exchanger " ZeoKarb 225 " (20—40 mesh; 8% cross-linked) (H form) or 1 g. of the anion-exchanger DeAcidite FF (20—40 mesh; 8% nominal cross-linking) (PO_4 form). After a period the resin was separated and the sorbed species were eluted and analysed for chromium or phosphate. A plot of the uptake against the time of ageing gave a smooth curve reaching a constant value (either a maximum or minimum), which was taken as the criterion for equilibrium.

Resins.—The strongly acidic monofunctional cation-exchanger " ZeoKarb 225 " was used for both the batch and the column experiments. Resins of varying degrees of cross-linking

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[1] Part I, Jameson and Salmon, *J.*, 1955, 360.
[2] Holroyd and Salmon, *J.*, 1956, 269.
[3] Vauquelin, *Ann. Chim. Phys.*, 1798, **25**, 194.

were employed; the best measure of this was provided by the weight-swelling values, measured by Pepper, Paisley, and Young's centrifuge method.[4]

Batch Experiments.—The technique was that outlined by Jameson and Salmon,[5] modified to permit more efficient elution of the sorbed species after the resin had been transferred to a column. The resin was kept in contact for some considerable time with successive small portions of the eluting agent. This method has the advantage of reducing the amount of eluting agent needed to achieve complete removal of the sorbed species and facilitating subsequent handling and analysis.

Column Experiments.—To the top of the resin column (1 × 35 cm.) was fitted a sintered-glass disc in order to trap any solid particles which could contaminate the resin bed and to prevent the resin particles from flowing into the rest of the apparatus on back-washing. The supply to the column was from a reservoir connected to the column through a mixing chamber, which was stirred magnetically. Concentrations of the solutions in the mixing chamber and the reservoir and the volume of the liquid in the mixing chamber were varied until they gave a clear separation of the complexes on the column. However, a theoretical expression was derived [6] for the exact concentration of the eluant entering the column at a given time t, *viz.*,

$$v_0 \ln [(c_0 - c_1)/(c - c_1)] = c$$

where c = concentration of eluant leaving mixing chamber at time t, c_1 = concentration of solution in the reservoir, c_0 = concentration initially of the solution in the mixing chamber, v = the volume delivered after time t, v_0 = volume of liquid in the mixing chamber (constant throughout experiment). Under the conditions used in the present study, the mixing chamber always contained water initially, *i.e.*, $c_0 = 0$. The equation may be rearranged to give the concentration at time t:

$$c = c_1(e^{v/v_0} - 1)/(e^{v/v_0})$$

Analysis.—Chromium was determined as before; [1] it was shown that nitric acid in the concentrations encountered did not interfere. The phosphate was determined as phosphomolybdate, dried at 110°, and weighed after breakdown of the complexes by treatment with ammonia (*d* 0·880) and a few drops of 100-vol. hydrogen peroxide, acidification, and prolonged boiling.

RESULTS AND DISCUSSION

Phase Diagram.—The system was studied at 70° for the range of solutions up to 66% of phosphoric oxide. Samples containing more than 20% were gel-like and separation into solid and liquid phases proved impossible. The results, given in Table 1 and Fig. 1, show little resemblance to those found at 40°.[1] The system of parallel or near-parallel tie-lines could be interpreted in one of the following ways: (i) The system is in metastable equilibrium. In the system Fe_2O_3–P_2O_5–H_2O at 25° various workers [7] found similar tie-lines which persisted up to 20% of phosphoric oxide, but it was shown by Jameson and Salmon [8] that such tie-lines were but one of a number of stages that the

TABLE 1. *Phase-diagram results of the system* Cr_2O_3–P_2O_5–H_2O *at* 70°.

Solution		Solid		Solution		Solid		Solution		Solid	
Cr_2O_3 (%)	P_2O_5 (%)	Cr_2O_3 (%)	P_2O_5 (%)	Cr_2O_3 (%)	P_2O_5 (%)	Cr_2O_3 (%)	P_2O_5 (%)	Cr_2O_3 (%)	P_2O_5 (%)	Cr_2O_3 (%)	P_2O_5 (%)
0·09	1·07	7·32	9·77	2·39	8·71	10·27	17·65	6·36	14·36	15·50	24·90
0·24	2·24	7·90	11·55	3·28	9·43	7·87	14·70	6·46	14·13	13·25	22·50
0·48	2·90	8·15	12·28	3·17	9·92	13·29	21·73	8·61	17·23	9·76	18·67
1·43	5·37	9·43	15·08	3·92	10·49	—	—	9·09	17·93	17·36	27·72
1·87	6·62	7·75	13·49	5·44	13·18	6·76	14·03				

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[4] Pepper, Paisley, and Young, *J.*, 1953, 4097.

[5] Jameson and Salmon, *J.*, 1954, 4013.

[6] Ernst and Redfern, unpublished work.

[7] Cameron and Bell, *J. Phys. Chem.*, 1907, **11**, 363; Carter and Hartshorne, *J.*, 1923, **123**, 2223; Salmon, *J.*, 1952, 2316.

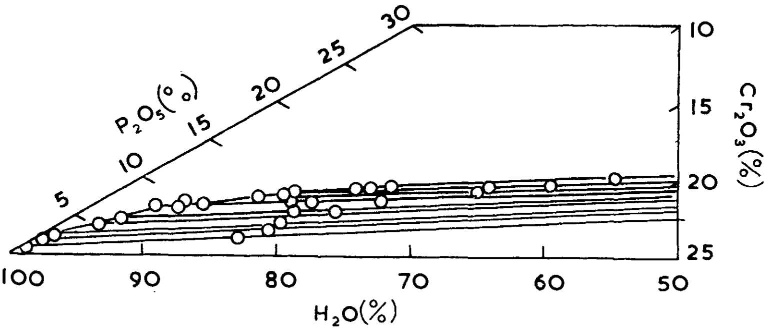
[8] Jameson and Salmon, *J.*, 1954, 28.

system went through before stable equilibrium was attained—in the present work care was taken to ensure that equilibrium had been truly attained.

(ii) That solid solutions were being formed between the green tertiary phosphate and one or more acid components. Solid solutions have been classified by Roozeboom [9] and by Ricci [10] as being of six types readily distinguishable by the use of the Roozeboom diagram, in which the percentage of A in the liquid is plotted against that in the solid in contact (the water content being ignored), *i.e.*, 100A/(A + B)%, where A and B are the two salts concerned. Several possibilities for A and B were tried but in no case could the present system be described as being one of the six types.

(iii) That a solid phase Cr_2O_3,P_2O_5,xH_2O has sorbed more or less phosphoric acid according to the composition of the liquid phase; Carter and Hartshorne [7] interpreted the parallel tie-lines in the ferric system in this way. If such adsorption is pictured as purely physical, it presumably depends on the surface area of the solid, and it is difficult to see how this would consistently lead to parallel tie-lines.

FIG. 1. Cr_2O_3–P_2O_5–H_2O *at* 70°.



(iv) The system is behaving as an ion-exchange material. Jameson and Salmon [8] interpreted the parallel tie-lines in the metastable ferric system as due to the fact that $H_6[Fe(PO_4)_3]$ which separated out initially acted as a cation-exchanger. Recent work [11,12] has shown that some hydrous oxides of ter- and quadri-valent metals show weakly basic anion-exchange properties, and that some phosphates and tungstates behave in a similar fashion as weakly acid-cation exchangers. No investigation of the structure has yet appeared, but it was suggested that the solid material consisted (*e.g.*, in the case of the zirconium phosphate) of zirconium atoms linked by bridging oxygen atoms: to the zirconium atoms, acid phosphate groups were attached and these had replaceable hydrogen ions for cation exchange.[12] The material in the present system was examined for possible ion-exchange properties. Solid material, isolated from the mixture used for the phase diagram at 70°, was loaded into a small column (1 × 10 cm.). Two such samples were treated with a dilute solution of chrome alum. Sample 1 sorbed 0·014 mmole of $[Cr(H_2O)_6]^{3+}$, and sample 2 0·046 mmole. In both cases it was shown that the solution became more acid on passage through the material. Subsequently, sample 2 was treated with a dilute solution of nitric acid (pH 1·5) and $[Cr(H_2O)_6]^{3+}$ ions were desorbed. The same sample was then treated with 0·1M-sodium chloride, and hydrogen ions were desorbed. All effluents from the two samples (about 0·5 g. dry weight) were checked for phosphate and in every case none was detected. In the light of this, and in view of the predominance of complex cations present in solutions in equilibrium with the solid material as shown by

[9] Roozeboom, *Z. phys. Chem.*, 1891, **8**, 521.

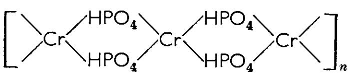
[10] Ricci, *J. Amer. Chem. Soc.*, 1935, **57**, 805.

[11] Kraus and Phillips, *J. Amer. Chem. Soc.*, 1956, **78**, 249, 694; Amphlett, McDonald, and Redman, *Chem. and Ind.*, 1956, 1314; 1957, 365; Anderson, *Trans. Faraday Soc.*, 1958, **54**, 130.

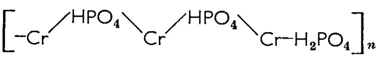
[12] Amphlett, McDonald, and Redman, *J. Inorg. Nuclear Chem.*, 1958, **6**, 220, 236.

the present studies, it is to be expected that the solid material consists of a polymeric network of one or a combination of both of the following types:

Type I



Type 2



Ion-exchange.—Jameson and Salmon[1] commented on the care that is needed in interpretation of the batch ion-exchange studies at 40° owing to several factors, *viz.*, the size of the complexes being sorbed, the time of ageing of the solution, and the time of contact of the solution with the resin. In all the present work fully aged solutions were used and the other two factors were investigated. If some steric factor is involved, the use of resins of various degrees of cross-linking should reflect the size of the complex ions being sorbed, in that tightly cross-linked (low weight-swelling) resins should preclude the entry of large ions. A range of solutions and resins of varying weight-swelling values being used, there was a marked fall in the amount of chromium and phosphate sorbed per equivalent of exchanger as the resin became more tightly cross-linked (see Fig. 2). The mole ratio $PO_4 : Cr$ also varied. Thus it appeared likely that a number of complexes competed for the exchange sites on the resin and that some of these were of considerable size. Increasing the time of contact of the solution with the resin caused a gradual rise in the amount of chromium and phosphate sorbed, especially for the medium cross-linked resins. In Fig. 3 this is compared with the rapid sorption of $[Cr(H_2O)_6]^{3+}$ from unaged solutions by the same resin. The shape of the curve for the uptake of the complexes indicates that the ions being sorbed are large and that entry is slow. It is also possible that the ions being sorbed undergo chemical attack on contact with the, initially, strongly acid media of the resin at room temperature, and that these smaller fragments are subsequently sorbed on the resin. The possibility that a number of complexes of similar type

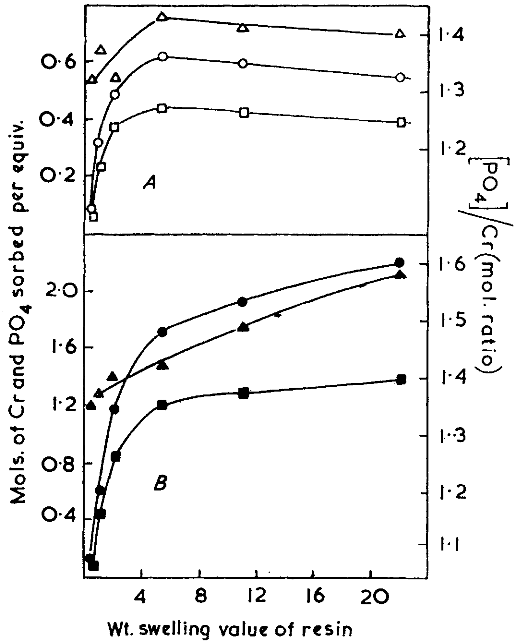


FIG. 2. *Sorption on ZeoKarb* 225 (H *form*) *from solutions aged at* 70° *for* 4 *days.*

(*A*) *Solution contained* 2·5% *of* P_2O_5 *and* 0·3% *of* Cr_2O_3.

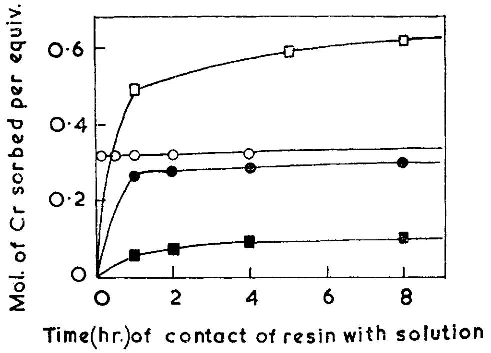
PO_4 *sorbed.* □ Cr *sorbed.* △ $[PO_4]/[Cr]$ *mole ratio species sorbed.*

(*B*) *Solution contained* 12·5% *of* P_2O_5 *and* 5·0% *of* Cr_2O_3.

● PO_4 *sorbed.* ■ Cr *sorbed.* ▲ $[PO_4]/[Cr]$ *mole ratio species sorbed.*

In every case resin and solution were in contact for 2 *hours.*

FIG. 3. *Sorption of* Cr *by ZeoKarb* 225 (H *form*) *from fresh and aged solutions after various times of contact.*



Weight-swelling value of resin	Moles/equiv. Cr sorbed	Condition of solution
1·98	○	Fresh
	□	Aged at 70° for 4 days
0·43	●	Fresh
	■	Aged at 70° for 4 days

Solution contained 5·0% *of* P_2O_5 *and* 1·0% *of* Cr_2O_3.

TABLE 2. *Ion-exchange chromatography: gradient elution of chromium*(III) *complexes in solutions of constant* P_2O_5 *concentration, after ageing at* 70°.

Solution Cr (*m*)	Solution PO_4 (*m*)	Complexes in order of elution	v_0 (ml.)	c_1 NH_4NO_3 (N)	c_1 HNO_3 (N)	Cr found (mmole)	PO_4 found (mmole)	Cr : PO_4 mole ratio	Probable ideal Cr : PO_4 mole ratio
0·039	2·113	A	550	1·00	—	0·054	0·109	1 : 2·02	1 : 2
0·196	2·113	A	575	0·66	—	0·196	0·406	1 : 2·07	1 : 2
		B		0·66	—	0·077	0·111	1 : 1·45	1 : 1·5
		C		0·66	—	0·065	0·088	1 : 1·36	1 : 1·33
0·392	2·113	A	580	0·66	—	0·182	0·364	1 : 2·00	1 : 2
		B		0·66	—	0·138	0·201	1 : 1·46	1 : 1·5
		C		0·66	—	0·112	0·156	1 : 1·38	1 : 1·33
		D		0·66	4	0·049	0·060	1 : 1·22	1 : 1·25
		G		—	8	0·101	0·051	1·99 : 1	2 : 1
0·588	2·113	A	580	0·66	—	0·073	0·179	1 : 2·47	1 : 2
		B		0·66	—	0·071	0·102	1 : 1·45	1 : 1·5
		C		0·66	—	0·038	0·050	1 : 1·33	1 : 1·33
		D		0·66	4	0·106	—	1 : 1·25 *	1 : 1·25
		E		0·66	4	0·144	0·160	1 : 1·12	1 : 1·125
		F		0·66	4	0·150	0·152	1 : 1·01	1 : 1
0·784	2·113	A	580	0·66	—	0·032	0·064	1 : 1·99	1 : 2
		B		0·66	—	0·087	0·140	1 : 1·61	1 : 1·5
		C		0·66	—	0·026	0·035	1 : 1·33	1 : 1·33
		D		0·66	4		Not detected		
		E		0·66	4	0·258	0·295	1 : 1·14	1 : 1·125
		F		0·66	4	0·177	0·178	1 : 1·00	1 : 1

2% Cross-linked ZeoKarb 225 (50—100 mesh) (H form) was contained in a column 1·2 × 33 cm. The results are given only on the main portion of the eluted complex: 0·5 g. samples of the resin were shaken with 10 g. of the fully aged solution for 2 hr., washed free from phosphate on a sintered-glass filter, and loaded on to the top of the prepared column. v_0 and c_1 have the significance given in the text.

* By inference; also indicated in some preliminary chromatographic work. Probable structures that may be assigned to the complexes:

A = $[H_2PO_4{-}Cr{-}H_2PO_4]^+$; B = $[H_2PO_4{-}Cr{-}HPO_4{-}Cr{-}H_2PO_4]^{2+}$; C = $[H_2PO_4{-}Cr{-}(HPO_4{-}Cr)_2{-}H_2PO_4]^{3+}$;
D = $[H_2PO_4{-}Cr{-}(HPO_4{-}Cr)_3{-}H_2PO_4]^{4+}$; E = $[H_2PO_4{-}Cr{-}(HPO_4{-}Cr)_6{-}H_2PO_4]^{7+}$;
F = $[H_2PO_4{-}Cr{-}HPO_4{-}Cr]^{3+}$; G = $[Cr{-}HPO_4{-}Cr]^{4+}$

In complexes B, C, D, and E the charge may be reduced by one or two units by the loss of a H^+ ion from one or both of the terminal phosphate groups, and by more units of charge if hydrogen ions are lost from the bridging phosphate groups.

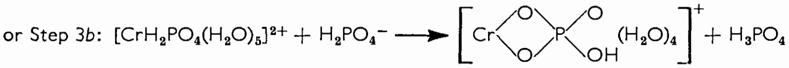
exists in solution, taken together with the likelihood of breakdown, makes it difficult to interpret the results of the batch studies in terms of possible complexes by Salmon's approach.[13] However, the complexes were sufficiently stable for separation chromatographically. Batch desorption and column studies were carried out to determine a suitable eluting agent. Some of the complexes were susceptible to breakdown by H^+ ions, and hence chromatographic development was initially by ammonium nitrate and later by a mixture of nitric acid and ammonium nitrate. The results are given in Table 2. The structures of A and G must be $[H_2PO_4\text{–}Cr\text{–}H_2PO_4]^+$ and $[Cr\text{–}HPO_4\text{–}Cr]^{4+}$ or $[Cr\text{–}PO_4\text{–}Cr]^{3+}$, and presumably the other complexes must be intermediate in character and in charge.

The major difference between the chromium(III)–phosphoric acid system at 0—40° and at 70° is the appearance of polynuclear complexes and the parallel tie-lines in the phase-diagram study, neither of which has been noted in the previous work.[1] This may be accounted for by the fact that phosphoric acid is a weaker acid at higher temperatures. Thus by applying Harned and Embree's equation [14] for the temperature-dependence of the ionisation constants of weak acids to phosphoric acid, it may be seen that K_1 and K_2 are decreasing above 43·1° (see Nims [15]). Thus it is clear that above this temperature a somewhat different situation exists in the system. The following mechanism for the formation of complexes is likely:

Step 1: $[Cr(H_2O)_6]^{3-} \longrightarrow [Cr(H_2O)_5]^+$ (see ref. 16)

Step 2: $[Cr(H_2O)_5]^{3+} + H_2PO_4^- \xrightarrow{\text{rapid}} [CrH_2PO_4(H_2O)_5]^{2+}$

Step 3*a*: $[CrH_2PO_4(H_2O)_5]^{2+} + H_2PO_4^- \longrightarrow [Cr(H_2PO_4)_2(H_2O)_4]^+$



Both steps 3*a* and 3*b* involve the loss of a second molecule of water from the chromium cation. Presumably 3*a* will be favoured in the present system since the formation of a stable four-membered ring depends, amongst other factors, on the radius of the unhydrated metal ion. The importance of this radius was established by Genge and Salmon [17] for phosphato-complexes of the tervalent metals which use $sp^3d_\gamma{}^2$-hybrid orbitals. They also showed that for an unhydrated metal ion a radius of 0·72 Å was the optimum for a ring of least strain. The experimental results were in accord with this deduction for metals using such hybrid orbitals. The authors pointed out, however, that their studies did not extend to those metals in which inner *d*-orbitals would probably be employed, *i.e.*, in $d_\gamma{}^2sp^3$-hybrid orbitals. Chromium(III), although similar to iron(III) in its ionic radius, more often resembles cobalt rather than iron, aluminium, gallium, and the tervalent rare earths, and it is likely that inner *d*-orbitals are employed by chromium and cobalt. Daniel and Salmon [18] prepared a phosphatotetramminecobalt(III) complex in which one PO_4 chelate ring, but no bis-chelate compound, appeared to be formed. Hence with cobalt(III) and possibly with chromium(III), only one four-membered ring, at most, can be formed with phosphate.

Most of the chromium complexes found in aged solutions of chromium(III) in phosphoric acid are cationic, having a $PO_4 : Cr$ mole ratio of $x : 1$ where $x > 1$, which implies that the phosphato-groups must have more than one associated hydrogen atom. This precludes the formation of chelate rings. Thus, on several counts, it seems unlikely that step 3*b* makes an important contribution to the overall equilibrium and it is probable that step 3*a*

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[13] Salmon, *Rev. Pure Appl. Chem.*, 1956, **6**, 24.
[14] Harned and Embree, *J. Amer. Chem. Soc.*, 1934, **56**, 1050.
[15] Nims, *J. Amer. Chem. Soc.*, 1934, **56**, 1110.
[16] Plane and Taube, *J. Phys. Chem.*, 1952, **56**, 33.
[17] Genge and Salmon, *J.*, 1959, 1459.
[18] Daniel and Salmon, *J.*, 1957, 4207.

is favoured. Further complexes may then be formed by suitable elimination reactions of the type:

$$[H_2PO_4{-}Cr{-}H_2PO_4]^+ + [H_2PO_4{-}Cr{-}H_2PO_4]^+ \longrightarrow [H_2PO_4{-}Cr{-}HPO_4{-}Cr{-}H_2PO_4]^{2+} + H_3PO_4$$

This is similar to that elimination reaction described by Bjerrum[19] in the process of the formation of polynuclear complexes of chromium involving hydroxyl bridging and referred to as "olation."

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[19] Bjerrum, *Z. phys. Chem.*, 1907, **59**, 336.