ALTHOUGH the comments of Dr. Brown on my communication are very encouraging for further theoretical investigations, it should be pointed out that the equation used by Brown to calculate the doubly degenerate $\bar{\nu}_2(E)$ vibration of the BH_4^- ion was derived for a tetrahedral ion or molecule which has a spherical and rigid electron distribution. This assumption is certainly not valid in the case of the BH_4^- ion in the $LiBH_4$ lattice. In this lattice the tetrahedral ion is considerably deformed, having the site symmetry C_s. In addition, it must be pointed out that the crystalline field in which any ion is embedded has a profound influence on the frequencies of vibrational modes (see, for example, refs. 1 and 2). The frequency of ν_2, calculated according to the formula derived by Brown, is that of the free tetrahedral BH_4^- ion and can only be compared, for example, with the Raman frequencies of BH_4^- in liquid ammonia.
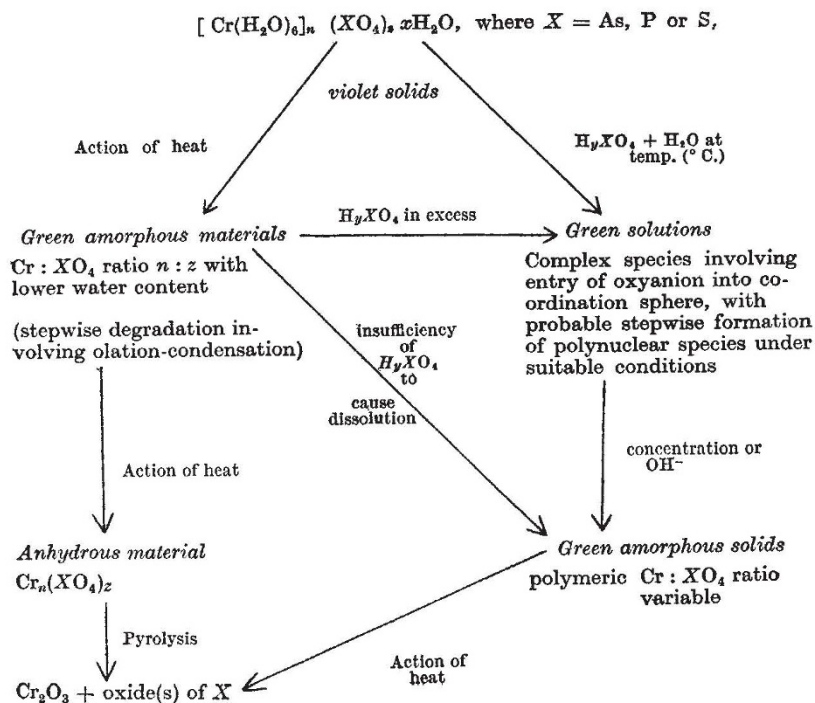
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[1] Strasheim, A., and Buijs, K., *J. Chem. Phys.*, **34**, 691 (1961).
[2] Ketelaar, J. A. A., Schutte, C. J. H., and Schram, B. L., *Spectrochim. Acta*, **13**, 336 (1959).

Chromium(III) – Oxyanion Systems

CERTAIN hexaquochromium(III) oxyanion compounds (in particular, the phosphate, arsenate and sulphate) have shown marked similarities in their behaviour on thermal degradation and in solutions with their corresponding oxyacids. This behaviour can best be explained on the basis of olation-condensation reactions which are believed to occur both in the solid state and in solution.

The behaviour may be represented schematically:

[$Cr(H_2O)_6]_n$ $(XO_4)_z$ xH_2O, where $X = As$, P or S,

violet solids

Action of heat

$H_yXO_4 + H_2O$ at temp. (° C.)

Green amorphous materials —— H_yXO_4 in excess ——→ *Green solutions*

$Cr : XO_4$ ratio $n : z$ with lower water content

(stepwise degradation involving olation-condensation)

Complex species involving entry of oxyanion into co-ordination sphere, with probable stepwise formation of polynuclear species under suitable conditions

insufficiency of H_yXO_4 to cause dissolution

Action of heat

concentration or OH^-

Anhydrous material $Cr_n(XO_4)_z$

Green amorphous solids polymeric $Cr : XO_4$ ratio variable

Pyrolysis

Action of heat

Cr_2O_3 + oxide(s) of X ←——

Work on the solution and solid phases of the systems: $Cr_2O_3-P_2O_5-H_2O$ at 0°, 40°[1], and 70°[2], $Cr_2O_3-As_2O_5-H_2O$ at 25°[3] has already been reported. The system $Cr_2O_3-SO_3-H_2O$ is being studied at 25° and 70°.

Thermogravimetric studies of hexaquochromium(III) phosphate, arsenate and sulphate indicate that the dehydration process is complex. Inflexions in curves of the loss in weight against temperature are interpreted as stages in a process of olation-condensation occurring in the solid phase, which is initiated by the entry of the oxyanion into the chromium(III) co-ordination sphere. Such a process is expected to result in the formation of cross-linked polymers incorporating groupings of the type:
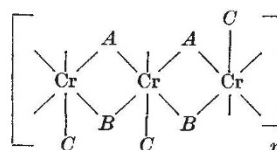
Where $A = HXO_4{}^{a-}$, $B = OH^-$ or $HXO_4{}^{a-}$ or no linkage, and $C = HXO_4{}^{a-}$, $H_2XO^{(a-1)-}$, or H_2O.

This type of structure accounts for the ion-exchange properties encountered in these systems[2,3]. X-ray studies have shown that the products of dehydration of these hexaquochromium(III) salts are amorphous and possess no long-range order. This might be accounted for by a random arrangement of the bridging groups. However, recrystallization occurs in these materials prior to complete dehydration to the phase $Cr_n(XO_4)_z$.

The kinetics of thermal decomposition have been studied by the method developed by Freeman and Carroll[4]. The results are presented in Tables 1–3, together with supporting evidence obtained from preliminary differential thermal analysis.

Infra-red studies of the products of progressive dehydration show that the characteristic absorption bands associated with water in the complex are initially extremely broad due to the effect of hydrogen bonding. In the course of the dehydration this band (3,750–2,100 cm.$^{-1}$) becomes modified in length and intensity, shortening occurring in the 3,750–3,100 cm.$^{-1}$ region. Finally the band disappears on complete dehydration (together with that due to the bending vibrations ($\sim 1,600$ cm.$^{-1}$)). The characteristic bands of the oxyanion undergo broadening and splitting in the course of dehydration—implying a lowering of T_d symmetry, which might be expected if the formation of HXO_4-groups were involved. Magnetic studies on the arsenate have shown that the compound obeys the Curie–Weiss law down to liquid-nitrogen temperatures and has a very small value of the Weiss constant θ. Progressive dehydration of this material