8. *Arsenates. Part I. Preparative, Phase-diagram, and Other Preliminary Studies of the System Chromium*(III)-*Arsenic Acid.*

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The preparation of hexaquochromium(III) arsenate is described and its stability and behaviour towards heat have been investigated.

In the phase diagram of the system Cr_2O_3–As_2O_5–H_2O for the range 1—29% As_2O_5, where both solutions and solids were green, the tie-lines were either parallel or divergent. The solid material which separated had ion-exchange properties.

Ion-exchange experiments on the green solutions indicated that both cationic and anionic complexes were present.

VARIOUS workers [1] have reported the preparation of a green, non-crystalline, ill-defined chromium arsenate which dissolved in acid solutions to give emerald-green solutions of uncertain character. Early attempts to correlate the data led to diverse conclusions.[2] Simon and Baumgartel,[3-5] in a systematic study, described a violet-grey, well-defined modification, and structural studies [4,5] led them to the structure $[Cr(H_2O)_6]AsO_4,H_2O$. Mention was made of rapid conversion of the compound either alone or on contact with water into a green modification of ill-defined water content, believed from tensimetric studies [5] to be polymeric. Pyrolysis and thermogravimetric studies by Guerin and Masson [6] yielded indefinite results. Measurements of pH and cryoscopic studies [4] on the emerald-green solutions were interpreted as indicating the presence of a complex species of the type $[Cr(H_2O)_nHAsO_4]^+$.

We tried to clarify these data and to compare the present system with that of the chromium–phosphoric acid system.[7,8] Also an improved method for the preparation of the violet-grey modification is reported.

EXPERIMENTAL AND RESULTS

Preparation and Properties of Violet-grey Chromium Arsenate.—Simon and Baumgartel's conditions [4,5] were found to be necessary but the method was somewhat uncertain, especially for larger quantities. The presence of alkali-metal ions (from the starting material) facilitated the conversion of the violet-grey into a green form of uncertain composition, and the alkali-metal ions could not easily be removed. The following method, using ammonium arsenate, reduced these tendencies. The preparation was carried out by mixing in the order given, 100 ml. portions of each of the following solutions, previously chilled in ice: M-ammonium dihydrogen arsenate; 2M-aqueous ammonia; 96% ethyl alcohol; M-hexaquochromium nitrate. After filtration the precipitate was washed successively with ethyl alcohol and ether. Analysis of a typical batch of the freshly prepared dried salt gave: Cr_2O_3, 25·50; As_2O_5, 38·23; H_2O, 36·37 {Calc. for $[Cr(H_2O)_6]AsO_4$: Cr_2O_3, 25·42; As_2O_5, 38·43; H_2O, 36·15%}.

Freshly prepared material was heated to constant weight at various temperatures, and the losses in weight were recorded. The results are given in Table 1. The thermogravimetric studies were carried out by using a Stanton thermobalance which was programmed for a linear temperature rise from 25—900° during periods varying from 3 to 12 hr. The results for the shorter periods indicated the presence of certain hydrates. Over a period of 10 hr. the effect

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[1] Schweitzer, *J. prakt. Chem.*, 1846, **39**, 269; Lefevre, *Compt. rend.*, 1890, **111**, 36; Prakash and Dube, *Z. anorg. Chem.*, 1932, **208**, 166.

[2] Dede, *Z. anorg. Chem.*, 1922, **125**, 28; Rosenheim and Thon, *Z. anorg. Chem.*, 1927, **167**, 1; Prakash *et al.*, *Allahabad Univ. Studies, Sci. Sect.*, 1932, **8**, 119; Brintzinger and Jahn, *Z. anorg. Chem.*, 1937, **230**, 416; Stalhane, Canad. P. 381,656.

[3] Simon and Baumgartel, *Holz. Roh-u-Werkstoff*, 1954, **12**, 453.

[4] Simon and Baumgartel, *Z. anorg. Chem.*, 1955, **282**, 307.

[5] Baumgartel, *Z. anorg. Chem.*, 1957, **290**, 133.

[6] Guerin and Masson, (*a*) *Bull. Soc. chim., France*, 1953, 440; (*b*) *Compt. rend.*, 1957, **245**, 429.

[7] Jameson and Salmon, *J.*, 1955, 360.

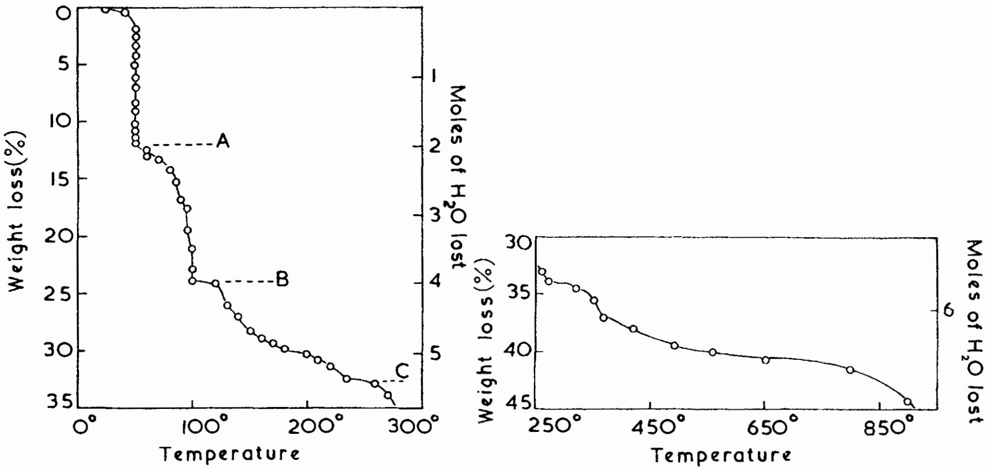
[8] Redfern and Salmon, unpublished work.

TABLE 1. *Degradation of hexaquochromium*(III) *arsenate by heating to constant weight.*

Temp. of heating	Approx. time of heating	Weight loss (%)	Mols. of H_2O lost per mol. of compound
0°	6 months	11·95	2
100	1 week	23·90	4
150	2 days	29·60	nearly 5
180	2 days	30·07	5
320°	5 weeks	33·21	5½
850	4 days	41·8	6 (and some As_2O_5
950	5 days	74·7	(Cr_2O_3 left)

was heightened. The results (see Fig. 1) indicate the tetrahydrate to be stable up to 50°, the dihydrate up to 120°, and the hemihydrate up to 330°. Above this temperature the compound loses As_2O_5 steadily until at 950° Cr_2O_3 is the stable solid phase.

FIG. 1. *Thermobalance study of hexaquochromium arsenate during* 10 *hours.*



A, $CrAsO_4,4H_2O$; *B*, $CrAsO_4,2H_2O$; *C*, $CrAsO_4,\frac{1}{2}H_2O$.

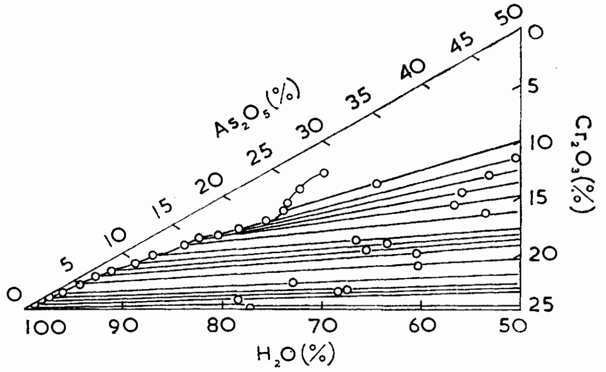


FIG. 2. Cr_2O_3–As_2O_5–H_2O *at* 25°.

Phase-diagram Studies.—The samples were contained in Pyrex boiling-tubes fitted with ground-glass stoppers and held in a lagged box in a lagged air-thermostat at 25° ± 0·1°. The solutions were prepared by dissolving the freshly prepared violet-grey chromium arsenate in solutions of arsenic acid, giving rise to an emerald-green solution immediately. In each case the arsenic acid solution was treated with small portions of the solid until no more would dissolve, then an excess of some 3—4 g. was added, and the mixture allowed to attain equilibrium during 6—8 weeks with frequent stirring. Alternate tubes in any given batch of twelve tubes were analysed at two or more weekly intervals. A smooth solubility isotherm was taken as the criterion of the attainment of equilibrium. For the range of solutions containing up to 27% of arsenic oxide no single solid phase can be isolated or identified (see Table 2 and Fig. 2). The

TABLE 2. *Phase diagram of the system chromic oxide–arsenic oxide–water at* 25°.

Solution			Solid phase		Solution			Solid phase	
Cr_2O_3 (%)	As_2O_5 (%)	pH	Cr_2O_3 (%)	As_2O_5 (%)	Cr_2O_3 (%)	As_2O_5 (%)	pH	Cr_2O_3 (%)	As_2O_5 (%)
0·10	0·60	2·20	11·25	11·40	1·68	11·20	1·71	10·60	22·80
0·15	0·95	2·08	9·85	11·65	1·90	11·83	1·48	—	—
0·20	1·78	1·97	14·10	16·95	2·50	13·70	1·50	14·80	31·70
0·25	2·30	2·00	14·45	18·15	2·54	15·05	1·30	12·25	31·00
0·28	2·55	1·96	10·65	14·42	3·37	16·35	1·52	11·60	32·50
0·41	3·36	1·91	11·10	15·90	3·72	17·80	1·50	11·55	35·35
0·46	3·85	1·95	10·75	16·40	4·41	20·00	0·90	11·25	38·40
0·57	5·05	1·68	15·72	23·75	4·35	21·85	0·85	6·50	29·05
0·78	6·45	1·74	14·70	24·75	3·92	22·60	0·42	8·45	56·80
1·05	7·60	1·70	12·05	22·50	3·23	24·60	0·14	4·95	50·60
1·50	9·60	1·65	12·30	24·30	2·89	27·10	0·04	—	—

system gave a series of parallel or diverging tie-lines similar to that encountered [8] in the system chromium(III)–phosphoric acid at 70°.

Ion-exchange Studies on the Solid obtained from the Phase-diagram Studies or from heating the Violet-grey Material at 110°.—As it was suspected that the solid material in the present system was behaving as an ion-exchanger, this possibility was further investigated. Once it had been established that the solid material isolated from the phase-diagram experiments possessed ion-exchange properties, the material used for subsequent studies was obtained by heating the violet-grey chromium arsenate at 110° for two weeks. The product, $CrAsO_4,2H_2O$, was lime-green. Weighed portions of sieved material (40—80 mesh) were loaded into small ion-exchange columns (9 × 1 cm.), back-washed to remove any adhering small particles, and washed with water. The product was not affected by water, or by acid up to 1N, even when allowed to remain in contact for some days but appeared to undergo a change in contact with dilute alkali.

Cation-exchange properties. The solid showed consistent ion-exchange properties towards H, K, Zn, and Cu^{2+} ions though very little towards Cr^{3+} itself. The results are given in Table 3.

TABLE 3. *Cation-exchange properties of green material having composition* $CrAsO_4,2H_2O$ *prepared by heating* $[Cr(H_2O)_6]AsO_4$ *at* 110° *for* 2 *weeks.*

Treatment	Behaviour
0·5N-HCl	H ions sorbed
H form with N-KCl	H ions desorbed; capacity 0·204 meq./g.
H form with 0·2N-KCl	H ions desorbed; capacity 0·192 meq./g.
H form with 0·05N-KCl	H ions desorbed; capacity 0·185 meq./g.
Zn form with N-HCl	Zn desorbed; 0·021 mmole/g.
Cu form with N-HCl	Cu desorbed; 0·018 mmole/g.
$[Cr(H_2O)_6]^{3+}$ form with N-HCl	Negligible desorption, *i.e.*, Cr not sorbed

The amount used in each experiment was approximately 1 g.; Cu and Zn forms were prepared by passage of 0·1N-sulphate solution through column. Sorption of Cu and Zn occurred with release of hydrogen ions. Metal estimated by standard EDTA solution.

Anion-exchange properties. The solid showed no anion-exchange properties either when fresh or after treatment with hydrochloric acid. No uptake of Cl^-, AsO_4^{3-}, or NO_3^- could be detected. However, treatment with 0·1N-alkali resulted in the uptake of hydroxyl ions and the release of arsenate ions which appeared to be reversible, or at least partly so. Passage of an arsenate solution resulted in a partial reversal of the process.

Batch Equilibrium Studies with Chromium Form of a Strong Cation-exchanger.—The amounts of metal removed from freshly prepared $[Cr(H_2O)_6]^{3+}$ form of ZeoKarb 225 (50—100 mesh) by arsenic, phosphoric, and perchloric acid after 7 days at 25° are shown in Fig. 3. The results indicate that complex-formation occurs between hexaquochromium(III) and arsenate ions in this time (cf. $[Cr(H_2O_6]^{3+}$–phosphate; [8] see also ref. 9 for a discussion of the method).

Uptake of Chromium and Arsenate on Cation- and Anion-exchangers from Solutions at 25°.—In these experiments 1·00 g. of De-Acidite FF in the arsenate form or 0·50 g. of ZeoKarb 225 in the hydrogen form was added to various solutions containing green chromium arsenates. After 14 days the chromium and arsenate contents of the resins were estimated after elution with

[9] Genge and Salmon, *J.*, 1957, 256.

6N-hydrochloric acid (cf. ref. 10). The results (see Table 4) show that in both cases chromium and arsenate were sorbed to a significant extent, indicating the presence of cationic and anionic complexes in the solutions.

Analytical Methods.—Chromium was determined, after oxidation to dichromate, by addition of an excess of standard ferrous ammonium sulphate solution followed by the back-titration of the excess by potassium dichromate. Chloride ions were shown not to interfere. Arsenate was determined after reduction to arsenite by using a saturated solution of sulphur dioxide (and subsequent boiling off of the excess) by titration with potassium bromate, with α-naphthaflavone as reversible bromometric indicator.[11]

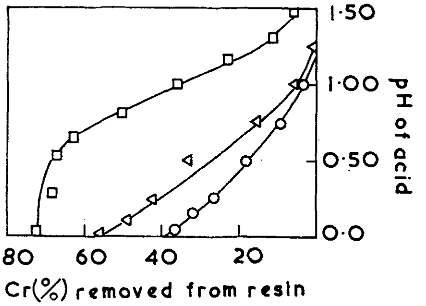


FIG. 3. *Removal of chromium from ZeoKarb* 225 *by various acids at* 25°.
□, H_3AsO_4; △, H_3PO_4; ○, $HClO_4$.

DISCUSSION

The violet-grey material presumably must be formulated as $[Cr(H_2O)_6]AsO_4$ and be similar to that prepared by Simon and Baumgartel[4] except that the different conditions employed mean that the last molecule of water which these workers found is absent from our material. This may account for the increased stability of our compound. From the results obtained on heating the freshly prepared substance, it is not yet possible to ascribe a definite structure to those hydrates which are stable at the temperatures indicated. The relative ease of loss of water from the hexahydrate is of interest. Plane and Taube,[12] in studies of the kinetics of the system $[Cr(H_2O)_6]^{3+}$–H_2O, noted that the provision of an anion in which electron transfer is possible greatly accelerated the rate of exchange of bound aquo-groups and presumably also of entrance of a charged ligand group into the co-ordination sphere of the molecule. Also there is the observation that there is rapid conversion of the solid violet-grey material into a green compound on contact with water, and that it is impossible to obtain a purple solution by dissolving the hexaquo-arsenate in arsenic acid. These facts are in direct contrast to those on the otherwise similar system chromium–phosphoric acid in which electron transfer does not appear to be possible.

It has been explained elsewhere[8] that the system of parallel tie-lines observed in some phase-diagram studies could be accounted for on the assumption that the solid phase was acting as an ion-exchange material. The appearance of a similar series in the present system, coupled with the observation that the green solid from the phase-diagram experiments or the solid obtained from heating the hexaquo-arsenate behaved as a weakly acidic cation-exchanger, seems to be reasonable proof of the assumption. The behaviour with sodium hydroxide may be accounted for by replacement of some of the arsenate bridges by hydroxyl bridges with the release of arsenate ions, if the material is assumed to possess a bridged polynuclear structure.

The results obtained from the preliminary batch experiments indicate that complex formation has taken place in solution, with formation of both anionic and cationic complexes in significant amount (Table 4).

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[10] Jameson and Salmon, *J.*, 1954, 4013.
[11] Tomicek, " Chemical Indicators," Butterworths, London, 1st edn., 1951, p. 543.
[12] Plane and Taube, *J. Phys. Chem.*, 1952, **56**, 33.

TABLE 4. *Uptake of chromium and arsenate by ZeoKarb* 225 *and DeAcidite FF from green solutions obtained by dissolving* $[Cr(H_2O)_6]AsO_4$ *in arsenic acid.*

Content of solution (mmole/ml.)				Found on resin	
Cr(III)	AsO_4	Resin form	Capacity (meq./g.)	Cr(III) mole/equiv.	AsO_4 mole/equiv.
0·530	1·190	ZeoKarb 225(H)	4·17	0·577	0·565
0·127	1·950	,, ,,	2·99	0·233	0·213
0·139	0·154	DeAcidite FF(Cl)	2·89	0·071	0·137
0·270	0·008	,, (Cl)	2·90	0·060	0·158

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