938. *Arsenates. Part II.*[1] *Thermogravimetric, Infrared, and Magnetic Studies of Some Solid Phases in the System Chromium*(III)–*Arsenic Acid.*

By G. M. LUKASZEWSKI and J. P. REDFERN.

Thermogravimetric studies of hexa-aquochromium(III) arsenate showed that dehydration and decomposition processes are complex. The kinetics of thermal decomposition have been investigated. The infrared spectra of the violet and the green solid phase in the system Cr_2O_3–As_2O_5–H_2O have been studied in the rock-salt region. A progressive splitting of the arsenate bands is interpreted in terms of a process of olation-condensation in the solid phase. The magnetic behaviour of various chromium(III) arsenates in the range of 280—85°K show, no divergence from the Curie–Weiss law and indicate the absence of oxy-bridges from these compounds.

PREPARATION of the compound $[Cr(H_2O)_6]AsO_4$ was described in Part I,[1] together with the phase diagram and ion-exchange and preliminary thermogravimetric studies. This work has been extended and Freeman and Carroll's method [2] has been applied to the various stages of dehydration and to the final stage of decomposition, in order to evaluate the kinetic parameters for each reaction. In addition, various stable materials from the thermogravimetric studies and certain green modifications have been investigated by means of infrared-spectral and magnetic measurements.

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[1] Part I, Lukazewski, Redfern, and Salmon, *J.*, 1961, 39.

[2] Freeman and Carroll, *J. Phys. Chem.*, 1958 **62**, 394.

EXPERIMENTAL

Preparation of Solids.—Hexa-aquochromium(III) arsenate was prepared as previously described.[1] The other materials used in the magnetic and infrared studies were prepared either by heating the hexa-aquo-compound to constant weight at the desired temperature or by treating appropriate amounts of it with arsenic acid to give the desired Cr : AsO_4 ratio. In the latter case, the solution was slowly evaporated, yielding a green precipitate. These materials possessed variable water contents, depending on the initial concentration of the reactants and on the rate of evaporation. After the solids had been washed successively with aqueous alcohol, alcohol, and ether they were air-dried. Chromium and arsenate were analysed as already described.[1] Some results are given in Table 1.

TABLE 1.

Preparations.

Material	Temp. of heating	Found (%)			Found
		Cr_2O_3	As_2O_5	H_2O	Cr : As : H_2O
A	See ref. 1	25·50	38·23	36·27	1·01 : 1 : 6·08
B	110°	33·60	50·63	15·77	1 : 1 : 1·99
C	180	36·38	54·83	8·79	1·01 : 1 : 1·03
D	300	38·10	57·27	4·64	1·01 : 1 : 0·52
E	450	39·61	59·84	0·55	1 : 1 : 0·05
L	—	20·32	55·65	24·03	1: 1·81 : 5·00

Materials B—E were prepared by heating compound A to constant weight at the temperature specified. Material L was prepared from a solution in which Cr : AsO_4 = 1 : 3, being precipitated with 96% alcohol.

Thermogravimetric Studies.—The hexa-aquochromium(III) arsenate was freshly prepared, washed with dry ether, and weighed directly into a clean dry platinum boat (1·5 × 1·5 cm., 0·25 cm. deep). The thermogravimetric studies were carried out on a Stanton thermobalance (model HT-D) which was arranged for a linear temperature rise between 25° and 1400°. A proportionating controller (supplied by the manufacturers) for the region 25—200° was used. Several trial thermogravimetric runs were made (with runs for 4, 8, 12, and 24 hr.) to determine the best conditions for the resolution of the various stages of the decomposition.[3] The results are given for a sample weight of 92·9 mg. from 24 hr. runs (rise $\sim$1° min.$^{-1}$) with chart speeds of 12 and 3 in.hr.$^{-1}$. Reference runs were carried out with the same platinum dish, and the necessary buoyancy corrections were applied. The total weight loss was 74·59% [hexa-aquochromium(III) arsenate to chromium(III) oxide requires 74·66%]. The *X*-ray powder photograph of the residue was identified as that of chromium(III) oxide (A.S.T.M. Index). The rate of loss of weight for each stage in the decomposition (determined either by a plateau, *i.e.*, no loss of weight for a finite time, or by an inflexion, *i.e.*, a rate of weight loss appreciably slower for a finite time) is plotted against temperature in Fig. 1A—D. These curves were used for the determination of the kinetic parameters (see below).

Infrared Studies.—The infrared measurements were made with a Hilger and Watts model H-800 spectrophotometer. Samples were examined from 4000 cm.$^{-1}$ (2·5 μ) to 650 cm.$^{-1}$ (15·5 μ) in the rock-salt region, as Nujol mulls mounted on a desiccated rock-salt disc. Calibration was by a polystyrene film; wavelengths are accurate to about $\pm$2·5 cm.$^{-1}$. The principal information obtained is given in Tables 2 and 3.

Magnetic Measurements.—The measurements were carried out on a temperature-variable Gouy balance over the range 293—80°K.[4] The samples were placed in Perspex Gouy tubes closed to a flat internal base at one end, the material being finely ground and carefully packed.[4] Measurements were carried out in an atmosphere of nitrogen in order to eliminate the correction for displaced air. The magnetic field (4000—500 gauss) was calibrated by a standard nickel chloride solution.[5] Magnetic susceptibilities were corrected (to give values of χ'_A) for the diamagnetic effect of the ligands surrounding the metal atom in each case. From the values

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[3] Lukaszewski and Redfern, *Lab. Practice*, 1961, **10**, 469.

[4] Earnshaw, *Lab. Practice*, 1961, **10**, 294.

[5] Nettleton and Sugden, *Proc. Roy. Soc.*, 1939, *A*, **173**, 313.

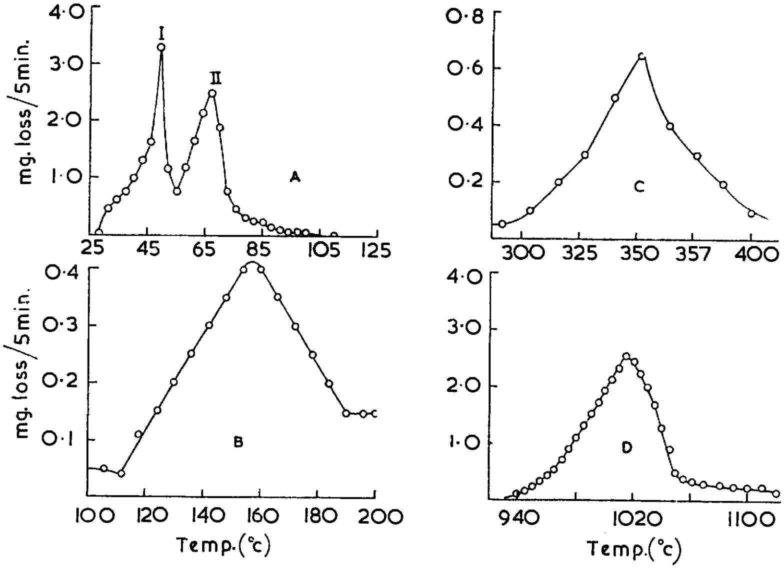

FIG. 1. Differential thermogravimetric curves of the decomposition stages of hexa-aquochromium(III) arsenate.

A, I, Reaction 1, loss at 55° is 12·1%. A, II, Reaction 2, loss at 105° is 24·1%. B, Reaction 3, loss at 300° is 30·1%. C, Reaction 4, loss at 420° is 33·2%. D, Reaction 6, loss at 1200° is 74·6%. Loss at completion of reaction 5 is 36·1% at 900°. (See Table 5.)

TABLE 2.

Infrared bands (cm.$^{-1}$) of hexa-aquochromium(III) arsenate and its thermal degradation products.

A	B	C′	D	E′	F
712m, sh	710w, sh	710w, sh	—	—	—
750 * vs, mb	730s, sh	725m, sh	725w, sh	725m, sp	725w, sh
	810w, sh	780w, sh	780m, sh	775m, sp	780m, sh
850w, sh	850 * vs, mb	850 * vs, mb	840s, sh	830m, sp	
	900w, sh	900w, sh	900 * vs, mb	875 * vs, sp	875 * vs, b
960w, sh	970w, sh	930w, sh	960w, sh	900m, sp	
1010w, sh				960w, sp	970w, sh
1080w, sh	1075w, sp	1050w, sh	1040w, sh	1000w, sh	
1150w, sp	1150w, sp	1155vw, sp	1160w, sp	1150m, sp	1160w, sp
1600s, mb	1655m, mb	1650m, mb	1650w, mb	1645vw, mb	1660vw
~2300s, vb	~2300m, vb	~2300m, vb	~2300w, vb	~2300vw, b	~2300vw
2150 (2300) † (3000) † 3750 } vs, vb	2500 (3275) † 3650 } vs, vb	2575 (3300) † 3625 } vs, b	2580 (~3450) † 3625 } s, b	2500 (~2700) † (~3190) † 3200 } s, b	~2700 † s, mb

For footnotes see Table 3.

of $1/\chi'_A$ and temperatures for each material the Weiss constant θ was calculated by the method of least squares. For each case the effective magnetic moment (μ_{eff}) at room temperature was calculated from the relationship:

$$\mu_{eff} = 2{\cdot}839\sqrt{(\chi'_A T)}. \tag{1}$$

The results are given in Table 4.

TABLE 3.

Infrared bands (cm.$^{-1}$) of material $Cr_2O_3,As_2O_5,22H_2O$ and its thermal degradation products.

G	H	I	J	K
—	650m, sh	—	—	665 * s, sp
665m, sh	710w, sh	—	725w, sh	735w, sh
710s, sp	725 * s, sp	735m, sh	750 * ms, sp	780 * vs, sp
750s, sp	765m, sp	760w, sh	775 * vs, sp	825w, sh
825 * vs, mb	825w, sh	800 * s, sp	810w, sh	850 * s, sp
900m, sh	850 * vs, mb			875w, sh
	910m, sh	900 * s, sp	910 * vs, sp	925w, sh
975w, sh	975w, sh	1015w, sh	960w, sh	950s, sp
1025w, sh	1025w, sh	1065w, sh	1025w, sh	975w, sh
1160s, mb	1170m, sp	1150w, sp	1125w, sp	1070w, sh
1600s, mb	1635m, mb	1650w, b	1675vw, vb	1175vw, sp
				—
1650 ~2300 2500 } s, vb	~2300s, b	~2300vw, b	—	—
2500 (~3510) † 3875 } vs, vb	2500 (~3200) † (3400) † 3650 } vs, vb	2500 (~2700) † 3500 3700 } s, vb	~2700w, b	~2700vw

A = $[Cr(H_2O)_6]AsO_4$; B, C′, D, E′, and F result from heating A to constant weight at 110°, 200°, 300°, 400°, and 700°, respectively.

G = $Cr_2O_3,3As_2O_5,22H_2O$; H, I, J, K result from heating G to constant weight at 200°, 600°, 800°, and 900°, respectively.

sp = sharp; b = broad.

* Principal peaks in band. † Well characterised broad peak in band approximately in the region of the given wavelength.

TABLE 4.

Magnetic measurements for various chromium(III) arsenate materials.

Compound	Temp. (K)	$1/\chi'_A$	Compound	Temp. (K)	$1/\chi'_A$
A (see Table 1)	288°	157·0	E (see Table 1)	294°	178·3
μ_{eff} = 3·85 B.M.	259	144·0	μ_{eff} = 3·65 B.M.	259·5	159·7
θ = 12·3°K	225	126·4	θ = 51°K	225·5	143·3
	183	104·0		187	133·5
	86	51·1		161·5	110·6
				124	92·1
B (see Table 1)	286°	158·1		91	71·0
μ_{eff} = 3·78 B.M.	260	144·7			
θ = 23°K	227	129·1	L (see Table 1)	290°	176·9
	181	107·5	μ_{eff} = 3·64 B.M.	260	160·0
	151	89·7	θ = 27°K	226	141·9
	85	54·2		186	118·9
				91	65·7

RESULTS AND DISCUSSION

Various distinct stages in the decomposition of hexa-aquochromium(III) arsenate are apparent from the change in sample weight with rise of temperature when the plateaux and points of inflexion are taken into account. At each stage analyses give a chromium : arsenic ratio of 1 : 1. Thus the various stages may be best represented by the equations of Table 5 (it is unlikely that arsenite is formed at any stage of the decomposition since the heating is always carried out under oxidising conditions). The kinetics of dehydration and decomposition were investigated by Freeman and Carroll's method.[2]

TABLE 5.

Reactions occurring in the thermal decomposition of hexa-aquochromium(III) arsenate.

Reaction	Activation energy (E^*) (kcal. mole^{-1})	Order of reaction (x)
(1) $CrAsO_4,6H_2O(s) \longrightarrow CrAsO_4,4H_2O(s) + 2H_2O(g)$	20·2 ± 0·5	0·4 ± 0·05
(2) $CrAsO_4,4H_2O(s) \longrightarrow CrAsO_4,2H_2O(s) + 2H_2O(g)$	36·2 ± 0·5	0·75 ± 0·05
(3) $CrAsO_4,2H_2O(s) \longrightarrow CrAsO_4,H_2O(s) + H_2O(g)$	19 ± 1	2·1 ± 0·2
(4) $CrAsO_4,H_2O(s) \longrightarrow CrAsO_4,\frac{1}{2}H_2O(s) + \frac{1}{2}H_2O(g)$	38 ± 2·5	0·9 ± 0·2
(5) $CrAsO_4,\frac{1}{2}H_2O(s) \longrightarrow CrAsO_4(s) + \frac{1}{2}H_2O(g)$	Could not be evaluated	
(6) $2CrAsO_4(s) \longrightarrow Cr_2O_3(s) + As_2O_5(g)$	183 ± 8	2·4 ± 0·4

In view of the complexity of the reactions it was considered desirable to investigate the applicability of their derivation to the present work. For the reaction:

$$\begin{array}{ccc} A_s \longrightarrow & pB_s + & qC_g \\ n_0 & px & qx \end{array} \tag{2}$$

where n_0 = initial number of moles of A, and x = number of moles of A decomposed after time t, and if n_a = number of moles of A at time t,

then,
$$n_a = n_0 - x, \tag{3}$$
and
$$w = qxM_c, \tag{4}$$
$$w_c = qn_0M_c, \tag{5}$$

where M_c = molecular weight of C, w = weight loss at time t, and w_c = weight loss at completion of the reaction. Dividing equation (4) by (5) and substituting for x from equation 3 give:

$$n_a = n_0 - n_0w/w_c. \tag{6}$$

When equation 6 is differentiated with respect to time, we obtain:

$$\mathrm{d}n_a/\mathrm{d}t = -(n_0/w_c)(\mathrm{d}w/\mathrm{d}t). \tag{7}$$

Freeman and Carroll [2] derived the equation:

$$-\frac{(E^*/\boldsymbol{R})\Delta T^{-1}}{\Delta \ln n_a} = -x + \frac{\Delta \ln(-\mathrm{d}n_a/\mathrm{d}t)}{\Delta \ln n_a} \tag{8}$$

[This equation was derived from the rate expression for the disappearance of reactant A from the mixture, namely,

$$-\mathrm{d}X/\mathrm{d}t = kX^x, \tag{9}$$

where X = concentration, mole fraction, or amount of reactant A, x = order of reaction with respect to A, and k = specific rate, assumed to be given by the expression:

$$k = Z \exp(-E^*/\boldsymbol{R}T), \tag{10}$$

where Z = frequency factor, E^* = energy of activation, and T = absolute temperature. Equation (8) arises from (9) and (10) in two cases, namely, (i) where X = mole fraction of A and (ii) where X = actual amount of A that has reacted at time t (in moles), *i.e.*, $X = n_a$. In the present treatment the latter case, where $X = n_a$, has been considered.]

Equations (7) and (8) are next combined with equation (11) which relates w and w_c

$$w_r = w_c - w, \tag{11}$$

to yield equation (12):

$$\frac{-E^* \cdot \Delta T^{-1}/2{\cdot}3\boldsymbol{R}}{\Delta \log w_r} = -x + \frac{\Delta \log \mathrm{d}w/\mathrm{d}t}{\Delta \log w_r} \tag{12}$$

Thus it is established that for a single-stage irreversible reaction the equation yielding E^* and x is independent of p and q and of the molecularity of the reaction. Thus a plot of $\Delta T^{-1}/\Delta \log w_r$ against $\Delta \log (dw/dt)/\Delta \log w_r$ should result in a straight line of slope $-E^*/2{\cdot}3\mathbf{R}$ and of intercept x.

The method of least squares was applied to the points obtained and the best lines are given for each reaction in Fig. 2. Some preliminary results have already been given.[6] The present results for the order of reaction and activation energies are given in Table 5. These were derived from the rising portions of the dw/dt curves only, as the later periods in the decomposition are probably not typical owing possibly to strong adsorption of the displaced material on the solid phase or to initiation of another process.

The infrared results show considerable broadening of the water (aquo) absorption bands caused by hydrogen bonding. This results in a diffuse band of strongly superimposed components, arising from symmetric (ν_1) and antisymmetric (ν_3) vibrations of water (~3400 cm.$^{-1}$) as well as overtones (~4350 cm.$^{-1}$). It is therefore difficult to distinguish between absorbed moisture and co-ordinated water in the region 4000—2500 cm.$^{-1}$. The water bending vibration (δ) ~1600 cm.$^{-1}$ is not a pure band, but shows interaction with other vibrations, as well as a shift to higher frequencies on progressive dehydration of these materials ~1650 cm.$^{-1}$. Absorption in the 2300 cm.$^{-1}$ region can be attributed to OH stretching frequency. On dehydration of both the violet and the green compound, a progressive modification of the water bands is observed, with weakening of the absorption at the 4000 cm.$^{-1}$ end and in the 2500 cm.$^{-1}$ region and termination in an absorption band at ~2700 cm.$^{-1}$. This behaviour is difficult to interpret but possibly indicates strong adsorption of displaced water on the solid phase. Hydrogen bonding between the aquo-groups and the charged ligand has the general effect of shifting the bending modes to higher frequencies. It is impossible to assess the metal–oxygen bond strength from a study of the 1000—700 cm.$^{-1}$ region [7] owing to superposition of the strong arsenate bands. Similarly it is difficult to distinguish the planar deformation (π) of bridging hydroxyl groups, if any, which is normally observed in this region.

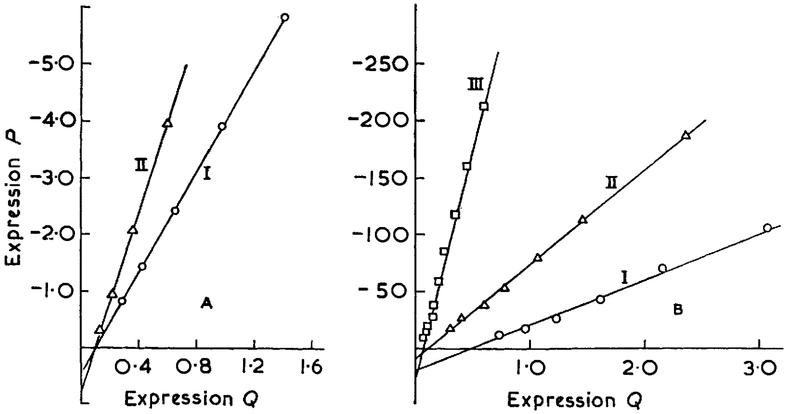

FIG. 2. Kinetics of decomposition of hexa-aquochromium(III) arsenate.
$P = \Delta \log (dw/dt)/\Delta \log w_r$. $Q = 10^3\Delta T^{-1}/\Delta \log w_r$. ($T$ is in °K.)
A, I, Reaction 1. A, II, Reaction 2. B, I, Reaction 3. B, II, Reaction 4.
B, III, Reaction 6. (See Table 5.)

Note.—The scale for Expression P in Fig. 2B should read $-5{\cdot}0$, $-10{\cdot}0$, $-15{\cdot}0$, $-20{\cdot}0$, $-25{\cdot}0$, and not as shown.

In the hexa-aquo-compounds the shape of the arsenate band at ~850 cm.$^{-1}$ indicates a slight lowering of the tetrahedral symmetry which increases on progressive dehydration. Band splitting concomittant with a shift to higher frequencies is observed both for the

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[6] Lukaszewski and Redfern, *Nature*, 1961, **190**, 805.

[7] Fujita, Nakamoto, and Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3963.

dehydration products of the hexa-aquo-compound and for the green modifications, implying a lowering of the T_d symmetry, caused by entry of the anion into the metal co-ordination sphere. This may be due to the formation in the solid of $H_2AsO_4^-$ or $HAsO_4^{2-}$ groupings (symmetry C_s), or even of both species. Under these conditions it is difficult to assign the split bands, in view of the lack of knowledge concerning the behaviour of the ligand field. However, comparison with other data on arsenate spectra[8] tends to support the above view. It is possible that the bands observed in the 2300 cm.$^{-1}$ region may be attributed to X–OH stretching modes.

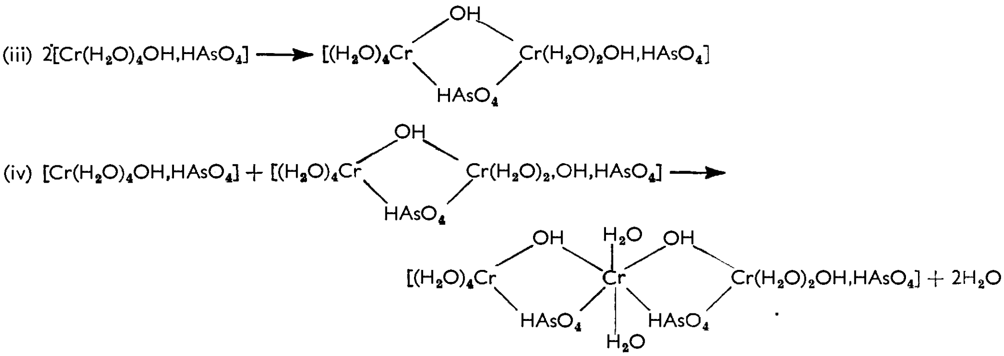
All the materials studied obey the Curie–Weiss law down to liquid-nitrogen temperatures (~80°K). A progressive increase in the value of θ is observed as the compound is successively dehydrated. This is probably due to the removal of the neutral ligand which acts as a magnetic diluent, allowing for freer interaction between the metal cations. Some interaction might be expected in the case of OH or $HAsO_4$ bridges but would not be as high as that expected if –O– links were present.[9] The greater value of θ for the green modification (produced by evaporation of a mixture of the hexa-aquo-compound and arsenic acid) could be explained by the increased number of bridges present.

It has been shown elsewhere[1] that $CrAsO_4,2H_2O$ has ion-exchange properties which might suggest a bridged polynuclear structure involving arsenate and perhaps hydroxyl bridging. The present work suggests that the partially dehydrated materials contain possibly OH^-, $H_2AsO_4^-$, $HAsO_4^{2-}$, or AsO_4^{3-} groups, but –O– bridges are excluded. The possible groupings may be present as bridging or monodentate ligands, or even, in the case of the $HAsO_4^{2-}$ and AsO_4^{3-} groups, as chelating ligands. The results suggest a complex process of olation in the solid analogous to that found for certain hydrated metal chlorides.[10]

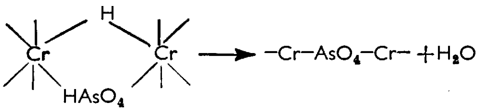
From the thermogravimetric and infrared data the following route of entry of the anion into the co-ordination sphere is proposed:

(i) $[Cr(H_2O)_6]AsO_4 \rightleftharpoons [Cr(H_2O)_5OH]HAsO_4$

(ii) $[Cr(H_2O)_5OH]HAsO_4 \longrightarrow [Cr(H_2O)_4OH,HAsO_4] + H_2O$



Such steps would account for the incremental water loss, albeit somewhat masked by the strong physical retention of water in the solid phase. Before complete dehydration a partial breakdown could occur, involving a slow fractional loss of water:



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[8] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253; Feher and Morgenstern, *Z. anorg. Chem.*, **1937**, **232**, 169.

[9] Earnshaw and Lewis, *J.*, 1961, 396.

[10] Castor and Basolo, *J. Amer. Chem. Soc.*, 1953, **75**, 4807.

The polymeric nature of the products in such reactions, and the presence of active groupings such as $HAsO_4$ and H_2AsO_4 with replaceable hydrogen would account for the ion-exchange properties found in the materials.[1]

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CHEMISTRY DEPARTMENT, BATTERSEA COLLEGE OF TECHNOLOGY,
LONDON, S.W.11.

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