Chromium Phosphates: Phase-diagram and Preliminary Ion-exchange Studies of the System: Chromic Oxide–Phosphoric Oxide–Water at 0° and 40°.

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Two series of compounds, one purple (derived from the hexaquochromic ion) and the other green (containing complex phosphatochromic ions), have been found to occur in the system chromic oxide–phosphoric oxide–water. A phase-diagram study of the system at 0°, where both solutions and solids were purple, has shown that in the range of solutions containing from 1% to 52% of phosphoric oxide the following are the stable solid phases: $Cr_2O_3,P_2O_5,12H_2O$; $2Cr_2O_3,3P_2O_5,51H_2O$; $Cr_2O_3,2P_2O_5,19H_2O$; $Cr_2O_3,3P_2O_5,18H_2O$. At 40°, when the solutions and solids were green, the following were found to be the stable solid phases in contact with solutions containing between 1% and 56% of phosphoric oxide: $Cr_2O_3,P_2O_5,12H_2O$; $Cr_2O_3,2P_2O_5,8H_2O$; $Cr_2O_3,3P_2O_5,10H_2O$. Attempts to study the system at 25° were abandoned since both solutions and solids remained indefinitely in a state between the green and the purple forms.

Ion-exchange experiments at 0° have shown the hexaquochromic ion to be the only species adsorbed by the cation-exchanger, and phosphate ions the only ones adsorbed by the anion-exchanger. The molar amounts of phosphate adsorbed per equivalent of resin from the chromic phosphate solutions were the same as from phosphoric acid solutions of similar concentrations. At 40° the adsorption of both anionic and cationic complexes was observed. Preliminary studies indicated these to be $[Cr(PO_4)_2,aq.]^{3-}$ and $[Cr(HPO_4),aq.]^{+}$ respectively.

No systematic study appears to have been made previously of the chromic phosphates, although several solid chromic phosphates have been reported. Thus both a green and a purple modification of the tertiary phosphate are known. The latter has been described by, *e.g.*, Rammelsberg (*Pogg. Annalen*, 1846, **68**, 149), Glühmann (*Annalen*, 1848, **65**, 149), Joseph and Rae (*J.*, 1917, **111**, 196), and Ness, Smith, and Evans (*J. Amer. Chem. Soc.*, 1950, **72**, 2813). All these workers formulated it as $Cr_2O_3,P_2O_5,12H_2O$ (or $CrPO_4,6H_2O$) and observed that it occurred as purple, hexagonal crystals (a description that accords with the present observations). A lavender-coloured amorphous variety has also been described by Rammelsberg and by Joseph and Rae (*locc. cit.*).

The degree of hydration of the green form was stated by Rammelsberg (*loc. cit.*) to be the same as for the purple modification, but Joseph and Rae (*loc. cit.*) ascribed it eight molecules of water, *viz.*, $Cr_2O_3,P_2O_5,8H_2O$.

The only other salt of orthophosphoric acid described is the compound $Cr_2O_3,2P_2O_5,19H_2O$, for which Haushofer (*Z. Krist.*, 1883, **7**, 263) has given goniometric measurements; the colour of this compound was said to be the same as that of chrome alum.

The original aim of the present work was to determine the solubility isotherm of the system chromic oxide–phosphoric oxide–water at 25°, but a difficulty was encountered in that at this temperature both solutions and solids remained indefinitely in a state intermediate between the purple and the green forms (the solids being mechanical mixtures) without, apparently, reaching equilibrium. However, it proved possible to obtain data for the appropriate phase diagrams at both 0° and 40° where both solutions and solids remained purple and emerald-green respectively.

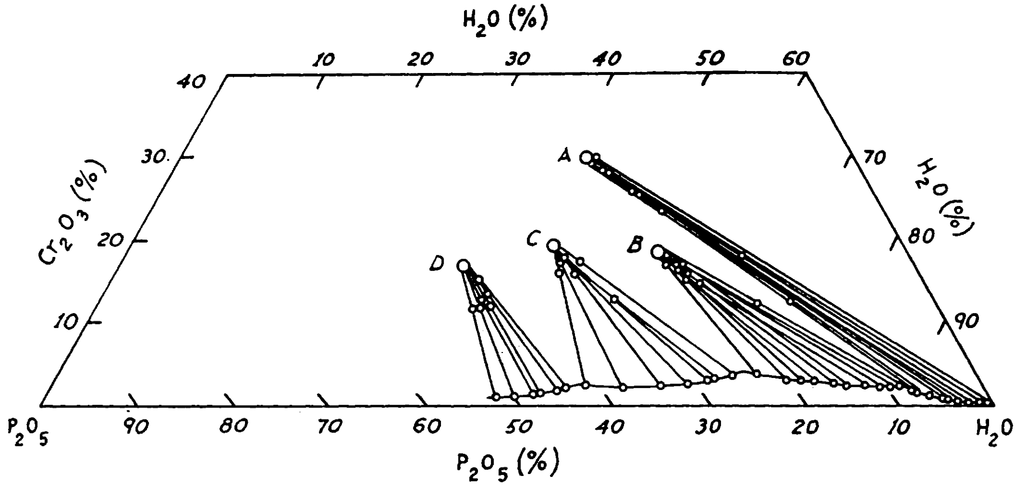
RESULTS.

Phase-diagram Studies at 0°.—A study of the system at 0° for the range of solutions up to 52% of phosphoric oxide has indicated the following as the stable solid phases (Table 1, Fig. 1): (*A*) $Cr_2O_3,P_2O_5,12H_2O$, as dull-purple, hexagonal plates, (*B*)

$2Cr_2O_3,3P_2O_5,51H_2O$, as black, irregular-shaped crystals, (*C*) $Cr_2O_3,2P_2O_5,19H_2O$, as purple, hexagonal-sectioned crystals, and (*D*) $Cr_2O_3,3P_2O_5,18H_2O$, as bright purple crystals.

Samples of the tertiary salt, $Cr_2O_3,P_2O_5,12H_2O$, were heated to constant weight at several temperatures and the loss in weight recorded. The results, which are plotted in Fig. 2*a*, differ from those of Joseph and Rae in showing a break in the curve corresponding to the formation of $Cr_2O_3,P_2O_5,8H_2O$ (at which point the solid becomes green), but these authors carried out their experiments in a dry atmosphere, whereas the present work was carried out under normal atmospheric conditions of humidity.

FIG. 1. Cr_2O_3-P_2O_5-H_2O *at* 0°.



A, $Cr_2O_3,P_2O_5,12H_2O$.
B, $2Cr_2O_3,3P_2O_5,51H_2O$.
C, $Cr_2O_3,2P_2O_5,19H_2O$.
D, $Cr_2O_3,3P_2O_5,18H_2O$.

TABLE 1. *The system chromic oxide–phosphoric oxide–water at* 0°.

Solutions			Moist solids		
P_2O_5 (%)	Cr_2O_3 (%)	$[PO_4]/[Cr]$	P_2O_5 (%)	Cr_2O_3 (%)	Type *
0·981	0·101	10·4	27·62	29·23	*A*
1·352	0·153	9·45	26·19	28·00	
2·50	0·325	8·25	26·62	28·53	
3·76	0·578	6·97	17·65	17·67	
4·47	0·647	7·40	22·81	23·83	
5·09	0·933	5·85	—	—	
6·22	1·31	5·11	24·88	26·02	
7·48	1·68	4·78	24·23	25·54	
7·59	1·77	4·61	14·96	12·59	
		†			
8·99	2·24	4·31	18·71	12·23	*B*
9·88	2·24	4·74	24·42	17·00	
10·81	2·36	4·91	23·11	14·84	
12·42	2·53	5·26	24·44	15·85	
14·22	2·77	5·50	25·40	18·01	
15·68	2·87	5·86	25·03	17·05	
17·85	3·03	6·31	25·57	17·72	
18·70	3·13	6·41	25·01	16·68	
20·21	3·26	6·64	24·66	15·61	
23·22	3·77	6·58	26·03	17·13	
25·66	3·53	7·80	34·83	17·56	*C*
28·01	3·18	9·43	36·47	17·88	
28·41	3·19	9·55	33·31	12·80	
30·98	2·91	11·4	35·89	16·22	
33·90	2·65	13·7	36·00	15·48	
38·06	2·54	16·1	36·87	17·44	
41·96	2·53	17·8	37·56	16·22	
44·03	1·95	24·2	46·72	15·32	*D*
44·91	1·86	25·9	46·51	13·46	
47·23	1·48	34·2	47·00	11·73	
47·41	1·47	34·6	47·51	12·56	
49·79	1·26	42·3	48·18	11·74	
51·77	1·17	47·4	48·77	11·65	

* Where *A* = $Cr_2O_3,P_2O_5,12H_2O$;
B = $2Cr_2O_3,3P_2O_5,51H_2O$;
C = $Cr_2O_3,2P_2O_5,19H_2O$;
D = $Cr_2O_3,3P_2O_5,18H_2O$.

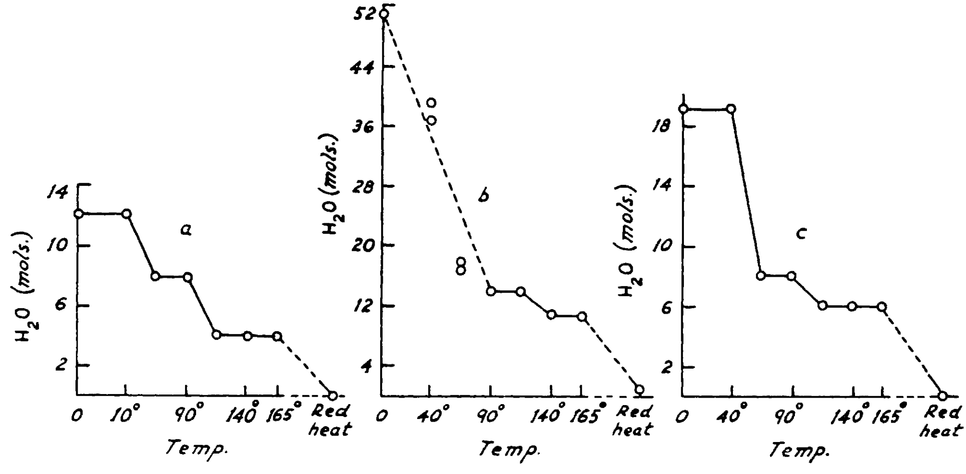
† The minimum value of the mol. ratio occurs at this transition point.

The compound $2Cr_2O_3,3P_2O_5,51H_2O$ has not been described before, and its degree of hydration cannot be fixed accurately by examination of the tie-lines (Fig. 1); the formula was decided on the basis of an examination of the phase diagram in conjunction with the results of experiments in which the compound was dried at various temperatures (see

Fig. 2*b*). The compound started to lose water rapidly at 40°, at which point it became partly green, but at each temperature it took too long to reach constant weight until a temperature of 95° was used; the solid was then wholly green. The loss of water at each break in the curve (Fig. 2*b*) corresponded to integral numbers of water molecules (*viz.*, 11 and 14 remain) when the original compound was assumed to contain 51 molecules of water.

The compound $Cr_2O_3,2P_2O_5,19H_2O$ has been described before by Haushofer (*loc. cit.*) and his description of it accords with the present observations. A dehydration curve is given in Fig. 2*c*; the solid became green at 65°.

FIG. 2. *System* Cr_2O_3-P_2O_5-H_2O *at* 0°; *dehydration curves for stable solids.*



(*a*) $Cr_2O_3,P_2O_5,12H_2O$. (*b*) $2Cr_2O_3,3P_2O_5,51H_2O$. (*c*) $Cr_2O_3,2P_2O_5,19H_2O$.

The compound $Cr_2O_3,3P_2O_5,18H_2O$ has not been described before. It forms bright purple crystals that dissolve readily in water to give a pale solution that gradually deposits hexagonal crystals similar in appearance to those of the tertiary salt. It is very hygroscopic.

Phase-diagram Studies at 40°.—The chromic phosphate system at 40° has been studied for the range of solutions containing up to 56% of phosphoric oxide and the following stable solid phases identified (Table 2, Fig. 3): (*E*) $Cr_2O_3,P_2O_5,12H_2O$, as a pale green, microcrystalline solid, (*F*) $Cr_2O_3,2P_2O_5,8H_2O$, as a dark green, semicrystalline solid, and (*G*) $Cr_2O_3,3P_2O_5,10H_2O$, as a bright green, crystalline solid.

TABLE 2. *The system chromic oxide–phosphoric oxide–water at* 40°.

Solutions			Moist solids		
P_2O_5 (%)	Cr_2O_3 (%)	$[PO_4]/[Cr]$	P_2O_5 (%)	Cr_2O_3 (%)	Type *
0·870	0·051	18·1	21·22	22·48	E
1·932	0·143	14·4	26·13	27·89	
3·44	0·340	10·9	26·44	28·51	
4·22	0·494	9·16	20·69	21·48	
7·43	1·24	6·44	20·38	19·50	
9·22	1·57	6·29	22·51	21·23	
11·13	2·66	4·48	21·96	21·52	
12·63	3·77	3·59	20·49	16·73	
15·88	6·18	2·75	18·89	12·53	
17·34	8·34	2·23	20·13	14·03	
18·84	9·19	2·19 †	23·41	20·39	
20·72	8·95	2·48	41·36	21·32	F
22·45	8·20	2·94	36·21	17·46	
25·24	7·48	3·61	33·05	13·55	
29·87	7·10	4·51	39·66	16·31	
33·01	7·43	4·76	—	—	
35·35	7·82	4·84	42·61	17·72	
38·83	8·44	4·93	44·98	19·03	
41·96	9·39	4·79	46·21	20·68	
43·11	9·81	4·71	46·99	19·60	
45·63	10·38	4·71	49·46	14·43	G
47·21	8·61	5·88	50·81	13·48	
49·11	7·57	6·95	53·93	15·86	
50·54	6·71	8·07	52·38	11·85	
51·76	5·97	9·28	53·89	12·67	
54·89	5·07	11·6	55·38	10·86	
56·13	4·98	12·1	56·00	9·23	

* Where $E = Cr_2O_3,P_2O_5,12H_2O$;
$F = Cr_2O_3,2P_2O_5,8H_2O$;
$G = Cr_2O_3,3P_2O_5,10H_2O$.

† The minimum value of the mol. ratio occurs at this transition point.

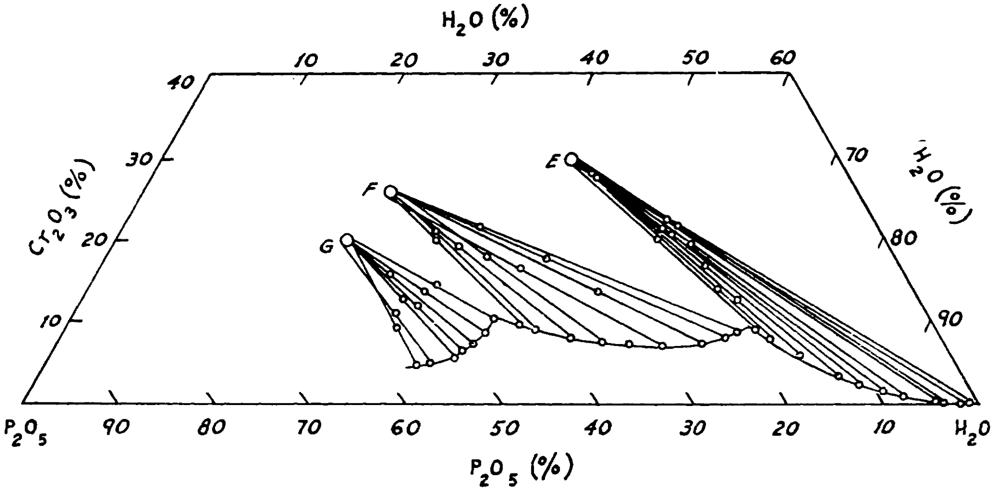
The tertiary salt, $Cr_2O_3,P_2O_5,12H_2O$, is stable towards water and exhibits no discernible crystal pattern.

The compound $Cr_2O_3,2P_2O_5,8H_2O$, has not previously been described. It is a dark green solid forming large ill-shaped crystals having only two well-defined faces and exhibiting conchoidal fracture. It is insoluble in water. A green compound of the same composition makes its appearance during the dehydration of the purple salt $Cr_2O_3,2P_2O_5,19H_2O$ (see Fig. 2*c*).

The compound $Cr_2O_3,3P_2O_5,10H_2O$ (which has not previously been described) is a bright green solid forming ill-defined crystals. These dissolve readily in water to give a light green solution which, on high dilution, yields a pale green amorphous precipitate.

Anion-exchange Experiments at 0°.—For these experiments 1·000-g. portions of Amberlite I.R.A.-400 in the phosphate form were added to various saturated solutions (100 ml. in each case) and left, with daily shaking, for three weeks. The solutions were prepared from 5M-phosphoric acid, the tertiary salt, and water according to the previously determined solubility isotherm.

FIG. 3. Cr_2O_3-P_2O_5-H_2O *at* 40°.



E, $Cr_2O_3,P_2O_5,12H_2O$. *F*, $Cr_2O_3,2P_2O_5,8H_2O$. *G*, $Cr_2O_3,3P_2O_5,10H_2O$.

The results, which are given in Table 3, show that no chromium was adsorbed on to the exchanger, but phosphate only, and that the amount of phosphate adsorbed was the same as that from pure phosphoric acid solutions of the same concentration (cf. Table 5*b*).

TABLE 3. *Adsorption of phosphate by resin I.R.A.*-400 (*phosphate*) (1·000 *g.*) *from chromic phosphate solutions at* 0° (100 *ml.*).

Solutions		Resin	
P_2O_5 (%)	$[PO_4]/[Cr]$	Capacity (m. equiv./g.)	Mol. of PO_4 * adsorbed per equiv. of resin
5	5·87	2·32	0·660
10	4·68	2·44	0·620
15	5·91	2·44	0·625
20	6·60	2·49	0·622

* No chromium was adsorbed.

Cation-exchange Experiments at 0°.—The results of similar experiments with the hydrogen form of the cation-exchanger Zeo-Karb 225 are given in Table 4. No adsorption of phosphate was observed and the adsorption of the tervalent chromium ion was almost independent of the pH. The exchanger was never completely saturated with the chromium ions and this was probably due to the blocking of some of the exchange sites by the large hexaquochromic ion, in which form it is most likely that the chromium is adsorbed.

TABLE 4. *Adsorption of chromium by Zeo-Karb 225-H* (0·500 *g.*) *from chromic phosphate solutions at* 0° (100 *ml.*).

Solutions			Resin	
P_2O_5 (%)	$[PO_4]/[Cr]$	pH	Capacity (m. equiv./g.)	Mol. of Cr * adsorbed per equiv. of resin
5	5·87	1·56	3·57	0·329
10	4·68	1·40	3·59	0·323
15	5·91	1·01	3·59	0·318
20	6·60	0·68	3·59	0·309

* No phosphate was adsorbed.

Anion-exchange Experiments at 40°.—The adsorption of chromium and phosphate by Amberlite I.R.A.-400 (in the phosphate form) from stable solutions (*i.e.*, of compositions decided on the basis of the solubility isotherm at 40°; since the solutions were made up from the purple tertiary salt they were initially aged at 40° for approximately three weeks) has been determined under equilibrium conditions. The results are given in Table 5*a* and those for a corresponding series of experiments with pure phosphoric acid solutions in Table 5*b*. A significant adsorption of chromium by the exchanger (Table 5*a*) indicates the presence in the green chromic phosphate solutions of anionic complexes.

TABLE 5. *Adsorption of chromium and phosphate by resin I.R.A.*-400 (*phosphate*) (1·000 g.).

(*a*) *From chromic phosphate solutions at* 40° (100 *ml.*).

Solutions		Resin						
			Mol. adsorbed/ equiv. of resin :		Capacity accounted for (%) *			
P_2O_5 (%)	$[PO_4]/[Cr]$	Capacity in (m. equiv./g)	Cr	PO_4	A	B	C	D
1	16·4	2·44	0·232	0·677	—	—	102	56
5	8·6	2·44	0·174	0·676	127	75	102	67
10	5·0	2·37	0·173	0·661	125	73	101	66
15	2·8	2·48	0·219	0·649	—	—	99	55
20	2·3	2·43	0·254	0·666	—	—	100	50
25	3·6	2·44	0·186	0·671	128	73	102	65

* Assuming the following to be adsorbed : A = $[Cr(PO_4)_3]^{6-}$; B = $[Cr(HPO_4)_3]^{3-}$; C = $[Cr(PO_4)_2]^{3-}$; D = $[Cr(HPO_4)_2]^{-}$ together with free phosphate.

(*b*) *From phosphoric acid solutions at* 40° (100 *ml.*).

Solutions : P_2O_5 (%)	1	5	10	15	20	25
Resin : Mol. of PO_4 adsorbed per equiv. of resin	0·651	0·660	0·642	0·641	0·655	0·647

Cation-exchange Experiments at 40°.—The results of similar experiments with the hydrogen form of the cation-exchanger Zeo-Karb 225 are given in Tables 6*a* and 6*b*. These results show an appreciable adsorption of phosphate (which varies with the time of contact of the resin with the solutions), thus indicating the presence of cationic phosphato-complexes.

TABLE 6. *Adsorption of chromium and phosphate by Zeo-Karb* 225-*H* (0·500 *g.*) *from chromic phosphate solutions at* 40° (100 *ml.*).

Solutions			Resin				
				Mol. adsorbed/ equiv. of resin :		Capacity accounted for (%) *	
P_2O_5 (%)	$[PO_4]/[Cr]$	pH	Capacity (m. equiv./g.)	Cr	PO_4	A	B
			(*a*) *After* 10—14 *days' contact with the resin.*				
1	16·4	1·54	3·30	0·368	0·157	79	95
5	8·6	1·18	3·54	0·281	0·022	80	82
10	5·0	1·00	3·58	0·285	0·037	78	82
15	2·8	1·04	3·64	0·372	0·161	79	96
20	2·3	1·10	3·58	0·430	0·288	71	101
25	3·6	0·62	3·59	0·367	0·275	55	83
			(*b*) *After* 3—4 *days' contact with the resin.*				
3	11·8	1·34	3·70	0·507	0·359	80	116
7·5	6·4	1·01	3·72	0·435	0·260	79	105
12·5	3·7	1·03	3·84	0·494	0·344	79	114

* Assuming the following to be adsorbed : A = $[Cr(HPO_4)]^{+}$ and B = $[Cr(H_2PO_4)]^{2+}$ or $[Cr(H_2PO_4)_2]^{+}$ together with $[Cr(H_2O)_6]^{3+}$ ions.

DISCUSSION

Nature of the Solutions.—The ion-exchange studies at 0° (Tables 3 and 4) fail to show the presence of either anionic or cationic phosphato-complexes. This observation, taken in conjunction with the purple colour of the solutions, suggests that the chromium is present as the hexaquochromic ion, $[Cr(H_2O)_6]^{3+}$. At the higher concentrations the solutions became emerald-green after about 12 weeks, although solutions containing up to about 35% of phosphoric oxide were still purple after about 6 months. The change in colour of the more concentrated solutions would appear to be partially reversible since such solutions, on dilution, often rapidly reverted to their original purple colour. This could be due to the fact that only one of the co-ordinated water molecules is replaced by an $H_2PO_4^-$ group to give $[Cr(H_2O)_5(H_2PO_4)]^{2+}$. (Such a process would be favoured by the high concentration of $H_2PO_4^-$ ions in these solutions.) The view that the phosphato-group here acts as a monodentate group finds support in the fact that when it does occupy two co-ordination positions it is much more difficult to displace: thus the green solutions obtained at 40° do not revert to the purple form either on dilution or during long periods at 0° except in the presence of strong mineral acid (nitric or perchloric acid).

In the case of the green solutions at 40° the nature of the ions present in solution is not so clear. The results of the anion-exchange experiments (Table 5) have been calculated in terms of the capacity of the resin for various possible complexes in a fashion similar to that employed in the study of the aluminium phosphates (Jameson and Salmon, *J.*, 1954, 4013), and they would seem to imply that it is the $[Cr(PO_4)_2]^{3-}$ ion that is adsorbed. In this respect it is of interest that the ratio of phosphate to chromium in stable solutions reaches a minimum value approaching two (Table 2) as compared with a value of three for the corresponding ratio in the ferric phosphate system (Jameson and Salmon, *J.*, 1954, 28) where the complex is a triphosphato one. The corresponding minimum is also three for the aluminium phosphate system (Jameson and Salmon, *J.*, 1954, 4013), but barely reaches a value of four in the chromic phosphate system at 0° (Table 1) where no phosphato-complexes are formed and the salts are those of a relatively weak base and a fairly strong acid. {If the minimum value of the ratio of phosphate to chromium has the significance just implied then the concentration of cationic complexes of the type $[Cr(HPO_4)]^+$ (see below) must be very low.}

Care is needed in the interpretation of the results of the cation-exchange experiments at 40° since the adsorption of the cationic complexes is marked by several unusual features. Thus, not only is the adsorbed material difficult to remove (requiring 3—4N-acid), but the time of contact of the resin with the solution appears to affect the adsorption (Table 6), and in addition the time for which the solutions are aged is probably a significant factor. The results of the experiments at 0° seem to suggest that the size of the hexaquochromic ion prevents its occupying all the available exchange sites of the resin and, if this is the case, then any ion containing both co-ordinated water and phosphato-groups would be expected to lead to this low effective capacity to an even greater extent. The constant (low) effective capacity for the $[Cr(HPO_4)]^+$ ion (Table 6) (it remains constant whatever the time of contact of the solution with the resin) suggests, therefore, that this is the ion initially adsorbed—the results obtained with a short time of contact between resin and solution appear to exclude the adsorption of both $[Cr(H_2PO_4)]^{2+}$ and $[Cr(H_2PO_4)_2]^+$ (at least in major amount). Subsequently, under the influence of the resin (*e.g.*, by acid catalysis by the sulphonic acid groups), a change in the species adsorbed occurs to give the hexaquochromic ion, possibly by means of a reaction of the type:

$$\overline{3[Cr(HPO_4)]^+} + H_3PO_4 \longrightarrow \overline{Cr^{3+}} + 2[Cr(HPO_4)(H_2PO_4)]$$

(where barred formulæ indicate the resin phase)

[Gustavson (*Svensk Kem. Tidskr.*, 1951, **63**, 167) has in fact reported that the functional groups of a cation-exchanger may act as ligand groups and even displace other groups originally bound in the complex.]

The minimum in the amount of chromium adsorbed by the anion-exchanger that is exhibited at about 7½% of phosphoric oxide in the solutions is presumably a concentration effect, since at this point the chromium content of the solutions is beginning to increase rapidly as the ratio of phosphate to chromium is decreasing (Tables 2 and 5), which factors might hinder the formation of anionic complexes. In the cation-exchange experiments (Table 6) it is not clear whether the similar dip in the adsorption of phosphate would persist with even shorter time of contact with the resin. In both cases the ageing of the solutions may well play a part.

Heating the solutions to temperatures much in excess of 40^c seems to change markedly the nature of the ions present in solution. The solutions become uncrystallizable (Vauquelin, *Ann. Chim. Phys.*, 1798, **25**, 194) and have only a very small concentration of adsorbable anionic and cationic complexes (Holroyd and Salmon, unpublished work). In the present work, therefore, none of the solutions was heated above 40°.

Nature of the Solid Phases.—Very little can be said as to the nature of the solids without *X*-ray or similar examination. The purple solids presumablyc ontain the hexaquochromic ion and phosphate ions, *e.g.*, the compound $2Cr_2O_3,3P_2O_5,51H_2O$ would be $[Cr(H_2O)_6]_2[HPO_4]_3,12H_2O$—although in this case the water content may be variable (and possibly zeolitic in nature).

In the green compounds at 40° the compound $Cr_2O_3,3P_2O_5,10H_2O$ is most probably $H_3[Cr(HPO_4)_3],2H_2O$, although no evidence for the triphosphato-ion is found in the range of solutions containing up to 25% of phosphoric oxide. From the anion-exchange experiments at 40° (Table 5), the compound $Cr_2O_3,2P_2O_5,8H_2O$ could quite well be $H_3[Cr(PO_4)_2(H_2O)_2],\frac{1}{2}H_2O$, and $Cr_2O_3,P_2O_5,12H_2O$ may be $[Cr(H_2O)_6][Cr(PO_4)_2(H_2O)_2],4H_2O$.

EXPERIMENTAL

Apparatus.—For the experiments at both 0° and 40° air thermostats were used. The samples were contained in "Pyrex" boiling-tubes closed with rubber bungs or with glass stoppers and held in a lagged box within the thermostats; the temperature variation was less than 0·1°.

Preparation of Solutions.—The solutions were prepared by dissolving the purple tertiary salt in solutions of phosphoric acid. This gave rise to deep purple solutions which, on being kept at 0°, deposited crystals and reached a state of equilibrium after about 6—8 weeks. The solutions could easily be supersaturated by warming them to 30° for a short time and dissolving the solid at this temperature before cooling them rapidly to 0°.

In the study of the system at 40° it seemed desirable (for the reasons given above) to avoid warming the solutions above this temperature. The solutions were therefore maintained at 40° and kept well stirred, more solid being added when necessary, until a supersaturated solution had been attained which would then crystallize out.

At both 0° and 40° the method of analysing alternate tubes in any given batch of 12 was employed. Two weeks were allowed to elapse between the analysis of the first and the second sets of solutions (and solids), and a smooth solubility isotherm was taken as a criterion of equilibrium. The time taken to reach equilibrium ranged from 6 to 10 weeks.

Preparation of the Purple Tertiary Chromic Phosphate.—Because of its nicely crystalline nature which made possible its preparation in a pure state, the compound used as starting material in all the present work was the purple tertiary salt, $[Cr(H_2O)_6]PO_4$, which was prepared as follows: "AnalaR" chromium potassium sulphate (120 g.) was dissolved in distilled water (1·5 l.). A solution of "AnalaR" disodium hydrogen phosphate (30 g.) was then added dropwise with continual (mechanical) stirring of the liquid. Immediately following this a solution of ammonium acetate (30 g.) in water (500 ml.) was added dropwise and the stirring continued for another 2 hr. The precipitate was washed several times by decantation and, finally, on a Büchner funnel, with cold water. A lavender-coloured solid (about 60 g.) was obtained; the product was nicely crystalline (small hexagonal plates) and gave no flame-test for sodium. Analysis of a typical batch of the air-dried material gave: Cr_2O_3, 29·74; P_2O_5, 27·74; H_2O, 42·50% (Calc. for $Cr_2O_3,P_2O_5,12H_2O$: Cr_2O_3, 29·80; P_2O_5, 27·83; H_2O, 42·37%).

Resins.—The strongly acidic, monofunctional cation-exchanger Permutit Zeo-Karb 225 and the strongly basic, monofunctional anion-exchanger Amberlite I.R.A.-400 were used. The former was in the hydrogen form and the latter in the form of its phosphate to avoid the introduction of foreign ions into the solutions on exchange. The resin used for the separation of chromium from phosphate in the case of the purple (*i.e.*, complex-free) solids and solutions was Permutit Zeo-Karb 215, a cation-exchanger having both phenolic and sulphonic acid groups as the active centres.

The technique was that previously employed for the study of the aluminium phosphates (Jameson and Salmon, *J.*, 1954, 4013) except that in elution of the species adsorbed at 40° 3—4N-nitric acid had to be used in place of 2N-nitric acid.

Analytical Methods.—Chromium was determined, after oxidation to dichromate, by addition of a standard ferrous ammonium sulphate solution, followed by back-titration of the excess with standard potassium dichromate solution.

Phosphate, in the case of the purple (*i.e.*, complex-free) system, was estimated by titration with standard bismuthyl perchlorate solution (M/20 approx.) with thiourea as indicator (Salmon and Terrey, *J.*, 1950, 2813) after removal of chromium by percolation of the solution through a column of Permutit Zeo-Karb 215 in the hydrogen form; perchloric acid was used to dissolve the solids and to stabilize the solutions.

The stable complexes present in the green solutions prevented the use of ion-exchange resins to effect the removal of chromium from these solutions and so the phosphate was precipitated from them as ammonium phosphomolydate, dried at 115°, and weighed. This procedure was adopted universally for small amounts of phosphate; perchlorates do not interfere.

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