A STUDY OF THE SULPHATO COMPLEXES FORMED BY DIGESTING CHROMIUM (III) SULPHATE IN HIGH CONCENTRATIONS OF SULPHURIC ACID

by

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To my wife, Ellen

ABSTRACT

The attack of chromite ore by sulphuric acid employing temperatures above the boiling point of the sulphuric acid solution, has been studied. The experimental data obtained in this research are adequately explained by the following mechanism; an initial protonic attack on the chromite lattice brings the metallic constituents into solution in the same ratio as they occur in the lattice; under sufficiently high acid concentrations and high temperatures various sulphatopolychromate (III) anions are formed whose hydrogen and other metal salts are insoluble and precipitate in a second step.

To further strengthen this explanation, typical compounds of the type postulated were prepared under similar conditions. Digesting chromium (III) sulphate with sulphuric acid, under similar digestion conditions, produced insoluble hydrogen salts of the sulphatopolychromate (III) anions whose properties corresponded to those of the insoluble materials produced in the digestion of chromite.

Chemical analysis of these hydrogen salts showed that three distinct classes of compounds were produced. The compounds of the first class have a sulphate to chromium equivalent ratio of two and contain coordinated sulphate and water groups. The compounds of the second class have a sulphate to chromium equivalent ratio of two or greater

and contain no coordinated water molecules. The third class of compounds has a sulphate to chromium equivalent ratio between one and a half and two and contain no coordinated water molecules.

The chemical composition of any compound is not sufficient to describe a compound and, therefore, infrared and pyrolysis studies were undertaken for these and the hydrates of chromium (III) sulphate in an attempt to establish, first, the characteristic infrared absorption spectrum of the sulphate ligand in compounds whose structures were known; second, to find pyrolysis intermediates which might resemble the sulphatopolychromate (III) salts, whose structures might be deduced by tracing their formation from known structures.

A simple thermobalance for studies over a pressure range of 0 to 60 atmospheres was designed and built for this purpose. This research did not require a thermobalance capable of operating at high pressures but this feature was incorporated in its design so that the machine would have greater versatility.

The results were interpreted in terms of olation-condensation reactions which were initiated by entry of the sulphate group into the chromium coordination sphere followed by polymerization with sulphate and perhaps water acting as bridging groups.

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INTRODUCTION

INTRODUCTION

The mineral chromite crystallizes with the spinel structure and may be formulated as $M(CrO_2)_2$. The most common metal (M) is iron (II) but may be replaced isomorphously by magnesium (II), manganese (II), and other divalent metals, whereas the chromium (III) may be replaced by trivalent metals such as aluminum (III) and iron (III). A ''high grade'' of chromite ore would contain approximately 50% chromic oxide and have a chromium to iron ratio of at least three to one. This ratio is the principle factor which determines whether or not the chromite is classified as ''low grade'' or ''high grade'' ore. The large chromite deposits in North America are classified as ''low grade'', due largely to the low value (1.5) for the chromium to iron ratio.

Utilization of these ''low grade'' ores is made feasible by sweetening with compounds such as $Na_2Cr_2O_7$, $CaO.Cr_2O_3$, $CaCrO_4$, Cr_2O_3, and CrO_3.[1a] Mechanical concentration and chemical benefication of these ores have found limited application; these methods have been comprehensively compiled by Udy[1b] and by Downes and Morgan [2]. The latter give a critical review of attempts at chemical benefication of North American chromite deposits; sulphuric acid leaching of these ores figures prominently in these methods. For sulphuric acid leaching of chromite to become an important industrial process, however, it is necessary that the leaching

and subsequent processes be cyclic.

The chromite lattice may be decomposed by boiling in strong sulphuric acid solutions, this process being accelerated by the addition of chromic anhydride (CrO_3).[4] Chemical benefication with an initial solution of the chromite in sulphuric acid chromic anhydride solution, followed by electrolytic oxidation of the chromium (III) to chromium (VI), and subsequent precipitation of CrO_3, has been developed by Elliot, Mather, and Wylie.[4, 5, 6, 7, 8] In order to establish a cyclic process, the iron (III), aluminum (III) and magnesium (II) acid sulphates are precipitated from concentrated acid solutions containing the chromic anhydride. This is followed by crystallization of the chromic anhydride, the supernatant acid solution is used for subsequent attack of the chromite, and the chromic anhydride may be used to sweeten the "low grade" chromite ore. The cost of crystallization processes and the loss of sulphuric acid in the acid sulphates prevents this process from becoming important in industry at the present time.

In order to curtail the cost of benefication, Downes and Morgan[2] leach a North American chromite concentrate with insufficient sulphuric acid for complete destruction of the chromite lattice. They outline optimum conditions for "preferential" removal of iron from the chromite lattice and optimum conditions for the rate of attack of the chromite

by sulphuric acid. They suggest that an acid concentration of 1:2 by volume, gives the best rate of attack of the lattice; this rate being determined from the amount of iron that is found in the resulting solution. A plot of the fraction of the total iron in solution, as a function of the acid concentration, shows a maximum at an acid concentration between 1:1 and 1:2. At lower acid concentrations the rate of attack is slower and at higher acid concentrations the appearance of the charge indicates that sulphation occurs but the amount of iron in the filtrate decreases. This process yields favourable chromium to iron ratios in the insoluble material left after such a digestion and favourable chromium recovery in the residue.

Downes and Morgan[2] report that all of the chromium will remain in solution during the digestion process provided excess acid beyond that required to convert all of the metals to the normal sulphates, is used. They also report a lower rate of attack at high acid concentrations, this rate being determined from the percentage of the total iron in the filtrate, which as they point out is not the total reaction but the rate at which the iron is ''preferentially'' removed from the lattice. The visual appearance of the insoluble material indicated that sulphation occurs at the higher acid concentrations. Since their data do not outline conditions for complete destruction of the chromite lattice, and do not

give evidence for the rate of attack of the chromite lattice, it was deemed desirable to outline first the conditions for complete attack and the optimum conditions required for this attack.

A more important reason for investigating this digestion process lies in establishing the nature of the insoluble material formed during the leaching process. The observations made by Downes and Morgan led them to conclude that the first step in the digestion process was an initial attack of the chromite lattice to form the normal sulphates of the metal constituents. After initial consumption of the acid, hydrolysis of chromium (III) and iron (III) ions occurs to form insoluble basic salts with the liberation of free acid, which then continues a ''preferential'' attack on the iron (II), magnesium (II), and possibly aluminum (III) oxides in the chromite lattice. Since chromite ore is not a mixture of oxides, one is skeptical about this ''preferential'' attack. Furthermore, they found that at higher acid concentrations sulphation occurs rapidly and a simultaneous sharp decrease in the amount of iron leached in the process. These observations are not consistent with a hydrolytic process.

To learn more about the attack of chromite by sulphuric acid, digestions employing elevated temperatures and various concentrations and amounts of sulphuric acid, were carried out in this investigation. It was immediately evident that

the digestion or leaching of the ore was a complicated process, and that the behaviour of this system could not be explained by a hydrolytic process.

It is a well established fact that heating solutions of chromium (III) sulphate causes ''masking'' of the sulphate and the chromium ions.[1, 12, 22, 31, 39] This ''masking process is evident in that barium chloride solutions will not precipitate all or any of the sulphate as barium sulphate and that sodium hydrogen phosphate will not precipitate all or any of the chromium (III) ions from these solutions.[12] These complexes contain coordinated sulphate and hydroxyl ligands, the number depending upon the age of the squeous solution, the concentration of the chromium (III) sulphate and prior thermal treatment of the solution. Both the sulphate and the hydroxyl group may act as bridging ligands in the formation of polynuclear complexes.[1, 12, 39] However, in the acid solutions, one would expect that the hydroxyl groups would not play an important role in any complexes that are formed or in the ''masking process''.

Recoura's work[10], in general substantiated by Whitney[11], shows that a series of acids may be obtained by digesting chromium (III) sulphate with sulphuric acid on a hot plate. He designates these as ''chromipolysulphuric acids'' which may be formulated as $Cr_2(SO_4)_3 \cdot n H_2SO_4 \cdot y H_2O$. The value of n is determined by the ratio of chromium (III)

sulphate and sulphuric acid employed in the digestion. If the molar ratio is 2, then the n value is 2. These water soluble acids do not show the characteristic reactions for the sulphate or the chromium (III) ion in solution and precipitate as the metal salt upon addition of a soluble metal salt to their solutions. Heating these acids at a temperature of 150°C causes conversion to a substance Recoura designated as the ''isomeric form'' of ''chromitetrasulphuric acid''.

These salts have received very little attention and therefore the permissible values of n are not clearly established. Wyrouboff[12a] considers all of these acids simply as mixtures of sulphuric acid and the ''chromitetrasulphuric acid'', whereas Whitney[11] considers the product formed whenever the molar ratio of chromium (III) sulphate to sulphuric acid is greater than 1.3 to be identical to Recoura's ''isomeric form''.

Udy[1c], in his textbook on chromium, suggests that the maximum number of sulphate ligands that can be coordinated to a chromium (III) ion in mononuclear complexes is three. This implies that, if octahedral coordination of chromium (III) is preserved, the sulphate group behaves as a bidentate chelating ligand. Fogel et al[22] report the formation of two inner inert complexes $[Cr(H_2O)_x\ SO_4]^+$ and $[Cr(H_2O)_x\ (SO_4)_2]^-$ in acid solution at temperatures below 80°C, but do not

designate the role that the sulphate ligands plays in these complexes. A search of the literature showed no structural information for any of these complexes produced in acid media. Therefore, the second part of this thesis deals with the preparation and properties of the compounds produced by digesting chromium (III) sulphate with sulphuric acid. In order to obtain more information about the structure of these materials they were subjected to pyrolysis and infrared spectral analysis.

The ''chromipolysulphuric acids'' contain a variable quantity of water depending upon the conditions of preparation.[10, 11] It is not known whether the water is ''constitutional water'' or ''water of hydration''. Udy[1d] suggests that the various forms of the hydrates of chromium (III) sulphate may be formulated as $[Cr_2(H_2O)_{12-2n}(SO_4)_n](SO_4)_{3-n} X H_2O$ where the value of X is usually between 4 and 5. The normal violet sulphate would have a zero value for n, whereas the green forms, containing coordinated sulphate ligands, could have values up to 3. Furthermore, if one continues this series by introduction of more sulphate groups into the coordination sphere, one obtains the ''chromipolysulphuric acids''.[12a] This formula implies that the maximum number of sulphate ligands that may enter into coordination is 6, and that the sulphate ligand functions only as a bidentate, likely chelating ligand, in these complexes.

Recoura[10], however, concludes that one mole of chromium (III) sulphate may combine with as many as six moles of sulphuric acid, whereas the above formulation would suggest that three is the maximum number of moles of sulphuric acid that may be coordinated. If a total of six moles of sulphuric acid can become coordinated to the two chromium (III) ions, it is impossible for the 9 $SO_4^=$ groups to act as bidentate ligands if octahedral coordination of the chromium (III) ions is preserved. In order to learn more about the role that the various constituents, water and sulphuric acid, play in these complexes, they were subjected to thermogravimetric analysis.

Thermogravimetric analysis is the science or art of weighing substances while they are being heated, usually at a uniform heating rate.[55] It requires a sensitive balance, which usually records the weight as a function of temperature or time automatically. This plot is commonly referred to as a ''thermogram''. A history of the development of this technique may be found in Duval's recent book on ''Inorganic Thermogravimetric Analysis''.[54] In some situations analysis of the thermogram enables one to assign a reasonable structural role for the various constituents in the compound. Thus, it is usually assumed that water lost upon pyrolysis at temperatures below 100°C, is ''water of hydration'', whereas water lost at higher temperatures is usually

''constitutional water''.[30, 31, 52, 54] Similarly, one would expect that absorbed sulphuric acid would be lost below its boiling point whereas constitutional or coordinated sulphate groups, as sulphuric acid, would be lost at higher temperatures. Furthermore, if, upon pyrolysis, coordinated groups, such as water or sulphate groups are lost in gaseous products, at least some constituents not volatilized must assume a different role in the pyrolysis products provided the central metal atom preserves the same coordination number as observed in the original compound. The different possible roles that the constituents assume in the pyrolysis products can be inferred from a knowledge of the composition of the material and the manner in which it decomposes, and may receive experimental verification from their infrared absorption spectra.

The infrared absorption spectrum of a sulphate ion depends upon the bonding that exists between itself and the other constituents in the solid state and especially on the symmetry of this bonding.[35, 34, 36, 37, 38] The infrared absorption spectrum of a monodentate sulphate ligand will be different from that of a bidentate sulphate ligand and so forth. Thus, an analysis of the infrared absorption spectrum of the various compounds containing coordinated sulphate ligands could enable one to assign possible structures for these compounds compatible with the data obtained from infrared spectral analysis and thermogravimetry.

EXPERIMENTAL PROCEDURES

EXPERIMENTAL PROCEDURES

DIGESTION OF CHROMITE

The chromite used in these experiments was a concentrate prepared from material taken from the Bird River chromite complex and supplied through the courtesy of the Research Department of the Hudson Bay Mining and Smelting Co. This concentrate assayed 41.8% Cr_2O_3, 26.5% FeO, 16.0% Al_2O_3 and 4.8% MgO and had a chromium-iron ratio of 1.36 to 1, and the particle size was about 80 mesh.

In order for the rate of attack of the chromite lattice by sulphuric acid to be conveniently rapid, one must maintain the temperature above the normal boiling point of the solution. These digestions were carried out in glass tubes sealed under atmospheric pressure. The sample of chromite concentrate and the desired quantity of sulphuric acid solution were placed in the tube and sealed. This sealed tube was then placed in a sand bath, which consisted of an ordinary iron pipe equipped with removable caps and filled with sand. A few small holes in the caps prevented pressures from building up inside the tube as it was heated. The steel pipe was deemed necessary to minimize the dangers of injury due toflying glass in the event of an explosion. The loaded pipe was then placed in a muffle furnace and maintained at the desired temperature for a predetermined length of time.

The regular occurrence of explosions at elevated

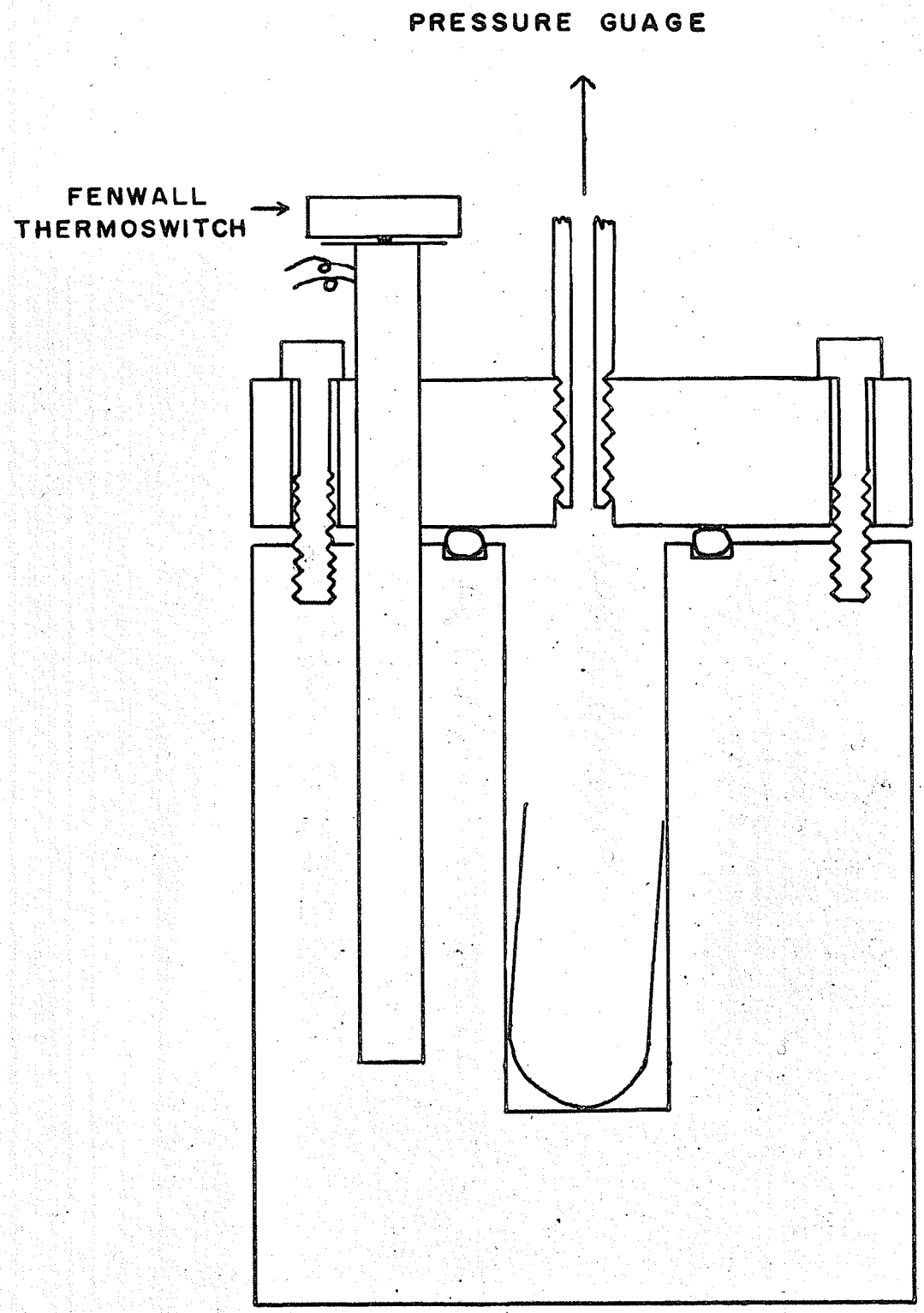
temperatures and low acid concentrations made it desirable to find a more suitable reaction vessel. The design of the vessel chosen for this purpose is shown in Figure 1. A simple steel pressure vessel, sealed by a Teflon "O" ring, was found to work satisfactorily. A glass tube, loaded with sulphuric acid solution and chromite concentrate, loosely closed with a wisp of glass wool to prevent mechanical spraying of the solution, was placed inside the steel pressure vessel, which in turn was sealed by a flat steel plate bolted to the steel vessel. It was found desirable to coat the "O" ring as well as the metal surfaces with a silicone grease; this prevented sticking of the "O" ring and seemed to facilitate the ease with which a proper seal could be obtained.

The sealed steel vessel was then placed in a thermostat, equipped with two heating elements, one of which was controlled by a Fenwall thermoswitch imbedded in the steel vessel and fed directly from a 110 volt line, whereas, the auxilliary heater was fed by a Variac so that heat could be supplied rapidly when bringing the system up to temperature, after which the power to the auxilliary was reduced to a point which gave minimum cyclic variation of time.

The vessel was equipped with a pressure gauge which was used to give a rough estimate of the rate of the reaction. As sulphuric acid is used up in the reaction, the vapor pressure increases, and levels off to a constant value as the

Figure 1

The Digestion Vessel


PRESSURE GUAGE
FENWALL
THERMOSWITCH

rate decreases. This was found to be a valid criterion for the completion of the reaction. Then, when the rate of the reaction had slowed down to a negligible value, the vessel was removed from the thermostat and allowed to cool, after which the contents were removed and analyzed.

After digestion of the chromite concentrate with sulphuric acid, the reaction vessel contained unattacked chromite, solution, and a finely divided acid and water insoluble substance. This latter, for lack of a more definitive designation, will be called ''altered chromite''. It will be shown later that this ''altered chromite'' consists of insoluble hydrogen and other metal salts of sulphato complexes of chromium (III). To determine the total weight of the insoluble material, the residue was washed with either hot water or hot dilute sulphuric acid solutions and dried at 110°C. The amount of insoluble residue was usually slightly larger when washed with acid than when washed with hot water. Under similar washing conditions these weights were reproducible to within a few per cent.

The main portion of the ''altered chromite'' was found to be insoluble in boiling water and in boiling sulphuric acid solutions. If the ''altered chromite'' was produced as a result of hydrolysis, as suggested by Downes and Morgan[2], it should dissolve in boiling sulphuric acid solutions. It is a well established fact that complexes of

chromium (III) are inert, but it has been our experience that the hydrolysis products produced by boiling alkaline solutions of chromium (III) sulphate, can be dissolved when boiled in sulphuric acid solutions, though admittedly, this occurs slowly. After some experimentation, it was found that boiling the ''altered chromite'' with 2 N sodium hydroxide solutions rendered these materials into an acid soluble gelatinous substance whose appearance was typical of precipitated metal hydroxides. Thus, solution of the gelatinous substance in dilute acid, followed by filtration, enabled us to separate the ''altered chromite'' from the unattacked chromite concentrate. The residue obtained in the above manner we have designated as unattacked chromite. The weight of the ''altered chromite'' is then the difference between the residue weight and the excess chromite concentrate. The composition of the ''altered chromite'' was determined from the filtrate obtained from the chromite separation.

ANALYTICAL TECHNIQUES

The determination of chromium (III) was done by back titrating with a standard solution of potassium dichromate after oxidation of the chromium (III) to chromium (VI) with ammonium persulphate, using silver ions as a catalyst[13a],

and addition of excess ferrous ammonium sulphate. The chromite concentrate contained trace amounts of manganese, which was oxidized to the permanganate ion in the oxidation of the chromium (III). The permanganate ion was, therefore, reduced by boiling the oxidized solution after the addition of 5 mls. of 1:3 hydrochloric acid.[13a]

The determination of iron was again through the use of a standard redox titration. To determine the total iron content, a redox titration was employed after reduction of the ferric ions with stannous chloride.[13b]

Sulphate was determined in all cases by precipitation and weighing as barium sulphate. Since chromium (III) co-ordinates the sulphate group in solution, it was found necessary to remove the chromium (III) ions. This was achieved by extraction of the chromium (III) acetylacetonate complex into chloroform. To test this method of analysis, a standard solution of sulphuric acid was prepared. Analysis of this solution by standard techniques of precipitating and weighing as barium sulphate,[13c] and by the following procedure, showed that the latter gave results which were 5 parts per thousand higher than the former.

Sufficient chromium was added to the sulphuric acid solutions in the form of potassium dichromate so that the $Cr:SO_4$ ratio would be near the value found in other typical samples. Sodium hydroxide solution was added so that the

resulting solution had a pH value between 4 and 5, as recorded on a Photovolt Model 110 Electronic pH meter. 5 mls. of ethyl alcohol and 5 mls. of acetylacetone were then added to the solution, to bring about the reduction of the chromium (VI) to chromium (III) and the formation of the acetylacetone complex.[16] In order for the reactions to proceed at a reasonable rate, the solutions were heated without boiling until the conversion to the complex was complete, as evidenced by the disappearance of the yellow colour of the chromium (VI) species. After cooling of the solution and the addition of 5 mls. of 1:3 hydrochloric acid, two successive extractions employing 25 mls. of chloroform, removed all of the acetylacetonate of chromium (III). This extraction is necessitated because of the low solubility of the complex in aqueous solutions. After extraction, the solutions were heated to remove any excess and dissolved chloroform. The sulphate was then precipitated as barium sulphate by the addition of barium chloride solution, and digested for a half hour followed by cooling, usually overnight. The precipitate of barium sulphate was collected in a sintered porous porcelain crucible, then ignited in a muffle furnace at 900°C.

In order to determine the sulphate content in the samples of "altered chromite", and other complexes of chromium (III), it is necessary to start with a solution free of coordinated sulphate groups. This was achieved by oxidizing

the chromium (III) to chromium (VI) with hydrogen peroxide in an alkaline solution which was necessary not only for the oxidation process but also, in many cases, to destroy the sulphato complexes in the ''altered chromite''. Following the oxidation process and the destruction of excess hydrogen peroxide by boiling, the pH of the solution was adjusted to a value between 4 and 5. In certain samples, such as anhydrous chromium (III) sulphate, alkaline solutions would not destroy the complex and in such cases a sodium carbonate fusion in platinum crucibles was necessary. Since the oxidation of chromium (III) occurs simultaneously for these samples the hydrogen peroxide oxidation was unnecessary, but prolonged boiling of an acidified solution was required to remove all of the carbonate ions from these solutions.

Aluminum was determined spectrophotometrically, employing a Beckmann Model DU Spectrophotometer, using alizarin Red-S in the presence of calcium.[14] Shapiro and Brannock[3] have shown that no interference will result from substances present in these samples. Magnesium was titrated with standard ethylenediamminetetraacetic acid, using Eriochrome Black T as indicator.[17]

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis of the various compounds was done on a thermobalance whose mode of operation and

description are found in the appendix. The thermograms in all cases have been obtained in an atmosphere of air unless a different atmosphere is specifically stated. In all types of thermograms, an inert atmosphere, usually nitrogen, was used under identical conditions as these obtained in an atmosphere of air, to make sure that the atmosphere played no important role in the decomposition of the substance.

INFRARED SPECTRAL ANALYSIS

The infrared absorption spectra were obtained using a Perkin Elmer Model 21 Infrared Spectrophotometer equipped with a sodium chloride prism. As absorbent, pressed pellets of the substance and potassium bromide, or a mull of the substance and Nujol, spread between two rock salt plates, were used. The potassium bromide pellets were prepared in a 1/2 inch potassium bromide die supplied by Beckmann Instruments Inc. as Catalog Number 5020. The technique used was that described in circular Number 518-A, supplied by the manufacturer. The maximum pressure applied to the die in the preparation of the pellets was 19,000-20,000 p.s.i.

In order to obtain sharp detailed spectra without scattering, it is necessary that the particle size of the solid substance be in the micron region. To obtain this reduction in size, many techniques have found application,[40] of these, the most convenient method consists of grinding a

mixture of the sample and potassium bromide in a Wig-L-Bug. However, grinding in the latter is not satisfactory for substances which decompose readily with the application of heat or vigorous grinding. The spectra obtained from the products of grinding $Cr_2(SO_4)_3$ $16H_2O$ in a Wig-L-Bug are shown in Figure 18. Experimentally, it was found that the hydrates in this investigation, which have low temperatures of dehydration, cannot be ground in a Wig-L-Bug, whereas, anhydrous substances or substances whose dehydration temperatures are above 100°C could be treated in a Wig-L-Bug without alteration of the sample.

Simple hand grinding of the hydrates with low decomposition temperatures proved unsuccessful. These samples, even though dry, tend to cake immediately, thus making it impossible to grind these substances. Mixing the sample with potassium bromide prior to grinding, prevents caking, but experimentation showed that better results could be obtained by grinding the mixture in a mortar and pestle in which the mixture was kept under ether. The use of ether ensures that the sample remains cool during the grinding process and results in a homogeneous mixture thus leading to a sharper spectrum.[23] Figure 19 shows the difference between spectra obtained from various grinding techniques. Hand grinding of the samples used in the mull technique, was started only after the mulling agent had been mixed with the sample. This prevents caking of the sample,

but also prevents the achievement of a good grind, because of the lubricating properties of the Nujol. For the compounds not altered by grinding, the Nujol was added only after a good grind had been obtained from the original powder. In the future, it might be advisable to prepare those hydrates which decompose readily by mixing them with potassium bromide or some other inert and infrared transparent substance, followed by grinding under ether. These samples can then be dried at room temperature or under vacuum followed by mixing with the Nujol.

Reagent grade potassium bromide was found to have a fairly strong absorption in the 1100 cm^{-1} region. This absorption is likely due to sulphate impurities in the potassium bromide. Since typical sample weights required to give good absorption spectra of the sulphate were in the range of 0.1 to 0.3 milligrams of compound for every 400 milligrams of potassium bromide, the amount of sulphate impurity, 0.0005% reported by the manufacturer, is quite sufficient to yield a substantial absorption band in the 1100 cm^{-1} which is the sulphate region. To prepare optical grade potassium bromide, the following method found application. A solution of ethyl alcohol and water, 50% by volume, was saturated with potassium bromide at a temperature near the boiling point of the solution. This solution was then allowed to cool sufficiently so that a good portion of the

potassium bromide precipitated, which was removed by rapid filtration and then discarded. The second crop of crystals which formed immediately after filtration was retained for spectroscopic purposes. These crystals were dried at 80°C followed by sufficient grinding so that the product could pass a 100 mesh sieve. The potassium bromide was then dried and stored in a drying oven at 200°C. The particle size of potassium bromide is generally recommended to be approximately 250 mesh for clear pellets but the experience in this laboratory showed that grinding of the potassium bromide after recrystallization was unnecessary. This is likely due to reduction of particle size during the ethanol precipitation as pointed out by Meloche and Kalbus.[23] In order to prevent contamination of the recrystallized potassium bromide, a mortar and pestle and sieves were thoroughly cleaned and then used for no purpose other than the grinding and sieving of the optical potassium bromide.

In preparing samples for infrared spectral analysis, an agate mortar and pestle were used to grind all samples. Experimentation showed that washing the mortar and pestle, followed by alcohol and ether rinses was not sufficient to render these spectroscopically clean if a water insoluble compound had been ground in it. For these latter salts, thorough scrubbing with Ajax Cleanser was sufficient to clean the mortar and pestle properly. To check for cleanliness,

optical potassium bromide was ground in the mortar and pestle prior to pelletization. The absorption due to this pellet was then determined in the infrared spectrophotometer, which showed no absorption in the 1100 cm^{-1} or sulphate region.

EXPERIMENTAL RESULTS

DIGESTION OF CHROMITE ORE

EXPERIMENTAL RESULTS

DIGESTION OF CHROMITE ORE

A) RESULTS

Table I shows the weights of ''altered chromite'' and unattacked chromite obtained under a variety of conditions. The amount of sulphuric acid is described in terms of ''percentages of equivalence'', an equivalent of sulphuric acid being calculated as the amount of sulphuric acid required to convert the concentrate completely to the normal sulphates. Thus, one gram of the chromite concentrate used in this work, would be equivalent to 1.751 gms. of pure sulphuric acid. Concentration of the sulphuric acid is described by a conventional volume ratio of concentrated sulphuric acid to water.

The weights of ''altered chromite'' as given in Table I refer to the weights of either acid or water insoluble material, other than chromite concentrate. To obtain this material the digestion products were treated with approximately 200 mls. of either dilute sulphuric acid solution or water and brought close to the boiling point of the solution. Heating was required for it was found that the fine precipitate would usually not settle and appeared to form a sol which, however, coagulated just below the boiling point of the solution. Some of the insoluble material produced in the digestion dissolves under these conditions and, therefore,

the weight of ''altered chromite'' plus the weight of unattacked chromite concentrate, given in Table I, does not refer to the total weight of insoluble material formed during the digestion, but to the weight of material insoluble under the washing conditions employed.

In order to separate the ''altered chromite'' from the unattacked chromite, the insoluble residue obtained after the soluble material had been removed as discussed above, was subjected to prolonged contact to boiling 2 N sodium hydroxide solution. This was then acidified and resulted in the solution of most of the insoluble material other than the unattacked chromite. Repeated alkali treatment was usually found unnecessary when hydrogen peroxide was added to the alkaline solution because the insoluble chromium (III) hydroxide was oxidized to a soluble chromium (VI) species, thus allowing continued attack on the ''altered chromite'' by sodium hydroxide.

The data suggest that the amount of chromite unattacked by sulphuric acid is determined primarily by the amount of acid present in the digestion. This is shown by comparison of runs using different percentage equivalence of acid as in run numbers 1, 9, and 16. When the acid used is about 50% of equivalence, the unattacked chromite is generally quite close to the amount anticipated from the stoichiometry, provided sufficient time is allowed for

equilibrium to be established. In no case was the attack great enough to indicate significant regeneration of sulphuric acid by hydrolysis: some silica is dissolved by the sodium hydroxide during the solution of the ''altered chromite'', thus accounting for the small apparent excess of attack. In no case was the excess attack great enough to indicate significant regeneration of sulphuric acid by hydrolysis.

Figure 2 shows a relationship between the amount of unattacked chromite and the sulphuric acid concentration, most effective attack occurring in the region of equal volume of sulphuric acid and water. A diminished rate of attack at lower acid concentration is anticipated in a presumably protonic attack on the chromite lattice; the falling off of the rate at higher concentrations is most readily rationalized on a purely mechanical basis, that is accumulation of insoluble products, because, as shown in Figure 3, the amount of ''altered chromite'' beginsto increase rapidly at sulphuric acid concentrations greater than 1:1. A decrease in the proton concentration at higher concentrations of sulphuric acid would also lead to a slower rate of attack. Wylie[4], in his investigation found that, for optimum conditions for chromite attack by sulphuric acid at 150°C, the amount of acid used should be at least 300% of equivalence and the acid concentration 75% by weight. Higher acid concentrations and smaller amounts (lower limit was not

Figure 2

Degree of attack of chromite as a function of acid concentration.

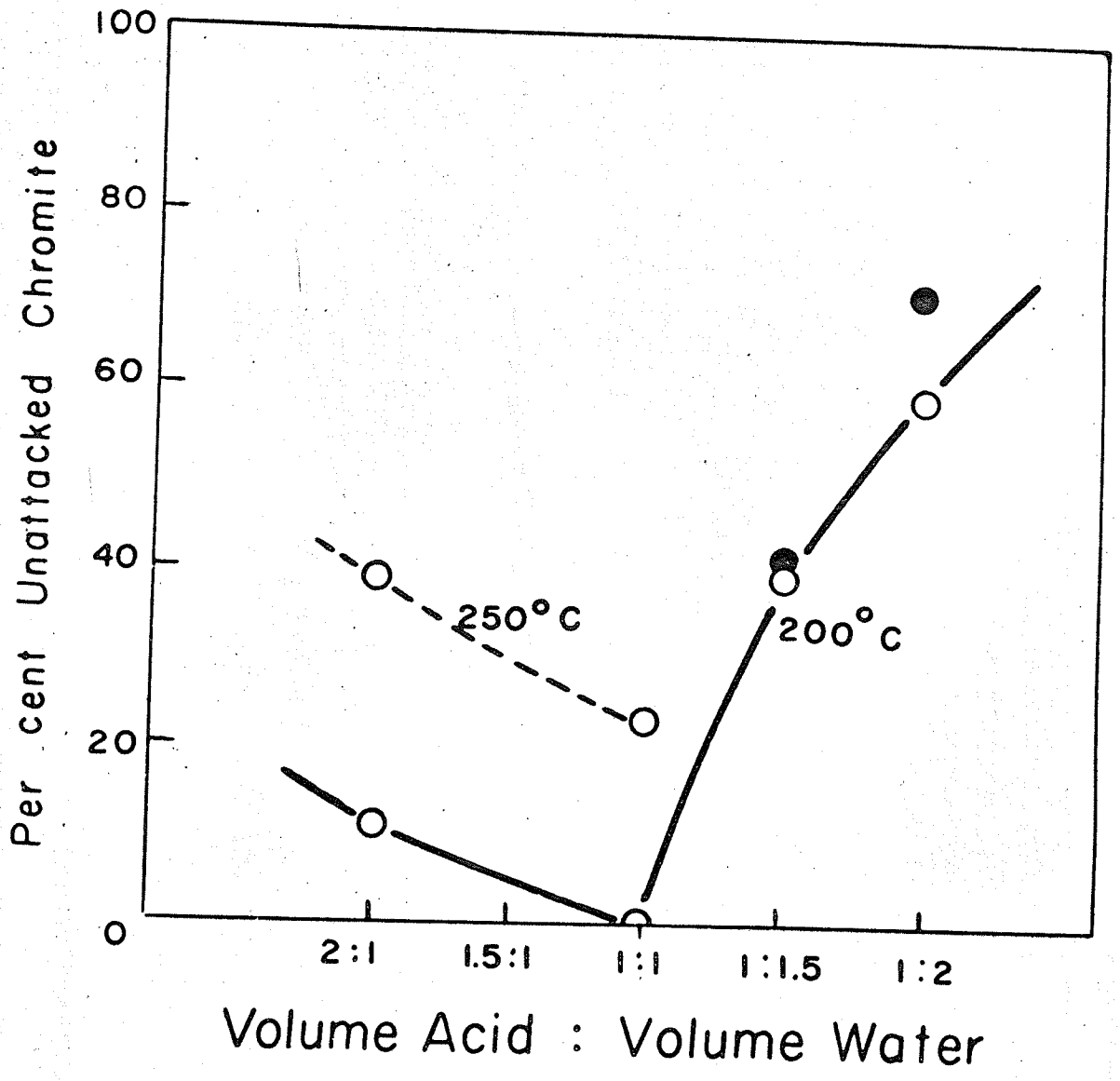
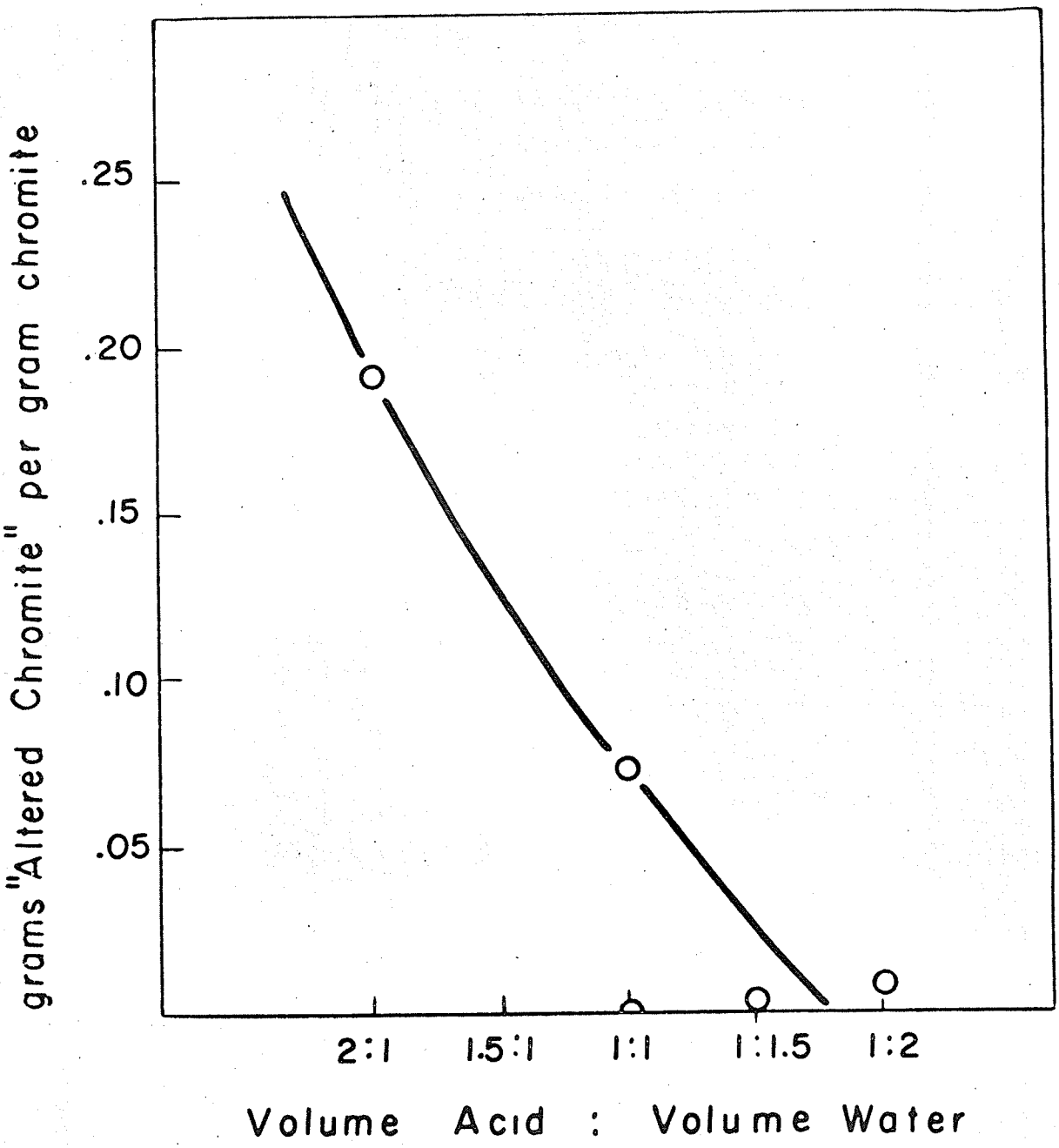

100
80
60
40
20
0
Per cent Unattacked Chromite
250° C
200° C
2:1
1.5:1
1:1
1:1.5
1:2
Volume Acid : Volume Water

Figure 3

Formation of ''altered chromite'' as a function of acid concentration.


grams "Altered Chromite" per gram chromite
.25
.20
.15
.10
.05
2:1
1.5:1
1:1
1:1.5
1:2
Volume Acid : Volume Water

given) of acid both brought about an increase in the amount of insoluble material which, presumably, is the same material designated here as ''altered chromite''. This decrease in the rate due to the formation of ''altered chromite'' is very evident in runs numbers 1 and 2. The slower rate of attack in 2 must be due to the formation of the ''altered chromite'' at an earlier stage than its formation in number 1. Two effects are responsible for this; first, the acid concentration, and second, the chromium (III) concentration are both higher in number 2 than in number 1 for a given degree of attack; the ''altered chromite'' will form at an earlier stage in the former thus decreasing the rate of attack on the chromite.

The dotted portion of Figure 2 shows that the rate of attack at higher acid concentrations drops as the temperature is increased to 250°C. Comparing runs numbers 1, 2, 3, and 4 in Table 1 shows how this increase in temperature simultaneously brings about a marked increase in the amount of ''altered chromite'' which is thought to coat the unattacked chromite thus preventing further attack by sulphuric acid.

Generally the weight of ''altered chromite'' increases as the temperature of the digestion increases and as the acid concentration increases. Figure 3 shows how the weight of ''altered chromite'' increases with an increase in acid

Table I

Products formed on sulphuric acid digestion of chromite

Run No.+	Conc. H_2SO_4:H_2O, ml/ml	% equivalence	Temp., °C	Time, hours	Unattacked chromite, g/g*	"Altered chromite", g/g*
1w	1:1	200	250	24	.256	1.76
2w	2:1	200	250	24	.386	1.06
3w	2:1	200	210	21	.105	.193
4w	1:1	200	210	21	.009	.057
5w	1:1.5	200	210	21	.380	.004
6w	1:2	200	210	21	.588	.013
7w	1:1.5	200	200	7.5	.406	.000
8w	1:2	200	200	7.5	.708	.000
9	1:1	100	250	24	.258	
10a	1:2	100	250	19	.362	.228
11w	1:2	100	250	19	.362	.310
12a	2:1	52.5	250	7.5	.477	.320
13w	2:1	52.5	250	7.5	.499	.158
14a	1.5:1	53.1	250	7	.484	.339
15w	1.5:1	53.1	250	7	.508	.189
16a	1:1	53.1	250	6	.424	.454
17w	1:1	53.1	250	6	.433	.458
18a	1:1	53.1	250	7	.424	.522
19a	1:1.5	40.6	250	7.5	.600	.324
20w	1:1.5	40.6	250	7.5	.619	.211
21a	1:1.5	52.5	250	19.5	.452	.419

* The weights of products are grams per gram of chromite in the digestion charge.

+ The symbol (w) after the number means that soluble products were removed with hot water, the symbol (a) means that dilute sulphuric acid was used.

concentration. The general increase in the weight of "altered chromite" is not evident in the runs employing 50% equivalence of acid. This is attributed to variations in the washing conditions and to the favoured formation of the hydrogen salts at high acid concentrations as in the digestions employing 200% equivalents.

The insoluble material which has been designated as

''altered chromite'' is formed whenever the acid concentration is high enough to give a reasonable rate of attack on chromite. This, presumably, is the same material that the Mines Branch workers consider to be hydrolysis products of the trivalent ions but which assumption is not consistent with their observation, substantiated in this work as well as that of Wylie[4], that the amount of this material increases with sulphuric acid concentration. The physical (finely divided, non-gelatinous grey green) and chemical (acid insoluble and altered by sodium hydroxide) properties are also suggestive that an alternate explanation is required. This was further demonstrated by digesting chromite concentrate with a solution of chromium (III) sulphate (1 gram of water per gram of the decahydrate) at 250°C, which digestion produced no acid insoluble precipitate other than the original chromite concentrate. Chemical analysis of two representative samples of the ''altered chromite'' are presented in Table 2, and the cation:anion ratio seems to indicate conclusively that hydrolysis cannot be a significant factor in the formation of the insoluble material. Complete analysis of the products was not generally made, partial analysis of the products showing that the results were quite constant within a given region of acid excess. The slight excess of cation over sulphate was typical of the runs using 50% equivalence of acid. This is ascribed to the hydrolysis

of the products during the manipulations subsequent to digestion, during the extraction of the soluble products the precipitate tended to develop a gelatinous nature, suggestive of an hydroxylation process. This behaviour was noticed as well for some sulphato complexes whose preparation and properties will subsequently be discussed.

Table II

Analysis of typical ''altered chromites''

From digestion No.	% Cr	Fe	Al	Mg	SO_4	Ratio equivalents, cations:anion
18a	7.25	9.56	4.39	1.82	60.0	1.12
2	10.37	6.43	2.42	1.55	68.2	.88

* Same as in Table I, page 29

The available facts are better explained on the postulate that the ''altered chromite'' is a mixture of the hydrogen, aluminum, magnesium, and iron (II) salts of sulphatopolychromate (III) anions. Recoura's work[10], in general confirmed by Whitney[11], substantiates the probability of this explanation, since he reports the preparation of a series of ''chromium polysulphuric acids'' under conditions rather similar to the digestion conditions, and observed that most of their salts were insoluble, and closely resembled the ''altered chromite'' in appearance. The work, published subsequently to ours, of Redfern and Salmon[41, 42, 43, 44], substantiates this assumption as well since they find analagous behaviour in the two systems, P_2O_5-Cr_2O_3-H_2O, and

As_2O_5-Cr_2O_3-H_2O. The formation and composition of such complexes will be a function of ligand concentration, central ion concentration[21] and of the relative concentrations of protons and other metals which can function as cations. This is completely consistent with the observation that high sulphate concentrations favour formation of the insoluble products, that the percentage of sulphate in these compounds is observed to increase when excess sulphuric acid is used, and that the removal of iron and chromium (III) is lowest with concentrated sulphuric acid, which is also the most favourable condition for the formation of these complexes.

To further strengthen this explanation, typical compounds of the type postulated were prepared under similar conditions. By digesting chromium (III) sulphate with sulphuric acid under various digestion conditions, as will be described subsequently, insoluble products, whose physical and chemical properties corresponded to those of the ''altered chromite'', separated. Since the residue produced in these digestions always contained anion equivalents in excess to those of chromium (III), they were assumed to be hydrogen salts. The hydrogen ions may be replaced by metal ions so that the metal cation and anion equivalents are identical in the metal salts of these sulphatopolychromate (III) anions.

B) DISCUSSION OF RESULTS

The hydrolysis mechanism proposed by Downes and Morgan[2]

for the attack of chromite by sulphuric acid would seem to profit by modification to the following scheme. The initial attack is a protonic attack of the chromite lattice, bringing the metallic constituents into solution in the same ratio as they occur in the lattice. Precipitation occurs in a second step. Sulphate complexes of chromium (III) are formed and under conditions of sufficiently high concentrations of chromium (III) and sulphate ions, these will include various anionic polynuclear species whose hydrogen and other salts are insoluble. High acid concentrations and high temperatures favour the formation of these salts. Attack of the chromite may become very slow after accumulation of these insoluble salts, hence, the failure to complete the decomposition of the chromite in a reasonable time when excess acid is used or when high temperatures are employed.

The more obvious weaknesses of the hydrolysis theory are: first, the precipitated iron is almost completely in the form of iron (II) which is not easily hydrolyzable; second, precipitation takes place when large amounts of unused acid are present; and, third, hydrolysis cannot account for the fact that the percentage of insoluble material increases as the concentration of the sulphuric acid increases.

In order to learn more about the second step in the proposed mechanism an investigation of the insoluble products formed during the digestion of chromium (III) sulphate with sulphuric acid was undertaken.

EXPERIMENTAL RESULTS

COMPLEXES OF CHROMIUM (III) SULPHATE

A) SULPHATO COMPLEXES

COMPLEXES OF CHROMIUM (III) SULPHATE

A) SULPHATO COMPLEXES

1) INTRODUCTION

Recoura[10] reports the preparation of a series of ''chromipolysulphuric acids'', $Cr_2(SO_4)_3$ n H_2SO_4 y H_2O, by evaporating to dryness mixtures of hydrated chromium (III) sulphate with sulphuric acid on a water bath. The value of n (up to a value of 6) is determined by the molar ratio of the hydrated chromium (III) sulphate and sulphuric acid used in the preparation, whereas the value of y is primarily determined by the length of time these mixtures are heated. Heating any of these acids for a long period of time at 150°C, converts the acid to what he termed the ''isomeric form of chromitetrasulphuric acid'' [$Cr_2(SO_4)_3$ H_2SO_4] which is insoluble in water. Whitney[11] suggests that the product that is formed whenever the molar ratio of sulphuric acid to chromium (III) sulphate is greater than three, is the product that Recoura designated as the ''isomeric form''. His experimental data on the conductance and freezing points of solutions of this salt, led him to conclude that this substance has a very high molecular weight and could, therefore, be called a colloid. He again substantiates Recoura's results in that addition of metallic salts such as $Hg(NO_3)_2$ or Cu Cl_2 to the solutions of these acids causes precipitation of the mercuric or cupric salt

of the ''chromitetrasulphuric acid''. Wyrouboff[12] considered all of these acids simply as mixtures of sulphuric acid and the ''chromitetrasulphuric acid''.

The acid sulphate $Cr_2(SO_4)_3\ H_2SO_4\ n\ H_2O$ is reported[12] to exist in two forms, the violet form, prepared from cold solutions of hydrated chromium (III) sulphate and sulphuric acid, and the green form prepared in vacuum. The green form contains coordinated sulphate groups whereas the violet form does not. Mather and Wylie[5] consider the chromium (III) sulphate to be in solid solution with compounds such as $Fe_2(SO_4)_3\ H_2SO_4\ 2\ H_2O$ and $Al_2(SO_4)_3\ H_2SO_4\ 15\text{-}17\ H_2O$ and $Al_2(SO_4)_3\ 16\ H_2O$. These solids were obtained by diluting three fold with water the digestion mixture of chromite and sulphuric acid (170°C) and allowing the solids and solution to equilibrate for a period of 2 to 4 weeks. The above solid phases may, therefore, not be identical to the solid phases produced at 170°C.

The chromic dihydroheptasulphate, $2\ Cr_2(SO_4)_3\ H_2SO_4$, has been prepared[12] by heating hydrated chromic oxide with concentrated sulphuric acid. If a large excess of acid is used the chromic oxide dissolves and then precipitates as a grey powder which is insoluble in water and is attacked with great difficulty by alkali. Some controversy exists about whether this material is the chromic dihydroheptasulphate or anhydrous chromium (III) sulphate.[12a]

Fogel et al[22] report the existence of two complexes, an inner inert complex $[Cr(H_2O)_2\ SO_4]^+$ and an outer sphere complex, or ion pair $(Cr(H_2O)_6^{+3},\ SO_4^{=})$ in dilute sulphuric acid solutions. The formation of an inert inner complex is postulated $[Cr(H_2O)_y(SO_4)_2]^-$ in more concentrated sulphuric acid solutions. Using ion exchange columns, they managed to separate the latter into its cis and trans isomers. Their studies were limited to temperatures below 85°C, and show that the mononuclear complex $H[Cr(H_2O)_y(SO_4)_2]$ is a soluble species and would, therefore, support Whitney's[11] conclusion that the isomeric form of ''chromipolysulphuric acid'' is in fact a polymer.

More recently, Lukaszeweski and Redfern[45] have studied the solid phases in equilibrium with solution in the systems Cr_2O_3-P_2O_5-H_2O and Cr_2O_3-As_2O_5-H_2O and observed that, in the presence of excess acid, amorphous solids with a variable ratio of $Cr:XO_4$ are formed. The temperatures employed by them in their phase study were limited to 0° and 70°C.[41,42,43,44] Their conclusion is that polymeric chains of $[H_2XO_4\text{-}Cr\text{-}\Big|H\ XO_4\text{-}Cr\Big|_n\text{-}H\ XO_4\text{-}Cr\ H_2XO_4]^+$ may be formed where X may be P or As. They suggest that similar behaviour will be observed for the Cr_2O_3-SO_3-H_2O system.

2) PREPARATION OF HYDROGEN AND ALUMINUM SALTS OF SULPHATOPOLYCHROMATE (III) ANIONS

Preparation of the hydrogen salts of sulphatopolychromate (III) anions was achieved by digesting chromium (III) sulphate with various concentrations of sulphuric acid, at different temperatures in either closed or open vessels. These preparations may conveniently be described as three distinct modes of preparation. The first method consists of digesting, in sealed tubes at temperatures between 200 and 250°C, chromium (III) sulphate with sulphuric acid whose concentration is greater than 11 molar. These digestions were maintained at the desired temperature for a day to ensure that equilibrium had been obtained. Precipitation of the product, however, usually occurred within the first few hours. After digestion, the precipitates were filtered and washed with cold water. To determine the lowest temperature required to precipitate this salt, a saturated solution of chromium (III) sulphate in 9.6 molar sulphuric acid (a volume ratio of water to sulphuric acid near 1) was digested in a vessel equipped with a condenser, at 135°C. Precipitation did not occur in the course of several weeks and, therefore, the solution temperature was increased daily in small steps. Formation of an insoluble product designated as R occurred at 180°C.

The second mode of preparation employs Recoura's "chromipolysulphuric acids" as starting material. The preparation of the latter consists of digesting chromium (III)

sulphate with relatively dilute (4 molar) sulphuric acid, in molar ratios of 1 to 1, up to 1 to 6, on a water bath until only a gummy glassy substance is left in the vessel. These materials were still moist when removed from the water bath and, therefore, they were placed in an air thermostat at 120°C in order to complete the drying process. It was noticed the ''chromipolysulphuric acids'' with n values of 6 and 5 crystallized in the course of several days of heating and the other members of this series, except for the first, crystallized upon further heating. It was noticed that the acids with higher n values crystallized more readily than the lower members of the series. The physical appearance of these crystallized products suggested that they were mixtures containing free sulphuric acid. These were, therefore, allowed to stay in the thermostat at 120°C for an extended period of time in the hope that all of the free sulphuric acid and absorbed water would volatilize. Higher temperatures were not employed in the drying process in order to prevent converting these acids to the product described by Recoura as the ''isomeric form of chromitetrasulphuric acid'' which according to Recoura is formed when these acids are heated to 150°C. These baked products which were less hygroscopic and less soluble than the starting materials belong to the second method of preparation. These products were not washed with water because of their solubility and

particularly for fear of alteration of the product due to hydroxylation.

The third method consists of digesting chromium (III) sulphate with a large excess of 9.6 molar sulphuric acid solution in an open vessel. The green decahydrate of chromium (III) sulphate was dissolved in acid then digested on a hot plate at a maximum temperature of 135°C. After precipitation appeared complete the solution was decanted and the precipitate washed with 9.6 molar sulphuric acid. After each washing a considerable length of time is required to allow the fine grey green precipitate to settle. After filtration the precipitate was kept at 135°C until no visible fumes of SO_3 were released.

The aluminum salts of the sulphatopolychromate (III) anions, were prepared by two different methods. The first method is identical to the first method described for the preparation of the hydrogen salt except that various concentrations of aluminum (III) sulphate were added prior to the digestion. The second method for the aluminum salt is identical to the third method described for the preparation of the hydrogen salt except that equal concentrations of aluminum (III) and chromium (III) sulphates were used in the digestion.

3) PHYSICAL AND CHEMICAL PROPERTIES

Generally, these products were not washed with hot water for fear of alterations occurring during this process. In attempts to wash these products with cold water, it was always noticed that the fine particles would not settle, rather, they formed what could be termed a colloidal dispersion or sol, this being identical to the behaviour observed for the ''altered chromite''. Heating caused flocculation to occur at a temperature just below the boiling point of water. This insoluble flocculent substance appeared very similar to precipitated aluminum hydroxide. There was no colour associated with the solution at this stage, but prolonged boiling caused the appearance of a pale green colour which was slowly intensified.

Table 3 shows the sulphate to chromium ratios for the products which have been obtained under various conditions of digestion, and pertinent data from chemical analysis and pyrolysis of these products, employing the thermobalance described in the appendix. The products are identified by the particular method and temperature of preparation, method of preparation number 1 refers to the first method, outlined previously, for the preparation of the hydrogen salts of the sulphatopolychromate (III) anions, these being the insoluble products obtained from solution as a result of digesting chromium (III) sulphate with sulphuric acid in sealed tubes.

Table 3

Pyrolysis Data for Hydrogen Salts of Sulphatopolychromate (III) Anions

Product	Method and temperature of preparation	Chromium to Sulphate ratio	Weight loss ratio of SO_3 to oxide residue	Weight loss ratio of SO_3 to sulphuric acid	Temperature interval for loss of sulphuric acid	Temperature of decomposition to Cr_2O_3 and SO_3	Mechanism
R	180	2.05	1.59 ± 0.05	2.42 ± 0.05	320-405°C	510°C	1
P	2-125	2.11-2.16	1.58	2.38	325-450	505	1
O	1-250	✱2.18	1.79	2.67	335-445	580	2
Z	1-250	✱2.25	1.80	2.42	330-460	590	2
U	1-250		1.77	2.41	330-440	590	2
Q	3-135	1.97-2.07	1.65	3.08	320-425	550	
T	3-330	1.79	1.75	10.9	355-440	585	3
S			1.72	9.70	340-440	585	3
W	3-135		1.58			585	
Y	altered chromite				300-450	530	
AA			1.65	slow loss from 470-545°C (4.40%)		545	

Heating rates employed are 230°C/hour

✱ These values obtained from the thermogram

The designation R refers to the product, thoroughly washed with hot water, obtained from the digestion at 180°C as previously described; this was the lowest temperature at which an insoluble product could be obtained from an initial 9.8 molar sulphuric acid solution. Chemical analysis of this product shows 18.5% chromium, 70.18% sulphate and the difference 10.9% water, giving a sulphate to chromium ratio of 2.05.

Baking at 125°C causes crystallization to occur for Recoura's ''chromipolysulphuric acids'' except for the ''chromimonosulphuric acid'' which bakes into a hard glass. The products obtained in this manner presumably contain excess acid (this excess depends upon the length of time baking is continued), which was not removed by washing for fear of producing alterations in the product. The product P is representative of the baked products described for the second method of preparation on page 38. Product P was prepared using a molar ratio of chromium (III) sulphate to sulphuric acid of 3 and is typical of a mixture which makes it very difficult to obtain a consistent set of analytical results. The product is hygroscopic and the slight excess of acid makes it sticky. The sample could, therefore, not be ground and stirring was not sufficient to produce a mixture. Chemical analysis of P gives a chromium content between 18.02 and 17.85% and sulphate between 70.23 and

71.32%, or a sulphate to chromium ratio between 2.11 and 2.16. Analysis of the weight losses in the thermogram of P and the residue weight show that this ratio should be 2.17 based on the assumption that all water is lost below 180°C. The 2% loss in weight between 470 and 495°C may, however, be due to loss of water; calculation of the chromium to sulphate ratio assigning this latter loss to water yields a ratio of 2.09.

The products O, Z, and U were all thoroughly washed with cold water; this was possible because the total amount of insoluble product obtained was small enough to enable filtration of the suspension. These products, stored in ordinary bottles in the laboratory after drying at 70°C, were not hygroscopic provided they had been washed properly. The small amount of material available made it inconvenient to determine the chemical composition by chemical analysis, which is, therefore, determined from the pyrolysis data. This approach is justified because there are no losses due to water in the temperature interval between complete loss of sulphuric acid and the decomposition to chromic oxide.

The product Q, prepared by the third method, was not washed with water and, therefore, the same difficulties in chemical analysis were encountered as in P. In addition, it was noticed that hot alkali and hydrogen peroxide would not completely oxidize the product; in order to get complete

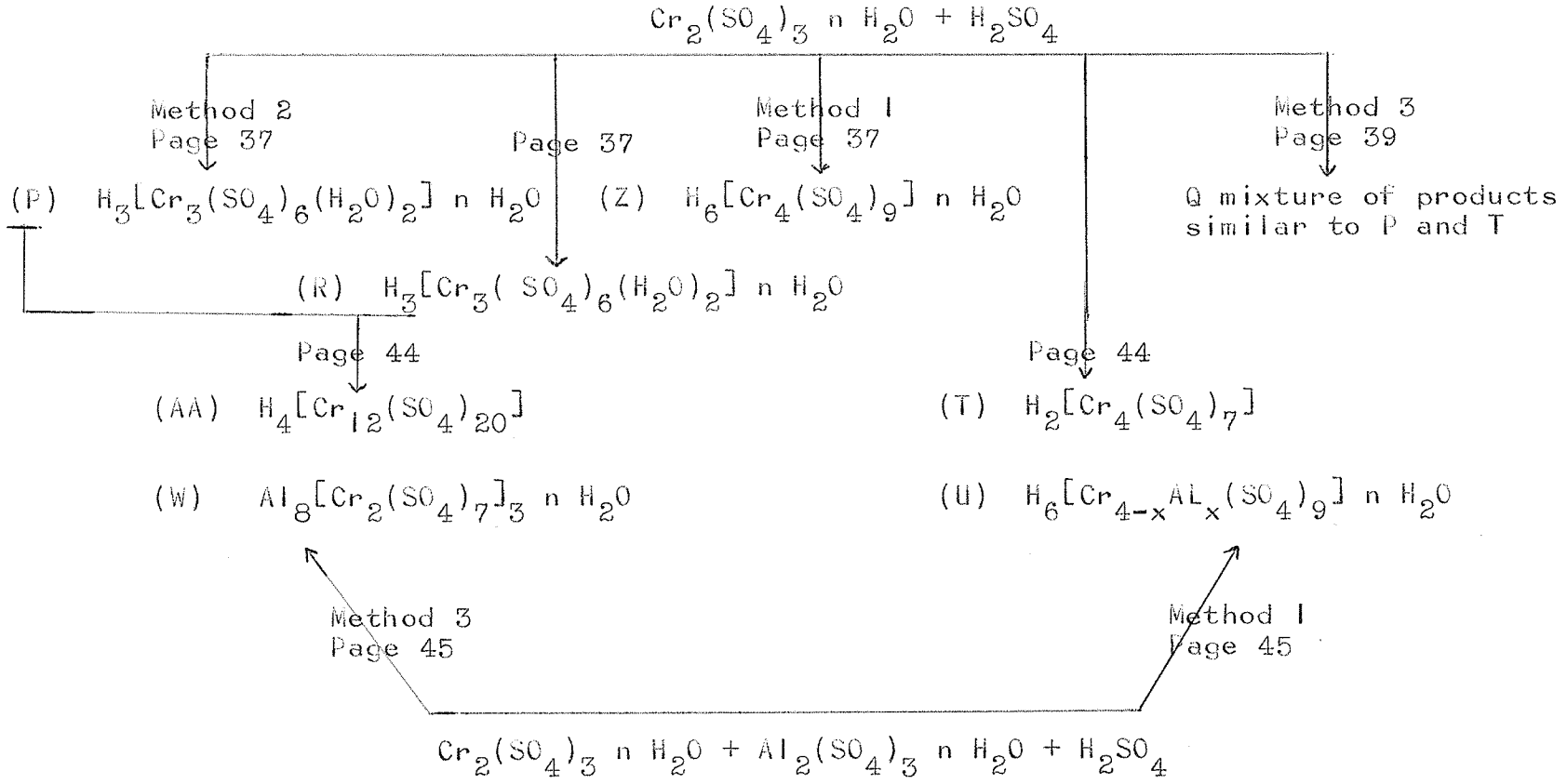
solution a small residue had to be subjected to a sodium carbonate fusion. Washing the product Q with large amounts of hot water left a residue S, whose infrared absorption spectrum (Figure 25) and thermogram were very similar to those of product T. Treating this product Q with hot sodium hydroxide solution, followed by solution of all acid soluble material leaves a residue AB whose infrared absorption spectrum is identical to that of T.

Product T was obtained by digesting chromium (III) sulphate with a large excess of sulphuric acid at the boiling point of the solution, 330°C, for several days, followed by thorough washing to remove all of the excess acid. Solution of this product was achieved only after it had been subjected to a sodium carbonate fusion. Chemical analysis of the product, 34.2% chromic oxide and 77.6% sulphate, corresponded closely in properties and analysis to the compound $H_2[Cr_4(SO_4)_7]$ (theoretical values 34.47 and 76.19) which was designated by Siewart[12a] as ''chromidihydroheptasulphate''.

Attempts to produce the anhydrous chromium (III) sulphate by heating insoluble products such as R and P in a muffle furnace at 400 to 450°C for 36 hours met with no success but produced the product AA whose chemical analysis showed the presence of excess sulphuric acid and a chromium to sulphate ratio of 1 to 1.65. Heating this at 500°C causes a small loss in weight to occur and the simultaneous

TABLE 9

Schematic representation for the formation of various hydrogen and metal salts of sulphatopolychromate (III) anions.



production of chromic oxide.

U was obtained by digesting 0.111 molar aluminum (III) and 0.368 molar chromium (III) sulphate with 14 molar sulphuric acid, in a sealed tube at 250°C. W was the insoluble product obtained by digesting an equimolar mixture of these same salts in excess sulphuric acid at 135°C. Chemical analysis showed a molar ratio of aluminum (III) sulphate to chromium (III) sulphate of 1.33 corresponding to the compound $Al_8[Cr_2(SO_4)_7]_3$ r H_2O. It is interesting to note that the thermogram showed no loss in weight in the temperature interval between 320°C and 450°C indicating that this latter product was definitely not a mixture of aluminum (III) sulphate and any of the insoluble products discussed previously.

Formation of these salts is favoured by high temperatures and high acid concentrations. At 200°C, digestion of 0.62 molar chromium (III) sulphate in 11 molar sulphuric acid produced no insoluble product, whereas the same digestion at 250°C did. Preparation of these insoluble products could be achieved at lower temperatures provided that they were digested in open vessels where concentration of the solution could occur. The products were insoluble in water and in acid solutions but upon exposure to boiling water, a pale green solution resulted. The rate at which solution occurred increased for the products obtained at low

temperatures; prolonged periods of boiling were required for the higher temperature products. The insoluble products with a sulphate to chromium ratio less than 2, obtained either from solution or by baking until fumes of sulphuric acid cease to appear, were completely inert to boiling water and to hot alkali solutions. Sodium hydroxide solutions altered the products with sulphate to chromium ratios of 2 or greater to an acid soluble gelatinous precipitate characteristic of chromium hydroxide. During the alteration process this gelatinous substance coated the original product and inhibited further reaction, therefore, hydrogen peroxide was added to oxidize the chromium (III) to chromium (VI) thus accelerating the alteration process. The appearance of the yellow colour of the chromate ion served as a good indicator in determining the rate of alteration, this rate being extremely slow for the high temperature products and relatively fast for the low temperature products.

Chemical analysis of these insoluble products showed that sulphate to chromium ratios near 2 were formed readily in these digestions, whereas ratios greater than 2 could be obtained only at temperatures near 250°C and high acid concentrations. The gummy, glassy and hygroscopic starting materials used in the second preparation probably have sulphate to chromium ratios greater than 2 and may correspond

to the ''chromipolysulphuric acids'' described by Recoura.[10] These materials were not investigated because they are water soluble and could, therefore, not correspond to the ''altered chromite''. The supposedly ''chromipolysulphuric acids'' crystallized upon heating at 120°C, the rate at which the crystallization process occurred increased for the acid as the value of n increased in the formula $Cr_2(SO_4)_3$ n H_2SO_4. The resulting materials, of which the product P is a typical example showed sulphate to chromium ratio near 2 may be the same compound that Whitney and Recoura call the ''isomeric form'' of ''chromitetrasulphuric acid''. The product R is very similar to the product P in that the sulphate to chromium ratio is near 2 and in that both products contain coordinated water molecules and their infrared absorption spectra are essentially identical. The product P, however, was more readily soluble and altered by sodium hydroxide than was the product R. This suggests that the products P and R are either different species or different polymers of the same species. If the product W is simply an aluminum salt of one of the ''chromipolysulphuric acids'', the conclusion of Recoura (that the metallic salts of these acids are less soluble than the acids) finds verification in this research. In very concentrated acid solutions and high temperatures (330°C), sulphate to chromium ratios less than 2 are preferred.

The properties, (water and acid insoluble, altered by sodium hydroxide, fine grey green), of the insoluble products with sulphate to chromium ratios of 2 or greater are identical to those of the ''altered chromite''. The latter, because of the mode of preparation, is not expected to contain large amounts of the sulphatopolychromate (III) acids, but is expected to contain mainly the salts of these acids because of the presence of large concentrations of other metal ions due to solution of the original chromite lattice. It was pointed out that the digestion of chromite, employing excess equivalents of sulphuric acid, produced an insoluble material containing an excess of anion equivalents to that of the cations, this excess generally being small. Thermogram Y on page 63 shows the pyrolysis curve of a sample of ''altered chromite'' containing this excess. The thermogram shows a small weight loss in the temperature interval of 300 to 450°C (this loss is probably due to loss of sulphuric acid resulting from the decomposition of the sulphatopolychromate (III) acids to form either anhydrous chromium (III) sulphate or some other intermediate) followed by decomposition to the oxides starting at 530°C. Figure 26 shows the infrared absorption spectrum for the ''altered chromite''. The large number of bands observed in the spectrum of the ''altered chromite'' compared to that observed in the other salts is not unexpected because the

former is a mixture of many salts.

In order to further characterize these insoluble products, they were subjected to pyrolysis in a thermobalance and to infrared spectral analysis. Since most of these insoluble materials contain water, it was deemed desirable to determine the temperature at which this water was lost. It is usually assumed that any water which is lost at low temperatures is lost as water of hydration or absorbed or occluded water, whereas, constitutional water or coordinated water is lost at higher temperatures. Thus, a knowledge of the temperatures required to drive off the water should enable us to determine the role that the water molecules play in these complexes. Furthermore, if the sulphate ligands are not all equivalent in the structure, this should again show up in the manner in which the material decomposes. The infrared absorption of the various constituents in these products depends very much upon the manner in which these species are chemically bound one to the other. Thus, an interpretation of the infrared absorption spectra of these insoluble products and the resulting products of pyrolysis should lead to possible structures for these complexes and will be the subject of the next several sections.

4) THERMOGRAVIMETRIC ANALYSIS OF THE HYDROGEN AND ALUMINUM SALTS OF SULPHATOPOLYCHROMATE (III) ANIONS

The pyrolysis data obtained from these products are most readily rationalized on the basis of three different mechanisms* of decomposition. These mechanisms were formulated as hypotheses on the basis of weight losses which occurred in the various steps and a knowledge of the composition of the material. These mechanisms were tested employing infrared spectral analysis as will be discussed subsequently.

All of these products lose weight between 50-120°C upon pyrolysis; this loss in weight is attributed to occluded and adsorbed water. Product number R loses 5.40% of its weight between 50-120°C. There is a further loss of 1.4%, which may be water or sulphuric acid between 210-310°C. Loss of sulphuric acid starts at 320°C and would appear to be complete at 410°C. There is, however, no plateau established in the temperature interval between the complete loss of sulphuric acid and the decomposition of the anhydrous sulphate; instead there exists a very slow loss up to 475°C where a plateau corresponding to the anhydrous sulphate is established, followed very shortly, 525°C, by loss of sulphur trioxide. The weight loss in the temperature interval, 410°C-495°C is 4.21%, corresponding to 2/3 of a mole of water per mole of chromium (III) sulphate; this loss plus

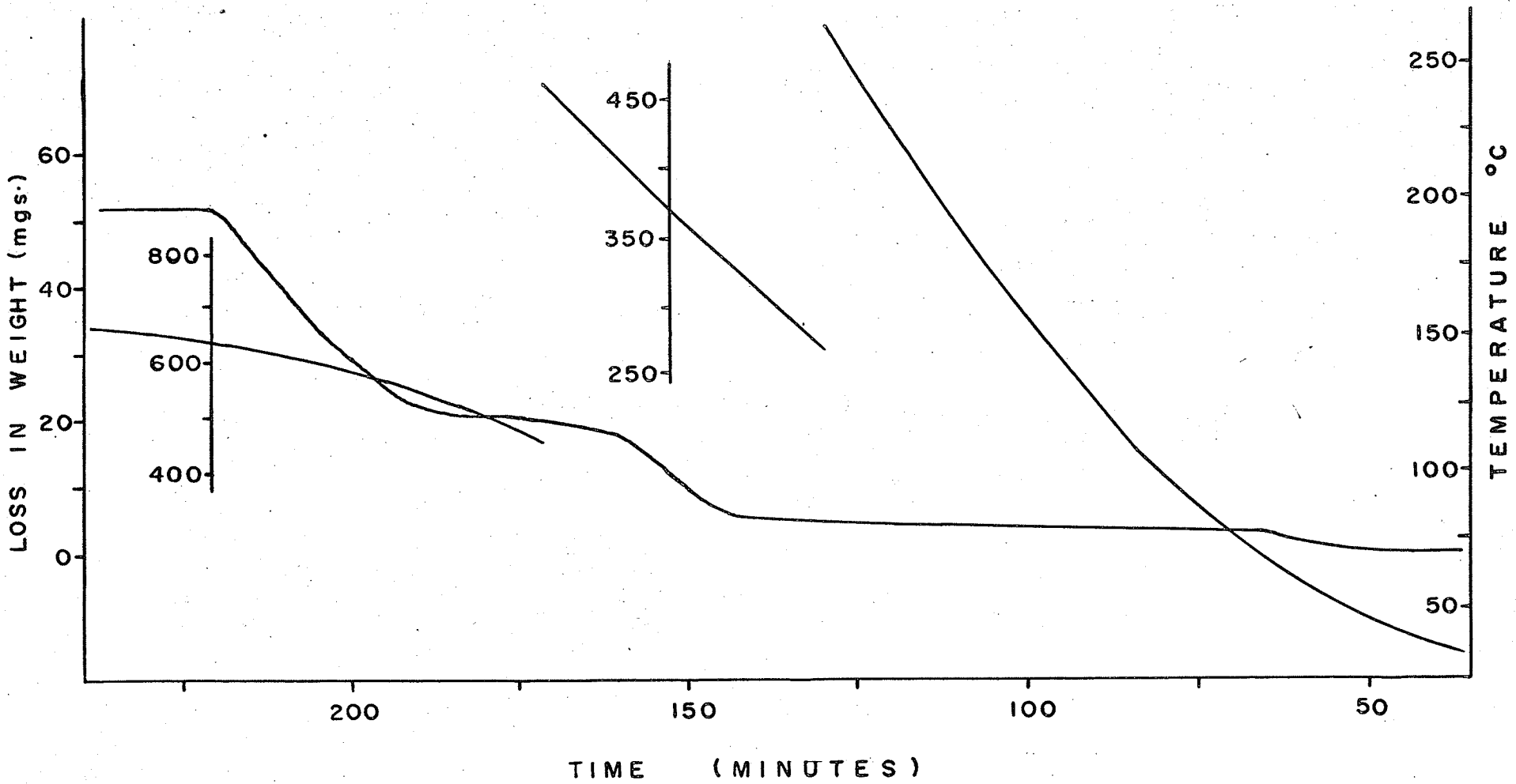
* The term mechanism is used as a synonym to represent a series of steps in the decomposition.

Figure 4

Thermogram for the product R

($H_3[Cr_3(SO_4)_6(H_2O)_2]$ n H_2O)

Sample weight = 78.1 mgs.


LOSS IN WEIGHT (mgs.)
60
40
20
0
800
600
400
450
350
250
250
200
150
100
50
TEMPERATURE °C
200
150
100
50
TIME (MINUTES)

the previous losses of water (total 11.0%) corresponds closely to the total water content of 10.9%. It is reasonable to assume that the assignments of the weight losses to the various constituents is correct, not only because of the close correspondence between the percentage of each constituent as determined from chemical analysis and from thermogravimetric analysis, but also, as will be shown later, because loss of water was not completed before the temperature had reached 470-480°C upon pyrolysis of the hydrates of chromium (III) sulphate. Analysis of the thermogram for product R leads to the following mechanism for decomposition.

1) $H_3[Cr_3(SO_4)_6(H_2O)_2]\ n\ H_2O \rightarrow H_3[Cr_3(SO_4)_6(H_2O)_2] + n\ H_2O$

2) $2\ H_3[Cr_3(SO_4)_6(H_2O)_2] \rightarrow [Cr_6(SO_4)_9(H_2O)_4] + 3\ H_2SO_4$

3) $[Cr_6(SO_4)_9(H_2O)_4] \rightarrow 3\ Cr_2(SO_4)_3 + 4\ H_2O$

4) $3\ Cr_2(SO_4)_3 \rightarrow 3\ Cr_2O_3 + 9\ SO_3$

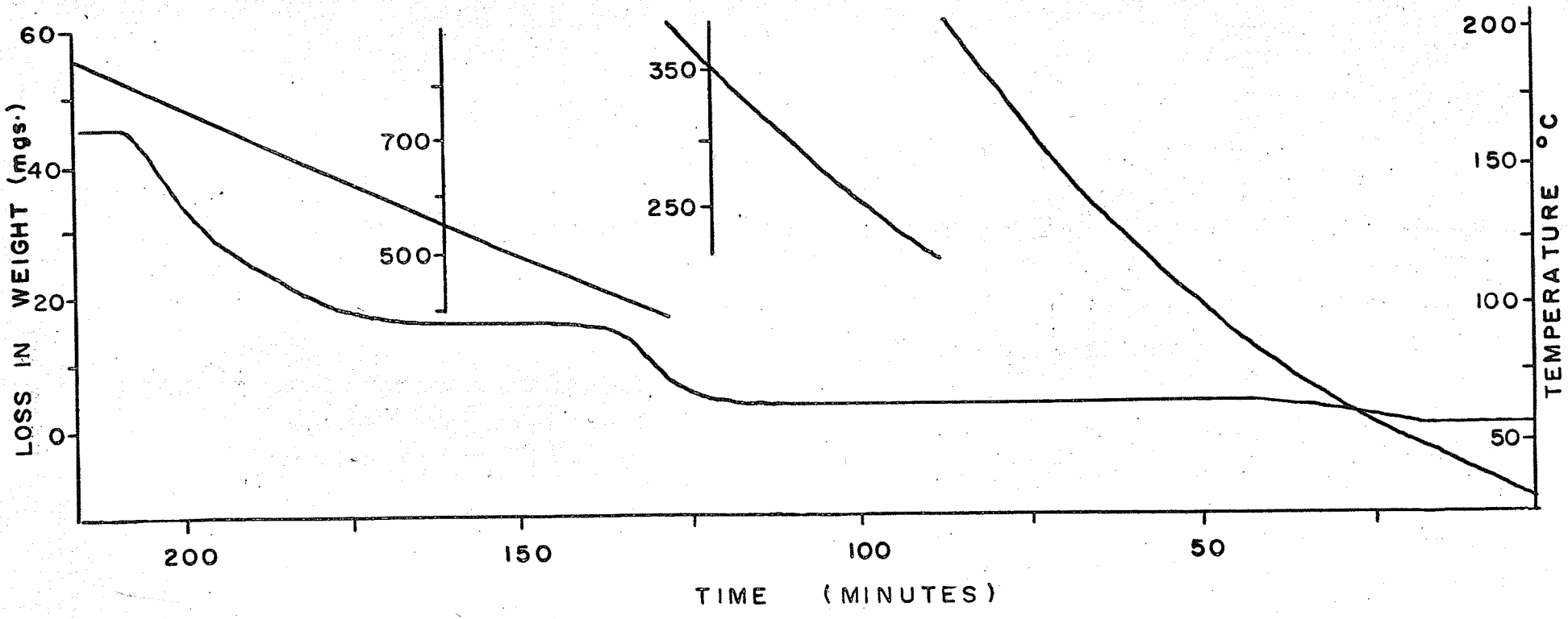
The theoretical weight loss ratio in step 4 to the residue weight of chromic oxide is 1.58 (1.59 for R, 1.58 for P) and 2.45 (2.42 for R, 2.38 for P) for the weight loss ratio of losses in step 4 to losses in step 2. Both products R and P fit the scheme rather well. The low values obtained for the ratio of weight losses of sulphur trioxide to that of sulphuric acid are likely due to the slight excess of

Figure 5

Thermogram for the product Z.

($H_6[Cr_4(SO_4)_9]$ n H_2O)

Sample weight = 61.5 mgs.


60
40
20
0
LOSS IN WEIGHT (mgs.)
700
500
350
250
200
150
100
50
TEMPERATURE °C
200
150
100
50
TIME (MINUTES)

sulphuric acid present in these samples. For product R, this ratio would have a theoretical value of 2.34 on the assumption that the known excess (0.05 moles) of sulphuric acid was all lost in this temperature interval.

The pyrolysis of the insoluble products obtained at 250°C have very neat thermograms, with very clearly defined plateaus. Thus the thermogram for the pyrolysis of Z shows a 6.4% loss in weight starting at 45°C and completed at 80°C followed by a plateau up to a temperature of 330°C. Loss of sulphuric acid starts at 330°C and is complete at 460° C. The thermogram then shows no further loss in weight up to a temperature of 590°C where the final decomposition to the chromium (III) oxide starts.

The products such as Z lose a variable amount of water below 100°C. Analysis of subsequent weight losses suggest the following mechanism.

1) $3\ H_6[Cr_4(SO_4)_9] \rightarrow H_4[Cr_{12}(SO_4)_{20}] + 7\ H_2SO_4$

2) $H_4[Cr_{12}(SO_4)_{20}] \rightarrow 6\ Cr_2O_3 + 2\ H_2SO_4 + 18\ SO_3$

The thermograms for these products show a stable plateau between the loss of sulphuric acid (Figure 5, page 53) and the decomposition to the oxide indicating no loss of water in this region. It should be noted that the average temperature at which the oxide is formed has shifted

to 585°C in the second mechanism from 510°C in the first mechanism. The theoretical weight loss ratios for this mechanism are 1.79 (1.79 for O, 1.80 for Z, 1.77 for U) for the losses in step 2 to the residue weight of oxide and 2.39 (2.76 for O, 2.42 for Z, 2.41 for U) for the ratio of the losses occurring in step 2 to those in step 1.

As mentioned previously, no chemical analysis was obtained for the products Z, O and U. The analysis is based entirely on the thermogravimetric results. It might be argued that step 2 in this mechanism is in fact a combination of steps 3 and 4 in mechanism 1, that is, in the last step both water and sulphur trioxide are lost simultaneously. In order to support this mechanism the product $H_4[Cr_{12}(SO_4)_{20}]$ was prepared and pyrolyzed. The product AA was prepared by heating products such as R and P, moistened with sulphuric acid in a muffle furnace, whose temperature was slowly increased up to a maximum of 400°C, for several days. Chemical analysis of this product (AA) shows a sulphate to chromium ratio of 1.65, comparing favourably with the theoretical value of 1.67 for the compound $H_4[Cr_{12}(SO_4)_{20}]$. The pyrolysis curve for AA (Figure 6) showed that this compound, upon decomposition, yields chromic oxide. Attempts to decompose $H_4[Cr_{12}(SO_4)_{20}]$ to the anhydrous $Cr_2(SO_4)_3$, by heating in a muffle furnace at 450°C met without success. Some decomposition was evident when AA was heated at 500°C for 24 hours

resulting in the formation of the green chromic oxide.

Product C appears to follow a different manner of decomposition. In view of the high value for the ratio of losses in step 2 to that in step 1, it is suggested that for C the first step should be

$$2\ H_8[Cr_6(SO_4)_{13}] \rightarrow H_4[Cr_{12}(SO_4)_{20}] + 6\ H_2SO_4$$

followed by decomposition of $H_4[Cr_{12}(SO_4)_{20}]$ as in mechanism 2.

The theoretical weight loss ratio for this step is 2.78 (2.76). The product, C, cannot be considered as an intermediate between the product R and Z, that is, one in which partial displacement of the water by sulphate groups has occurred. If it were such an intermediate, then the decomposition to the oxide should not proceed through the compound $H_4[Cr_{12}(SO_4)_{20}]$. It is therefore likely, that the product C is a compound different from that of R and Z. Further discussion regarding the validity of this assumption will be given later.

The products T and S with sulphate to chromium ratios less than 2 would seem to decompose by a third mechanism.

1) $2\ H_2Cr_4(SO_4)_7 \rightarrow H_2[Cr_8(SO_4)_{13}] + H_2SO_4$

2) $H_2[Cr_8(SO_4)_{13}] \rightarrow 4\ Cr_2O_3 + H_2SO_4 + 12\ SO_3$

The theoretical weight loss ratios are 1.74 (1.75 for T, 1.72 for S) and 10.79 (10.9 for T, 9.70 for S).

The decomposition of Q does not correspond to any of these three mechanisms, but this correspondence is not expected, for it was shown previously that this product was a mixture. The pyrolysis data and the infrared absorption spectrum are easily rationalized on the assumption that Q is a mixture of $H_2[Cr_2(SO_4)_4]$ and $H_2[Cr_4(SO_4)_7]$.

The two insoluble products U and W, containing aluminum (III) ions, differ in pyrolysis behaviour. The thermogram for U resembles the thermograms such as Z in that it has well defined plateaus and shows no detectable weight loss between 440 and 590°C. The weight losses observed in this thermogram are readily rationalized if one assumes that the aluminum (III) ion isomorphously replaces the chromium (III) ion in the product Z. The weight loss ratio observed for the loss in weight at temperatures above 590°C to the loss in weight in the temperature interval of 330-440°C was 2.41 compared to the value of 2.38 for the mechanism discussed for the decomposition of product Z. The weight loss ratio for the loss above 590°C to the residue weight of oxides was 1.85. This value was recalculated so that it could be compared directly with the values obtained for the hydrogen salts. Chemical analysis of the residue of chromium (III) and aluminum (III) oxide showed 90.61%

Figure 6

Thermogram for the product AA.

($H_4[Cr_{12}(SO_4)_{20}]$)

Sample weight = 93.4 mgs.

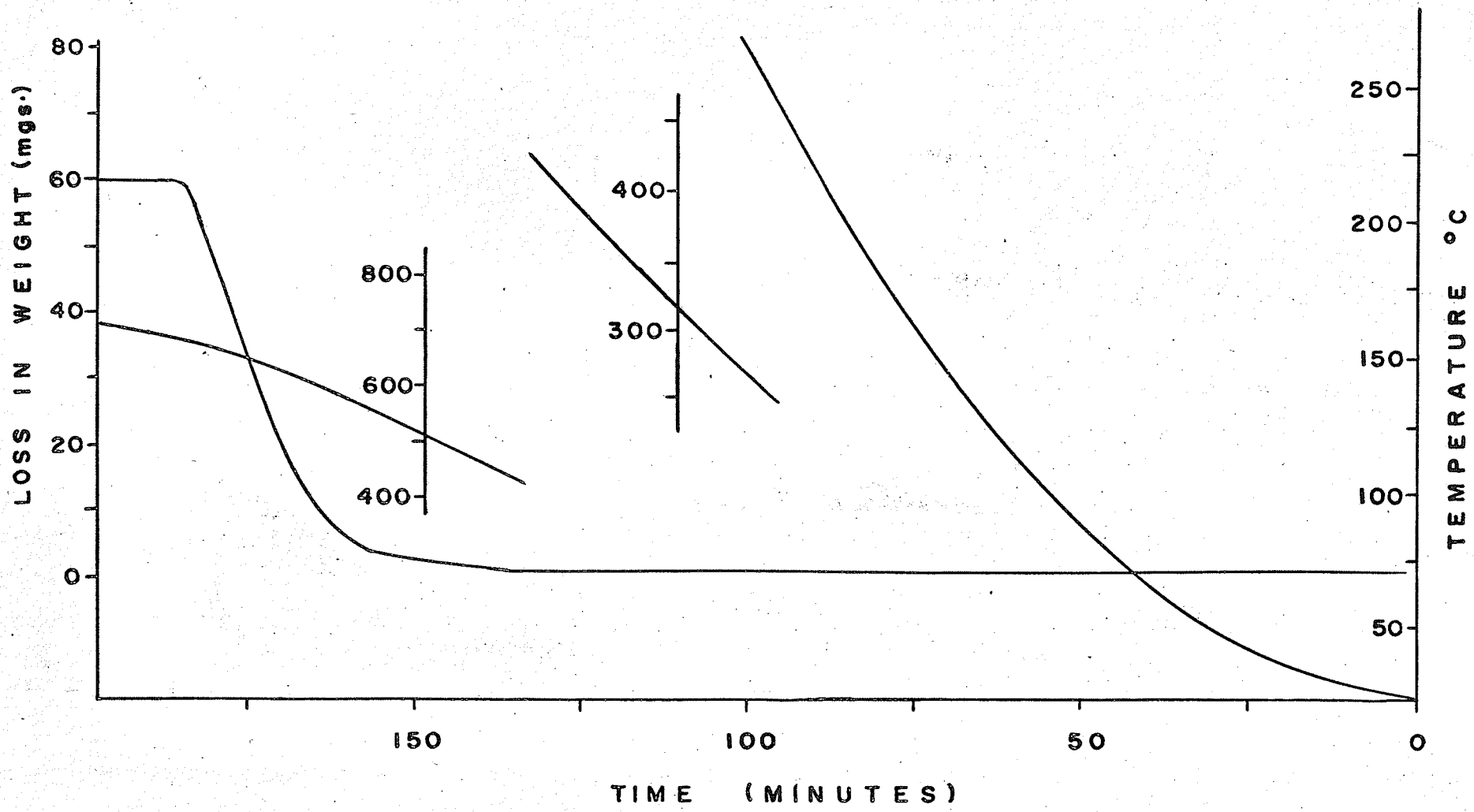
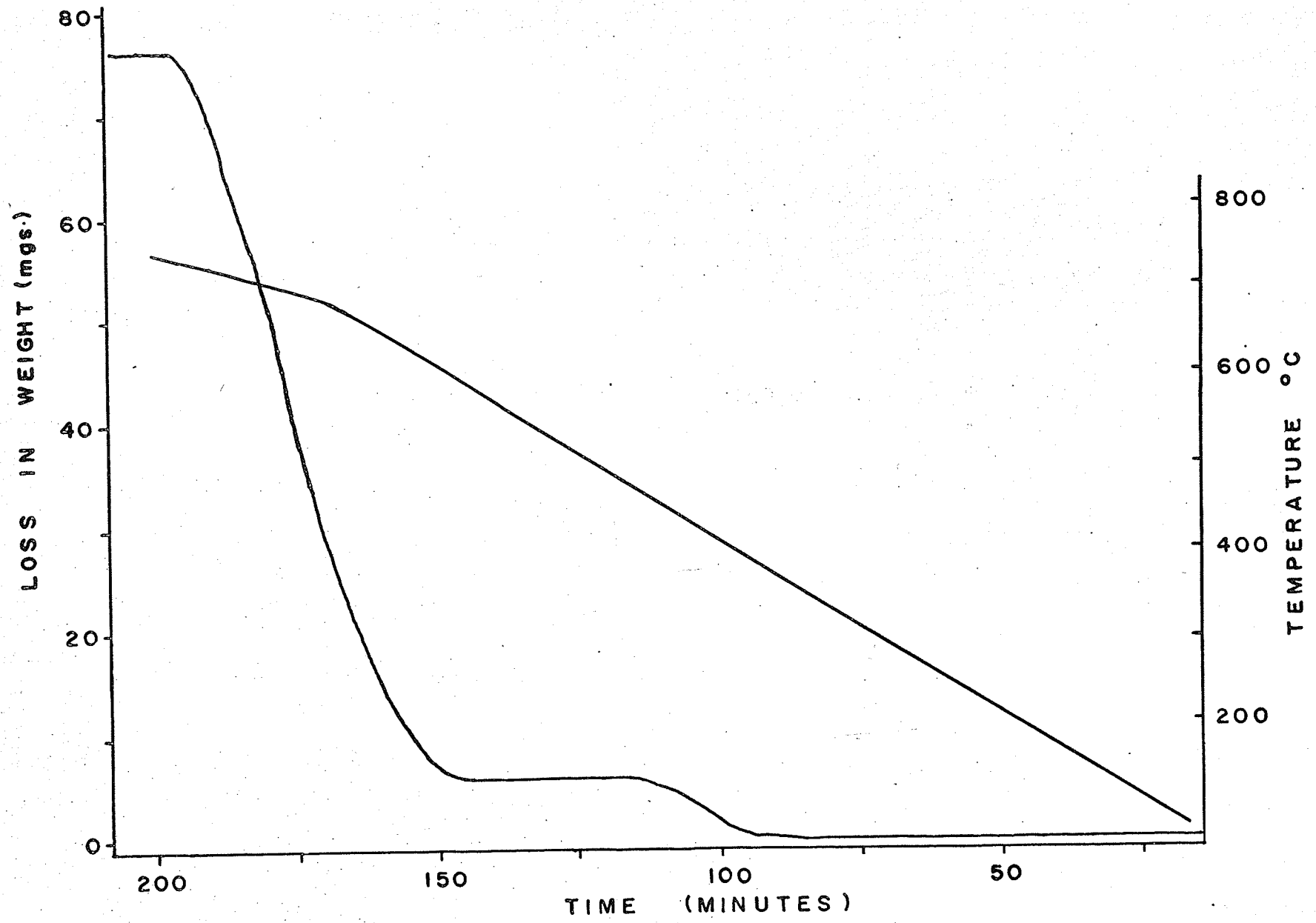

LOSS IN WEIGHT (mgs.)
80
60
40
20
0
800
600
400
400
300
250
200
150
100
50
TEMPERATURE °C
150
100
50
0
TIME (MINUTES)

Figure 7

Thermogram for the product T.

($H_2[Cr_4(SO_4)_7]$)

Sample weight = 116.0 mgs.


80
60
40
20
0
LOSS IN WEIGHT (mgs.)
800
600
400
200
TEMPERATURE °C
200
150
100
50
TIME (MINUTES)

Cr_2O_3 and the difference 9.39% Al_2O_3. 1.000 gram of the mixed oxides is, therefore, equivalent to

$$1.000 \times \frac{90.61}{100} + 1.000 \times \frac{9.39}{100} \times \frac{152}{101.9} = 1.046$$

gram of Cr_2O_3. The residue weight of mixed oxides was converted to an equivalent weight of Cr_2O_3 by multiplying the residue weight by 1.0462. This is equivalent to dividing the ratio of 1.85 by 1.0462 which gives the value of 1.77 given in Table 3. The experimental values of 2.41 and 1.77 compare favourably with the theoretical values of 2.38 and 1.79 and, therefore, suggest that U decomposes by the same mechanism as does the product Z.

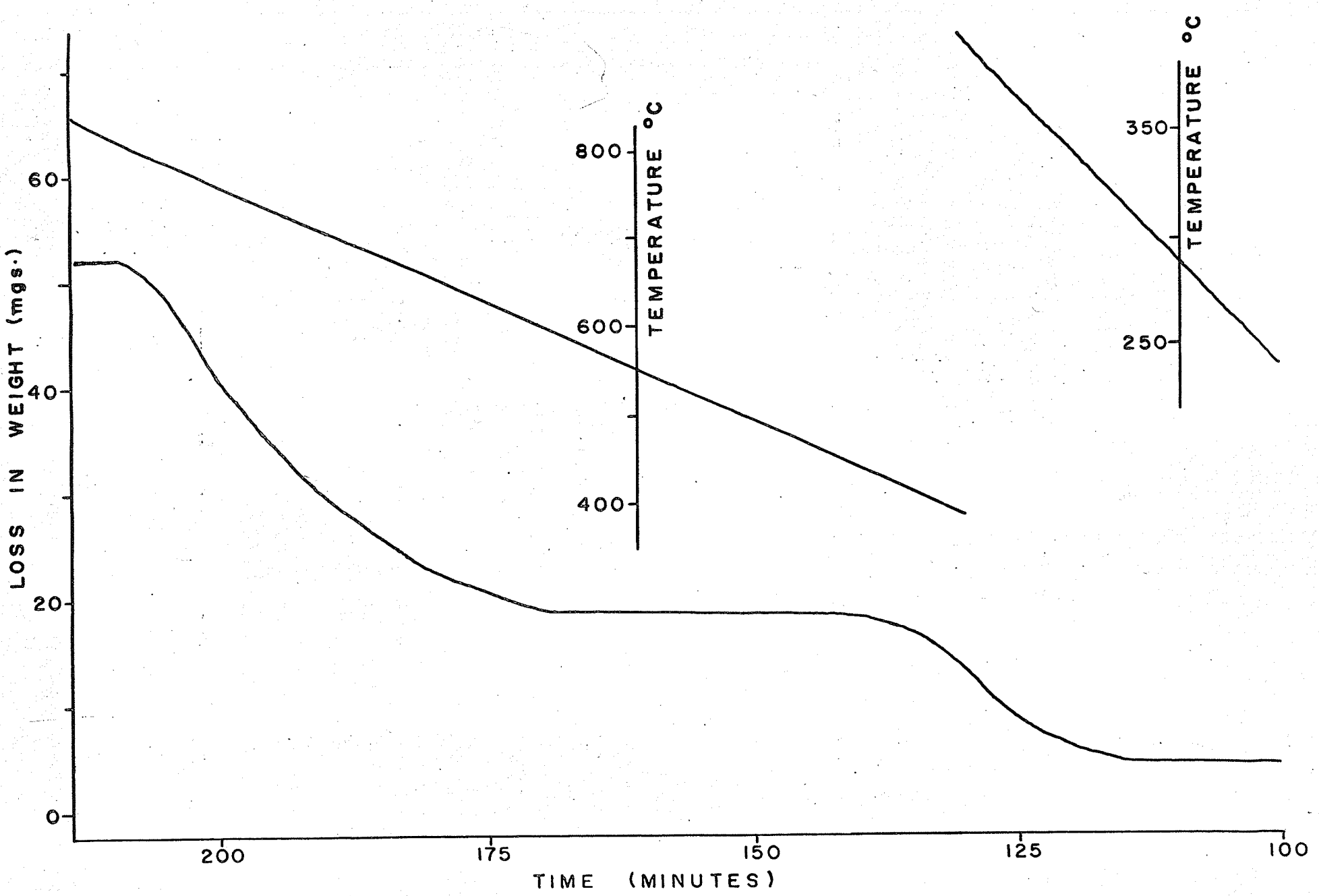
The product W, whose provisional empirical formula may be written as $Al_8[Cr_2(SO_4)_7]_3$ starts to decompose at a temperature of 585°C, and yields the oxides of chromium (III) and aluminum (III), and sulphur trioxide. If the anion $[Cr_2(SO_4)_7]^{-8}$ exists, its decomposition to form the intermediate anhydrous $Cr_2(SO_4)_3$ or the anions $[Cr_{12}(SO_4)_{20}]^{-4}$ or some other anion would not be detected as a weight loss in its thermogram as observed for the products Z and R because this decomposition would be accompanied by the formation of anhydrous aluminum (III) sulphate and not a loss of sulphuric acid as in Z and R. Differential thermal analysis should be helpful in proving the existence of the

Figure 8

Thermogram for the product U.

($H_6[Cr_{4-x}Al_x(SO_4)_9]$ n H_2O)

Sample weight = 69.8 mgs.


LOSS IN WEIGHT (mgs.)
60
40
20
0
800
600
400
TEMPERATURE °C
350
250
TEMPERATURE °C
200
175
150
125
100
TIME (MINUTES)

anion. The data obtained for this product do, however, suggest that this anion exists. Assuming that it does not exist, one must then conclude that the product W is a mixture. The conditions under which it was prepared are the same conditions employed to prepare products such as Q. Therefore, if W is a mixture, the mixture would have to contain hydrogen salts of the sulphatopolychromate (III) anion (not anhydrous chromium (III) sulphate) and either anhydrous aluminum (III) sulphate or some other aluminum salt. The pyrolysis of such a mixture must show a loss of sulphuric acid prior to decomposition to the oxides of the metals, and must show an anion-cation ratio greater than unity. Since there is no loss of sulphuric acid prior to the decomposition to the oxides, and since chemical analysis shows no anion excess to that of metallic cations, one must conclude that the product W is not a mixture containing the product Z. It is, however, possible that the product W is a mixture of anhydrous aluminum (III) sulphate and an aluminum salt of one of the sulphatopolychromate (III) anions. The infrared absorption spectrum for W, however, suggests that this is not the case. The evidence suggests that this is a salt of the ''chromiheptasulphuric acid'' or $Cr_2(SO_4)_3 \ 4 \ H_2SO_4$ which precipitates during the digestion and is consistent with Recoura's observation that the metallic salts of the acids are less soluble than the acids themselves.

Figure 9

Thermogram for the product W.

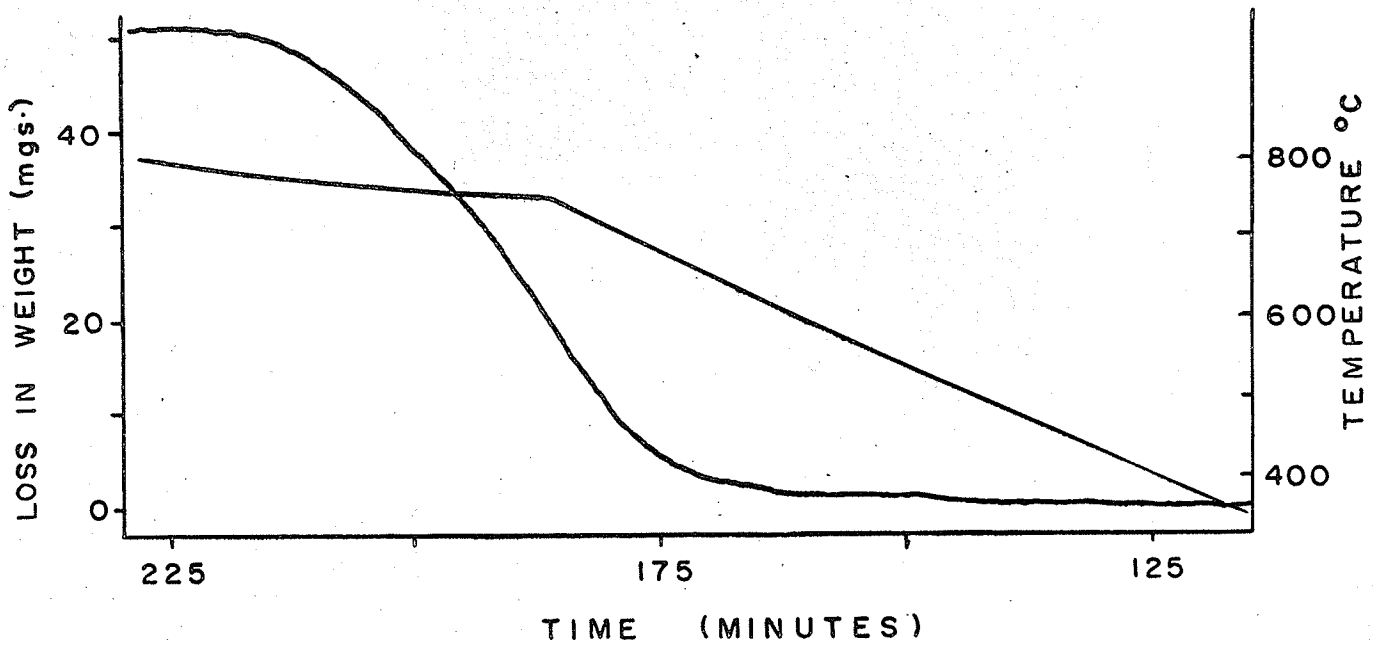
$(Al_8[Cr_2(SO_4)_7]_3 \; r \; H_2O)$

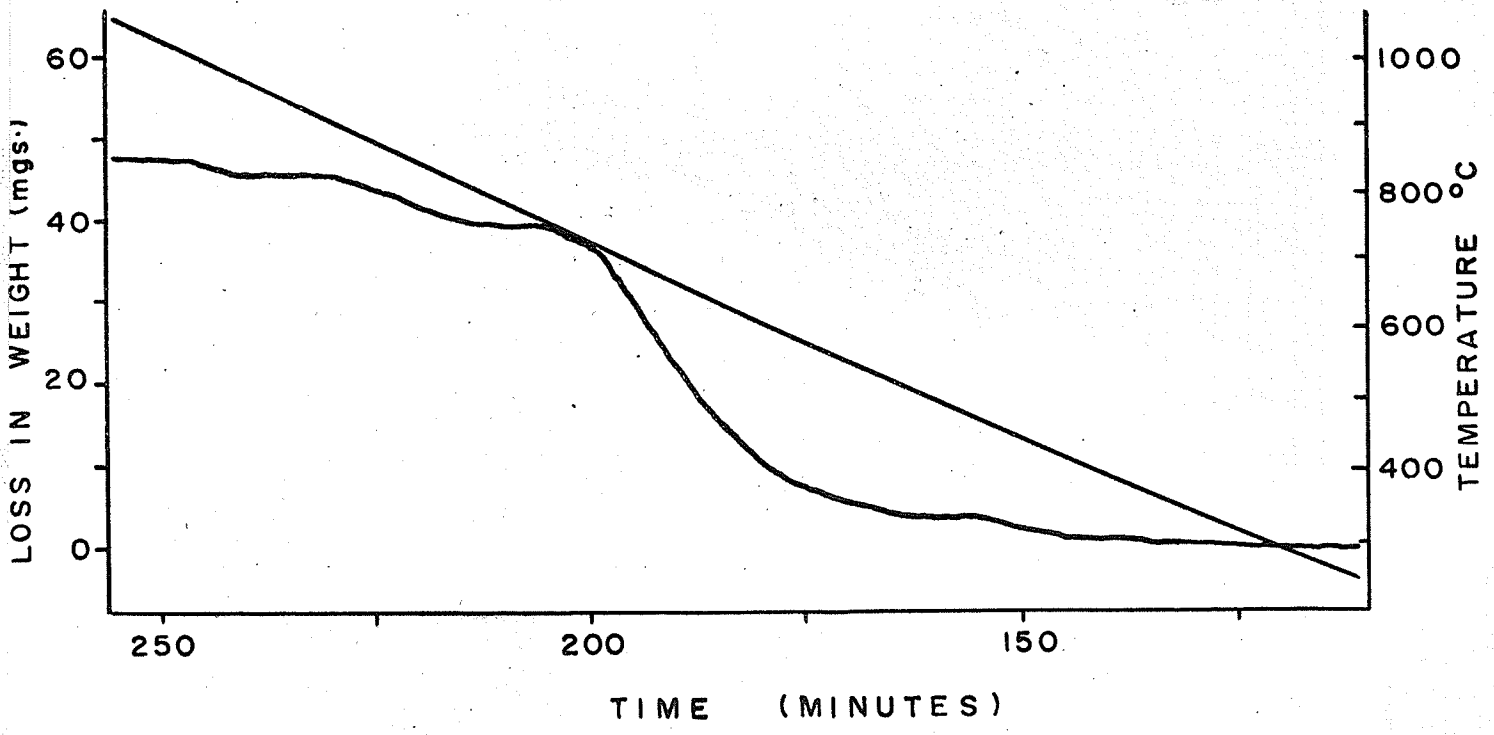
Sample weight = 77.1 mgs.

Figure 10

Thermogram Y for ''altered chromite''

Sample weight = 97.0 mgs.


LOSS IN WEIGHT (mgs.)
40
20
0
TEMPERATURE °C
800
600
400
225
175
125
TIME (MINUTES)


LOSS IN WEIGHT (mgs.)
60
40
20
0
TEMPERATURE
1000
800 °C
600
400
250
200
150
TIME (MINUTES)

5) DISCUSSION OF RESULTS

The results obtained from the digestion of chromium (III) sulphate with sulphuric acid demonstrate that the formation of insoluble products is favoured by high temperatures and high concentrations of sulphuric acid, these being the same conditions favouring the formation of ''altered chromite''. The sulphate to chromium equivalent ratio in these insoluble products is invariably larger than 1.5, indicating that precipitation occurs as a result of sulphation and not hydroxylation.

Thermogravimetric analysis of these insoluble products suggests that three distinct species or classes of compounds (excluding the glasses or ''chromipolysulphuric acids'') are produced under various digestion conditions. The first class of compounds such as R and P have a sulphate to chromium ratio of 2 and contain coordinated water groups. The second class of compounds such as O, Z and U, have a sulphate to chromium ratio larger than 2 and have only sulphate groups coordinated to the chromium ion. The third class of compounds such as T and AA have a sulphate to chromium ratio between 1.5 and 2.0 with no water coordinated to the chromium ions.

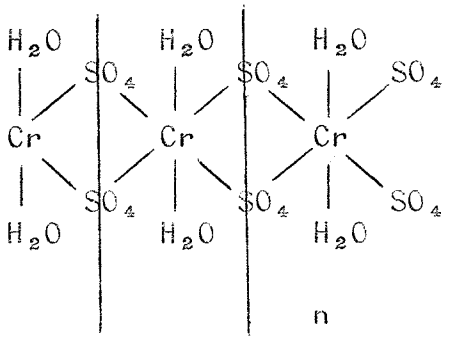
It is impossible to say much about the metal salts of these acids, although product W suggests that the metal salts of these sulphatopolychromate (III) acids with sulphate to chromium ratios much larger than 2 are less soluble than

the acids. The rare occurrence of anion excess to that of cations in the ''altered chromite'' would suggest this as well. The sample of ''altered chromite'', Y, containing such an excess decomposes with a loss in weight due to sulphuric acid at a temperature of 300-450°C.

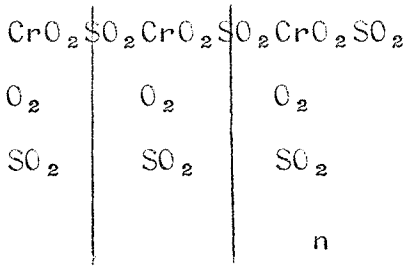
Recoura[10] reports the preparation of a series of ''chromipolysulphuric acids'' which he formulates as $Cr_2(SO_4)_3$ n H_2SO_4 y H_2O and suggests that the maximum value for n is 6. The violet and green forms for the hydrated chromium (III) sulphates may be formulated as $[Cr_2(SO_4)_n(H_2O)_{12-2n}](SO_4)_{3-n}$ 4 H_2O.[1d] The violet form would have an n value of zero, and the various green forms, n values of 1 to 3. Many other formulations including polynuclear products have been reported for the hydrates of chromium (III) sulphate.[12b, 39] The sulphate group can behave as a monodentate, a bidentate, a chelating or as a bridging ligand in these complexes.[1, 12, 22, 35, 36, 39]

An empirical formula must be supplemented by a structure before one can claim to have described a compound. It is evident that many possible structures could be formulated for these compounds. As an example, we can take the compound having a sulphate to chromium ratio of 2. Assuming that water can be used either as water of coordination or water of crystallization, one could formulate the compound as $H[Cr(SO_4)_2]$ n H_2O in which the sulphate groups

act as tridentate ligands. Another possible formulation is the following $H[Cr(H_2O)_2(SO_4)_2]$ where the sulphate groups act as chelating bidentate ligands with the two waters in either cis or trans positions. One could have a polymer chain with or without water molecules coordinated to the chromium ion as in



or



These structures are all possible structures and, therefore, it is necessary to obtain more information regarding the role that the sulphate groups play in the complex and also the number of water molecules in each complex. It was for this reason that the products were subjected to pyrolysis in a thermobalance and to infrared spectral analysis.

The infrared absorption spectrum of the sulphate group changes very markedly as the sulphate group changes

its role from that of a free ion to a monodentate or a bidentate ligand in its compounds.[29, 35, 36] Analysis of the infrared absorption spectra of the hydrogen salts of the sulphatopolychromate (III) ions should, therefore, tell us something about the role that the sulphate ions play in these compounds. Complete analysis of the infrared absorption spectra of any compound, however, requires a prior knowledge of the crystal structure[24] and since this is not available for these compounds, it was decided to compare the infrared absorption spectra of these compounds with those of the hydrates of chromium (III) sulphate. This investigation was undertaken in an attempt to (1) characterize the infrared absorption of mono - bi - etc. sulphate ligands coordinated to chromium (III) ions by observing the spectra of chromium (III) sulphates whose structures were known and (2) to find pyrolysis intermediates, which might resemble the "altered chromite" or the hydrogen salts of sulphatopolychromate (III) anions, whose structure might be deduced by tracing its formation from a known structure. For this reason, a complete discussion of the pyrolysis of the normal violet chromium (III) sulphate, and the infrared absorption spectra of the normal hydrate and its pyrolysis products will be given before an interpretation of the infrared absorption spectra of the sulphatopolychromate (III) acids is attempted.

EXPERIMENTAL RESULTS

COMPLEXES OF CHROMIUM (III) SULPHATE

B) HYDRATES OF CHROMIUM (III) SULPHATE

B) HYDRATES OF CHROMIUM (III) SULPHATE

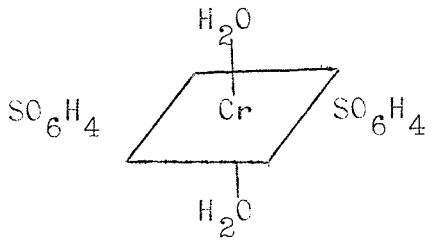
1) INTRODUCTION

The hydrates for chromium (III) sulphate may be formulated as $Cr_2(SO_4)_3$ n H_2O. The value of n depends upon the manner in which the hydrate is prepared. The common hydrates are customarily referred to as the normal violet sulphate and the green sulphates. For the normal violet sulphate n values between 14 and 18 have been reported.[1d, 12b] All of the sulphate ions in the violet salt can be precipitated with barium chloride from its solutions, indicating that the sulphate ion is not coordinated to the chromium ions. The formula for the violet salt is therefore often written as $[Cr(H_2O)_6]_2(SO_4)_3$ X H_2O. The value of X depends upon the manner of preparation and storage of the hydrate. The green hydrate can be prepared by simply heating the violet salt at temperatures as low as 55°C in air or 30°C in vacuum.[1d, 12b] Some of the sulphate ions are ''masked'' in the green hydrate, that is, the sulphate ions will not be completely precipitated by barium chloride. The number of sulphate groups that are ''masked'' depends very much upon the manner in which the green form was prepared. Three green hydrates are formulated by Udy[1d] as $[Cr_2(H_2O)_{10}SO_4](SO_4)_2$ X H_2O, $[Cr_2(H_2O)_8(SO_4)_2]SO_4$ X H_2O, $[Cr_2(H_2O)_6(SO_4)_3]$ X H_2O.

The latter salt may be converted to $[Cr_2(H_2O)_3(SO_4)_3]$ by heating at 80°C and all of the hydrates are converted to the anhydrous $Cr_2(SO_4)_3$ when heated to a temperature near 400°C.[1d, 12b] The solubility of the hydrates decreases as more sulphate groups become coordinated and as more of the water molecules are lost.

The formulas given above for the green hydrates show that two water molecules are displaced from the coordination sphere of the chromium (III) ion. There is, however, no experimental proof that the sulphate ligand in fact behaves as a bidentate ligand in these solids, but it must unless loss of octahedral coordination is admitted, especially in the compound $Cr_2(SO_4)_3$ 3 H_2O. Heating the hydrates of chromium (III) sulphate results in the loss of water and usually the simultaneous coordination of the sulphate groups. The recent investigations by Harmelin[30] of the pyrolysis of a violet salt of chromium (III) sulphate and the infrared absorption spectra of the various hydrates and the anhydrous material produced in the pyrolysis lead to the conclusions that in the normal violet sulphate $Cr_2(SO_4)_3$ 14 H_2O, six of the water molecules are bound directly to the sulphate groups to form the $H_4SO_6^=$ ion. Four of the water molecules form weak bonds with the chromium (III) ions, two may act as bridges between the chromium (III) ions and another four water molecules form strong bonds with

the chromium (III) ions. It is suggested that the structure for this hydrate must be very similar to the structure proposed by Harmelin and Duval[31] for the potassium chrome alum which they consider to be $K[Cr(H_4SO_6)_2(H_2O)_2]$ 6 H_2O containing the complex ion



Their experimental results, however, do not justify the structure proposed for the chromealum. A detailed discussion of their work is given in appendix 2.

The pyrolysis data obtained by Harmelin[30] may be summarized in the following set of equations.

1) $Cr_2(SO_4)_3$ (16-18) H_2O $\xrightarrow{35 \rightleftharpoons 80°C}$ $Cr_2(SO_4)_3$ 14 H_2O

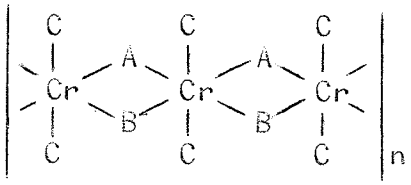
2) $Cr_2(SO_4)_3$ 14 H_2O $\xrightarrow{115 \rightleftharpoons 170°C}$ $Cr_2(SO_4)_3$ 4 H_2O

3) $Cr_2(SO_4)_3$ 4 H_2O $\xrightarrow[\text{slower than in 2}]{170 \rightleftharpoons 540°C}$ $Cr_2(SO_4)_3$

4) $Cr_2(SO_4)_3$ $\xrightarrow{570 \rightleftharpoons 730°C}$ $Cr_2O_3 + 3\ SO_3$

Harmelin's[30] attempts to produce the $Cr_2(SO_4)_3$ 6 H_2O hydrate by slow dehydration of the normal violet sulphate met without success. Instead, she noticed only a much slower rate of dehydration once this composition had been obtained.

Lukaszeweski[45] suggests that pyrolysis of the hexaaquochromium (III) oxyanion compounds (in particular the phosphate, arsenate, and sulphate) involves olation - condensation reactions in the solid similar to those observed in solution, which are initiated by the entry of the sulphate ion into the chromium (III) coordination sphere, resulting in the following structure.



where A = HXO_4^{a-}

B = OH^- or HXO_4^{a-} or no linkage

C = HXO_4^{a-}, H_2XO_4 or H_2O

The infrared absorption spectra for the pyrolysis materials show broadening and splitting of the characteristic XO_4^- absorption bands indicating a lowering of symmetry for the XO_4^- groups. Lukaszewski does not attempt a detailed analysis of the infrared absorption spectra which would give evidence supporting the proposed structures for these compounds.

The pyrolysis data obtained by him for the hydrate $[Cr(H_2O)_6]_2(SO_4)_3 \cdot 4\ H_2O$ may be summarized in the following

1)	$Cr_2(SO_4)_3$ 16 H_2O	60⇒100°C	$Cr_2(SO_4)_3$ 15 H_2O
2)	$Cr_2(SO_4)_3$ 15 H_2O	120⇒170°C	$Cr_2(SO_4)_3$ 10 H_2O
3)	$Cr_2(SO_4)_3$ 10 H_2O	170⇒390°C	$Cr_2(SO_4)_3$ 5 H_2O
4)	$Cr_2(SO_4)_3$ 5 H_2O	390⇒450°C	$Cr_2(SO_4)_3$ 1.5 H_2O
5)	$Cr_2(SO_4)_3$ 1.5 H_2O	450⇒530°C	$Cr_2(SO_4)_3$ 1 H_2O
6)	$Cr_2(SO_4)_3$ 1 H_2O	530⇒635°C	$Cr_2(SO_4)_3$
7)	$Cr_2(SO_4)_3$	635⇒780°C	Cr_2O_3 + 3 SO_3

X-ray studies of these hydrates indicate that they are amorphous but recrystallize prior to complete dehydration. The amorphous nature is attributed to random arrangement of the bridging groups.

2) DISCUSSION OF RESULTS

a) PREPARATION OF THE HYDRATES

The mode of preparation of the hexadecahydrate of chromium (III) sulphate or the normal violet sulphate used was the method of Higby.[12b] 100 mls. of concentrated sulphuric acid were added to 400 mls. of water and cooled to 15°C. This solution was then saturated with chrom alum. 160 mls. of concentrated sulphuric acid were added from a burette at such a rate as to maintain the temperature of the solution between 15 and 20°C. The small crop of crystals formed at this stage were discarded and the precipitate formed after the addition of another 100 mls. of concentrated sulphuric acid were kept for further purification. The impure violet sulphate was then dissolved in 150 mls. of 25% ethyl alcohol-water solution followed by the addition of sufficient alcohol to give a resulting 60% ethyl alcohol solution. After several such recrystallizations the violet sulphate was deemed sufficiently pure to be used. Chemical analysis of the impure violet sulphate showed a sulphate to chromium ratio of 1.59, whereas the recrystallized product had a ratio of 1.52 compared to the theoretical value of 1.50. The impurities impart a green colour to the alcoholic solutions and are probably species of ''green chromium (III) sulphate'' and other sulphato complexes of chromium (III) formed as a result of the production of local high temperatures

during the addition of concentrated sulphuric acid. e.g. $HCr(SO_4)_2$ The hydrate was found by analysis to be $Cr_2(SO_4)_3$ 16.3 H_2O.

Hydrates with n values of 4.58 and 2.17 were prepared by very slow dehydration of the ''normal violet sulphate'' (16.3 hydrate) in a drying oven. Placing the 16.3 hydrate in a drying oven at 65 or 75°C for several hours produced the 13.7 hydrate. This hydrate, however, continues to show a loss in weight when left in the drying oven. The weight loss was too slow to reach a limit as for example at 65°C loss in weight was still occurring after 11 months. The hydrate left in the oven at this time had an n value of 5.65. The hydrate having an n value of 4.58 was obtained at 75°C and the hydrate with n equal to 2.17 at 200°C.

b) THERMOGRAVIMETRIC ANALYSIS

(I) RESULTS

The pyrolysis data obtained for the 16.3 hydrate under various heating rates are given in Tables 4a and 4b. Thermogram C'' in Table 4b is a continuation of thermogram C' which in turn is a continuation of thermogram C. The sample weight used in C necessitated readjustment of the thermobalance because the weight loss up to a temperature of 140°C gave full scale deflection of the recorder. A typical thermogram obtained for the 16.3 hydrate is shown in Figure 11. The data may be conveniently summarized in the following.

1. Loss of water starts at 30°C and continues up to a temperature of 50°C. The thermograms showed an inflection point at 40°C which corresponded to an average weight loss of 3%. The percentage weight loss refers to a percentage of the original sample weight. The plateau at 50°C showed an average weight loss of 7.21%. The composition of the hydrate at this plateau corresponds to $Cr_2(SO_4)_3$ 13.57 H_2O and appears stable up to 85°C.
2. A very rapid weight loss occurred between 85 and 110°C, followed immediately by a more gradual loss of water. The intersection of these two slopes showed a weight loss near 31% at a temperature of 110°C, provided the heating rate was slow. For faster heating rates the

TABLE 4a

Pyrolysis data for $Cr_2(SO_4)_3$ 16.3 H_2O

Thermogram	Maximum Temperature	Heating rate °C/hour	% of original sample weight of the hydrate lost at Intersection(I_1) (☆°C)	Plateau(P) (☆-☆°C)	Intersection(I_2) (☆°C)
H	97	5.4	3.01 (37) 6.94 (42)	8.25 (50-86)	30.16 (97) plateau
A	120	14	2.81 (38)	6.74 (49-85)	30.79 (110)
C	160	23	3.00 (47)	6.89 (53-85)	31.26 (116)
K	175	41	2.80 (39)	7.17 (53-88)	31.10 (120)
L	650	325		7.00 (60-85)	33.6 (145)
J	625	42		7.44	30.70 (110)
N	640	36		6.41	31.08 (110)

(☆-☆°C) indicates that the plateau is stable in the region from ☆°C to ☆°C.
(☆°C) indicates the temperature for the intersection of two slopes.
Intersections and Plateaus as marked in figure 11.

TABLE 4b

Pyrolysis data for $Cr_2(SO_4)_3$ 16.3 H_2O

Thermogram	Maximum Temperature	Heating rate °C/hour	% of original sample weight of the hydrate lost at Intersection(I_2) (☆°C)	Plateau(P_2) (☆-☆°C)	Final Plateau (☆°C)	
C	160	23			34.47 (160)	
C'	220	23			37.29 (220)	
C''	700	300	40.47 (370)	43.46 (480-530)	(675)	
K	175	41	31.96 (140)		34.67 (175)	
L	650	325		43.05 (470-520)	(625)	
J	625	42	32.56 (145)	42.33 (340-380)	(600)	
					47.35 (425)	Intersection
N	640	36		42.67 (330-375)	(595)	
					47.11 (445)	Intersection

(☆-☆°C) indicates that the plateau is stable in the region from ☆°C to ☆°C.
(☆°C) indicates the temperature for the intersection of two slopes.
Intersections and Plateaus as marked in figure 11.

weight loss increases (L).

3. For slow heating rates a pseudo-plateau was established near 140°C showing an average weight loss of about 32% (theoretical value for the loss of 12.3 molecules of water is 32.34%.)

4. For fast heating rates the pseudo-plateau mentioned in 3 was not established, instead the gradual loss in weight mentioned in 2 continued up to a temperature of 470°C. Here one obtained a plateau for the anhydrous chromium (III) sulphate. The weight loss being 43.0%, compared to the theoretical value of 42.83%.

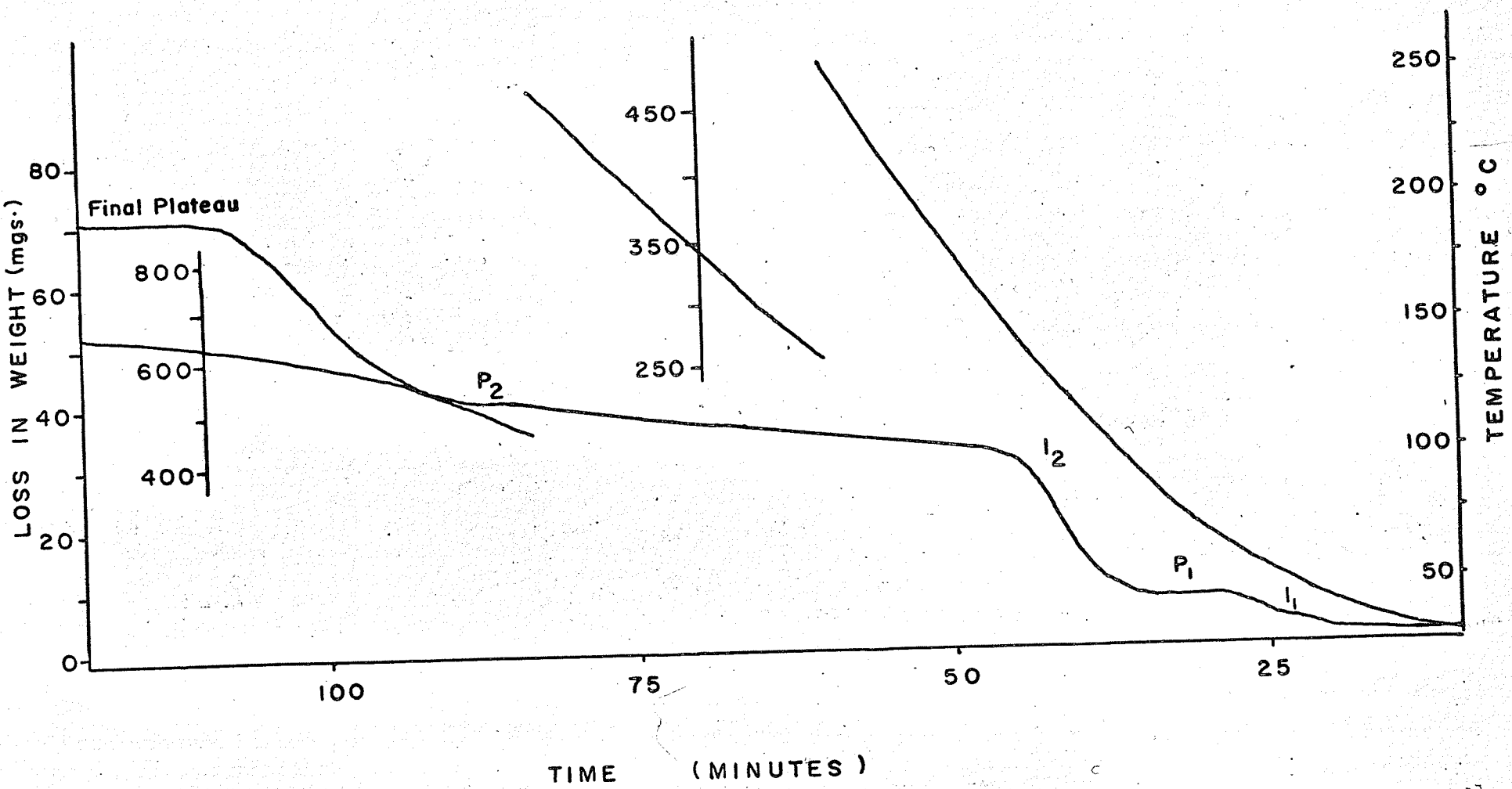
5. The anhydrous chromium (III) sulphate began to decompose at 530°C and was completed at 625°C. These temperatures varied somewhat with the rate of heating. There were two very obvious exceptions in thermograms N and J, these two will be discussed later.

Since the weight losses observed below 80°C represent a small fraction of the total loss (near 9%) occurring upon complete pyrolysis, they may include a fairly large percentage error. In order to check this weight loss two samples were placed in a drying oven at 65 and 75°C resulting in the formation of the 13.7 and 13.6 hydrates respectively, when left in the oven for several hours. The weight losses observed were 6.6% at 65°C and 7.0% at 75°C. These results lack precision but they show conclusively that the hydrate

Figure 11

A typical thermogram for $Cr_2(SO_4)_3$ 16.3 H_2O

Sample weight = 97.6 mgs.


LOSS IN WEIGHT (mgs.)
80
60
40
20
0
Final Plateau
800
600
400
450
350
250
P_2
I_2
P_1
I_1
250
200
150
100
50
TEMPERATURE °C
100
75
50
25
TIME (MINUTES)

obtained below 80°C has an n value near 13.5.

The weight losses in the temperaure interval of 145 to 470°C were very slow and represented one-eighth of the total weight loss obtained upon pyrolysis. In order to investigate this region in more detail, the hydrates with n values of 13.8, 4.58 and 2.17 were prepared by slow dehydration of the 16.3 hydrate in a drying oven. The 13.8 hydrate was prepared by heating the 16.3 hydrate at a maximum temperature of 45°C for several weeks. The hydrate with an n value of 4.58 was prepared by heating the 16.3 hydrate at 75°C for four weeks. The product formed during the initial stages of dehydration is hygroscopic and very soluble but as dehydration proceeds the product loses its hygroscopicity and becomes difficultly soluble in water. Heating the 16.3 hydrate for two weeks at 200°C produces the hydrate with an n value of 2.17. All of these hydrates still showed slow weight losses at their respective temperatures. The odd values of 13.8, 4.58 and 2.17, for the hydrates, have no significance. Other values could be obtained by longer or shorter heating periods at the respective temperatures. The hydrates must of course reach a limiting n value for the respective temperatures but these were not determined. These observations agree with those of Harmelin[30] namely, the pyrolysis curves for the violet chromium (III) sulphate do not show a plateau

corresponding to the 6 hydrate ($Cr_2(SO_4)_3$ 6 H_2O). The pyrolysis data for these partially dehydrated products is given in Table 5.

All of the thermograms obtained by pyrolyzing the 16.3 hydrate show a gradual loss in weight in the temperature interval from 145°C to the temperature required to produce the anhydrous chromium (III) sulphate (except for thermogram number C'' where a slight change in the rate of weight loss is noticeable). The intersection of the two slopes occurs at a weight loss corresponding to 40.47%. The theoretical weight loss for 15.3 molecules of water is 40.21%, thus indicating that the last step in the dehydration process is the loss of one mole of water per mole of $Cr_2(SO_4)_3$. The intersection of two slopes in thermogram number D (for the 13.8 hydrate) at 380°C and a weight loss of 36.44% (theoretical value for the loss of 12.8 molecules of water is 36.13%) and the intersection in thermogram E (for the 4.58 hydrate) at 425°C and a weight loss of 14.21% (theoretical value for the loss of 3.58 molecules of water is 13.58%) indicates that the last molecule of water is lost in a separate step. Thermogram number M (for the 2.17 hydrate) shows a stable plateau for the temperature interval of 350-400°C, with a weight loss of 4.43%. The theoretical value for the loss of 1.17 molecules of water is 4.89%.

The thermograms D Figure 12 and E Figure 13 show changes in the rate at which the last four molecules of water are lost upon pyrolysis. These changes are more pronounced in E than in D and lead to the stable plateau in thermogram M Figure 14. One may attribute the absence of these changes of slope in the thermograms for the 16.3 hydrate to the fact that upon pyrolysis, extremely long periods of time are required for any rearrangements to take place in the solid and, therefore, the products $Cr_2(SO_4)_3$ 2.17 H_2O and $Cr_2(SO_4)_3$ 4.58 H_2O, obtained by slow dehydration, are in fact, not identical to the pyrolysis products having the same stoichiometry. Evidence to support this view is found in the fact that the infrared absorption spectrum of $Cr_2(SO_4)_3$ 2.17 H_2O became well defined only after it had been kept at a temperature of 200°C for a week. Lukaszewski[45] gives a similar interpretation of his work on the oxyanions; namely, the pyrolysis products are amorphous but recrystallization occurs before the anhydrous salt is formed.

The decomposition of $Cr_2(SO_4)_3$ 16.3 H_2O, implied by the thermogravimetric studies, follows this pattern.

1) $Cr_2(SO_4)_3$ 16.3 $H_2O \xrightarrow[30-50°C]{} Cr_2(SO_4)_3$ 13.5 H_2O + 2.8 H_2O

2) $Cr_2(SO_4)_3$ 13.5 $H_2O \xrightarrow[80-110°C]{\text{very fast}} Cr_2(SO_4)_3$ 4.5 H_2O + 9 H_2O

TABLE 5

Pyrolysis data for hydrates of chromium(III) sulphate

Thermogram	Maximum Temperature	Heating rate °C/hour	% of original sample weight of the hydrate lost at Intersections (☆°C)	Plateau(☆-☆°C)	Final Plateau °C
D	695	350	28.25(150) 32.77(237) 36.44(380)	39.28(455-540)	660
E	700	200	12.02(350) 14.21(425)	17.54(480-540)	670
M	670	70	0.0(220) 4.43(350-400)	9.42(445-495)	625

(☆-☆) indicates that the plateau is stable in the region from ☆°C to ☆°C.

(☆) indicates the temperature for the intersection of two slopes.

Thermogram number	Theoretical value for loss of
D is obtained from $Cr_2(SO_4)_3$ 13.8 H_2O	13.8 H_2O is 38.93%
E is obtained from $Cr_2(SO_4)_3$ 4.58 H_2O	4.58 H_2O is 17.37%
M is obtained from $Cr_2(SO_4)_3$ 2.17 H_2O	2.17 H_2O is 9.06%

Figure 12

Thermogram number D for $Cr_2(SO_4)_3$ 13.8 H_2O.

Sample weight = 106.9 mgs.

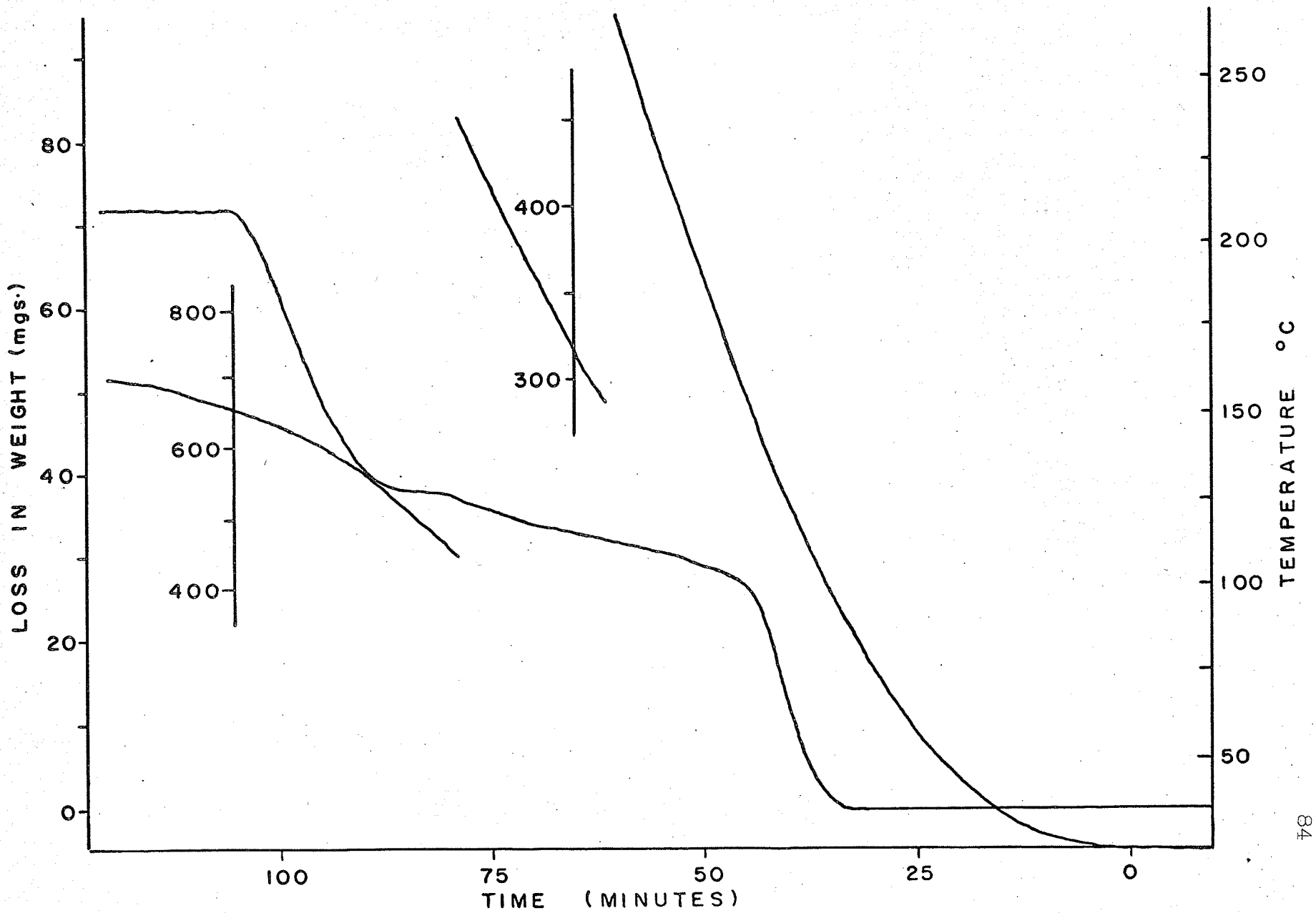

LOSS IN WEIGHT (mgs.)
80
60
40
20
0
800
600
400
400
300
250
200
150
100
50
TEMPERATURE °C
100
75
50
25
0
TIME (MINUTES)

Figure 13

Thermogram number E for $Cr_2(SO_4)_3$ 4.58 H_2O

Sample weight = 151.0 mgs.

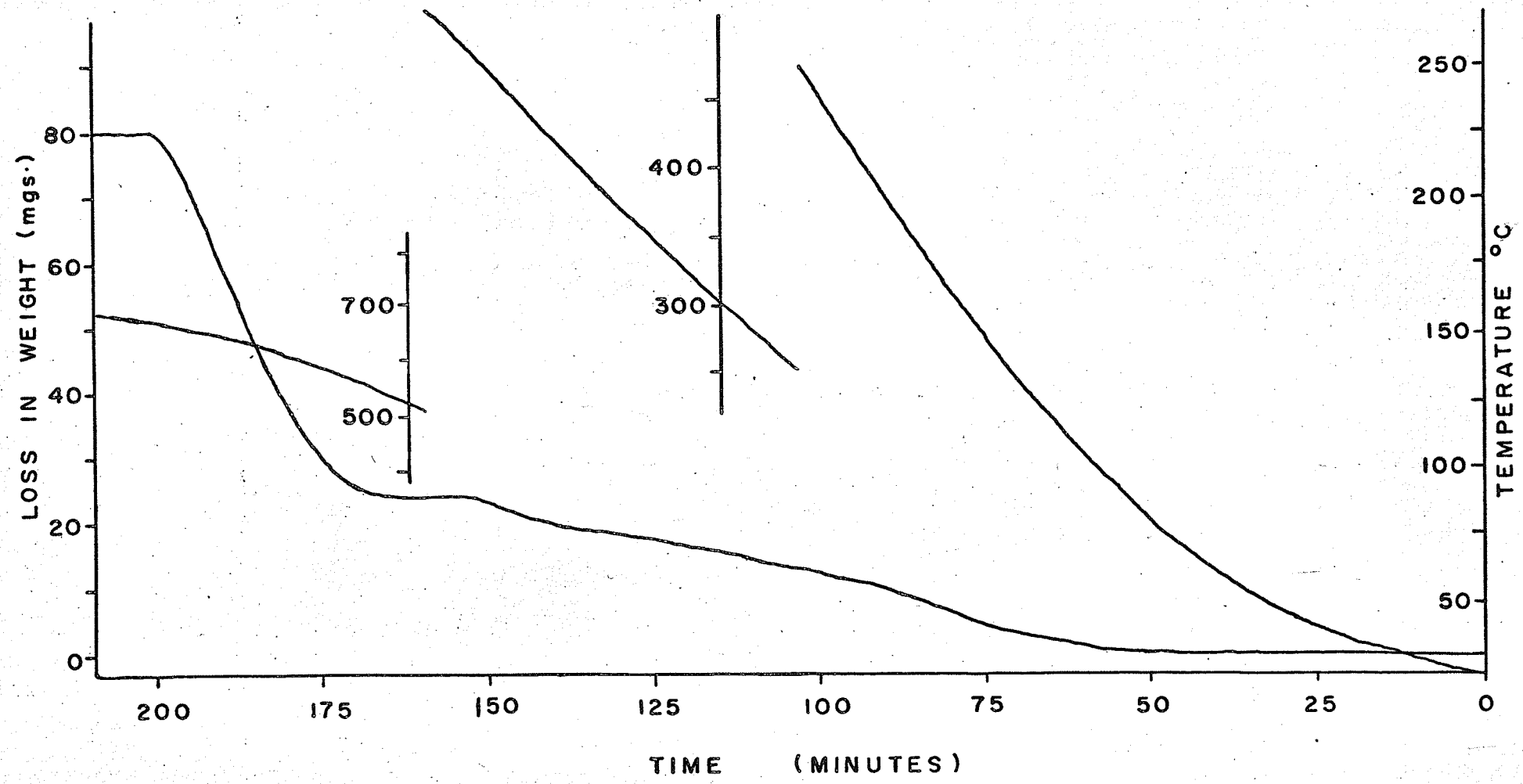
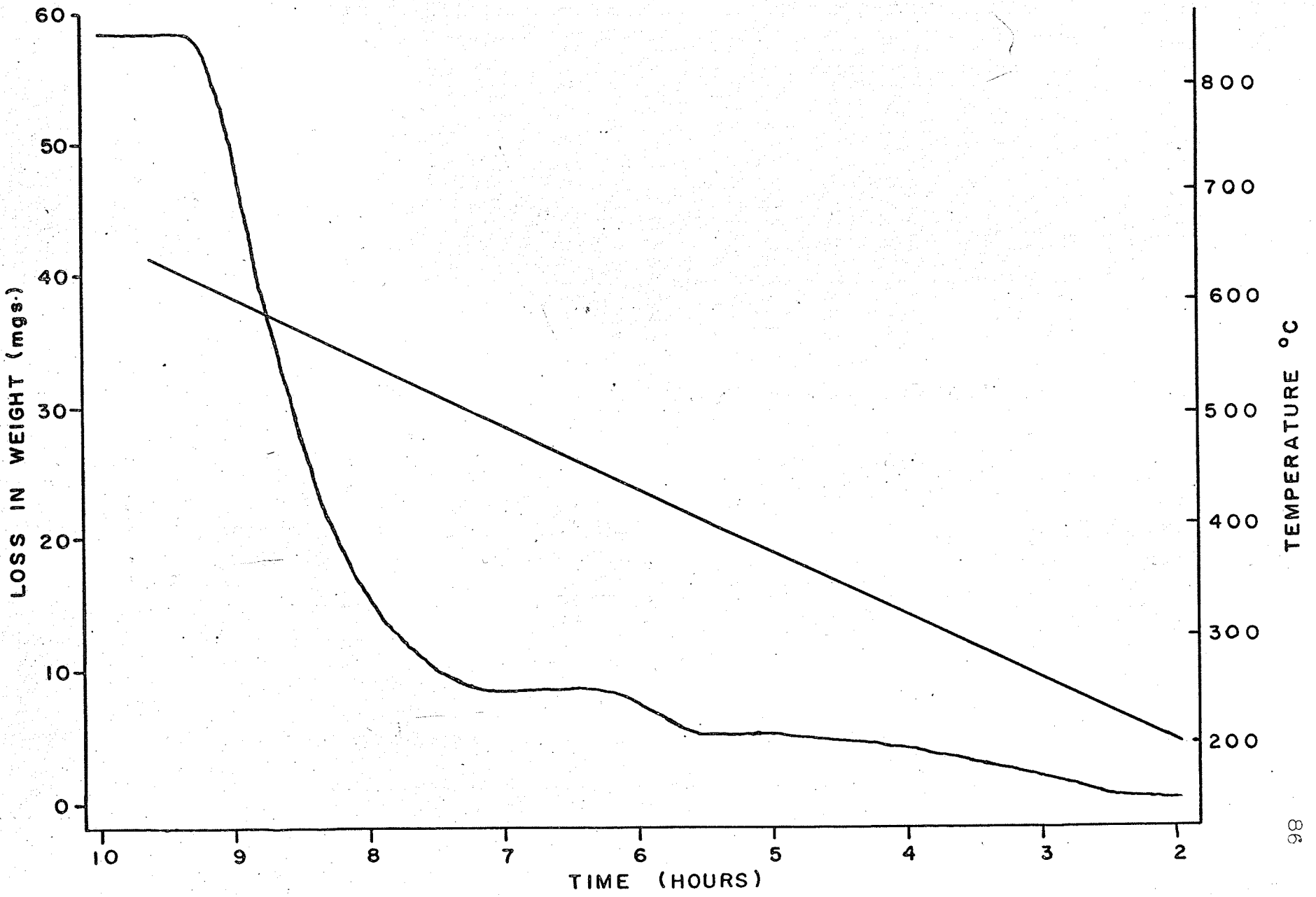

LOSS IN WEIGHT (mgs.)
80
60
40
20
0
700
500
400
300
250
200
150
100
50
TEMPERATURE °C
200
175
150
125
100
75
50
25
0
TIME (MINUTES)

Figure 14

Thermogram number M for $Cr_2(SO_4)_3$ 2.17 H_2O

Sample weight = 91.7 mgs.


LOSS IN WEIGHT (mgs.)
60
50
40
30
20
10
0
TEMPERATURE °C
800
700
600
500
400
300
200
10
9
8
7
6
5
4
3
2
TIME (HOURS)

3) $Cr_2(SO_4)_3\ 4.5\ H_2O \xrightarrow[110\text{-}140°C]{\text{fast}} Cr_2(SO_4)_3\ 4.0\ H_2O + 0.5\ H_2O$

4) $Cr_2(SO_4)_3\ 4.0\ H_2O \xrightarrow[140\text{-}470°C]{\text{very slow}} Cr_2(SO_4)_3 + 4\ H_2O$

5) $Cr_2(SO_4)_3 \xrightarrow{525\text{-}625°C} Cr_2O_3 + 3\ SO_3$

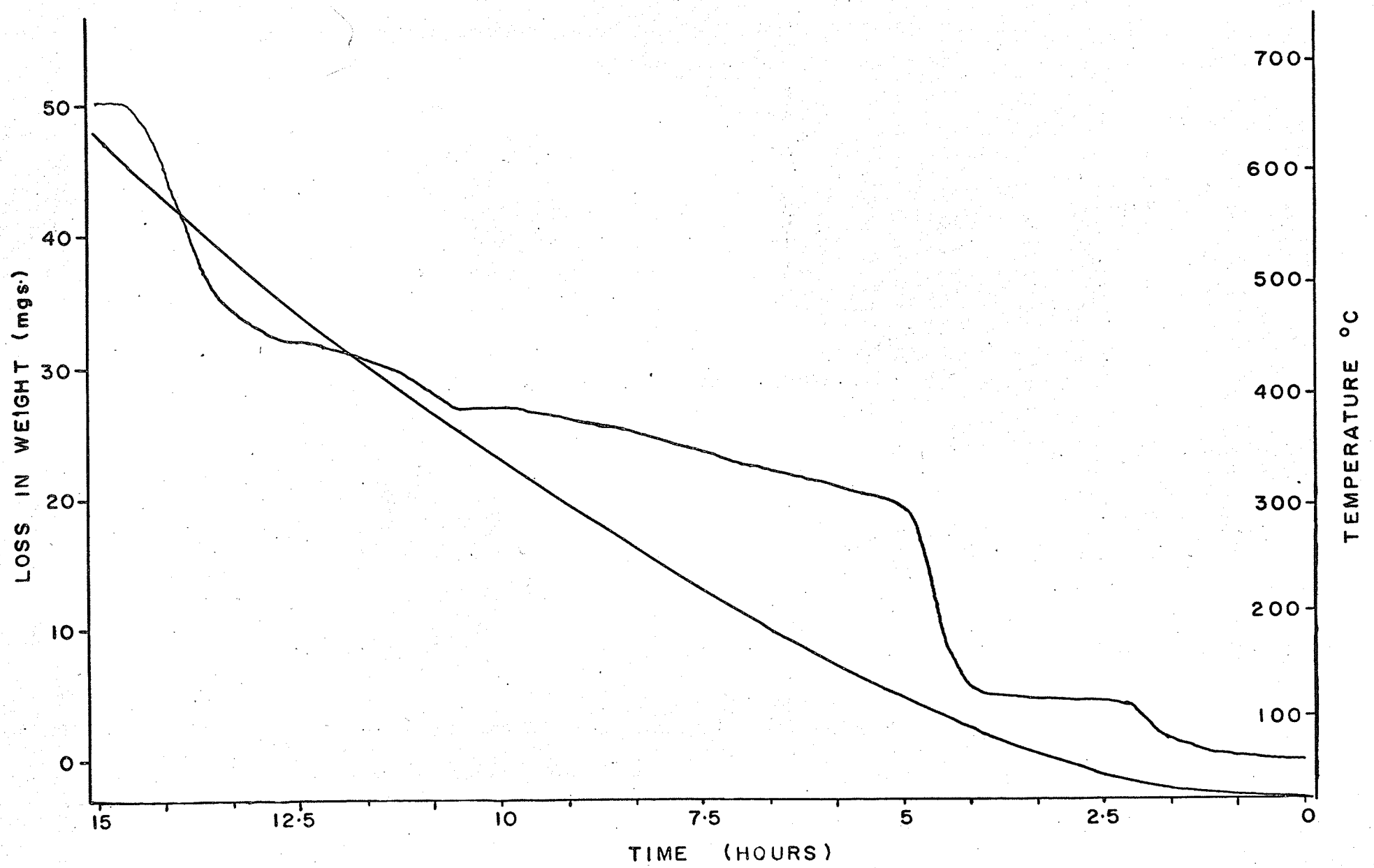
The decomposition of the 4.58 and 2.17 hydrate would be similar except that these would now definitely show the existence of the mono hydrate, $Cr_2(SO_4)_3\ H_2O$.

The two thermograms J,(Figure 15) and N show weight losses corresponding to the above scheme, but the temperature at which all of the water has been lost has dropped to 340°C in J and 330°C in N, compared to the temperatures near 470°C for the other thermograms. Furthermore, these two thermograms, J and N, show weight losses stoichiometrically explainable as loss of SO_3 (step 5) starting at a temperature of 380°C, well below the temperature of 525°C observed in other thermograms employing fast heating rates. The thermograms J and N show a change in the rate at which SO_3 is lost; this change in slope occurs at a temperature of 425°C and 445°C and at 47.3 % and 47.1 % weight loss. This change in slope occurs when only 16% of the sulphur trioxide has been lost. These differences must be attributed to the slow heating rates employed in obtaining thermograms J and N. The low temperature at which all of the water is

Figure 15

Thermogram number J for $Cr_2(SO_4)_3$ 16.3 H_2O

Sample weight = 63.7 mgs.


LOSS IN WEIGHT (mgs.)
50
40
30
20
10
0
15
12·5
10
7·5
5
2·5
0
TIME (HOURS)
700
600
500
400
300
200
100
TEMPERATURE °C

lost in thermograms J and N may find an explanation in terms of the following: assuming that the mechanism whereby the last four molecules of water are lost is a complex process, one might expect that for fast heating rates there is not sufficient time for rearrangements to take place and that water is split out by simple bond cleavage rather than displacement of the coordinated water by an oxygen from a sulphate group. For fast heating rates one would then expect ''holes'' in the coordination sphere which presumably strengthen the Cr-O-S bonds and, therefore, require higher temperatures for the decomposition to the chromium (III) oxide and sulphur trioxide. Loss of a pair of electrons from the coordination sphere of the chromium (III) ion as the water molecule is lost would increase the effective nuclear charge on the chromium (III) ion and, therefore, strengthen the Cr-O-S bonds.

A plateau in any thermogram is usually taken as evidence for the existence of a definite compound. For example, the plateau from 50-80°C is taken as evidence for the existence of the $Cr_2(SO_4)_3$ 13.5 H_2O hydrate. Such a plateau in a thermogram, however, does not insure that the compound is stable over the temperature interval of the plateau. This is quite evident from the weight losses observed for the $Cr_2(SO_4)_3$ 16.3 H_2O hydrate which when kept at a temperature of 65°C for an extended period and

resulted in the formation of the 5.65 hydrate. A plateau in a thermogram, therefore, does not prove that a compound is stable, instead the plateau gives evidence only for the slow rate of decomposition. From thermogram N it is evident that the anhydrous $Cr_2(SO_4)_3$ decomposes at a very slow rate at temperatures below 445°C and at a slightly higher rate at higher temperatures. One may, therefore, conclude that the plateaus, found in the thermograms employing fast heating rates, do not necessarily give evidence for the existence of a stable form of anhydrous $Cr_2(SO_4)_3$ and that the high temperatures given in Tables 4 and 5 at which decomposition of the anhydrous $Cr_2(SO_4)_3$ starts, are therefore, not necessarily the lowest temperatures at which decomposition occurs.

Further proof for this explanation was found in attempts to produce the mono hydrate and anhydrous chromium (III) sulphate. Thermogram M showed a plateau corresponding to the mono hydrate in the temperature interval of 350 - 400°C. Since the thermograms J and N had not been obtained at this time it was concluded that heating the 16.3 hydrate at a temperature of 350°C might produce the monohydrate. If the mono hydrate was not produced anhydrous chromium (III) sulphate or some other hydrate with an n value less than unity was expected because all of the thermograms so far had shown that final loss of water did not occur below

temperatures of 470°C. The product obtained by heating the 16.3 hydrate at 350°C for 24 hours had a sulphate to chromium ratio of 1.35 indicating that decomposition of anhydrous chromium (III) sulphate had occurred. Since decomposition of anhydrous $Cr_2(SO_4)_3$ occurs in a muffle furnace at temperatures as low as 350°C, one must conclude that the temperatures obtained for this decomposition in the thermograms employing fast heating rates do not reflect the minimum temperatures at which decomposition is possible but the temperature at which decomposition is first detected under the conditions of pyrolysis. This serves to emphasize the conclusions of others in the field, namely that one should refer to the decomposition temperatures as ''procedural decomposition temperatures or p.d.t.''.[46] Thus, the ''p.d.t.'' for anhydrous $Cr_2(SO_4)_3$ is found by Lukaszewski[45] to begin at 635°C and is completed at 780°C and by Harmelin[30] to begin at 570°C and is completed at 730°C.

(2) CONCLUSIONS

The pyrolysis data for the normal violet sulphate show that a plateau in a thermogram does not necessarily prove the existence of a thermally stable compound. The existence of a plateau in a thermogram may simply mean that under the conditions of pyrolysis, no weight loss is detected in the temperature interval of the plateau. Proof for the thermal stability of the compound must be obtained otherwise. The anhydrous $Cr_2(SO_4)_3$ will decompose at temperatures as low as 350°C. This would indicate that it is impossible to produce pure anhydrous $Cr_2(SO_4)_3$ by dehydration of the hydrates of chromium (III) sulphate by heating to a temperature near 400°C as reported in the literature.

The thermograms for the pyrolysis of the 16.3 hydrate show plateaus corresponding to the 13.5 hydrate and the anhydrous chromium (III) sulphate. Maintaining these two products at the respective temperatures corresponding to the plateaus in the thermogram causes very slow decomposition of the material. The thermograms show no plateaus which may be taken as evidence for a relatively stable hydrate with n values between 13.5 and 0. The thermograms show only that the rate at which the water is lost decreases as dehydration proceeds. The hydrates obtained by extremely slow dehydration under isothermal conditions do show plateaus corresponding to the hydrate with an n value of 1, indicating that the

products produced in the thermobalance may be amorphous whereas the products produced by extremely slow dehydration may have had time to crystallize.

The procedural thermal decomposition of $Cr_2(SO_4)_3$ 16.3 H_2O, employing a heating rate of 36°C per hour may be represented in the following steps.

1) $Cr_2(SO_4)_3$ 16.3 H_2O $\xrightarrow{30\Rightarrow 50°C}$ $Cr_2(SO_4)_3$ 13.5 H_2O + 2.8 H_2O

2) $Cr_2(SO_4)_3$ 13.5 H_2O $\xrightarrow[\text{very fast}]{80\Rightarrow 110°C}$ $Cr_2(SO_4)_3$ 4.5 H_2O + 9 H_2O

3) $Cr_2(SO_4)_3$ 4.5 H_2O $\xrightarrow[\text{fast}]{110\Rightarrow 145°C}$ $Cr_2(SO_4)_3$ 4.0 H_2O + 0.5 H_2O

4) $Cr_2(SO_4)_3$ 4 H_2O $\xrightarrow[\text{very slow}]{145\Rightarrow 335°C}$ $Cr_2(SO_4)_3$ + 4 H_2O

5) $Cr_2(SO_4)_3$ $\xrightarrow[\text{slow}]{375\Rightarrow 595°C}$ Cr_2O_3 + 3 SO_3

c) INFRARED SPECTRAL ANALYSIS

(I) INTRODUCTION

In order to determine the symmetry of a ligand in a crystal lattice, site group or factor group analysis based on a knowledge of the crystal structure is required. Nakamoto et al,[35] however, state that the effect of coordination upon the absorption due to the ligand will be much greater than the perturbations due to the crystal field and that, therefore, ignorance of site group or factor group analysis may be tolerated when using infrared analysis to determine the symmetry of a ligand in a crystalline lattice. The free sulphate ion is a regular tetrahedron belonging to the point group T_d; it has nine modes of vibrations, shown in Figure 16, giving rise to four fundamental frequencies. Coordination of one of the oxygens of the sulphate group to a metal lowers the symmetry and causes: first, the appearance of new bands and splitting of degenerate modes; second, frequency shifts of the bands, and third, intensification of the spectrum.

TABLE 6

Correlation table between T_d, C_{3v} and C_{2v} symmetry

	ν_1	ν_2	ν_3	ν_4
T_d	A(R)	E(R)	F(IR)	F(IR)
C_{3v}	A(IR)	E(IR)	A(IR) + E(IR)	A(IR) + E(IR)
C_{2v}	A(IR)	A(IR) + A(R)	A(IR) + B(IR) + B(IR)	A(IR) + B(IR) + B(IR)

(IR), infrared active. (R), raman active

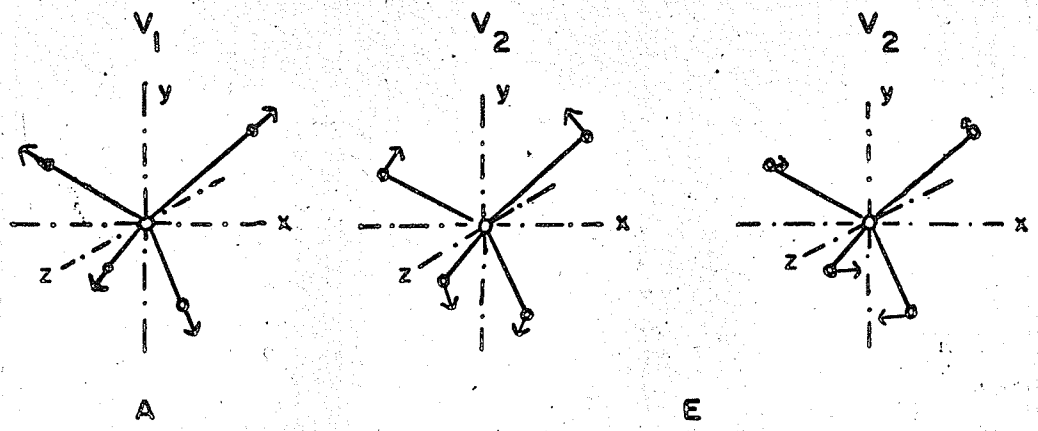
The symbols A,E,B and F refer to the symmetry types of vibration, only certain symmetry types being allowed. A complete discussion of their significance may be found in Herzberg's text.[34,p 104-123] For our purpose it is sufficient to realize that A and B refer to nondegenerate, E to doubly degenerate, and F to triply degenerate modes of vibration. The symmetry of the molecule is described in terms of a point group, T_d, C_{3v}, C_{2v} etc., in which the molecule has a certain combination of symmetry elements, such as 3 fold axis of rotation, mirror planes, etc. A discussion of these may also be found in Herzberg's text.[34,p5-12]

Table 6 shows that the free sulphate ion (T_d) has two infrared active modes of vibration ν_3 and ν_4. The values in solution are 1104 cm^{-1} for ν_3 and 613 cm^{-1} for ν_4.[34] The sulphate ion coordinated as a monodentate ligand with C_{3v} symmetry should cause the appearance of two new bands ν_1 and ν_2 and at the same time split ν_3 and ν_4 into two bands. When the sulphate group acts as a bidentate ligand with C_{2v} symmetry, ν_1 becomes active, ν_2 should split into two active bands, while ν_3 and ν_4 each split into three bands. The experimental work of Nakamoto et al[35] and Barraclough and Tobe[36] is consistent with these theoretical predictions.

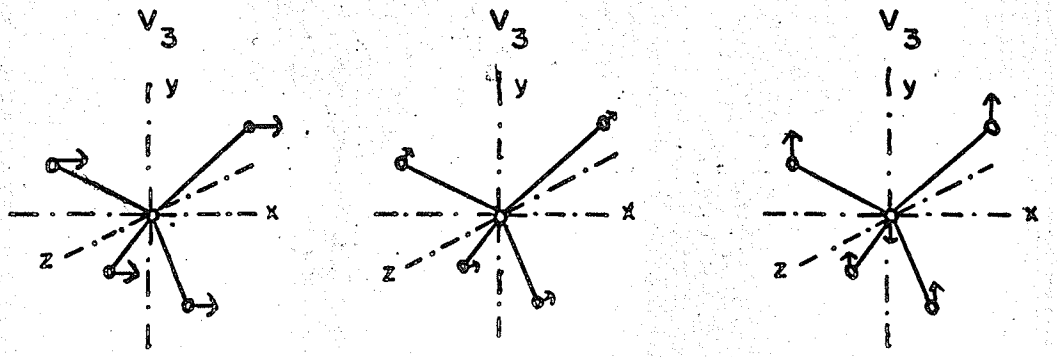
It was noticed by Nakamoto et al, by Ross, and by ourselves, that invariably the infrared spectra of the sulphate group shows absorption bands with either a doublet or triplet

Figure 16

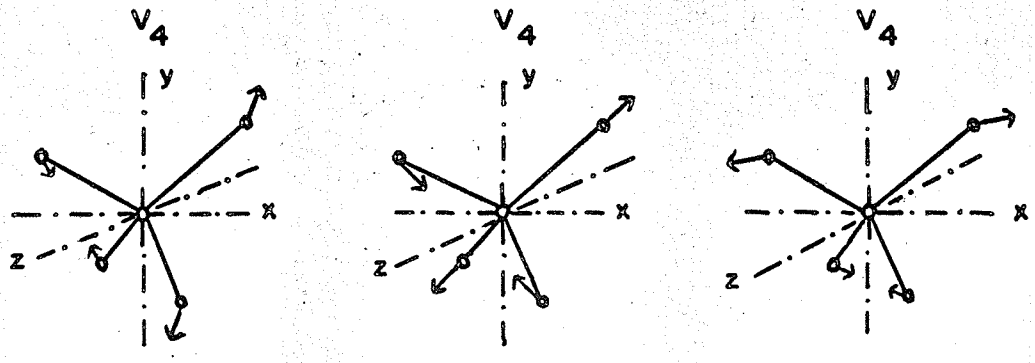
Normal vibrations of the sulphate ion



A E



F



F

structure, appropriate for C_{2v} or C_{3v} symmetry, in the crystalline state. In these compounds, such as potassium sulphate and gypsum, coordination cannot be the cause of this apparent reduction in symmetry. Nakamoto et al observe that the characteristic v_1 frequency (973 cm^{-1}) of the sulphate ion, is present in the compound $[Co(NH_3)_6]_2(SO_4)_3$ 5 H_2O. They attribute the appearance of this band to the perturbations of the crystal field on the sulphate ion.

Ross,[28] in his investigation of various hydrated and anhydrous sulphates and perchlorates, shows that the frequencies v_3 and v_4 mostly display the triplet structure appropriate for C_{2v} symmetry. He lists three reasons for the lowering of the symmetry from the regular tetrahedron observed in solution. They are: '' first, distortion of the $SO_4^=$ tetrahedron in the crystal lattice; second, covalent bonding of the sulphate to the metal, through one or more oxygen atoms and third, a non uniform field due to water molecules around the cation''. His conclusion, that, whereas an assymmetric crystal field is of importance, the major cause for the splitting must be due to distortion of the tetrahedron in the crystal lattice, is based on the large splitting observed in the anhydrous sulphates, particularly barium and strontium sulphate.

Since the sulphate ion invariably shows bands characteristic of C_{2v} or C_{3v} symmetry in the crystalline

state, is it still possible to use infrared spectral analysis to determine the symmetry of the sulphate ligand and assign its reduction in symmetry to coordination ? The affirmative answer of Nakamoto et al would still appear valid, that is, coordination usually causes: first, appearance of new bands and splitting of degenerate modes due to lowering of symmetry; second, frequency shifts of the bands; and third, intensification of the spectra. The fundamentals active in the free ion increase their intensity whereas the newly allowed bands have weak or medium intensity. Evidence to support this view may be found in the magnitude of the splitting observed for the ν_3 frequency of the sulphate ion in potassium sulphate (Figure 19) 1115, 1143 and 1162 cm^{-1} (1093, 1124 and 1149 cm^{-1}, Ross[28]) whereas, the splitting due to coordination is much more drastic as shown by the chelating sulphate;[36] 1075, 1176 and 1211 cm^{-1} in $[Co(en)_2SO_4]Br\ 2\ H_2O$, or the bridging sulphate[35] 1050-60, 1105 and 1170 cm^{-1} in $[(NH_3)_4Co\langle^{NH_2}_{SO_4}\rangle Co(NH_3)_4](NO_3)_3$. The intensity of the ν_1 band is drastically different for these two effects. Coordination of the ligand gives a strong band for the ν_1 frequency whereas its intensity is very weak when allowed due to crystal field perturbation.

Scrocco and Mathieu[37], using site group analysis, predict the spectra of strontium, barium and lead sulphates. Their prediction is based on a knowledge of the crystal

structure of these isomorphous salts, and the perturbing effect of the crystal field on the fundamental modes of vibration. These predictions are verified in their experimental work except for lead sulphate where they find that the intensities of the bands are drastically different from those predicted by the zero order of approximation. They find that the splitting of degenerate modes of vibration in the sulphate group increases as the polarizability of the associated cation increases and interpret this as greater distortion of the sulphate ion in lead sulphate than in barium sulphate which is greater than in strontium sulphate. Duval and Lecomte[38], on the other hand, consider the spectra of barium and lead sulphates to be characteristic of the spectra in which the sulphate group possesses regular tetrahedral symmetry. Scrocco and Mathieu find also that the splitting of the nine fundamental modes into eighteen modes as a result of coupling between the four sulphate groups in the unit lattice, decreases as the polarizibility of the cation increases. They attribute this decrease to shielding of the electromagnetic radiation by the polarizible cation.

Ross[28] attributes the triplet structure observed for the sulphate ion in gypsum to distortion of the sulphate ion in the gypsum lattice. Hass and Sutherland[24], using the method of site group analysis, have shown that this triplet structure is predicted from knowledge of the site symmetry

of the sulphate group in gypsum, and consideration of the perturbing effect of the crystal field. They show as well, that in gypsum there are a total of six infrared active frequencies, excluding overtones and combination bands, observed for water which has only three non degenerate modes of vibration in the free state: these arise due to coupling between the four molecules of water in the unit cell. They attribute the large splitting of the water frequencies, compared to the splitting between two associated bands for the sulphate, observed in gypsum, to the direct coupling that exists for the water molecules and the nonexistence of such coupling for the sulphate groups.

These results pose two questions: first, is the splitting of degenerate modes of vibration of the sulphate ion in the crystal lattice due to distortion of the ion in the lattice or is it due to crystal field perturbation effects. second, since the large splitting observed for water, compared to that of the sulphate in gypsum, can be attributed to direct coupling between the water molecules, does this mean that similar effects (that is the appearance of new bands for the degenerate or nondegenerate modes of a ligand placed in a symmetrical crystal field) should be observed, as a result of direct coupling provided by coordinated metal ions or should this coupling be of less importance as coordination occurs as suggested by the work of Scrocco and Mathieu ?

There is no x-ray evidence to show that the sulphate ion is distorted in the gypsum crystal lattice.[24] The infrared and Raman absorption spectra of gypsum are in good agreement with that predicted from site group analysis. Similarly, the spectra of barium and strontium sulphate agree with the spectra predicted from site group analysis and the calculated intensities using a zero order approximation agree well with the experimental values. This does not mean that the splitting of the degenerate modes is not due to distortion, but the experimental work of Hass and Sutherland, and of Scrocco and Mathieu, confirms that one needs to consider only the perturbation of the crystal field in predicting the spectra of the sulphate ion in the crystalline state, where coordination of the sulphate ion is absent. Ross's criticism of Nakamoto et al for neglecting the possibility of distortion being one of the prime factors causing reduction of symmetry in the compound $[Co(NH_3)_6]_2$-$(SO_4)_3 5\ H_2O$, does not appear justified.

From the correlation for T_d, C_{3v}, and C_{2v} symmetry, Table 6, it is easy to predict the qualitative form of the spectrum when coordination causes reduction of the symmetry of the sulphate ligand to either C_{3v} or C_{2v}. What happens when all four of the oxygens from the sulphate group become coordinated in a manner such that the sulphate ligand finds itself in a strong symmetrical crystal field ?

The answer to this problem may be found in the selection rules for the crystalline state. '' The selection rules for the absorption of infrared radiation by a small molecule in the gaseous state depend only on the symmetry properties of the individual molecules; the corresponding rules for the same molecule in the crystalline state depend, in addition, on the symmetry of the crystal and on the number and position of the molecules in the unit cell'', Hass and Sutherland.[24] Since the selection rules depend upon the symmetry of the crystal and the number of molecules in the unit cell, one may expect to find bands other than those predicted from the symmetry of the ligand alone. The splitting for these bands will not be as large as that expected for bands which appear due to reduction of symmetry, but may show a considerable magnitude of splitting as a result of direct coupling between the sulphate groups by the coordinated metal ion, very similar to that observed for the water molecules in gypsum. The intensity of these bands will be low compared to the intensity of bands resulting from coordination, in which reduction of symmetry occurs, but not as low as observed for the bands allowed due to perturbation of the crystal field as in barium, strontium and potassium sulphate.

One may, therefore, conclude that the infrared absorption spectra of inorganic sulphates may be classified

in three distinct classes. The first class will include the ionic sulphates. Their spectra will show the appearance of new bands, not found for the free sulphate ion, due to reduction of symmetry by the perturbation of the crystal field. The splitting of these bands may be fairly large, but usually less than 100 cm^{-1} (91 cm^{-1} for $SrSO_4$, 83 cm^{-1} for $BaSO_4$, Mathieu and Scrocco[37]). The splitting of bands due to coupling of the sulphate groups in the unit cell will usually be quite small and the intensity of newly allowed bands, such as the breathing frequency ν_1, will be low.

The second class of compounds will encompass the coordination compounds, in which the sulphate ligand has reduced symmetry. The bands newly allowed as a result of reduction in symmetry will have intensities comparable to those observed in the free sulphate ion. The splitting as a result of reduction in symmetry will be fairly large, usually greater than 120 cm^{-1}. The shift of the 1104 cm^{-1} band for the free sulphate will usually be much larger than that observed in the ionic compounds.

The third class will include the coordination compounds in which the sulphate group exists in a symmetrical crystal field. The splitting of bands allowed due to coupling between the sulphates (these if present in the second class are hidden by other bands) will be much smaller than the splitting observed in the second class and may even be smaller than those in the first class, i.e. those due to reduction

of symmetry in the first class. The last class may include the anhydrous sulphates of the transition metals and others where symmetrical coordination of the sulphate ligand to the metal occurs.

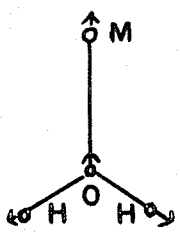
The results obtained for lead sulphate by Scrocco and Mathieu show that the calculated intensities, considering the sulphate ion to have regular tetrahedral symmetry, did not agree with the experimental values, the latter showing a much greater intensity than that calculated. The largest splitting of degenerate modes of vibration in lead, barium and strontium sulphate was observed for lead sulphate. Accepted ideas of bonding would suggest that the cation sulphate bond would be ionic for strontium and barium sulphate and covalent for lead sulphate as is suggested by their polarizability. Lead sulphate is, therefore, properly classified as belonging to our class 2, whereas barium and strontium sulphate are best considered as belonging to class 1. The experimental work of Scrocco and Mathieu lends support to this classification of the spectra. Similarly, the work of Duval and Lecomte[38], and our own, indicate that the spectra of the anhydrous sulphates of the transition metals, which are more complicated than our class 1, are best considered as belonging to the third class.

The gaseous water molecule has three fundamental modes of vibration, as shown in Figure 17, which are all

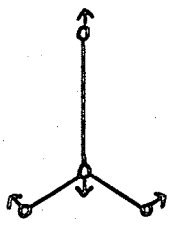
Figure 17

Vibration modes for the water molecule

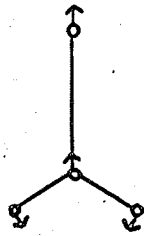
COORDINATED WATER MOLECULE



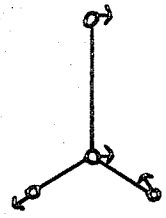
V_1



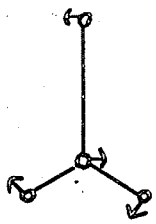
V_2



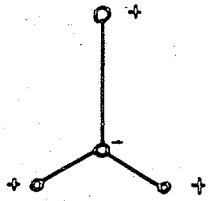
V_3



V_4

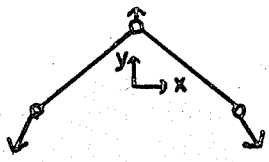


V_5

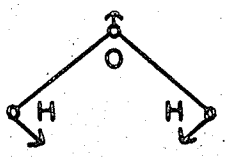


V_6

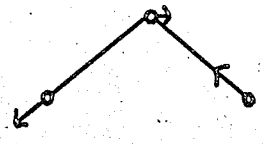
FREE WATER MOLECULE



V_1



V_2



V_3

infrared active. The gaseous molecule absorbs infrared radiation at 3657(v_1), 3756(v_3)and 1595(v_2) cm^{-1}.[24] In the solid and liquid state, the absorptions due to the stretching vibrations v_1 and v_3, are shifted to lower frequencies, whereas the absorption due to the bending or deformation mode v_2 shifts to a higher frequency.[27] The magnitude of the shifts that are observed in various hydrates depend upon the strength of the hydrogen bond that the water molecules form with the constituents of the solid state.[25, 26]

The rocking, wagging and twisting modes, shown in Figure 17, give rise to infrared absorption when water becomes coordinated to a metal ion. Absorption due to these modes is possible only if water forms a strong coordinate bond with the metallic cation and if the water molecule forms strong hydrogen bonds to the associated anion.[29] Thus, absorption at 795 cm^{-1} for $Ni(glycine)_2$ 2 H_2O, at 875 cm^{-1} for $Cu(SO_4)$ 5 H_2O, and 965 and 1012 cm^{-1} for $K[Cr(C_2O_4)_2(H_2O)_2]$ 3 H_2O, is assigned to these modes by Fujita et al.[29]

(2) RESULTS

EXPERIMENTAL PROCEDURES

Good resolution of the absorption bands can be obtained only if the particle size of the absorbent has been reduced to the micron region.[40] The reduction in particle size is most readily achieved by grinding the sample in what is commonly called a Wig-L-Bug or amalgamator. This grinding process, as discussed previously (page 18), was found to be unsatisfactory for the 16.3 hydrate. In order to obtain good resolution of the absorption bands for the 16.3 hydrate, three different methods were tried. The first consisted of simple grinding of the hydrate in an agate mortar and pestle, resulting in the spectrum marked as number 1 in Figure 19. Spectrum number 2, obtained by mixing the hydrate and potassium bromide followed by grinding of this mixture, shows the appearance of a new band at 1060 cm^{-1}, not evident in spectrum number 1. It was thought that this band might be due to alteration of the sample during the grinding process because this band is also evident in the spectra obtained from the grinding products in the Wig-L-Bug (Figure 18), therefore, to insure that the sample remained cool during the grinding process the mixture of potassium bromide and the sample was ground under ether. This last method produces a spectrum (number 3) which shows good resolution of the bands, and was found to

Figure 18

Infrared absorption spectra; samples prepared by grinding $Cr_2(SO_4)_3$ 16.3 H_2O in a Wig-L-Bug.

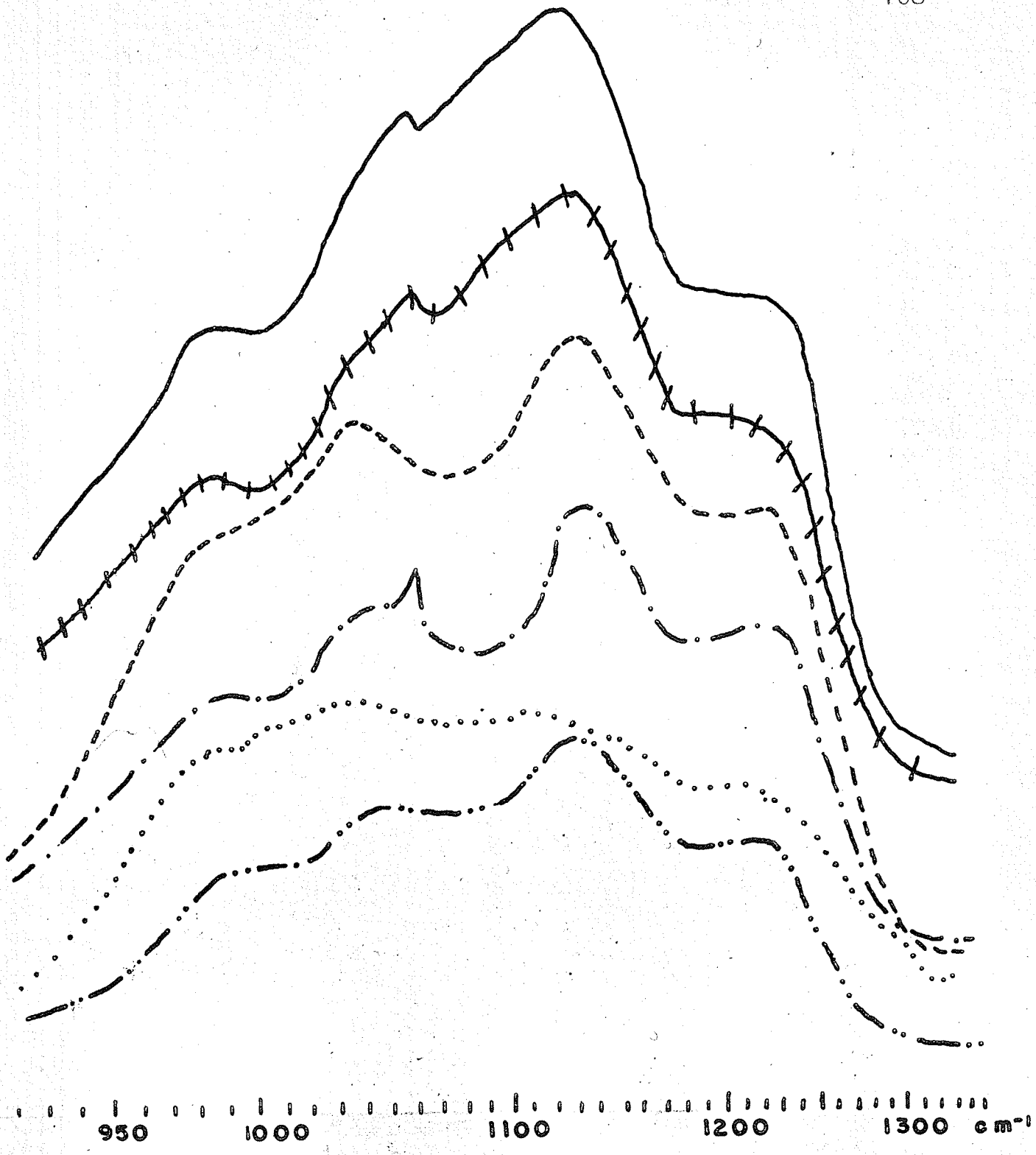
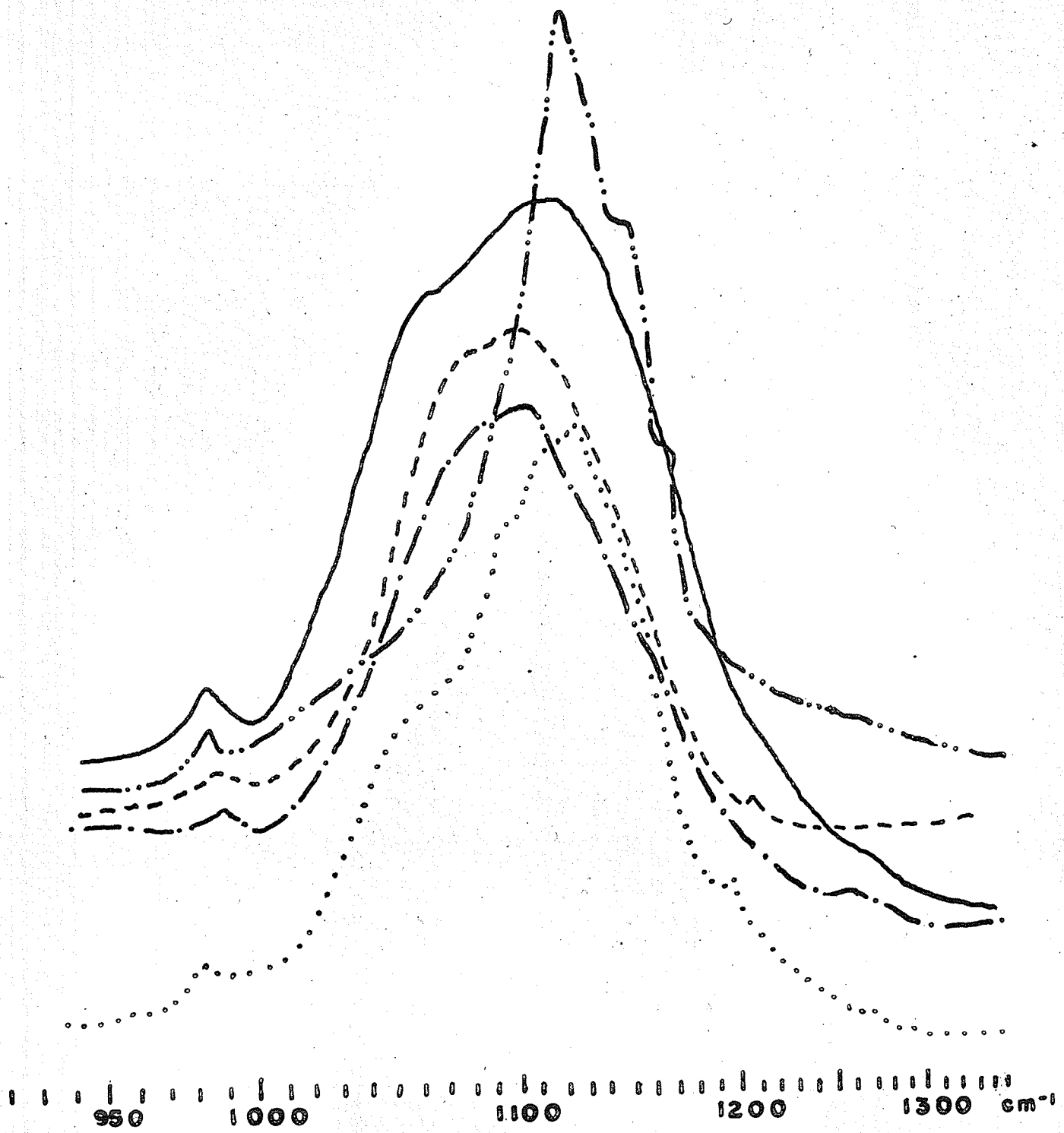

950
1000
1100
1200
1300 cm⁻¹
5 minutes
12 minutes
38 minutes
40 minutes
n= 4·6
n= 5·8 Nujol

Figure 19

Infrared absorption spectra for $Cr_2(SO_4)_3$ 16.3 H_2O

Method 1, 2 and 3 as described on page 107

Method 4 as described as page 112


950
1000
1100
1200
1300
cm⁻¹
Method 1
Method 2
Method 3
Method 4
K_2SO_4

produce satisfactory results in all samples where this was used. Its advantages, however, were not appreciated until most of this work was completed. This method has found application in other laboratories[23] and should prove very useful in the preparation of inorganic compounds which are soluble in volatile organic liquids, for solution of the sample in the volatile liquid followed by rapid evaporation of this liquid should leave a fine powder and, consequently very little scattering and good resolution of the bands.

The spectra in Figure 19 show features that occurred very frequently in the spectra of these compounds. The main absorption band in spectrum number 1 is seen to lie at slightly lower frequencies than the band in spectrum number 2 and the composite of bands in spectrum number 3. There is no resolution of the 1060 cm^{-1} band in spectrum number 1 as observed in numbers 2 and 3. This lack of resolution may be seen as well in the two spectra of the 4.6 hydrate as shown in Figure 18. Poor resolution and slight shifting of the bands to lower frequencies is often associated with scattering due to large particle size and has been observed in many of our spectra for the samples where it was obvious that a poor grind of the sample had been obtained.

Meloche and Kalbus[23] in their investigation of the infrared absorption spectra of inorganic compounds, found

anomalous behaviour, due to exchange, between the spectra obtained by the potassium bromide and the Nujol mull techniques. The latter consisted of mixing the ground sample with a mineral oil, whose absorption was then determined after it had been spread between two rock salt plates. The anomalous behaviour was evident in the appearance of absorption bands due to potassium sulphate in the absorption spectrum of a sulphate compound and was explained as due to ion exchange between the sulphate and the bromide ion. Their conclusion was that the major factor in this exchange was the presence of moisture in the sample, in potassium bromide, and moisture picked up in the grinding process, and was most evident in the hydrates with low temperatures of dehydration and generally absent from anhydrous materials. In this investigation the potassium bromide was stored at 200°C and all samples, where possible, were dried at 65°C prior to preparation for spectral analysis, in order to minimize this exchange.

Examination of the spectra in Figure 19 shows that a band at 985 cm^{-1}, presumably due to potassium sulphate, is present in spectra numbers 2 and 3 and absent in number 1, indicating that ion exchange has occurred in the first two. It is evident that this exchange must occur in the grinding process of the sample when mixed with potassium bromide because if this exchange occurred during the pelletization process when pressure is applied to the sample in the die,

then spectrum number 1 should show this band as well. Since it does not, one may conclude that the exchange process takes place during the grinding process. The presence of the 985 cm^{-1} band need not cause any difficulty in the interpretation of the spectrum provided its existence is recognized. The spectrum of the exchange products, however, may contain bands other than those due to potassium sulphate or the original hydrate. It is the recognition of these bands which are of concern in the interpretation of the spectra in which exchange is evident. It was deemed necessary, therefore, to examine the spectrum (number 4, page 109) of this hydrate employing the mull technique, but it was found that the spectrum produced was no better than that obtained by the pellet technique in which the sample was ground by itself. The reason for this is obvious, because in order to prevent caking of the hydrate during the grinding process, the hydrate was mixed with the mineral oil prior to grinding; the latter acts as a lubricant and, therefore, prevents the effective reduction in particle size. This spectrum represents the best one obtained by this method and shows the same features as observed for spectrum number 1 in Figure 19. This spectrum indicates that the 1060 cm^{-1} band might be present, in that widening of the spectrum occurs in this region, but the resolution is such that

this conclusion is pure conjecture. Thus we have two spectra numbers 1 and 4 in which ion exchange is absent, indicating the possible nonexistence of an absorption band at 1060 cm^{-1} and two spectra numbers two and three, in which ion exchange is evident and which show the existence of this band. It would seem that the obvious source of this band is an absorption due to a compound of chromium(III) bromide, but the two spectra which do not show the 1060 cm^{-1} band, show behaviour, shifts to lower frequencies and simultaneous poor resolution, often associated with large particle size.

Assuming that this band (1060 cm^{-1}) is due to absorption of the products resulting from the ion exchange process, which as shown previously, occurs during the grinding process, one must expect the intensity of this particular band to increase as the grinding of the sample in potassium bromide becomes more violent. In other words, examination of the spectra of the grinding products obtained in the Wig-L-Bug, should show an increase in the intensity of the 1060 cm^{-1} band as the hydrate is subjected to longer periods of grinding. These spectra should also show the appearance of the main absorption band at 1115 cm^{-1} for potassium sulphate if the latter is produced in any appreciable amounts. Examination of the spectra in Figure 18 does not verify this prediction. Instead, the exact opposite behaviour is observed in that the 1060 cm^{-1} band disappears as grinding

proceeds and there is no evidence of the 1115 cm^{-1} band. The apparent discrepancy between the 38 and 40 minute grind is due to the sample size used in the two runs. The latter contains approximately three times the amount of material (sample plus potassium bromide) and, therefore, the grinding would be more gentle. Since the 1060 cm^{-1} band disappears upon grinding one may conclude that this band is not due to absorption by exchange products (if any) formed in the grinding process.

The spectra obtained for the 16.3 hydrate indicate clearly the need for small particle size in determining the infrared absorption of any compound. This work indicates that those hydrates which decompose readily, are best ground when mixed with a carrier such as potassium bromide, under a volatile organic liquid. This work supports the conclusion, of Meloche and Kalbus[23], that the results obtained by the pellet technique should be used with caution, and that these results be checked by other methods. This has been achieved in these spectra by comparison of the mull and pellet spectra. For the 16.3 hydrate, where these two do not agree, a reasonable interpretation of this discrepancy has been advanced. The best spectrum obtained for the 16.3 hydrate is number 3 in Figure 19. Since the 985 cm^{-1} band presumably due to potassium sulphate, appears in this spectrum, one is not able to assign all of these bands to the hydrate of

chromium (III) sulphate, but it is reasonable to assume that most of the bands in this composite set must belong to the hydrate, especially since this composite does not contain the main peak of potassium sulphate at 1115 cm^{-1}.

For the other hydrates no anomalous behaviour was observed. The conclusions of Meloche and Kalbus are verified in this work in that the hydrate with the lowest temperature of dehydration is the only compound that showed the anomaly. The absorption spectra of the 4.58 hydrate in Figure 18 employing the mull technique, and the pellet technique show identical patterns except for poor resolution in the mull spectrum. The spectra of all the hydrates of interest are shown in Figure 20 and a schematic representation of their bands in Table 7. These are the best spectra that have been obtained and have been compared to the spectra in which the product was subjected to mild grinding; these showing no behaviour different from that shown other than much poorer resolution very similar to that shown for the 4.58 hydrate in Figure 18.

The absorption bands of the series of chromium (III) sulphates obtained by dehydration of the 16.3 hydrate, in the 2000 cm^{-1} to 3800 cm^{-1} region are shown in Figure 21 and compiled in Table 7. Some of these spectra show two peaks at 2850 and 2950 cm^{-1} which are due to the absorption

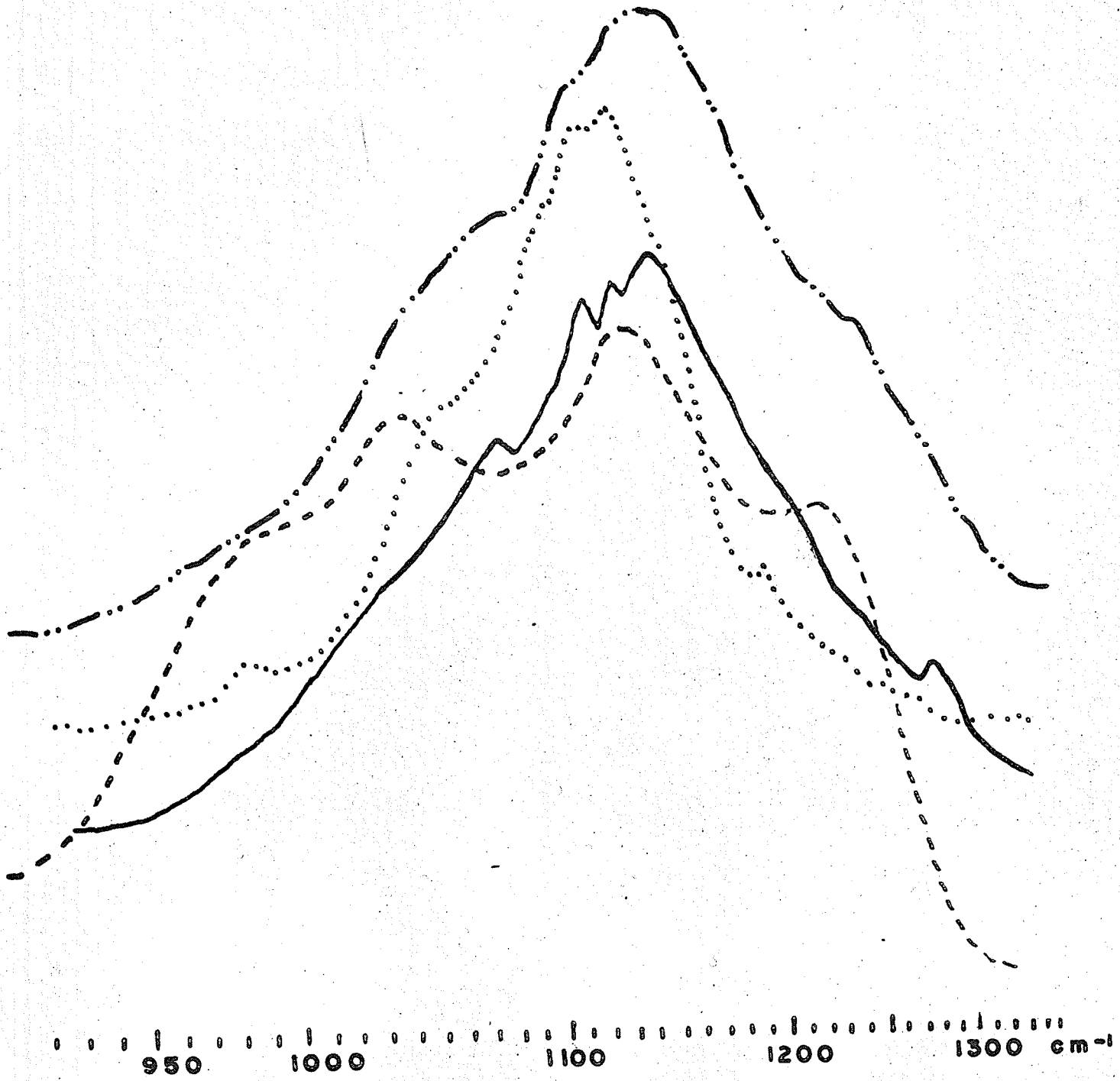
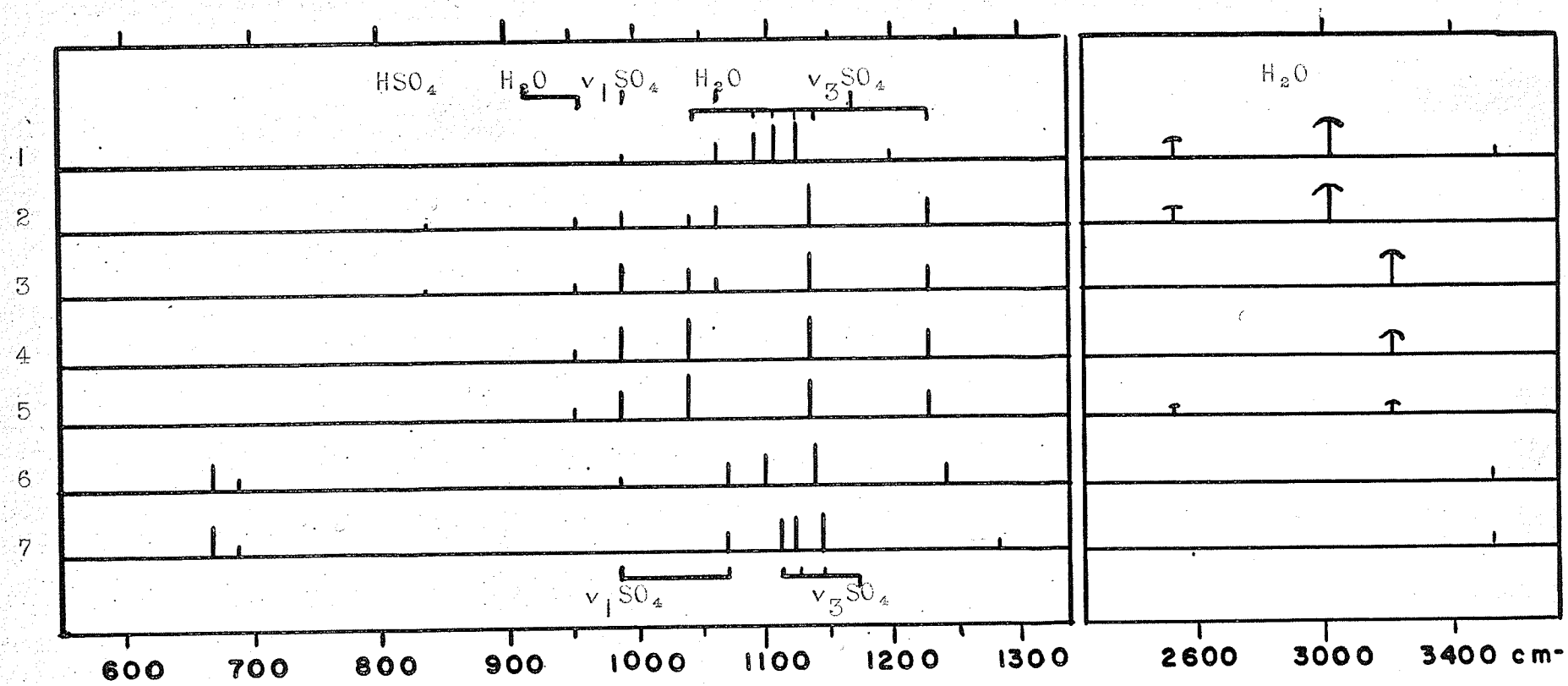

950
1000
1100
1200
1300 cm-1
n = 16·3
n = 4·6
n = 2·1
n = 0

TABLE 7

Schematic representation of the infrared absorption bands for various hydrates of chromium (III) sulphate



1) $Cr_2(SO_4)_3$ 16.3 H_2O

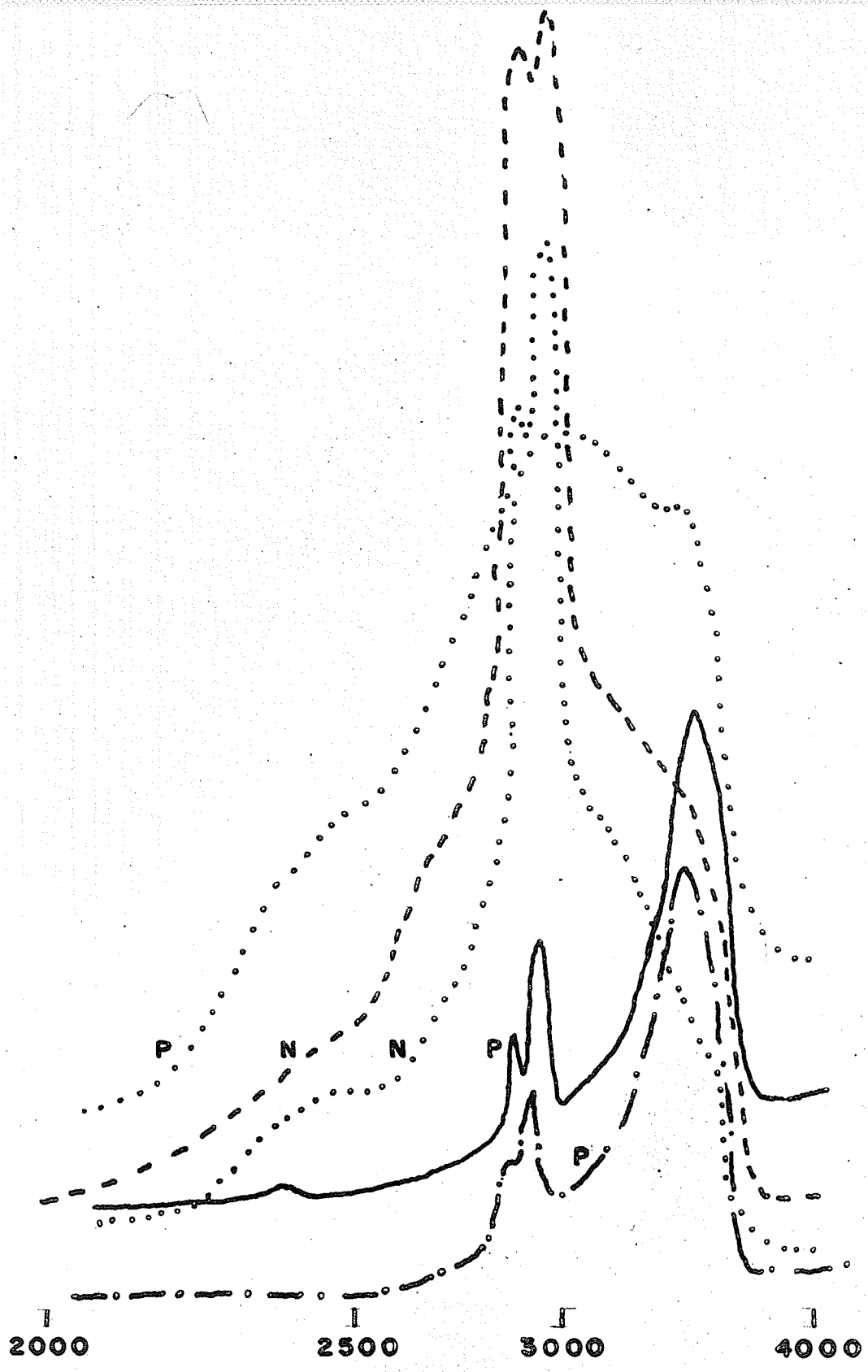
$Cr_2(SO_4)_3$ 16.3 H_2O ground in Wig-L-Bug for 2) 10 minutes 3) 40 minutes 4) 38 minutes

5) $Cr_2(SO_4)_3$ 4.6 H_2O 6) $Cr_2(SO_4)_3$ 2.1 H_2O 7) $Cr_2(SO_4)_3$

by the mulling agent used in mulling samples. As noted previously, the mortar and pestle had to be scrubbed with Ajax cleanser to render it clean after a water insoluble compound had been ground in it. To test this cleaning procedure a pellet pressed from potassium bromide which had been ground in the mortar and pestle after cleaning was examined in the spectrograph. These blanks showed no absorption in the sulphate region but occasionally showed these two peaks. Their source was not immediately evident but since they are the same two peaks observed in the mulling agent and since the agate mortar and pestle is the same one used for mulling samples, these two bands may be due to the mulling agent. Unfortunately it took some time to realize the difficulty in rendering the mortar and pestle ''spectroscopically clean'' and, therefore, contamination resulted.

Figure 21

Infrared absorption spectra for various hydrates of chromium(III) sulphate. (water region)



n = 16·3 ·····

n = 4·6 – – – –

n = 2·1 —·—·

n = 0 ——

P = KBr Pellet

N = Nujol mull

INTERPRETATION OF WATER BANDS

Table 7 shows the infrared absorption spectra of a series of hydrates of chromium (III) sulphate. All spectra obtained by the pellet technique show absorption bands at 3450 cm^{-1} and 1620 cm^{-1} (not shown) even when no sample is introduced into the potassium bromide. These two bands may be attributed to the symmetric and antisymmetric vibrations of water, invariably present in the potassium bromide, and to the bending or deformation mode of water. The 3450 cm^{-1} band is due to the antisymmetric stretching (v_3), whereas the tailing observed on the lower frequency side is due to the symmetric vibration (v_1). It is of interest to note that the stretching vibrations have been lowered from the values observed in gaseous water, v_1(3657 cm^{-1}) and v_3(3756 cm^{-1}), and the bending mode, v_2, has been raised from 1595 cm^{-1}.[24]

All hydrates with n greater than 12 show two bands, one centered near 3000 cm^{-1} and another near 2500 cm^{-1}, and a strong shoulder at 3500-3600 cm^{-1}, evident only in the Nujol mull spectra of the 16 hydrate and the anhydrous sulphate. A possible assignment would attribute the 3500-3600 cm^{-1} to water of wetting or of absorption present in these compounds. The frequencies observed for this water are very close to those observed in liquid water, 3450 and 3220 cm^{-1}. The presence of the water of wetting was evident in the pyrolysis of this

hydrate in that it lost water below 50°C to produce the 13.5 hydrate. A possible assignment of the two bands, 3000 and 2500 cm^{-1} would be to the stretching vibrations v_1 and v_3 of water, drastically modified by hydrogen bonding to the sulphate ions in the lattice and by coordination to the chromium (III) ions. The band at 1640 cm^{-1} would be the deformation frequency v_2, again modified as are v_1 and v_3. This is in agreement with the general observation that hydrogen bonding lowers the numerical values of the stretching frequency and increases the value of the deformation frequency.[24,25,26] These are admittedly, very large shifts, but not totally unexpected since in ice v_1 has the value of 3400 cm^{-1}.[27,p82] Jones[57] obtained a very broad band at 2800-3200 cm^{-1} for the absorption of water in $LiOH \cdot H_2O$ and others[25,26] have found bands as low as 1500 cm^{-1} where extreme hydrogen bonding exists.

A different interpretation is required, however, for the following reasons. The separation of frequencies v_1 and v_3 is found to be 100 cm^{-1} in the gaseous state, 226 cm^{-1} in the liquid state, and 180 cm^{-1} in the solid state.[27,p83] In gypsum, where each water molecule is hydrogen bonded to two sulphate groups, the difference between the lowest and highest component for v_1 and v_3 is 135 cm^{-1}.[24] Both v_1 and v_3 vibration frequencies are due to the stretching of the O-H bonds and hence any changes causing frequency shifts in

one vibration should cause similar shifts in the other. The bands in the spectra (Figure 21) are sufficiently broad that one band would contain the absorption due to the two vibration frequencies, v_1 and v_3, if the separation of these two frequencies is of this magnitude. The two bands must then be assigned to two non-equivalent sets of water present in the crystal lattice. It was evident from the pyrolysis data that 13.5 molecules of water were different from the 2.8 molecules of water which were lost below 50°C. Of these 13.5 molecules, 12 probably provide octahedral coordination for the two chromium ions, thus leaving 1.5 molecules of water strongly hydrogen bonded to the sulphate groups. Taking into account the intensity of the two bands, one must assign the larger of the two, at 3000 cm^{-1}, to the coordinated water and the 2500 cm^{-1} must then be assigned to the water hydrogen bonded to the sulphate ions. This assignment is intuitively unsatisfactory, because the lower the force constant for the O-H bond the lower the frequency of absorption.[25,26] This implies that the water molecules hydrogen bonded are held more strongly than those coordinated to the chromium ions. Also the above assignment does not agree with the observation that the 5.65 hydrate still shows the 2500 cm^{-1} band with a very low intensity, though it is impossible to envisage the same distribution of water as exists in the 16 hydrate. One must look for a more acceptable assignment.

Before a new assignment is possible it is best to look at the complete spectrum of the 16 hydrate. All of the bands in Figure 20, except the band at 1060 cm^{-1} may be assigned to absorption of the sulphate group; the 1060 cm^{-1} band is best regarded as due to absorption of water. For the moment we will anticipate the ultimate assignment of this band, which is due to the rocking, wagging and/or twisting mode of water and it becomes infrared active only if strong covalent bonding between the metal ion and water exists and is intensified by hydrogen bonding of the water to the associated anions in the lattice. This means that the lattice contains water molecules coordinated to the chromium ions and simultaneously hydrogen bonded to the sulphate group.

From the pyrolysis data we know that 13.5 molecules of water are rather firmly held in the lattice of the 16 hydrate, 12 of these can provide octahedral coordination for the two chromium (III) ions and 1.5 can serve as water bridges between two sulphate groups to form $(H_2S_2O_9)^{-4}$, $(O_3SO\text{---}H\text{-}O\text{-}H\text{---}OSO_3)^{-4}$. This arrangement would lead to C_{3v} symmetry for the sulphate group. Since the coordination of the water molecules to chromium ions is expected to increase the positive character of the protons in water, it is probable that these will form hydrogen bonds with the sulphate group as well. If it is assumed that the three oxygens, other than the one already hydrogen bonded , form

such hydrogen bonds, the twelve water molecules coordinated to the chromium ions would then form two nonequivalent sets of water. Of the 24 protons or O-H bonds in the lattice per 2 chromium ions, 9 would be bonded as discussed above, 3 for each of the 3 sulphate ions and 15 would be bound only to an oxygen atom which , of course, is coordinated to the chromium ion. The 9 hydrogen-oxygen bonds would have lower force constants than would the other fifteen and the latter would then be assigned to the absorption band at 3000 cm^{-1} and the former to the band at 2500 cm^{-1}. It is difficult to say where the absorption due to the 1.5 molecules of water which act as hydrogen bridges should occur. Their contribution to the intensity of a band will of necessity be small, and may contribute to either of the bands or even have a band of its own which because of its low intensity has not been observed. This distribution leads to reasonable relative intensity of the two bands as observed in the spectra, and provides as well for the infrared activity of the 1060 cm^{-1} band.

Fujita et al[29] show that the N-H stretching frequency is lowered whereas the rocking mode is shifted to higher values by coordination of NH_3 to a metal. These effects are increased as a result of hydrogen bonding to the associated anion or to neighbouring complex ions. For the iodide, bromide and chloride salts, this effect increases in the

order of their ability to form hydrogen bonds. The effect of coordination of the metal is shown to parallel the stability of the complexes, i.e. the most stable complex exhibits the greatest shift in frequency. These same effects seem to operate in the aquo complexes for in order that the rocking, wagging and twisting modes be observable in the sodium chloride region (650-4500 cm^{-1}) both coordination and hydrogen bonding must be present. If either of them is weak the absorption due to these modes will not be observed.[29] Fujita et al[29] assign two infrared active bands at 965 and 1012 cm^{-1} to coordinated water in the compound $K[Cr(ox)_2(H_2O)_2]$ 3 H_2O. These bands result from the wagging, twisting and rocking modes, which become infrared active when water becomes coordinated. The latter compound is likely to contain weaker $Cr-OH_2$ bonds than does $[Cr(H_2O)_6]_2(SO_4)_3$ n H_2O because the coordinated oxalate ion transfers charge to the chromium ion in the formation of a covalent bond and as a result weakens the $Cr-OH_2$ bond. Similarly the small charge on the oxalate or neighbouring complex ions will form weaker hydrogen bonds than would the sulphate group. The frequency of absorption due to these modes would, therefore, be higher in the 16 hydrate of chromium (III) sulphate than in potassium diaquodioxalatochromate (III). The 1060 cm^{-1} band finds a reasonable assignment when attributed to one of the wagging, rocking or twisting modes of coordinated

water, and its disappearance upon grinding is to be expected, for as the sulphate group becomes coordinated to the chromium ions, the $Cr-OH_2$ bond becomes weaker as a result of charge transfer from the sulphate to the chromium ion, resulting in a smaller coordination effect. Simultaneously the effect of hydrogen bonding would become less. If the above assignment is correct, one should expect to see this band shift to lower frequency and eventually disappear as coordination of the sulphate group proceeds upon dehydration and a simultaneous shift to higher frequencies is expected for this vibrational frequency of the water. Examination of the data in Table 7 shows that the 1060 cm^{-1} band is not evident in the hydrates with n values less than 4.58. The absorption increases in the 950 cm^{-1} region as dehydration proceeds and then disappears again for the hydrates with n values less than 4. The 2500 cm^{-1} band gradually disappears and the 3000 cm^{-1} band shifts to a higher frequency (3200 cm^{-1}) as dehydration of the hydrate proceeds.

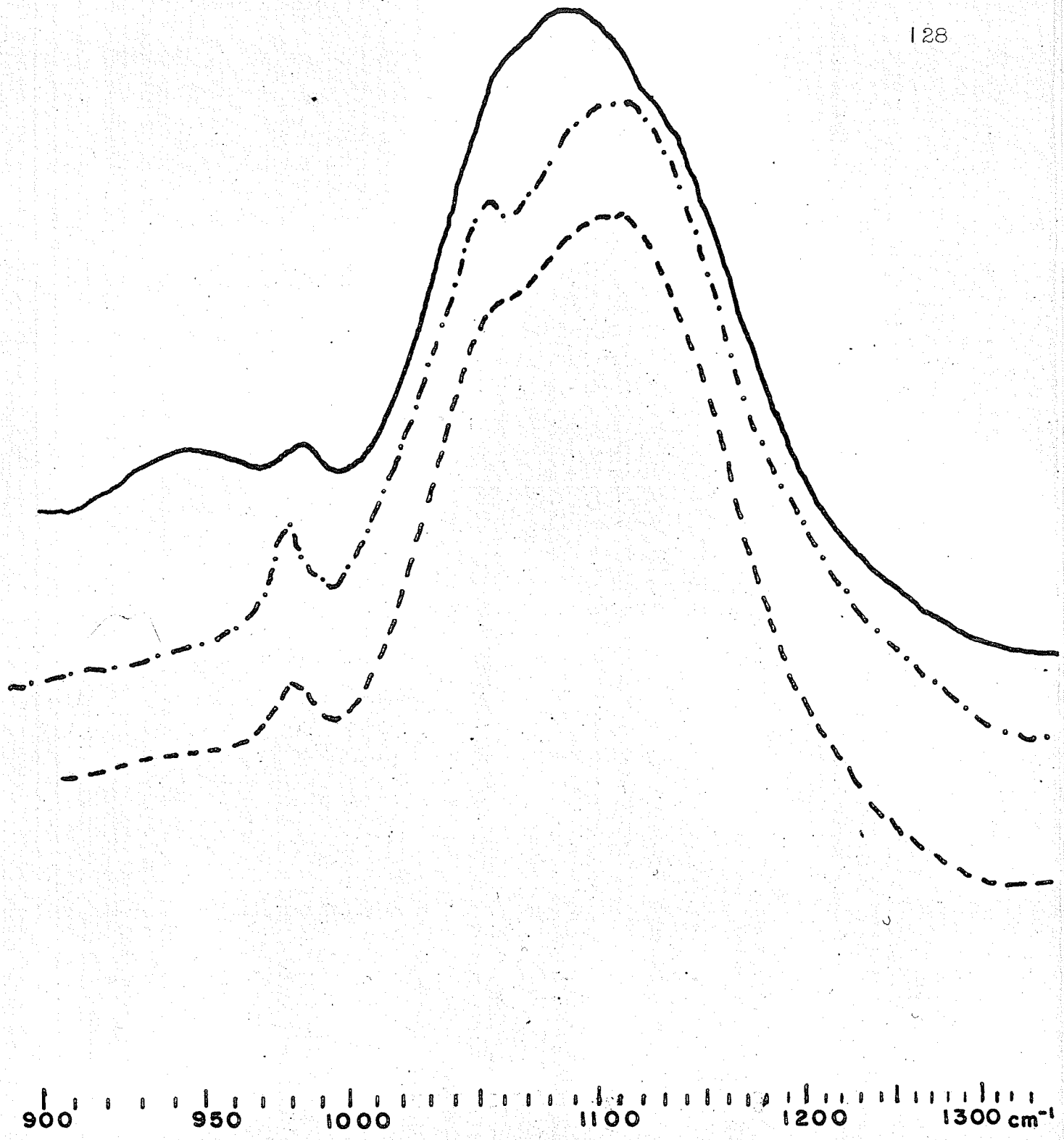
Harmelin's observation[30] on the hydrates of chromium (III) sulphate agree with the above observations but she reports the presence of a band at 940 cm^{-1} in the spectra of the hydrates with n values between 14-18. This band is reported as well by Harmelin and Duval[31], who also report the presence of this band in chromealum. The

16.3 hydrate and recrystallized chromealum do not show the presence of this band in our spectra. It was noticed, however, that several recrystallizations of the 16 hydrate were required before a satisfactory chromium to sulphate ratio (1.52) was obtained in its preparation. The impure product had a sulphate to chromium ratio of 1.59 and showed a broad, low intensity absorption band at 940-950 cm^{-1}. (Figure 22) This band appears in the dehydrated products and its presence is first noted in the 12.1 hydrate. It is likely that this band at 940 cm^{-1} is due to partially dehydrated forms such as $(Cr(SO_4)_2(H_2O)_6)^-$, and not to the dodecahydrate of chromium (III) sulphate. They do not report the presence of the 1060 cm^{-1} band but in view of the difficulty of reducing the particle size of this hydrate, it may be that they encountered difficulty in obtaining good resolution.

There is no reason to exclude the existence of hydroxyl groups or hydroxyl bridges in the partially dehydrated forms of chromium (III) sulphate. Scargill[32] has shown that the deformation mode (δ OH) of M-O-H (coordinated hydroxyl group) tends to zero intensity as the metal oxygen distance increases (i.e. as the hydroxyl group becomes more ionic) and that δ OH increases and the vibration frequency of the hydroxyl group (ν_{OH}) decreases as the hydrogen bond to the associated anion becomes stronger. He assigns the ν_{OH}

Figure 22

Infrared absorption spectrum for potassium chrom alum, for impure and recrystallized violet chromium(III) sulphate.


900
950
1000
1100
1200
1300 cm⁻¹
Impure violet chromium(III) sulphate
Potassium chrom. alum
Recrystallized violet chromium(III) sulphate

frequency to bands between 3200 cm^{-1} and 3500 cm^{-1}, and the δ OH frequency to bands between 925 cm^{-1} and 1000 cm^{-1}, in nitrosyl ruthenium complexes. It is possible, therefore, to assign the 950 cm^{-1} band to the presence of hydroxyl groups in the partially dehydrated forms but absent in the 16 hydrate. If these hydroxyl groups are formed one must have the simultaneous production of bisulphate or coordinated bisulphate groups. Potassium and sodium bisulphate show two very strong absorption bands near 850 cm^{-1} and four strong bands between 1000 and 1300 cm^{-1}.[33] The absorption spectra of the partially dehydrated products show four bands in the 1000 to 1300 cm^{-1} region, but there are no absorption bands near 850 cm^{-1}, except in the spectra obtained from the two products of grinding (numbers 2 and 3, Table 7). The general absence of absorption bands near 850 cm^{-1} for these partially dehydrated products suggests that bisulphate groups are not present. The most logical explanation for the fleeting appearance of the 835 cm^{-1} band is that in the initial stages of dehydration, hydroxyl and bisulphate groups are formed, but as coordination of the sulphate group proceeds, hydrogen bonding between the bisulphate and the hydroxyl groups will make it meaningless to speak of the H^+ as being bonded to the OH^- or the $SO_4^=$ group.

The interpretation of the infrared absorption due to the water present in the 16.3 hydrate leads to the following

conclusions. The first band at 3500-3600 cm^{-1} appears only as a shoulder and is assigned to the lattice water in the hydrate. The second band centered near 3000 cm^{-1} is assigned to the v_1 and v_3 symmetric and antisymmetric stretching vibrations of coordinated water molecules, which are not hydrogen bonded to the sulphate groups. The third band, centered near 2500 cm^{-1}, is assigned to the stretching frequencies, v_1 and v_3, of water molecules coordinated to chromium ions and hydrogen bonded to the sulphate groups. The fourth band, centered near 1640 cm^{-1} and relatively broad, is assigned to the deformation mode v_2 for water. A fifth band at 1060 cm^{-1} is assigned to the rocking, wagging and/or twisting mode of coordinated water hydrogen bonded to the sulphate group.

As dehydration proceeds one notices the gradual disappearance of the 1060 cm^{-1} band and the 2500 cm^{-1} band with a simultaneous shift to higher frequncy (3200 cm^{-1}) of the 3000 cm^{-1} band. A new band appears at 950 cm^{-1} which is assigned to the coordinated water molecules in the partially dehydrated forms. The 950 cm^{-1} band disappears again for n values below 4. The band at 3200 cm^{-1} disappears as dehydration proceeds to completion.

INTERPRETATION OF SULPHATE BANDS

An absorption spectrum due to a sulphate ion (ligand), in the series of hydrates of chromium (III) sulphate may be placed in one of the three distinct classes enumerated on page 103. The 16 hydrate belongs to the first class and shows three bands at 1090, 1105, and 1125 cm^{-1} all with a high intensity and a very low intensity band at 980-90 cm^{-1} (Figure 19). The latter may be assigned to the breathing frequency, v_1, of the sulphate and the three strong bands may be assigned to the triply degenerate mode of vibration v_3. The small splitting of v_3 and the low intensity of the v_1 frequency indicate that this hydrate is properly placed in our first class which one might call the free sulphate in the crystalline state or, synonymously the ionic sulphate in solids. This pattern characteristic of C_{2v} symmetry represents slight reduction (perturbation) in symmetry due to the crystal field or hydrogen bonding. The 1190 cm^{-1} band is obviously an overtone of v_4 (610 cm^{-1} Harmelin[30]) in keeping with the low intensity usually observed for these bands.

The hydrates with n values between 4 and 6 belong to the second class. These spectra show four absorption bands of comparable intensity (Figure 20). The first, assigned to the breathing frequency v_1 at 980 cm^{-1}, is infrared active in these compounds. The three bands at 1040, 1135, and

1230 cm^{-1} are assigned to the triply degenerate ν_3 vibration of the sulphate, which show a total splitting of 190 cm^{-1}. This large splitting and intensification of the spectra would leave no doubt that reduction of symmetry has occurred as a result of coordination of the sulphate ligand. The triplet structure indicates that the sulphate possesses C_{2v} symmetry, but it is impossible to say whether the bidentate sulphate ligand acts as a bridging or a chelating group.

The absorption spectra of the grinding products obtained by grinding the 16 hydrate in a Wig-L-Bug show quite clearly the transition from the 16 hydrate to the compounds of the second class (Figure 18). The 5 and 10 minute grinds clearly represent a transition stage, whereas the 38 and 40 minute grinds are identical to the second class, except for the small peak at 1060 cm^{-1}, previously assigned to absorption by water, in the 40 minute grind.

The spectrum of the 2.1 hydrate (Figure 20) would appear to represent a transition state between the hydrates containing 4 and 0 molecules of water. The bands are poorly defined and the spectrum shows strong shoulders at positions corresponding to the bands for the 4-6 hydrates. The spectra of the anhydrous chromium (III) sulphates, shown in Figure 20, resemble somewhat the spectra of the first group, except that the frequencies have been shifted to higher values.

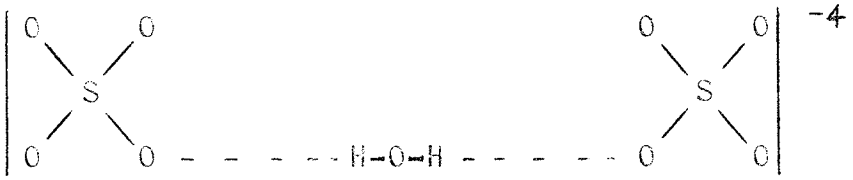
There are, in addition, more bands in the form of strong shoulders which have not been properly resolved, lack of resolution for this compound is not thought to be due to lack of reduction of particle size but rather due to some random arrangement of the sulphate ligands in the solid state.

The spectrum of anhydrous chromium (III) sulphate shows two unresolved bands at about 1040 and 980 cm^{-1} as well as unresolved absorption bands between 1150 and 1280 cm^{-1} in addition to a doublet at 1070 cm^{-1}, a triplet at 1112, 1125 and 1140 cm^{-1}, and a low intensity band at 1285 cm^{-1}. The latter five bands are identical to those reported by Harmelin[30] for the anhydrous chromium (III) sulphate. Harmelin[30] assigns the 1285 cm^{-1} band to the first harmonic of ν_4, the 1070 cm^{-1} band to ν_1 and the triplet to ν_3. These assignments lead to the conclusion that this spectrum is characteristic of a sulphate ligand possessing C_{2v} symmetry. This assignment, however, is not in keeping with our classification because the splitting observed for the triplet (28 cm^{-1}) is too small to be indicative of reduction in symmetry due to coordination and the other bands even though they are not resolved must be accounted for. It is not suggested that coordination of the sulphate group does not occur in the anhydrous sulphate. In fact, it is thought that all four oxygens are coordinated

to chromium ions, but coordinated in such a manner as to preserve the T_d symmetry expected for a regular tetrahedron. Whatever the structure is, strong coupling must exist between the sulphate groups and, therefore, the complexity of this spectrum may be explained by the selection rules given by factor group analysis of the crystalline state. This spectrum is essentially identical to the spectrum of the product AA whose spectrum shows better resolution as shown in Figure 28. Arguments to support an interpretation of this spectrum will be advanced later. For the present, these conclusions will only be stated. The sulphate group in the anhydrous chromium (III) sulphate possesses C_{2v} symmetry, not as a result of coordination but due to lattice requirements. This means that the sulphate ligand is symmetrically coordinated but that the sulphate ligand lies along a C_{2v} symmetry axis of the crystal.

d) THE MECHANISM OF DECOMPOSITION

The first step in the dehydration process involves a 7.2% weight loss which is attributed to loss of lattice water. Thus, with reference to the formulation of the hydrate as $Cr_2(SO_4)_3$ n H_2O one obtains the hydrate having an n value of 13.5. The rate at which water is lost between 50° and 80°C is so slow that one observes a plateau in the thermogram for this temperature interval. Twelve of the 13.5 water molecules provide regular octahedral coordination for the two chromium (III) ions, while the other 1.5 molecules of water are hydrogen bonded to the sulphate ions in the following manner:



The other six oxygens from the above ion $H_2S_2O_9^{-4}$, though not necessarily all, are hydrogen bonded to the coordinated water molecules. One could thus write several formulas for the hydrate, $Cr_2(SO_4)_3$ 13.5 H_2O or $[Cr(H_2O)_6]_4$ $(H_2S_2O_9)_3$. Harmelin[30] reports that the first loss in weight occurs in the temperature interval from 35 to 80°C and is such that the resulting hydrate always has an n value of 14 and is stable up to a temperature of 115°C whereas Lukaszeweski[45] reports the loss of 1 molecule of water between 60 and 100°C resulting in the formation of the

15 hydrate which is stable up to 120°C. The second loss of water occurs in a series of fast steps. The one and a half molecules of water per mole of $Cr_2(SO_4)_3$ hydrogen bonded to the sulphate groups, and some of the coordinated water would seem to be lost simultaneously. It is evident, from the infrared absorption spectra of the pyrolysis products formed in the second stage, that coordination of the sulphate group occurs simultaneously with water loss. The infrared absorption spectra show a symmetry characteristic of either a chelating or a bridging group for the sulphate ligands. The disappearance of the 1060 cm^{-1} band at this stage is not unexpected because the mode of vibration giving rise to this band is very sensitive to the strength of the $Cr-OH_2$ bond and to the hydrogen bonding between the water and the associated anion.[29] The absorption due to water is shifted to lower frequency (950 cm^{-1}) and suggests that either the resulting $Cr-OH_2$ bond has been weakened or that hydrogen bonding has become less, or both. It might be noted that Harmelin[30] reports that the infrared absorption spectrum of the deuterated hydrate does not show the band at 940 cm^{-1} and, therefore, assigns this band to absorption by water. Since the last four molecules of water are lost only at higher temperatures, one might ask, is it reasonable to assume, as we have done, that the $Cr-OH_2$ bond is weaker in the 4 hydrate than in the higher hydrates? This is a valid

assumption because loss of water is presumed to result through displacement of the coordinated water molecule by an oxygen from the sulphate groups. Loss of water, therefore, is not governed by the strength of the $Cr\text{-}OH_2$ bond but by the ease whereby this displacement can occur. This will largely be determined by the steric difficulties encountered in the displacement.

Since the hydrate with an n value of 4 that is produced in the second stage of pyrolysis will dissolve only upon prolonged boiling in an acidified solution, it is suggested that this hydrate is not a mononuclear but a polynuclear complex.[1e] The mononuclear species $[Cr(H_2O)_x\ SO_4]^+$ and $[Cr(H_2O)_y\ (SO_4)_2]^-$ have been shown to be water soluble complexes by Fogel et al.[22] Different mechanisms which might be postulated for the decomposition of the hydrate will be limited by the following considerations, namely: the hydrate with an n value of 4 will be polynuclear and contain bidentate sulphate ligands.

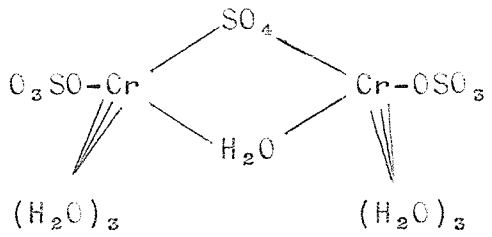
Mechanism I

Step 1 $[Cr(H_2O)_6]_4(H_2S_2O_9)_3 \xrightarrow{fast} [Cr(H_2O)_6]_4(SO_4)_6 + 3\ H_2O$

Step 2 $2\ [Cr(H_2O)_6^{+++} + 3\ SO_4^{=} \xrightarrow{fast}$

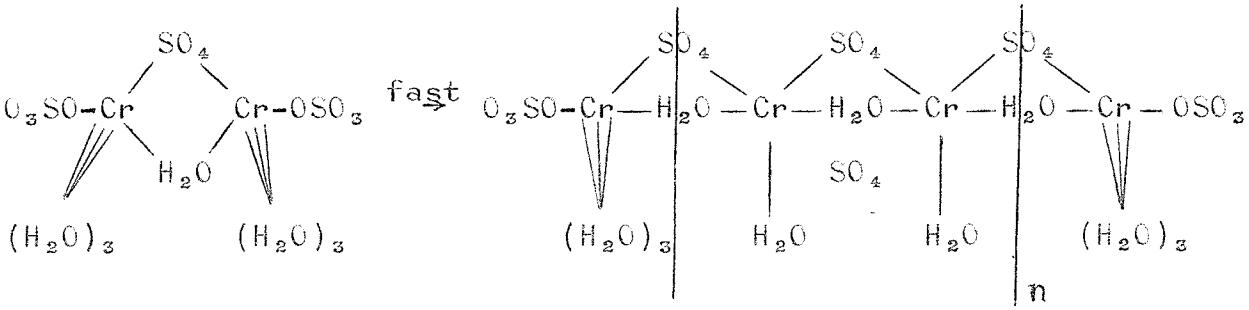
$$[Cr(H_2O)_5SO_4]^+ + [Cr(H_2O)_4(SO_4)_2]$$

Step 3 $[Cr(H_2O)_5SO_4]^+ + [Cr(H_2O)_4(SO_4)_2]^- \xrightarrow{fast}$



+ H_2O

Step 4



In this mechanism, as the polymer chain grows, the total water content approaches an n value of 4 very rapidly. It is easy to see why the intersection of the two slopes observed in the thermogram should have the value of 31%. The total loss of water up to this point, 31% of the original sample weight represents 11.8 moles, thus leaving the hydrate with 4.5 molecules of water in a polymer chain containing a total of 12 chromium ions. The terminal sulphate groups could become chelating groups, displacing one water molecule from the coordination sphere of the terminal chromium ion.

A second mechanism which results in both bridging and chelating sulphate ligands could result from the following steps

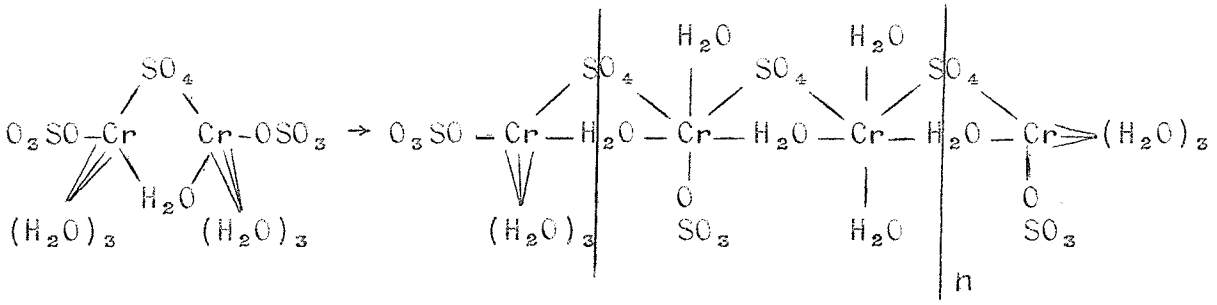
Mechanism 2

Step 1 as in mechanism 1

Step 2 as in mechanism I

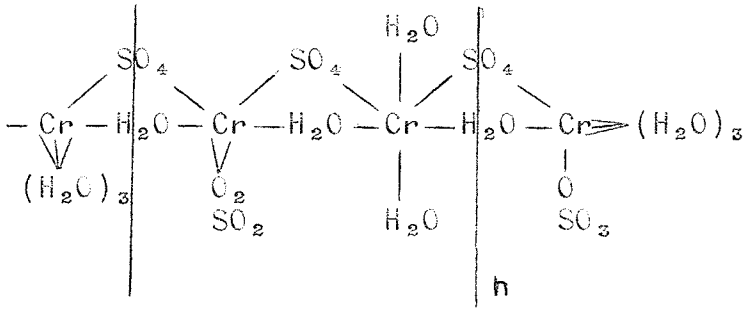
Step 3 as in mechanism I

Step 4



Step 5

Product in Step 4 →



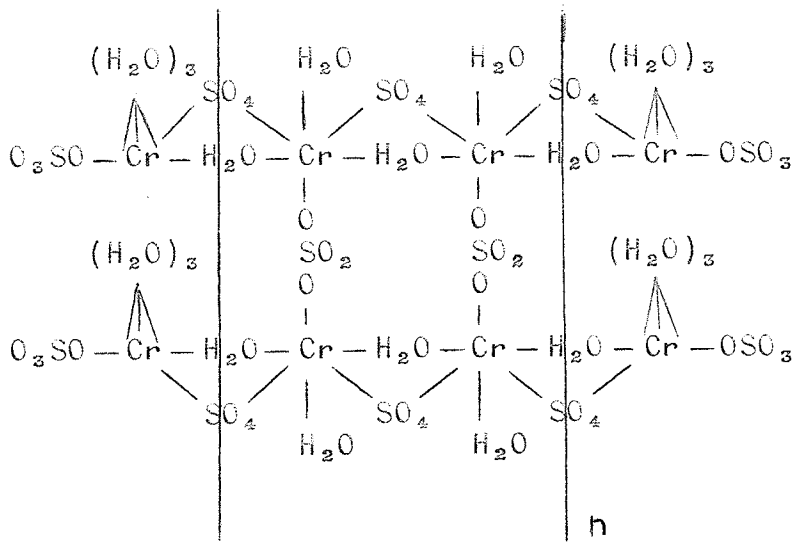
The resulting structure has only one bridging sulphate group between each pair of chromium ions, thus for every three sulphate groups two are bridging groups and the third group is a chelating group. Again, the terminal sulphate groups would become chelating ligands. This structure again leads to a hydrate which may be formulated as $Cr_2(SO_4)_3$ 4 H_2O.

Mechanism 3

Steps I to 4 - as in Mechanism 2

Step 5 involves the cross linking of two polymeric chains

2 [polymeric chains as in products step 4] →



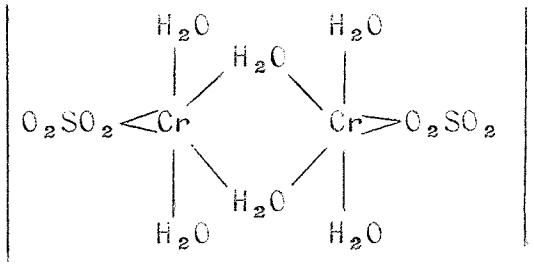
The hydrate representing this structure will again approach an n value of 4 very rapidly as r increases. In fact, it would not be surprising to see this structure approach an n value of three by forming another bridging water group between two consecutive chromium atoms and the elimination of one water molecule for every bridge formed. This possibility did not exist in the first two mechanisms. However, cross linking of polymer chains is apt to be slow and therefore in this mechanism the rate should be much slower after the hydrate with an n value of 5 has been obtained. The intersection of the two slopes occurs at an n value of 4.5 and therefore this mechanism does not agree with the experimental facts.

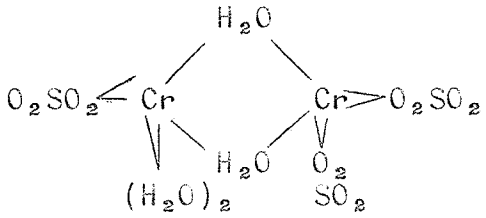
A fourth mechanism which does not involve long range order can be achieved in the following mechanism.

Mechanism 4

1) $[Cr(H_2O)_6]_4(H_2S_2O_9)_3 \xrightarrow{fast} 2[Cr(H_2O)_6]_2(SO_4)_3 + 3\ H_2O$

2) $2\ [Cr(H_2O)_6]^{+++} + 2\ SO_4^{=} \xrightarrow{fast} 2\ [Cr(H_2O)_4SO_4]^{+} + 4\ H_2O$

3) $2\ [Cr(H_2O)_4(SO_4)]^{+} \xrightarrow{fast}$  $+ 2H_2O$

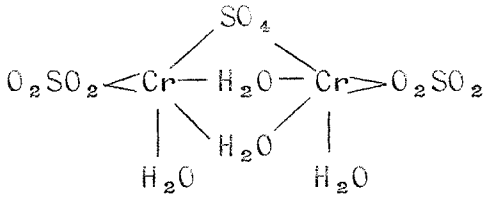
4) Product in 3 + $SO_4^{=} \xrightarrow{slow}$  $+ 2\ H_2O$

or the last sulphate could enter as a bridging group as in mechanism 5.

Mechanism 5

Steps 1 to 3 as in Mechanism 4

Step 4 [reactant as in step 4 above] →

→  $+ 2\ H_2O$

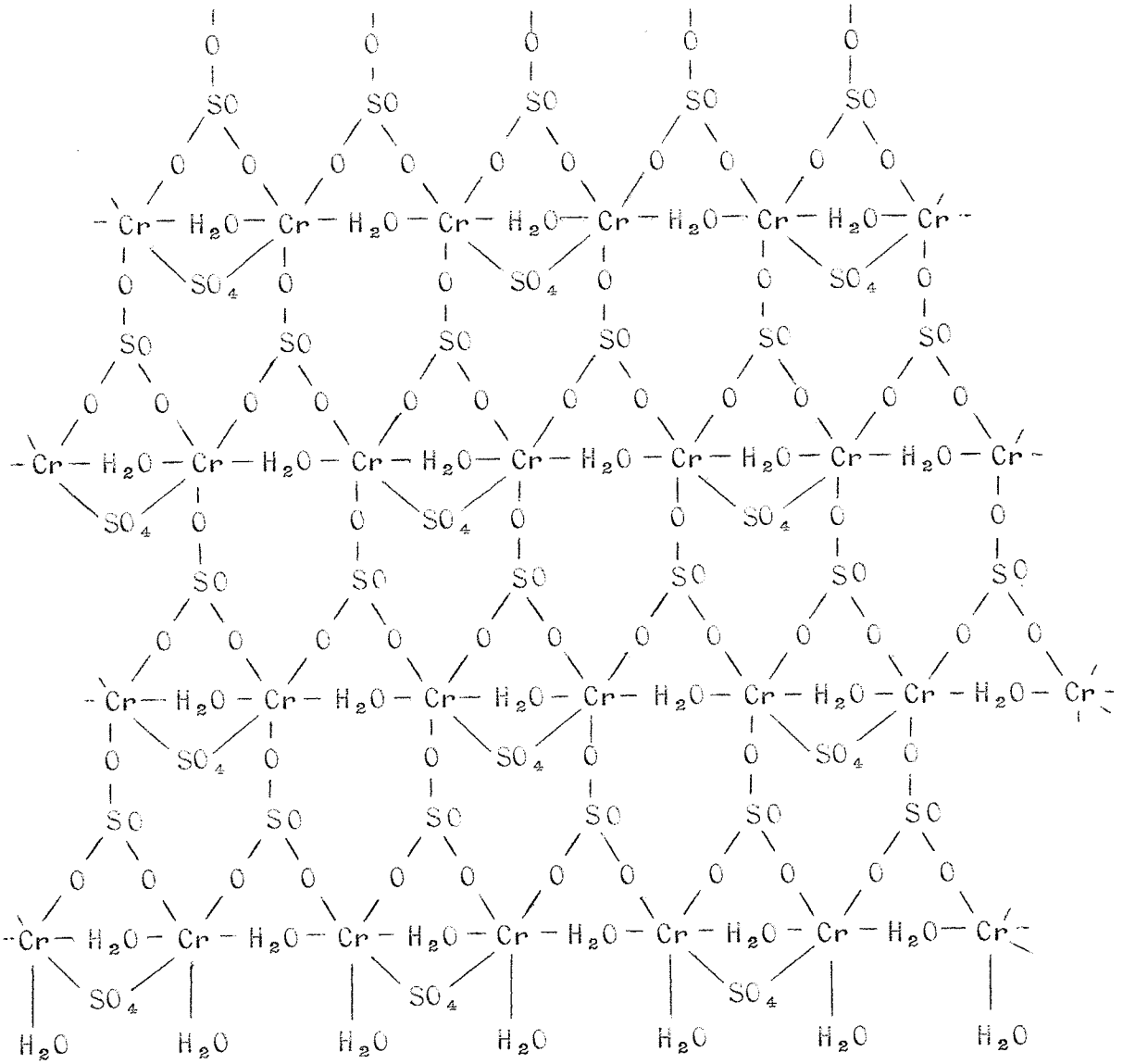
Both mechanisms 4 and 5 lead to a hydrate with an n value of 4 and result in the formation of neutral molecules. The five mechanisms proposed here are the only ones that this author has been able to deduce which are consistent with the experimental results.

In all of these structures, one might object to

showing the water molecules as bridging groups. These are usually described as ''ol'' or the bridging hydroxyl groups, however, as mentioned previously, as a result of hydrogen bonding, it is meaningless to specify the proton as being located on the OH^- or the $SO_4^=$ group.

In order to decide which of the five mechanisms would be favoured, one should know the crystal structure of the original hydrate and the structure of the tetrahydrate. The rate of formation of the polymer chains will depend upon the arrangement, in the original lattice, of the various units that compose the polymer chain. If their positions in the lattice are such that rearrangement is not necessary before coordination of the sulphate ion occurs, then the rate of formation of the chains will be a fast process. On the other hand, if rearrangement must occur, then the mechanisms which do not produce long chains will be preferred.

In Mechanism I, the slow rate of dehydration observed for the loss of the last four molecules of water is due to cross linking of the polymer chains to form sheets, followed by cross linking of the sheets, and as a last step possible rearrangement of the Cr-O-S bonds. Thus the next logical step in mechanism I would result in cross linking of parallel polymer chains to give the following sheet like structure.



This structure leaves us with two moles of water, per mole of $Cr_2(SO_4)_3$, with a third of the sulphate groups as bidentate and the other two-thirds as tridentate ligands. Upon further dehydration, these sheets could become cross linked, thus eliminating one molecule of water per mole of $Cr_2(SO_4)_3$. In this structure, two-thirds of the sulphate groups would act as tridentate ligands and the other third

as quadridentate ligands. The last step would have to entail breaking of the chromium sulphate bonds followed by rearrangement and elimination of the last mole of water.

In mechanism 2 the next step could result from a set of parallel chains becoming cross linked to a second set of parallel chains where the second set of parallel chains runs at right angles to the first set. This would be followed immediately by elimination of all water molecules as all four oxygens from the sulphate ligands become co-ordinated to the chromium ions. This would result in the formation of parallel chains of

$$\begin{array}{l} ---O_2SO_2CrO_2SO_2CrO_2SO_2--- \\ \quad\quad\;\; O_2 \quad\quad O_2 \\ \quad\quad\;\; S \quad\quad S \\ \quad\quad\;\; O_2 \quad\quad O_2 \end{array}$$

cross linked to parallel chains of

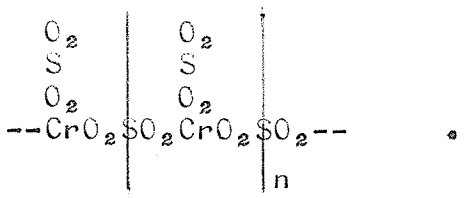
$$---O_2SO_2CrO_2SO_2CrO_2SO_2Cr---$$

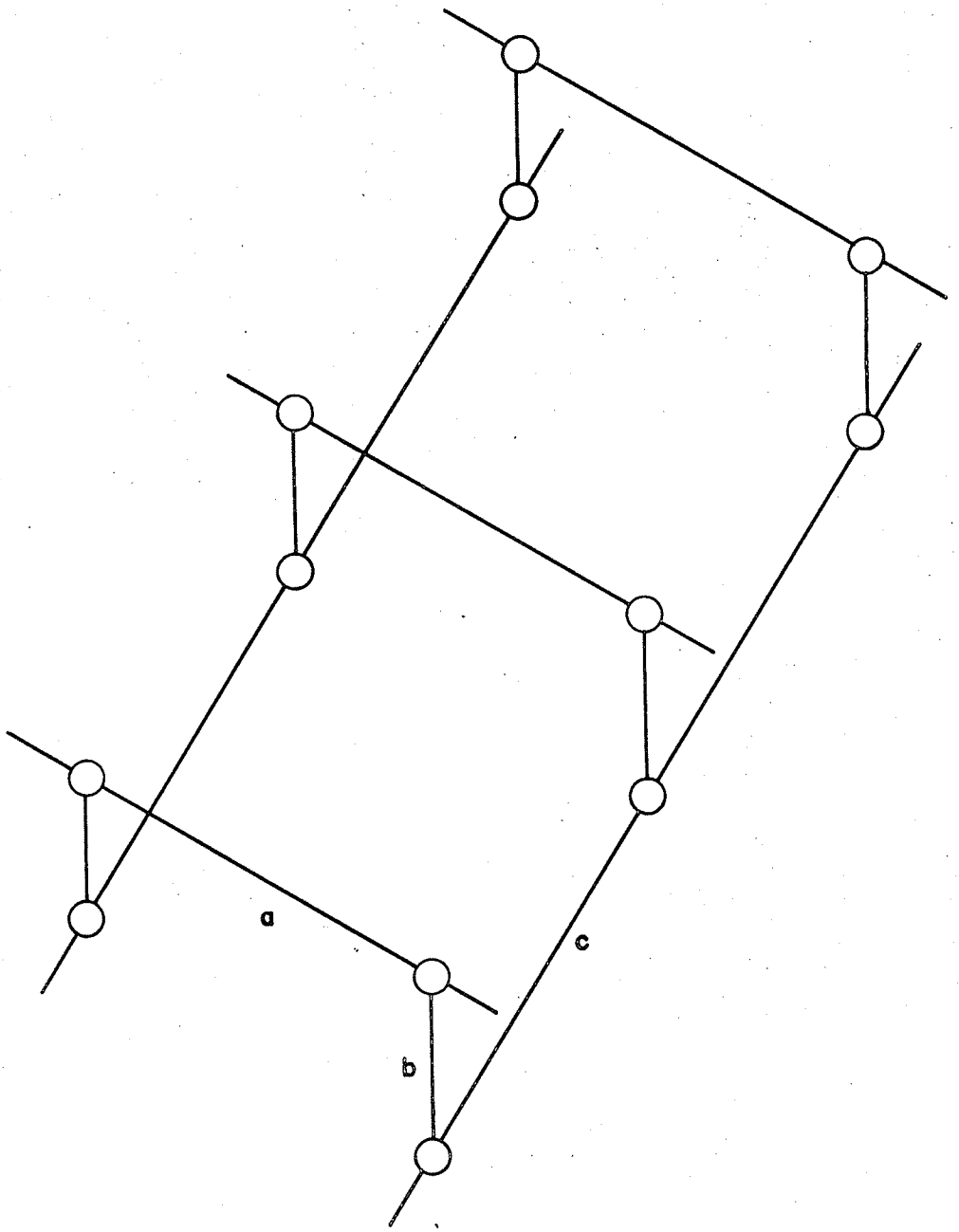
This final structure for the anhydrous $Cr_2(SO_4)_3$ has all of the sulphate ligands equivalent in that it acts as a chelating ligand to one chromium (III) ion and as a chelating ligand to a second chromium (III) ion. The resulting structure is shown in Figure 23.

It is difficult to envisage the next step in mechanism 3, and since it is inconsistent with the experimental data, this mechanism will not receive further consideration. It is also difficult to see how mechanism 4 could lead to a

Figure 23

Possible structure for anhydrous chromium(III) sulphate starting with chains of $--CrO_2\$O_2CrO_2\$O_2--_n$ and





○ Cr atom

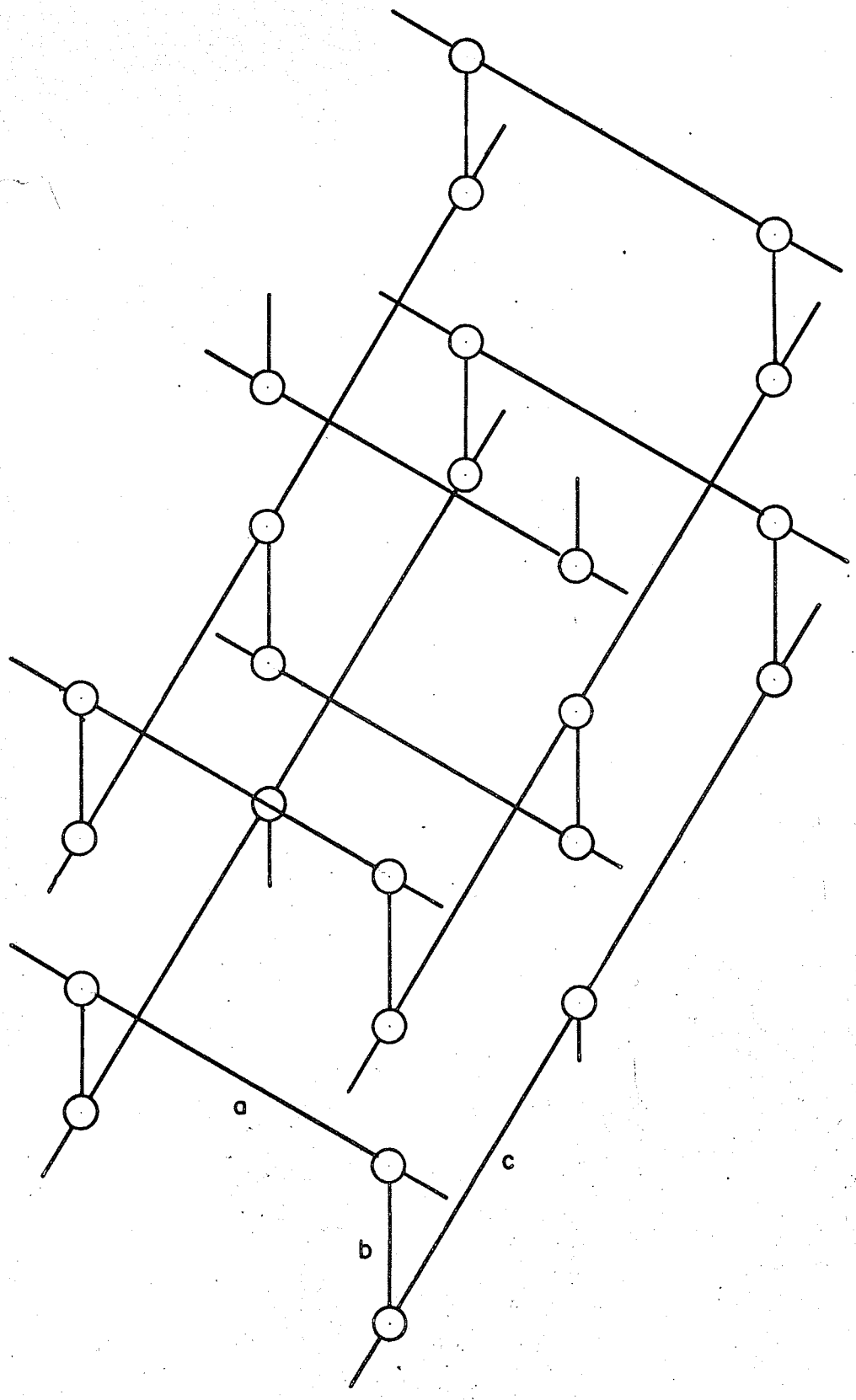
a = b = c

—— Tetradentate SO_4

Figure 24

Possible structure for anhydrous chromium(III) sulphate starting with chains of $--CrO_2|SO_2CrO_2|SO_2--_n$ and

$$--CrO_2\left|\begin{matrix}O_2\\S\\O_2\end{matrix}\right|SO_2CrO_2SO_2CrO_2\left|\begin{matrix}O_2\\S\\O_2\end{matrix}\right|SO_2--_n \quad .$$



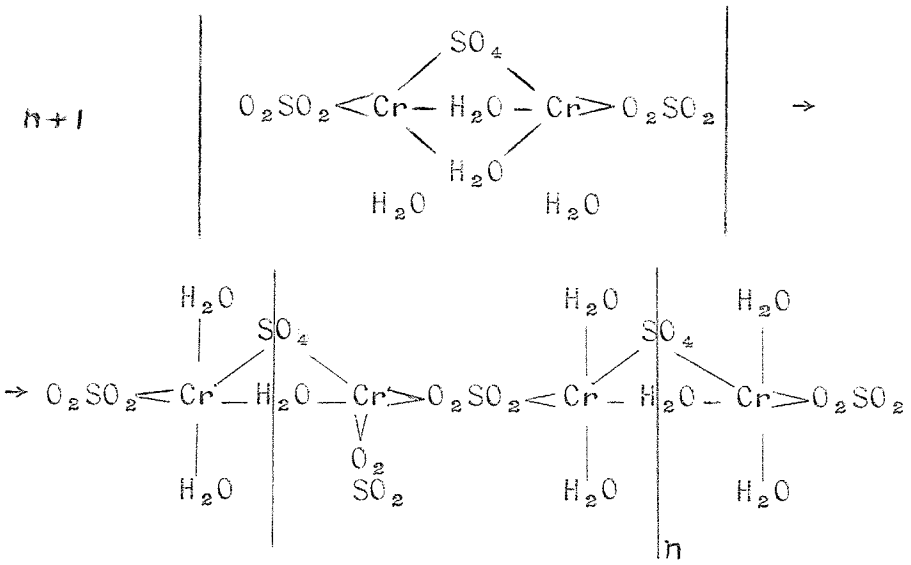
○ Cr atom

a = b = c

—— Tetradentate SO_4

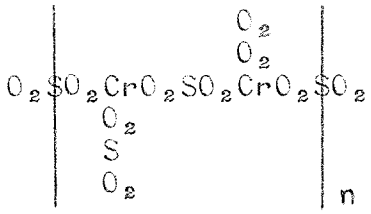
reasonable structure for anhydrous chromium (III) sulphate without the simultaneous rupture of both of the water bridges. In mechanism 5, however, it is easy enough to visualize the formation of polymer chains as the next step in that mechanism.

Step 5 in Mechanism 5



The last step in this mechanism could result in the cross linking of two parallel sets of chains, each set running at right angles one to the other, followed by displacement of the bridging water groups as the four oxygens from each sulphate group becomes coordinated. This would result in the same final structure as in mechanism 2 which is shown in Figure 23.

If the first set of parallel chains in mechanisms 2 and 5 have every alternate sulphate ligand on opposite sides of the polymer chain



the structure in Figure 24 would result from cross linking of this chain with $O_2SO_2CrO_2SO_2CrO_2SO_2Cr$.

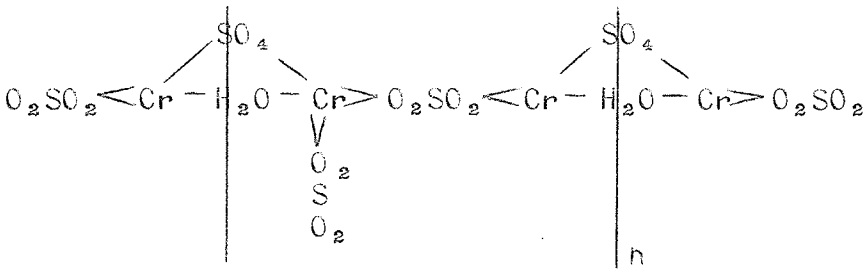
Since the anhydrous chromium (III) sulphate and the insoluble products obtained by digesting chromium (III) sulphate with concentrated sulphuric acid, such as the ''dihydroheptasulphate'' $[Cr_2(SO_4)_3]_2\ H_2SO_4$, and the product AA, whose formula may be written as $H_4[Cr_{12}(SO_4)_{20}]$, all have the same infrared absorption spectra, and since the latter, as will be shown, apparently results from cross linking of polymer chains to give nearly identical structures, it will be assumed that the mechanisms for the decomposition of chromium (III) sulphate which show only the formation of polymer chains to produce the 4 hydrate, need to be considered. This means that we need to consider only mechanisms 2 and 5. There is only a very minor difference in these two mechanisms, the difference between the two mechanisms is, essentially, that in mechanism 5, the rate at which the polymer chains are formed is considered to be a slow step and results only after the 4 hydrate has been produced.

These two mechanisms adequately explain the experimental results obtained from the pyrolysis and the

infrared spectra of the 16 hydrate and the pyrolysis products. The first loss of water other than water of hydration involves a total of 9.5 molecules of water per mole of $Cr_2(SO_4)_3$. This loss results from the displacement of six coordinated water molecules by the three sulphate ligands, and a further loss due to the formation of bridging water groups. The effect of coordination on the symmetry of the sulphate ligand is very evident in the infrared absorption spectrum for sulphato groups. Thus, upon dehydration, the spectrum of the sulphate ligand which in the 16 hydrate is the spectrum of a "free" ion, or an uncoordinated group perturbed by the crystal field and hydrogen bonded to the coordinated water molecules, changes to a spectrum which is typical of a coordinated bidentate sulphate ligand. The effect of coordination of the sulphate is also evident in the infrared absorption due to the water. Thus, the band at 1060 cm^{-1} assigned to the rocking, wagging or a twisting mode of coordinated water, shifts to a lower frequency, 950 cm^{-1}, and the valence vibrations v_1 and v_2 shift to a higher frequency 3200 cm^{-1} from 3000 cm^{-1}. These shifts are all in accord with that expected on theoretical grounds as the coordinate bond formed by water and the chromium (III) ion becomes weaker and as the effect of hydrogen bonding decreases. The absorption band at 2500 cm^{-1} assigned to the valence vibrations of the water molecules which are coordinated and hydrogen bonded to the sulphate groups in

the 16 hydrate disappears, as expected, for the 4 hydrate.

The slow rate of dehydration for the last 4 molecules of water could result from the cross linking of chains in mechanism 2 and to the formation of polymer chains in mechanism 5. The infrared absorption observed for the 2 hydrate is interpreted as a superposition of two spectra, one similar to that observed for the 4 hydrate, and the other similar to the anhydrous $Cr_2(SO_4)_3$. The polymer chain formed in mechanisms 2 and 5 would predict such a spectrum. Furthermore, the gradual disappearance of the water bands, as noticed, would be expected as they are slowly displaced by the sulphate ligands. Mechanism 5 will explain the formation of the monohydrate as observed for the thermogram number M. A sixth step in mechanism 5 involves the cross linking of a parallel set of chains to a second set of parallel chains, set at right angles to the first, resulting in the elimination of the nonbridging water molecules, and leaving only the bridging water molecules. Thus, each chain would be



The chromium atoms do not all show octahedral co-ordination but when these are cross linked they would have

octahedral coordination. The final step would then entail displacement of the bridging water molecules by the bidentate bridging sulphate ligands.

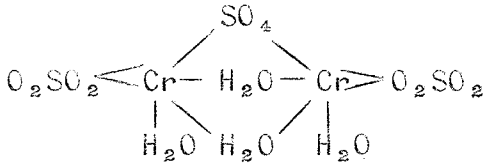
3) CONCLUSIONS

The pyrolysis of the hexadecahydrate of chromium (III) sulphate, which may be formulated as $[Cr(H_2O)_6]_4[H_2S_2O_9]_3\ 5\ H_2O$, occurs in a series of steps which may be described as condensation reactions.

The first step in the pyrolysis, starting at a temperature of 30°C, involves the loss of 2.5 molecules of water of hydration or formation of the 13.5 hydrate which may be formulated as $[Cr(H_2O)_6]_4(H_2S_2O_9)_3$.

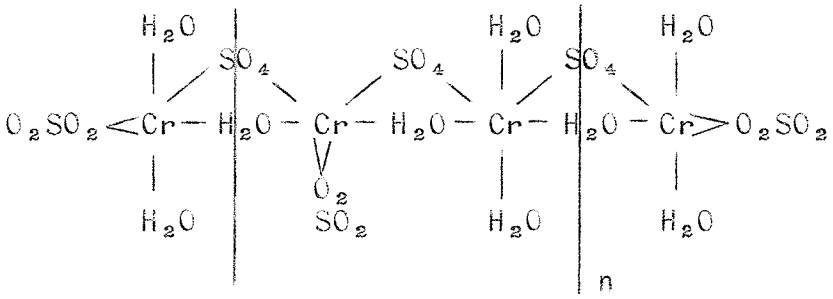
The second step, which involves a series of fast condensations, results in the formation of the 4 hydrate, $Cr_2(SO_4)_3\ 4\ H_2O$, whose structure is either

a)



or

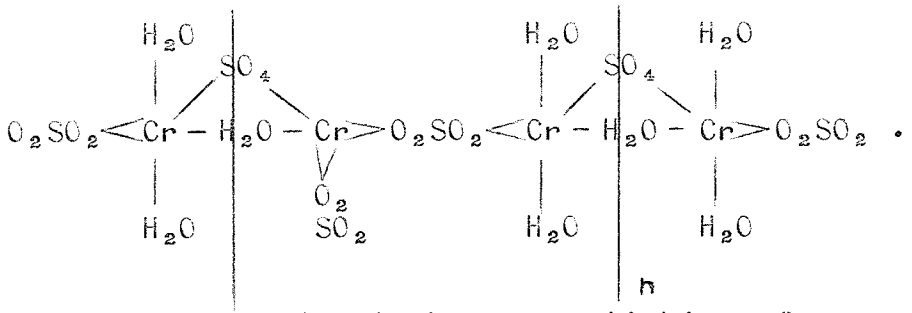
b)



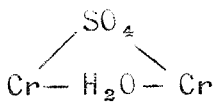
The temperatures at which the condensation is observed depends upon the pyrolysis conditions and occurs between 80 and 145°C for a heating rate of 36°C/hr.

Further dehydration proceeds very slowly and results

from further condensation reactions for the structure (a) above, to form long polymer chains of



This is followed immediately by cross linking of a set of these parallel chains to another set of parallel chains (at right angles to the first set) to give a layered structure similar to that in Figure 23, or a three dimensional network as in Figure 24. This cross linking results in the elimination of the nonbridging water molecules as the sulphates from one chain become coordinated to the second chain. Further dehydration for the structure (b) above, results from the cross linking of parallel sets of chains as given above. The final result of cross linking gives the dihydrate of chromium (III) sulphate. The structures would be as shown in Figures 23 or 24 in which every alternate set of chromium (III) ions in a chain would possess the grouping



instead of CrO_2SO_2Cr as shown for the monohydrate and this grouping for every pair of chromium (III) ions in a chain for the dihydrate. The mono and di-hydrates are observed

only for extremely slow heating rates. A heating rate of 36°C/hr. is not slow enough to show the formation of the monohydrate.

The loss of the last molecule of water then occurs as the bridging bidentate sulphate ligand becomes coordinated as a tetradentate ligand displacing the bridging water molecules. The last step in the pyrolysis involves the decomposition of the anhydrous chromium (III) sulphate to chromium (III) oxide and sulphur trioxide at a temperature of 375-595°C for a heating rate of 36°C/hr. No data exists for the crystal structure of anhydrous chromium (III) sulphate. If the crystal structure were known the validity of these mechanisms could find support but this support will have to wait until a complete analysis of the structure has been made from x-ray diffraction measurements.

EXPERIMENTAL RESULTS

COMPLEXES OF CHROMIUM (III) SULPHATE

C) INFRARED ABSORPTION SPECTRA OF HYDROGEN SALTS OF SULPHATOPOLYCHROMATE (III) ANIONS

C) INFRARED ABSORPTION SPECTRA OF HYDROGEN SALTS OF SULPHATOPOLYCHROMATE (III) ANIONS

1) DISCUSSION OF RESULTS

The infrared absorption spectra of the insoluble products formed in the digestion of chromium (III) sulphate in sulphuric acid are shown in Figures 25, 26, 27 and 28 and are compiled in Table 8. As discussed previously, the product P was thought to contain absorbed sulphuric acid; the spectrum of the product P, in Figure 27 does not, however, show any absorption bands due to the sulphuric acid. Two peaks at 850 cm^{-1} and 875 cm^{-1}, not shown, with an intensity equal to the intensity of the peaks shown in Figure 27, are present in the spectrum of sulphuric acid. These two peaks are absent in the spectra of P, indicating that infrared absorption due to sulphuric acid is definitely absent for in this region the bands due to sulphuric acid would not be obscured by absorption by P.

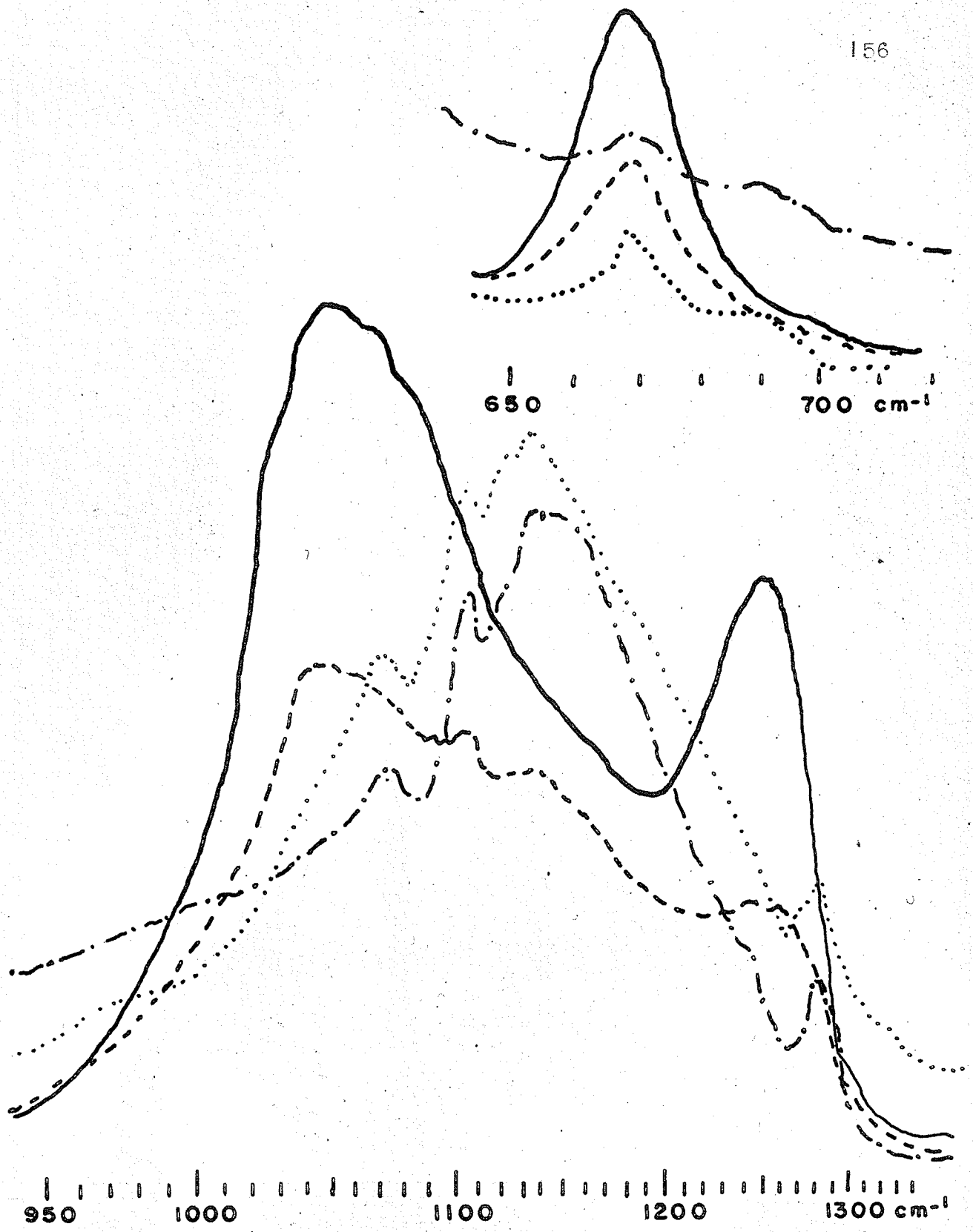
Comparison of the spectra of P, R, and Z, shows the gradual disappearance of the 1070 cm^{-1} band and the 1280 cm^{-1} band with simultaneous strengthening of the 1040 cm^{-1} and the 1260 cm^{-1} bands in going from P to R to Z. The disappearance of the two bands parallels the solubility and the ease of alteration of the products by sodium hydroxide. It was products P and R which showed water losses in the temperature interval of 400-500°C and decomposed via mechanism I; that is, these products, upon pyrolysis, produced the anhydrous

Figure 25

Infrared absorption spectra of various hydrogen salts of sulphatopolychromate (III) anions.

Products Q, S, and AB are discussed on page 44.

T has an emperical formula of $H_2[Cr_4(SO_4)_7]$.


650
700 cm⁻¹
950
1000
1100
1200
1300 cm⁻¹
Q
S
T
AB

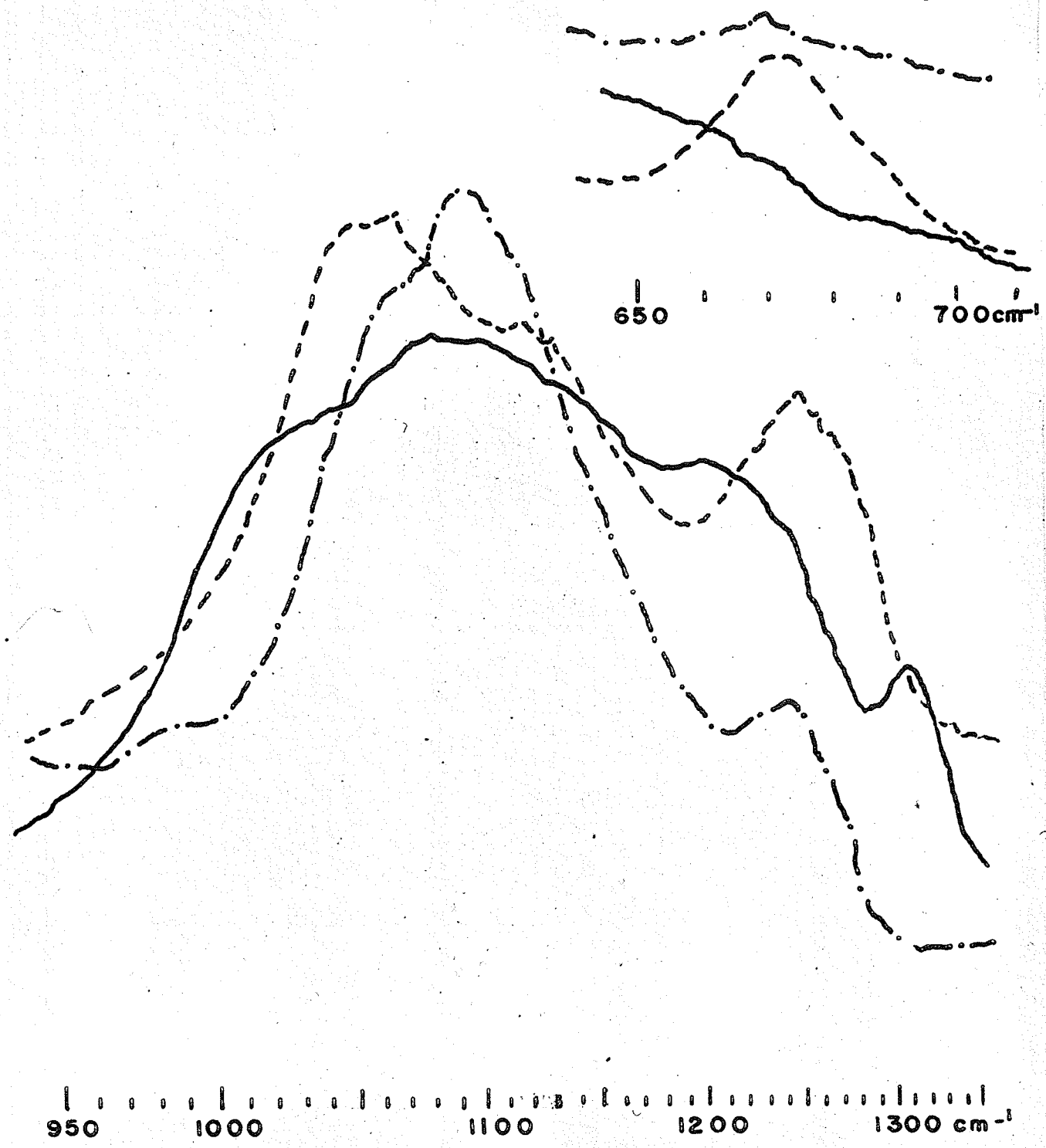

650
700cm⁻¹
950
1000
1100
1200
1300 cm⁻¹
U
W
Y

Figure 27

Infrared absorption spectra of various hydrogen salts of sulphatopolychromate (III) anions.

P and R have the emperical formula $H_3[Cr_3(SO_4)_6(H_2O)_2]$ n H_2O

Z has the emperical formula $H_6[Cr_4(SO_4)_9]$ n H_2O

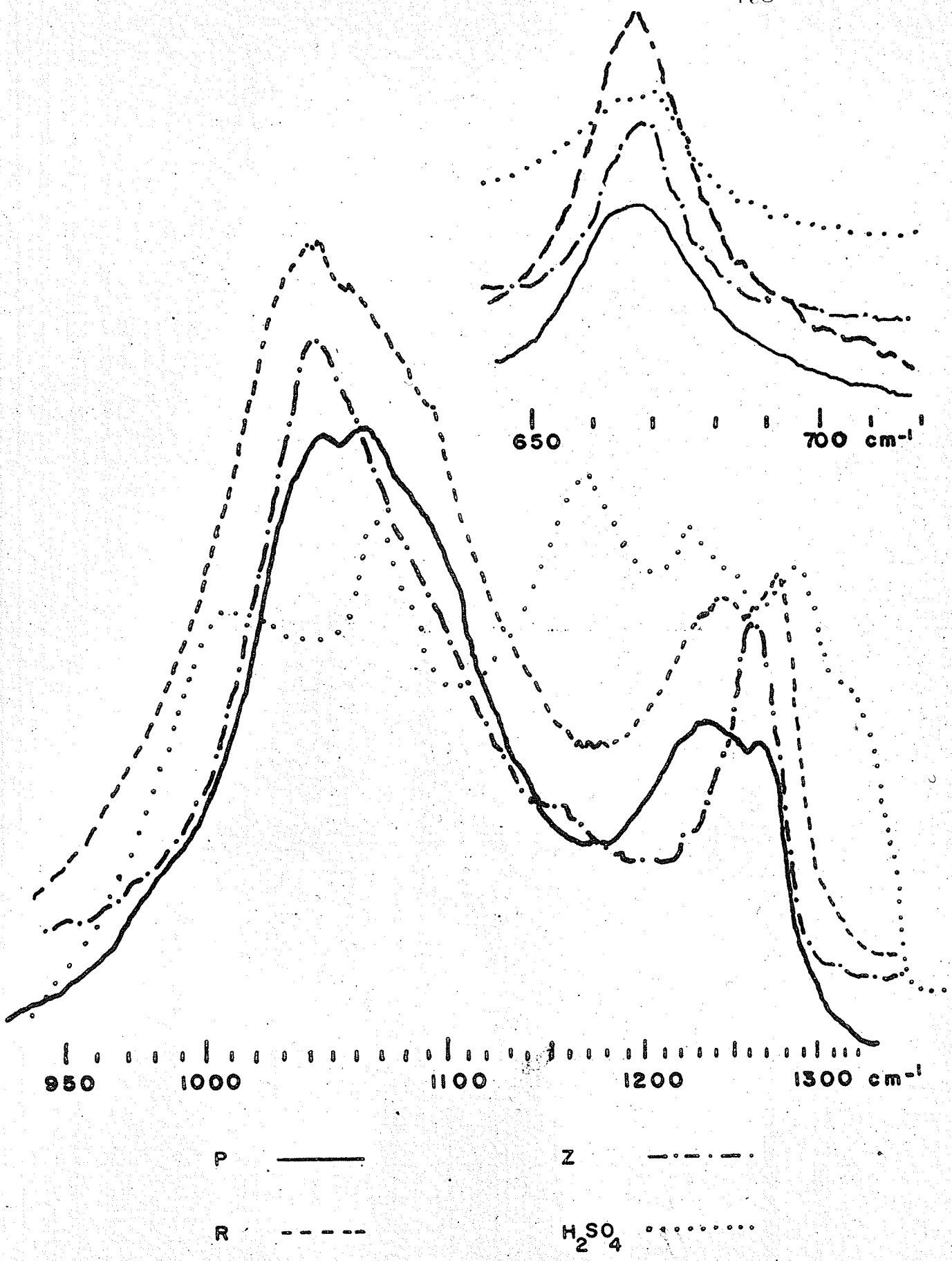

650
700 cm⁻¹
950
1000
1100
1200
1300 cm⁻¹
P
Z
R
H2SO4

Figure 28

Infrared absorption spectra of $Cr_2(SO_4)_3$ and $H[Cr_3(SO_4)_5]$.

Infrared absorption spectrum for $Cr_2(SO_4)_3$ and the product AA ($H[Cr_3(SO_4)_5]$).

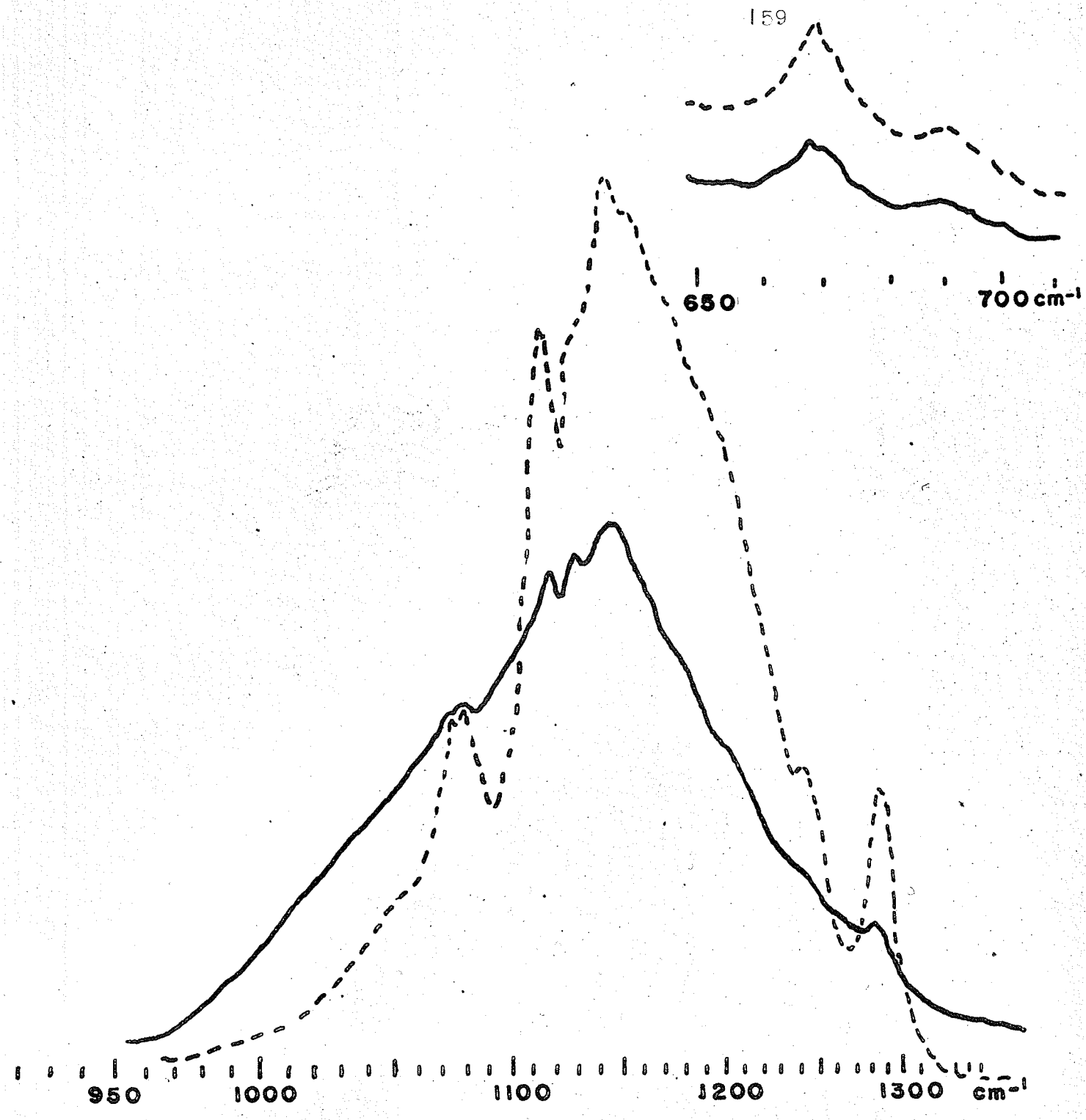
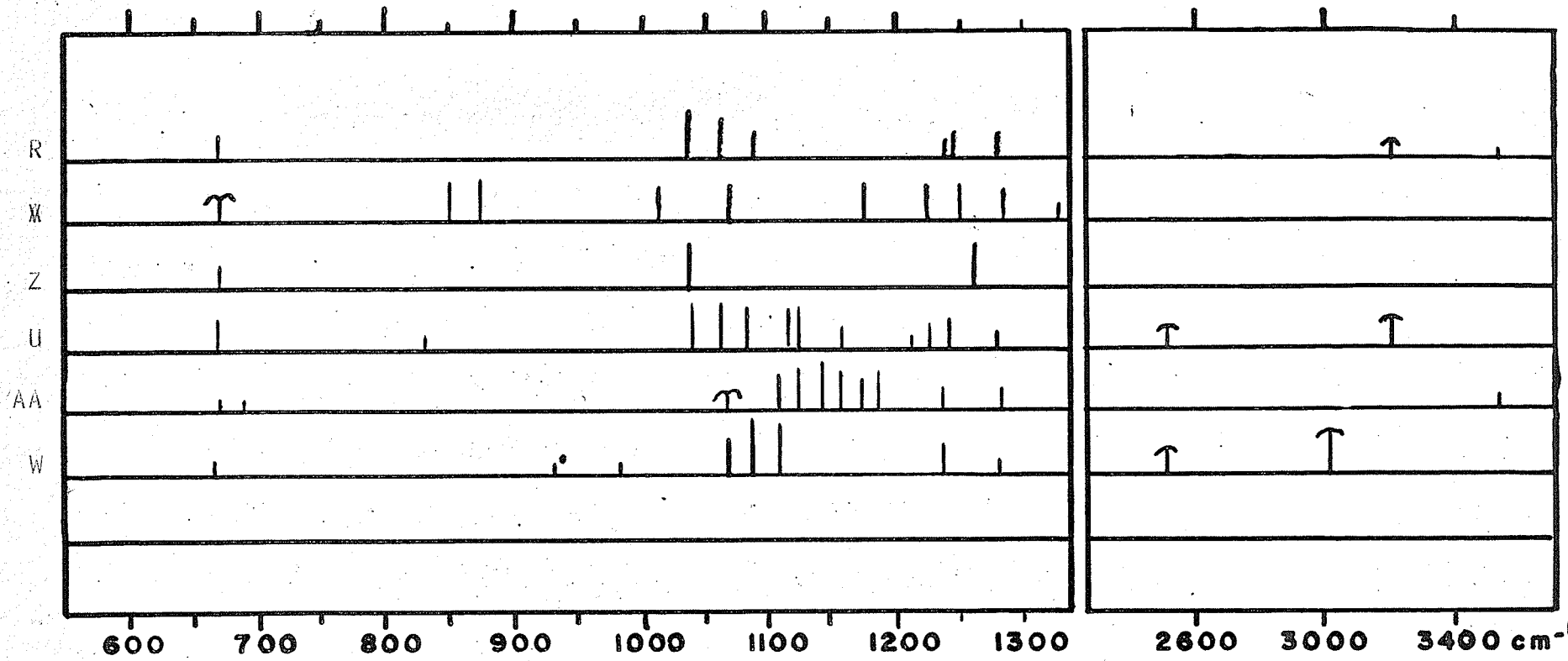

650
700 cm-1
950
1000
1100
1200
1300 cm-1
AA
Cr2(SO4)3

TABLE 8

Schematic representation of the infrared absorption bands for various hydrogen and metal salts of sulphatopolychromate (III) anions.



R) $H_3[Cr_3(SO_4)_6(H_2O)_2]$ X) H_2SO_4 Z) $H_6[Cr_4(SO_4)_9]$ AA) $H[Cr_3(SO_4)_5]$

U and W are aluminum salts as described in the text

chromium (III) sulphate, whereas the product Z contains no water and decomposes via mechanism 2 in which the intermediate $H_4[Cr_{12}(SO_4)_{20}]$ was produced upon pyrolysis. The two bands, at 1040 cm^{-1} and 1260 cm^{-1}, present in all three products are, therefore, assigned to the sulphate group. The absence of the two bands at 1070 cm^{-1} and 1230 cm^{-1}, in product Z, would suggest that these two might best be assigned to water present in P and R. Assignment of these bands to water need not be the only explanation. These three spectra indicate that there are no changes in the symmetry of the sulphate group in going from product P to R to Z, such as was observed for the sulphate group in going from the violet sulphate $Cr_2(SO_4)_3$ 16 H_2O to the green sulphate $Cr_2(SO_4)_3$ 4 H_2O.

The infrared absorption spectrum of product Z does not yield to an easy interpretation. The two bands at 1040 and 1260 cm^{-1} could be assigned to the triply degenerate ν_3 vibration of the sulphate ligand which gives rise to two bands, one being doubly degenerate and the second one non-degenerate when the symmetry of the sulphate group is reduced to C_{3v} symmetry. Table 6 shows, however, that the nondegenerate breathing frequency (ν_1) becomes infrared active when the symmetry is reduced to C_{3v}. The spectrum for product Z does not show any absorption in this region and therefore, the above assignment is not justified.

It is obvious that we are dealing with a coordinated sulphate group in the product Z. Since the breathing frequency v_1 is absent from the spectrum and since the selection rules for our first and second class of compounds are governed by the correlation given in Table 6, one must conclude that if the selection rules for infrared absorption by the products such as Z are those outlined for class one or two, then the sulphate group must have regular T_d symmetry. It is, however, impossible to conceive a structure in which the sulphate group would have T_d symmetry for the product Z. In order to explain the spectrum for the product Z, one must resort to factor group analysis which requires a prior knowledge of the crystal structure.

If we assume that the sulphate group has C_{3v} symmetry in the product Z, then the site group analysis, which considers the occupant of the site just as if it were an independent molecule having the symmetry of the site, would predict that the breathing frequency v_1 would be infrared active and that the v_3 frequency should give rise to two infrared active bands. Site group analysis, however, only yields an adequate interpretation for the grosser details of the spectrum. Differences between the predicted and the actual spectrum can be explained only by resorting to an analysis of the unit cell or factor group analysis. These differences correspond essentially to coupling of vibrations between

occupants of the different sites in the lattice.[48, 49, 50] Winston and Halford[48] point out that if a vibration is assigned infrared inactivity in the site analysis, it must also be inactive in factor group analysis. A vibration which is assigned infrared activity in site analysis, however, may not necessarily have activity in factor group analysis. It is possible that the absence of the breathing frequency v_1 is due to the coupling that exists between the sulphate groups, thus causing it to be infrared inactive. Furthermore, they point out that a vibration which is degenerate under site group analysis will still be degenerate under factor group analysis, and that motions may become more degenerate under factor group than they are under site group analysis. A band under site analysis may become duplicated under factor group analysis, the number of times not to exceed the number of sites in the unit cell. This means that if the sulphate group possessed C_{2v} symmetry, this would definitely be evident in the spectrum of the compound. It is concluded, therefore, that the spectrum of the product Z is the spectrum one would expect for a sulphate group possessing C_{3v} symmetry, a breathing frequency v_1 is not observed because of its infrared inactivity as a result of coupling between the sulphate groups in the unit cell.

If octahedral coordination of the chromium (III) ion

is preserved in the compound Z, ($H_6[Cr_4(SO_4)_9]$), twenty-four coordination sites must then be distributed between the nine sulphate groups. This means that each sulphate ligand would, on the average, be two and two-thirds dentate in the complex, or we could say that six of the nine sulphate groups are tridentate and the other three are bidentate ligands, or that seven and one-half of the nine sulphate groups would be tridentate and one and one-half monodentate. The sulphate ligands cannot all be equivalent but they can all have the same symmetry (C_{3v}) if the product contains only mono and tridentate ligands. Other combinations are possible in which the sulphate ligands could behave as tetradentate and bidentate ligands, although all possible combinations predict that it is impossible for all of the sulphate ligands to be equivalent.

The products Z and O are two typical examples of the products formed in the digestion at 250°C. Both Z and O decompose to give the intermediate $H_4[Cr_{12}(SO_4)_{20}]$, yet the sulphate to chromium ratio for these two are 2.25 and 2.18 respectively. As mentioned on page 56, the product O cannot be considered to be a mixture of product R and Z even though the sulphate to chromium ratio might suggest such a mixture. Since the products of digestion at 250°C show identical properties except for the loss of different weights of sulphuric acid in the first step of pyrolysis, it will be

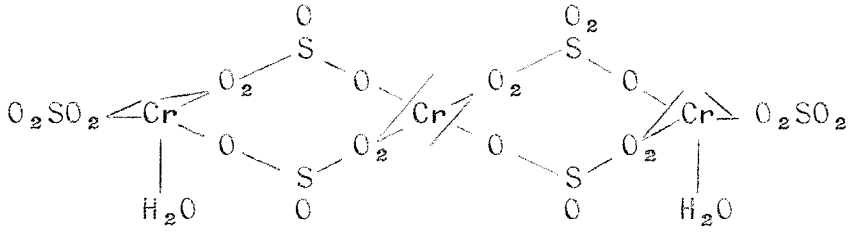
assumed that the basic structures of these products are the same. The structures will show minor variations accounting for the different sulphate to chromium ratios. The experimental results obtained by this author showed sulphate to chromium ratios between 2.14 and 2.29. These results, however, were all obtained employing chromium (III) concentrations near 0.62 M and sulphuric acid concentrations between 11 and 14 molar. A more detailed investigation of the insoluble products formed using other concentrations of the reactants is necessary to establish the limiting sulphate to chromium ratios allowed for the products with a Z type structure.

The products P and R have infrared absorption spectra very similar to that of the product Z. Each of the two bands at 1040 and 1260 cm^{-1} in product Z appears to be split into three bands in the product R. This splitting might be due to coupling of three sulphate groups in the unit cell, coupling which does not exist in the unit cell of Z. The differences may also be attributed to interaction of the sulphate groups with the coordinated water molecules present in the product R. The differences in the two spectra do not suggest that we have a major change in the coordination of the sulphate groups.

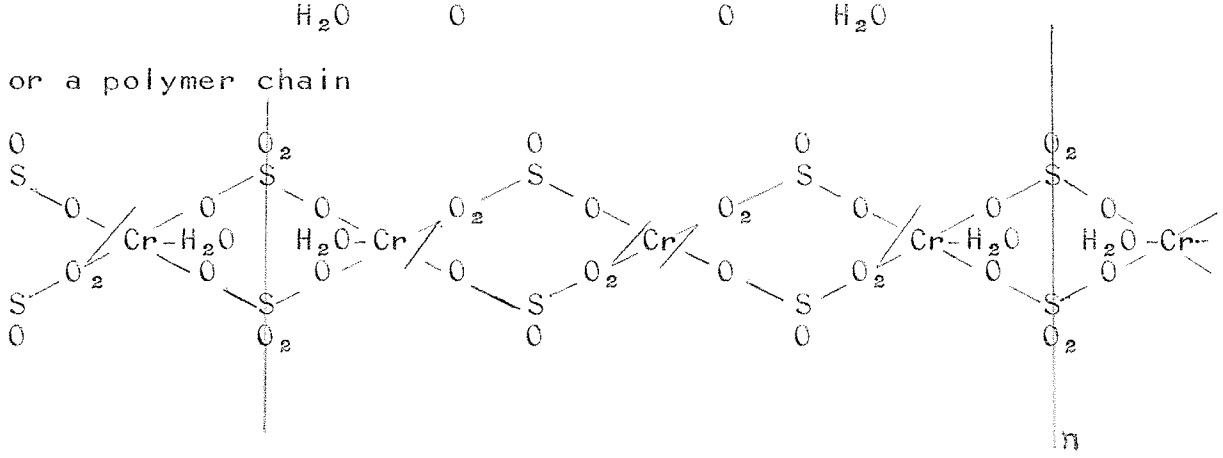
The product R may be formulated as $H_3[Cr_3(SO_4)_6(H_2O)_2]$. It is not known whether the water molecules function as

bridging or bidentate groups or as monodentate groups. There are a total of eighteen coordination sites that must be satisfied if chromium has octahedral coordination. If the water molecules behave as bidentate ligands, then each sulphate group would, on the average, be two and one-third dentate. That is, four of the six sulphate groups would be bidentate and the other two tridentate. If this were true then the spectrum for product R should be the spectrum for a sulphate group having C_{2v} symmetry. The spectrum of R, however, was interpreted as being due to a sulphate ligand possessing C_{3v} symmetry. If the water molecules are monodentate, then the average sulphate group would be two and two-thirds dentate or four of the six sulphate groups would be tridentate and two would be bidentate.

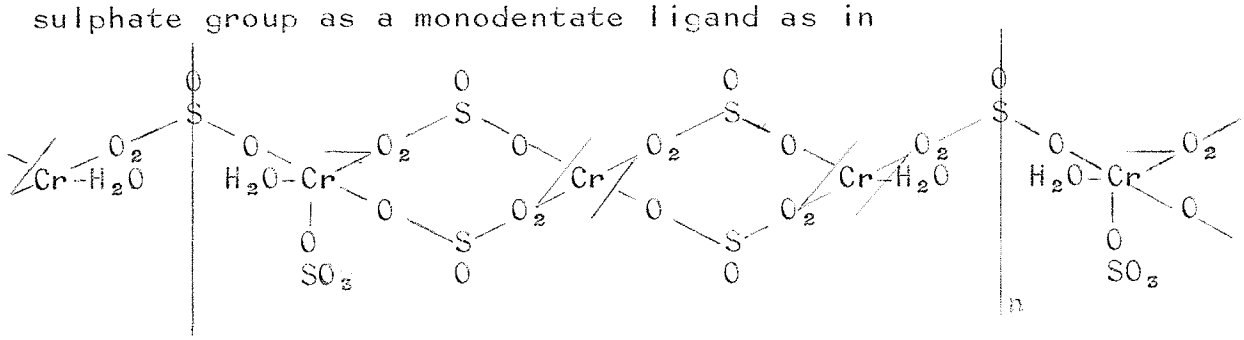
A possible structure for the product R is



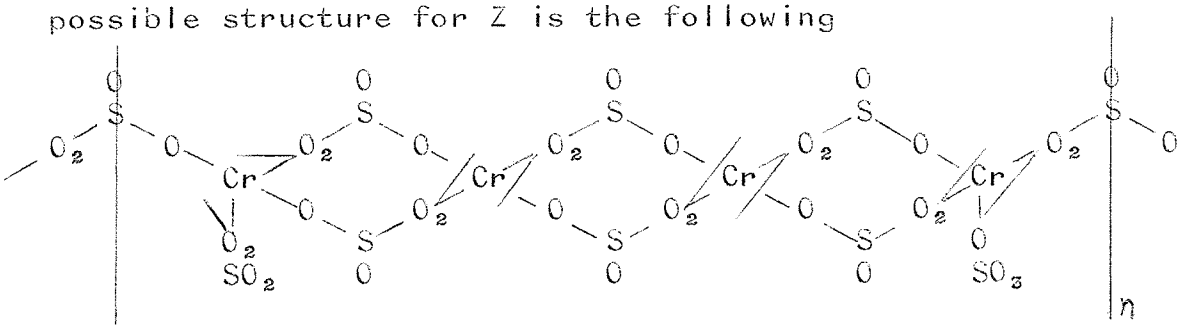
or a polymer chain



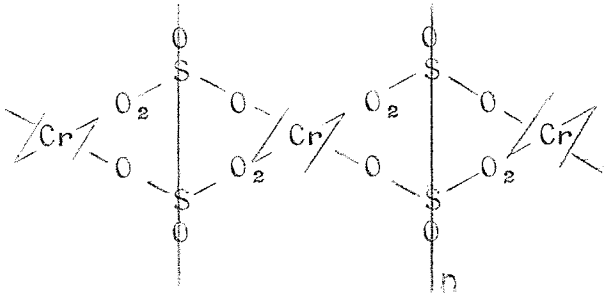
In both of these structures, four of the six sulphate groups per three chromium (III) ions are tridentate while the other two are bidentate. One could have five sulphate groups acting as tridentate ligands and the sixth sulphate group as a monodentate ligand as in



The products formed at higher temperatures, 250°C, such as O and Z, are thought to form polymer chains similar to the polymer chain shown for R in which the water molecules have been replaced by coordinated sulphate groups. Thus a possible structure for Z is the following



The structure has seven of the nine sulphate groups as tridentate ligands, one as a bidentate, and another as a monodentate ligand. One could think of product Z resulting from the sulphation of the following polymer chain



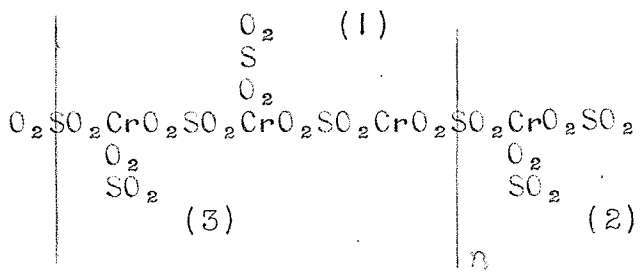
The product Z is formed by the addition of a sulphate group to every fourth chromium atom, whereas the product O by addition to every sixth chromium atom. Furthermore the products such as R can now be considered to result from the introduction of water molecules to two out of every three chromium atoms. The two bands at 1070 cm^{-1} and 1230 cm^{-1} may, therefore, be due to absorption by the sulphate ligands possessing C_{3v} symmetry whose vibration frequencies are modified as a result of hydrogen bonding.

There is no doubt that products T, AB, and AA represent different products from those of P, R, and Z, as shown by their different absorption spectra. It is evident that the sulphate group must have changed its symmetry in going from the product Z to AA. It is, however, rather surprising to see that the spectra of the three products T, AB, and AA, and the anhydrous chromium (III) sulphate produced by dehydration of the normal violet chromium (III) sulphate are all essentially the same. These products all have a sulphate to chromium ratio less than 2; 1.5 for the anhydrous chromium (III) sulphate, 1.65 for the product AA, and 1.79 for product T. The x-ray powder photographs for AA and the anhydrous chromium (III) sulphate are identical except for a darker background in the latter indicating that scattering occurred. The broad bands observed in the infrared absorption spectrum for the anhydrous chromium

sulphate may also be due to imperfect crystallinity.

Since the spectra of the compounds with sulphate to chromium ratios between one and one-half and two all have essentially the same infrared absorption spectra, it is thought these products must all have the same basic structure. In the anhydrous chromium (III) sulphate, three sulphate groups must satisfy the coordination site for the two chromium atoms. This means that if octahedral coordination is preserved (there is no reason to suspect that it isn't) then each sulphate group must be tetradentate.

In the product AA, each sulphate must be 3.6 dentate, that is, four out of five sulphate groups will be tetradentate with the fifth one being bidentate. The structure of this product may result from cross linking of sets of parallel chains running at right angles to a second set of parallel chains in a manner similar to that for the anhydrous $Cr_2(SO_4)_3$. The polymer chain could be the following



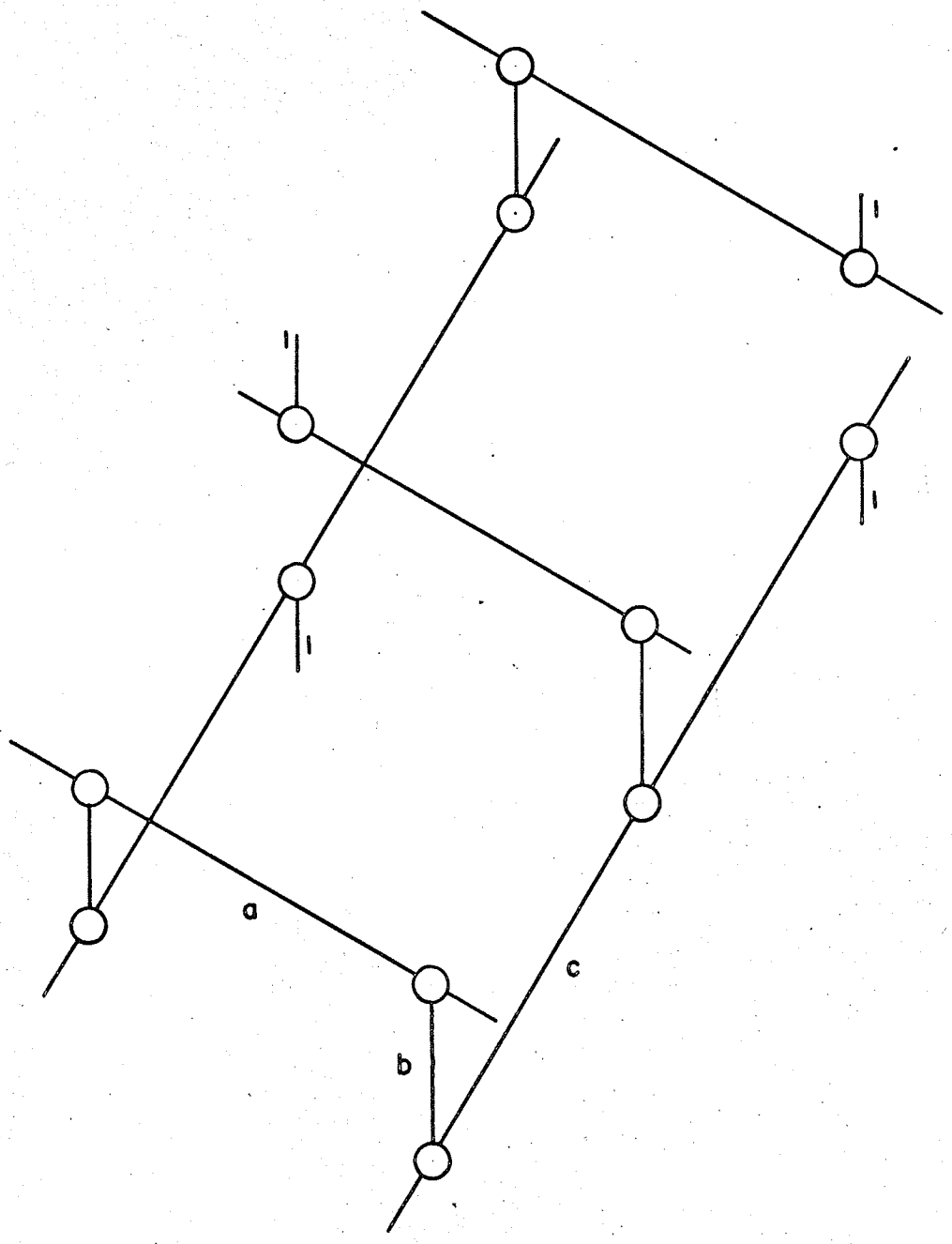
The sulphate group marked as (1) would act as tetradentate ligands while the two marked as (2) and (3) as bidentate ligands. This structure is shown in Figure 29.

If this is the true structure for this compound, one should expect to find other products with variable sulphate to chromium ratios and one can then assign a similar structure to the product T in which more sulphate groups would act as bidentate ligands. One could look at the structure for the product AA as being identical to that of the anhydrous $Cr_2(SO_4)_3$, except that every third chain in both of the parallel sets has been removed.

It would seem that there are a total of six bands, 1112, 1125, 1140, 1155, 1173 and 1185 cm^{-1} which comprise the main absorption for the compound AA. If these bands are all due to the v_3 vibration of the sulphate group, multiplied, due to coupling between the sulphate groups in the unit cell, it would mean that there are a total of six sulphate groups in a unit cell if the sulphate group possesses T_d symmetry. The band at 1070 cm^{-1}, a doublet, and the band at 1245 or 1285 cm^{-1} may be due to the chelating sulphate groups which possess C_{2v} symmetry. The infrared absorption pattern for the product AA definitely does not suggest co-ordination of the type observed for the hydrate $Cr_2(SO_4)_3\ 4\ H_2O$ in which the sulphate group possessed C_{2v} symmetry. It is, however, possible that the site symmetry for the sulphate group is C_{2v}. One could assign the doublet at 1070 cm^{-1} to the v_1 breathing frequency and the three bands at 1112, 1125, and 1140 cm^{-1} to the v_3 vibration of

Figure 29

Possible structure for $H[Cr_3(SO_4)_5]$.



○ Cr atom

a = b = c

—— Tetradentate SO_4

—|— Bidentate SO_4

the sulphate group. This splitting pattern is predicted in Table 6 for a sulphate group possessing C_{2v} symmetry. Each of these bands could be duplicated in the spectrum as a result of coupling between the two sulphate groups in the unit cell. The reduction in symmetry, however, must be due to lattice requirements rather than coordination of only two of the oxygens in the sulphate ligand. The small splitting that is observed, 28 cm^{-1}, and the low intensity of the 1070 cm^{-1} band suggests that this spectrum belongs to the third classification discussed on page 103. The infrared absorption spectra for the products T, AB, AA and the anhydrous $Cr_2(SO_4)_3$, therefore, suggests that the sulphate ligand may not possess T_d symmetry in these compounds, that its reduction in symmetry is not due to unsymmetrical coordination but due to lattice requirement or perturbation by the crystal field.

The spectra for the products U, W, and Y, are shown in Figure 26. As discussed previously, the product U decomposed in a manner very similar to that of the product Z, and suggested that one might consider product U as identical to the product Z in which the aluminum (III) ion replaced the chromium (III) ion isomorphously. However, the spectra of the two products, U and Z, are slightly different. Two strong absorption bands at 1115 and 1240 cm^{-1} are found in the spectrum of U, in addition to two bands at 1040 and

1260 cm^{-1}, which are the two absorption bands found in the spectrum of the product Z. One would expect that the replacement of a chromium (III) ion by an aluminum (III) ion in the product Z, should produce some changes in the spectrum of the compound, but it is difficult to predict what these changes would be. Substitution by the smaller aluminum (III) ion 0.57A° (chromium 0.65) should produce some distortion of the sulphate ligands coordinated to this particular lattice site and hence reduce the symmetry of these particular sulphate groups. The additional bands found in the spectrum of U, compared to the bands in the spectrum Z, may then be due to the sulphate groups which are coordinated to the aluminum (III) ions. It is possible that the product U is a mixture of the product Z and some other aluminum salt of one of the sulphatopolychromate (III) anions or mixture of the product Z and the compound $Al_2(SO_4)_3H_2SO_4$ whose existence has been reported by Mather and Wylie.[5]

The spectrum for the product W, whose provisional chemical formula may be written as $Al_8[Cr_2(SO_4)_7]_3$, is shown in Figure 26. The spectrum shows a weak band at 990 cm^{-1}, another band as a strong shoulder at 1065 cm^{-1}, a strong band at 1090 cm^{-1}, a medium band at 1240 cm^{-1}, and shoulder at 1260 cm^{-1}. No attempts will be made to interpret this spectrum, it is given only to show the difference between

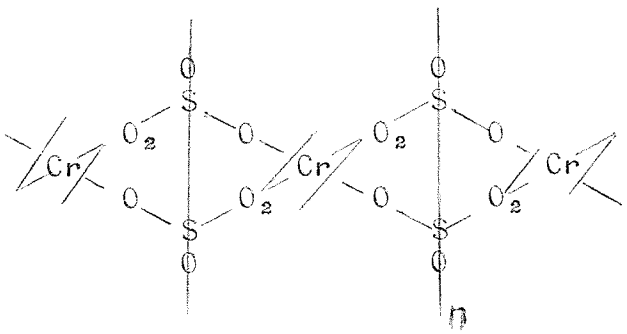
the two insoluble digestion products U and W which both contain aluminum ions. The product U was obtained by digesting a one to three molar ratio of aluminum (III) and chromium (III) sulphate in 140 molar sulphuric acid at 250°C whereas product W was prepared by digesting an equimolar ratio of these two salts in a large excess of sulphuric acid at 135°C. The absorption spectrum for aluminum (III) sulphate shows three fairly strong absorption bands at 1050, 1136, and 1218 cm^{-1}, and a weak, poorly defined band at 980 cm^{-1}.[51] The spectrum of product W does not suggest that it is a mixture of aluminum (III) sulphate and some aluminum (III) salt of one of the sulphato-polychromate (III) anions because even though the product W has absorption bands in the region corresponding to the aluminum (III) sulphate, their relative intensities are such that they would negate such a conclusion. The three bands in aluminum (III) sulphate at 1050, 1136, and 1218 cm^{-1} are of comparable intensity with the 1136 cm^{-1} band showing slightly stronger absorption. The thermogravimetric and infrared absorption results obtained for products U and W suggest that it should prove a very interesting system to study in further detail.

The spectrum for the product Y shown in Figure 26 shows considerable complexity. This is not surprising since this product, a sample of ''altered chromite'' must represent

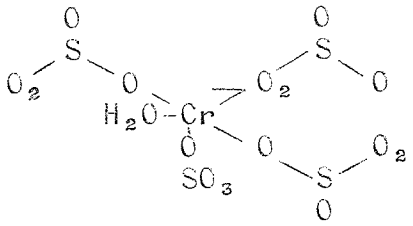
a mixture of various salts formed in the attack of the chromite lattice.

2) CONCLUSIONS

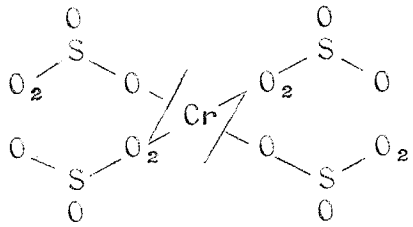
Analysis of the infrared absorption spectra of the hydrogen salts of the sulphatopolychromate (III) anions supports the conclusion, obtained from the analysis of the thermogravimetric results, that their salts may be divided into three classifications. The first class of compounds have sulphate to chromium ratios of 2 and contain co-ordinated water groups in the complex. The presence of the coordinated water caused the appearance of two bands at 1070 and 1230 cm^{-1}, not evident in the second class of compounds which have a sulphate to chromium ratio greater than 2 and show only two absorption bands at 1040 and 1260 cm^{-1}. The two bands at 1070 and 1230 cm^{-1} are not assigned to absorption by the water molecules, but are thought to arise from the sulphate groups which may be hydrogen bonded to these water molecules or they may arise because of a different coupling mode present in the first class and absent in the second class. The infrared absorption spectra of the compounds in both the first and the second class are interpreted as the spectra characteristic of a sulphate ligand possessing C_{3v} symmetry. It is suggested that all of these compounds have the same basic polymer chain in which the sulphate ligand acts as a tridentate bridging ligand.



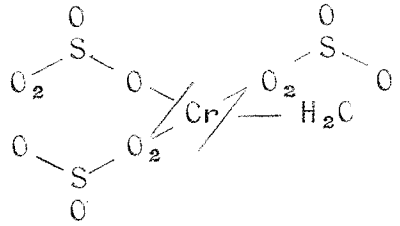
The compound R in the first class has two coordinated water molecules for every three chromium (III) ions. Introduction of these water molecules into the basic chain results in one-third of the chromium (III) ions having a monodentate sulphate ligand, a coordinated water molecule and three bridging tridentate sulphate ligands.



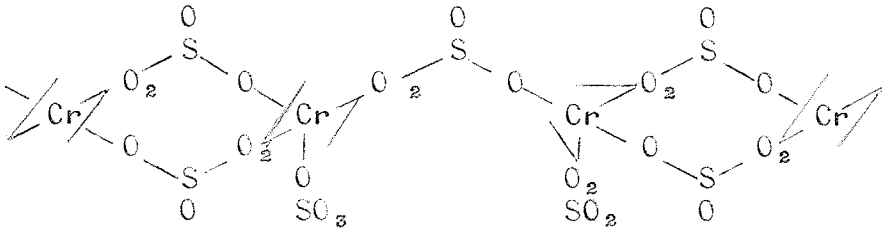
One third of the chromium (III) ions have four bridging tridentate sulphate ligands



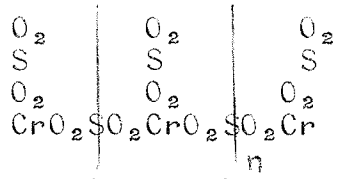
and one third of the chromium (III) ions have a bridging water molecule and three tridentate sulphate ligands



For the second class of compounds which have sulphate to chromium ratios greater than 2, the value for this ratio is determined by the number of sulphate ligands that are introduced into the chain. For each sulphate ligand introduced, the chain is disrupted and gives rise to the following link in the chain



The third class of compounds formed, which have a sulphate to chromium ratio between 1.5 and 2, all show the same absorption pattern. This spectrum was interpreted as being due to a symmetrically coordinated tetradentate sulphate ligand, but whose absorption was characteristic of a ligand possessing C_{2v} symmetry and not T_d symmetry. The reduction in the symmetry of the site was, however, attributed to lattice requirements or due to crystal field perturbation rather than unsymmetrical coordination. The various compounds that comprise this class were all assigned a basic structure consisting of parallel chains of



cross linked to a second set of parallel chains of

$CrO_2SO_2CrO_2SO_2Cr$. Cross linking of the two chains above results in the formation of the anhydrous chromium (III) sulphate. The formation of compounds with sulphate to chromium ratios greater than 1.5 may be considered to result from the periodic removal of one of the chains from the second parallel set. Thus, if every third chain was removed from the anhydrous chromium (III) sulphate and every sulphate ligand from the first set of chains, which should be linked to the missing chain, acted now as a bidentate ligand, one obtains the compound AA whose formula may be written as $H[Cr_3(SO_4)_5]$.

The experimental work for the aluminum (III) salts of the sulphatopolychromate (III) anions suggests that several different salts and possibly sulphatopolyaluminate (III) anions are formed under various digestion conditions. The infrared absorption spectrum of W suggests that the aluminum (III) salts of the sulphatopolychromate (III) anions with sulphate to chromium ratios greater than 2, precipitate as insoluble materials under conditions where the hydrogen salts of the sulphatopolychromate (III) anions are soluble. Under digestion conditions in which the aluminum (III) ion concentration is much smaller than the chromium (III) concentration, insoluble materials are found in which the aluminum (III) ion isomorphously replaces the chromium (III) ion or which may contain sulphatopolyaluminate (III) anions.

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

The experimental data obtained from the digestion of chromite concentrate with sulphuric acid suggested that the mechanism involved an initial protonic attack of the chromite lattice, bringing the metallic constituents into solution in the same ratio as they occurred in the lattice. Precipitation occurs in a second step due to the formation of insoluble sulphato complexes of chromium (III) which include various anionic polynuclear species whose hydrogen and other salts are insoluble. These insoluble materials, referred to as ''altered chromite'', represent a mixture of the various salts formed during the digestion. In order to strengthen this explanation, chromium (III) sulphate was digested under conditions similar to the digestion of the chromite concentrate resulting in the formation of insoluble products whose properties were the same as those of the ''altered chromite''.

It is a well established fact that coordination of the sulphate group to the chromium (III) ion occurs readily in solution.[1, 10, 11, 12, 39, 51] Tai and Underwood[51] report the formation of the inner inert complexes $[Cr(H_2O)_xSO_4]^+$ and $[Cr(H_2O)_x(SO_4)_2]^-$ in sulphuric acid solutions at temperatures below 80°C. The ''chromipoly-sulphuric acids'' reported by Recoura[10] are coordination compounds of chromium (III), and sulphate ions but the

structure of these complexes has not heretofore been established. Whitney[11] regards the ''isomeric form of chromipolysulphuric acid'' as a polynuclear complex with a large molecular weight. This research has established that complexes containing sulphate to chromium ratios near 2 are the predominant insoluble hydrogen salts formed under the digestion conditions employed for the attack of chromite and are assumed to be identical to the ''isomeric form''. Since the mononuclear anionic species $[Cr(H_2O)_x(SO_4)_2]^-$ is soluble[51], the assumption that the insoluble products are polynuclear would appear to be valid. Thus digestion of chromium (III) sulphate with sulphuric acid causes coordination of sulphate ligands to the chromium (III) ions with the possible formation of various mononuclear species such as $[Cr(H_2O)_4(SO_4)_2]^-$, $[Cr(H_2O)_2(SO_4)_2]^-$, and $[Cr(H_2O)_5(SO_4)]^+$. A second step in the digestion then involves polymerization of the monomers and subsequent chain growth, followed by precipitation of the heavier polymers.

The insoluble hydrogen salts formed during the digestion of chromite are complexes with sulphate to chromium ratios near 2, since these are the insoluble products produced by digesting chromium (III) sulphate and sulphuric acid under identical conditions. Chemical analysis of the ''altered chromite'', however, shows anions to be in excess of metallic cations only if a large excess of acid has been

employed in the digestion. This excess is attributed to the presence of the hydrogen salts in the ''altered chromite''. Since the ''altered chromite'' consists mainly of the metal salts of the sulphatopolychromate (III) anions, one must concur with Recoura's[10] conclusion that the metal salts are less soluble than the hydrogen salts. The metallic salts which constitute the ''altered chromite'' do not necessarily contain the same anions as do the insoluble hydrogen salts. This is evident from the analysis of the product W whose chemical analysis corresponds to $Al_8[Cr_2(SO_4)_7]_3$ n H_2O. Digesting chromium (III) sulphate under identical conditions used to prepare the above aluminum salt produces an insoluble hydrogen salt with a sulphate to chromium ratio near 2. If the product W was an aluminum salt of the insoluble acid produced under these conditions, it should have a composition corresponding to $Al[Cr(SO_4)_2]_3$. The formation of an aluminum salt of a sulphatopolychromate (III) anion with an apparent sulphate to chromium ratio much greater than 2 is most readily rationalized on the assumption that various sulphatopolychromate (III) anions are produced in solution and that the hydrogen salts of the anions with sulphate to chromium ratios much greater than 2 are soluble, whereas, the metal salts such as aluminum (III) are insoluble. A study of the various anions produced in these digestions should be possible by separating the

various species present in the solutions using anion exchange columns and thus prove or disprove the above assumption. This research does not give a complete description of the various anionic polymeric species formed during the digestion process nor a complete description of the insoluble metal and hydrogen salts that are formed in the digestion, but it has established that the insoluble hydrogen salts invariably have a sulphate to chromium ratio near 2 and that polynuclear anionic species with sulphate to chromium ratios larger than 2 are likely formed and may be precipitated from solution by metallic cations.

The dehydration or pyrolysis of the hydrates of chromium (III) sulphate is considered to occur through a series of condensation reactions. This process is considered to be similar to reactions occurring in aqueous solutions of chromium salts which undergo hydrolysis.[45, 52] If this assumption is valid, the pyrolysis products obtained upon dehydration of chromium (III) sulphate should be identical to the products obtained upon hydrolysis of aqueous chromium (III) sulphate solutions. Furthermore, if the insoluble products obtained in the digestion of chromite were the hydrolysis products as suggested by Downes and Morgan,[2] then the pyrolysis products of the chromium (III) sulphate should have similar infrared absorption spectra to the insoluble products obtained in the digestion of chromite

ore or of chromium (III) sulphate with sulphuric acid. Since the infrared absorption spectra of these various products are not similar, one must again conclude that precipitation does not occur as a result of hydrolysis in the digestion of chromite concentrate with sulphuric acid.

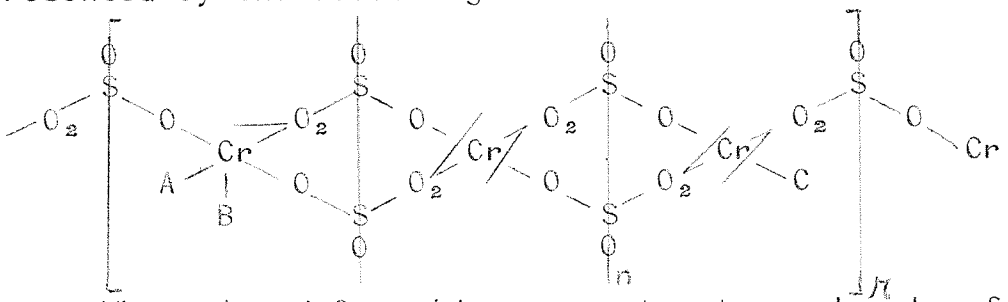
CONCLUSIONS

CONCLUSIONS

This research has established that the mechanism for the digestion of chromite concentrate with sulphuric acid proceeds, through an initial protonic attack of the chromite lattice, bringing the metallic constituents into solution in the same ratio as they occur in the lattice. At sufficiently high concentrations of acid and high temperatures, various anionic polynuclear species are formed, and precipitate as insoluble metal or hydrogen salts. Precipitation of the hydrogen salts in the digestion is favoured by high acid concentration, high temperatures and an excess acid beyond that required to dissolve the chromite. The metallic salts precipitated in the digestion process will not necessarily contain the same sulphatopolychromate (III) anions as do the insoluble hydrogen salts, instead they likely contain anions whose hydrogen salts are soluble.

The hydrogen salts of the sulphatopolychromate (III) anions may be precipitated under conditions of high temperatures and high acid concentrations, and may be divided into three groups. The insoluble salts obtained from solution at temperatures below 180°C, constituting the first group, invariably contain coordinated water molecules, whereas the insoluble salts produced at temperatures of 250°C, the second group, contain no coordinated water molecules.

The lower temperature products invariably have a sulphate to chromium ratio of 2, whereas, the higher temperature products have a ratio slightly larger than 2, the highest value obtained in this research being 2.29. The pyrolysis data and infrared absorption spectra for these salts and their pyrolysis products suggest that their salts may be represented by the following formula



Where A and C would represent water molecules for the insoluble products obtained below 180°C and B, a monodentate sulphate ligand. The value of n determines the chain length of the repetitive unit in the polymer and has a value of unity in the polymer $H[Cr_3(SO_4)_6(H_2O)_2]$. For the insoluble products obtained at 250°C, A with B would represent a bidentate chelating sulphate ligand, whereas C would represent a monodentate sulphate ligand and n would have a value of 2 for the polymer with sulphate to chromium ratio of 2.25.

Attempts to produce anhydrous chromium (III) sulphate by dehydrating the normal violet sulphate in boiling concentrated sulphuric acid were unsuccessful, instead the ''chromidihydroheptasulphate'' or hydrogen heptasulphato-

tetrachromate (III), $H_2[Cr_4(SO_4)_7]$ is produced. The thermal decomposition of the insoluble hydrogen salts obtained at 250°C produces hydrogen pentasulphatotrichromate (III), $H[Cr_3(SO_4)_5]$. The anhydrous materials, including $Cr_2(SO_4)_3$, constitute the third group. Structures compatible with the experimental results for the anhydrous chromium (III) sulphate are shown in Figures 23 and 24. The compound $H[Cr_3(SO_4)_5]$ is assigned an identical structure except that every third chain of $O_2SO_2CrO_2SO_2Cr$ has been removed from both of the parallel sets of chains. Removing every other chain of $O_2SO_2CrO_2SO_2Cr$ from both of the sets of parallel chains would give a possible structure for the compound $H_2[Cr_4(SO_4)_7]$.

Upon pyrolysis, the first group of hydrogen salts of sulphatopolychromate (III) anions lose water of hydration at temperatures below 120°C, followed by loss of sulphuric acid in the temperature interval from 320-450°C. The co-ordinated water molecules are expelled immediately after loss of sulphuric acid and is usually complete near 480°C. The anhydrous chromium (III) sulphate then decomposes starting at temperatures near 520°C.

The second group loses water of hydration at temperatures below 100°C, and sulphuric acid in the temperature interval of 320-450°C, to form the product $H[Cr_3(SO_4)_5]$ which starts to decompose near 585°C to form the chromium

(III) oxide, sulphuric acid, and sulphur trioxide.

Upon pyrolysis of the hexadecahydrate of chromium (III) sulphate which may be formulated as $[Cr(H_2O)_6]_4(H_2S_2O_9)_3$ 5 H_2O, it loses its water of hydration at temperatures below 50° C. Starting at 80°C, coordinated water, and water, hydrogen bonded to the sulphate groups, are lost simultaneously, resulting in a series of fast condensation reactions to produce a polymeric chain in which the sulphate ligands function as bridging groups and give a polymer containing four molecules of water per mole of chromium (III) sulphate. This polymer is not stable at 145°C and continues to lose water slowly up to 335°C where the anhydrous chromium (III) sulphate is produced, provided the heating rate is no greater than 36°C/hr. The anhydrous chromium (III) sulphate starts to decompose at 375°C.

APPENDIX I

A SIMPLE THERMOBALANCE FOR STUDIES OVER A PRESSURE RANGE OF 0 TO 60 ATMOSPHERES

Reproduced from the following publication:

Wendall J. Biermann and Menno Heinrichs

Canadian Journal of Chemistry 40, 1361 (1961)

A SIMPLE THERMOBALANCE FOR STUDIES OVER A PRESSURE RANGE OF 0 TO 60 ATMOSPHERES

ABSTRACT

A design is presented for a thermogravity balance usable to a pressure of 1000 p.s.i. The mass sensitive element is a tool steel cantilever rod, the displacement of which is measured by a linear variable differential transformer. Thermograms for the pyrolysis of calcium oxalate, chromium (VI) oxide, and Mohr's salt are included to show typical performances.

A search of the literature to find a thermogravity balance design which would enable us to study solid-gas reactions over an extended temperature and pressure range disclosed only one design, that reported by Rabatin and Card.[15] This design employs a modified torsion balance as the mass sensitive element and an optical lever - photoelectric cell transducer system to develop a voltage proportional to mass, for automatic recording. While there is no question of the intrinsic excellence of their design, the construction of their balance would seem to offer a major challenge to the machine shop facilities available in most university laboratories.

In the present design, the mass sensitive element is a tool steel cantilever rod, rigidly fixed on one end and undergoing varying displacement on the free end as the sample, supported on the free end, changes mass. The amount

of displacement is determined by a linear variable differential transformer (LVDT), whose output is demodulated and fed to a recording potentiometer. Easy zero adjusting of the transducer after closing and pressurizing the system is incorporated in the design, overcoming the major criticism of Rabatin and Card[15] to the application of an LVDT as a displacement transducer.

The cross-sectional drawing of Figure 30 shows the mechanical construction of the thermobalance. Since recent papers by Newkirk[46] and Garn[18] outline in detail various general considerations regarding the design of thermogravity balances, it would seem superfluous to repeat them here. Suffice it is to say that the present design is in harmony with their various suggestions.

DESCRIPTION OF THE APPARATUS

THE PRESSURE VESSEL

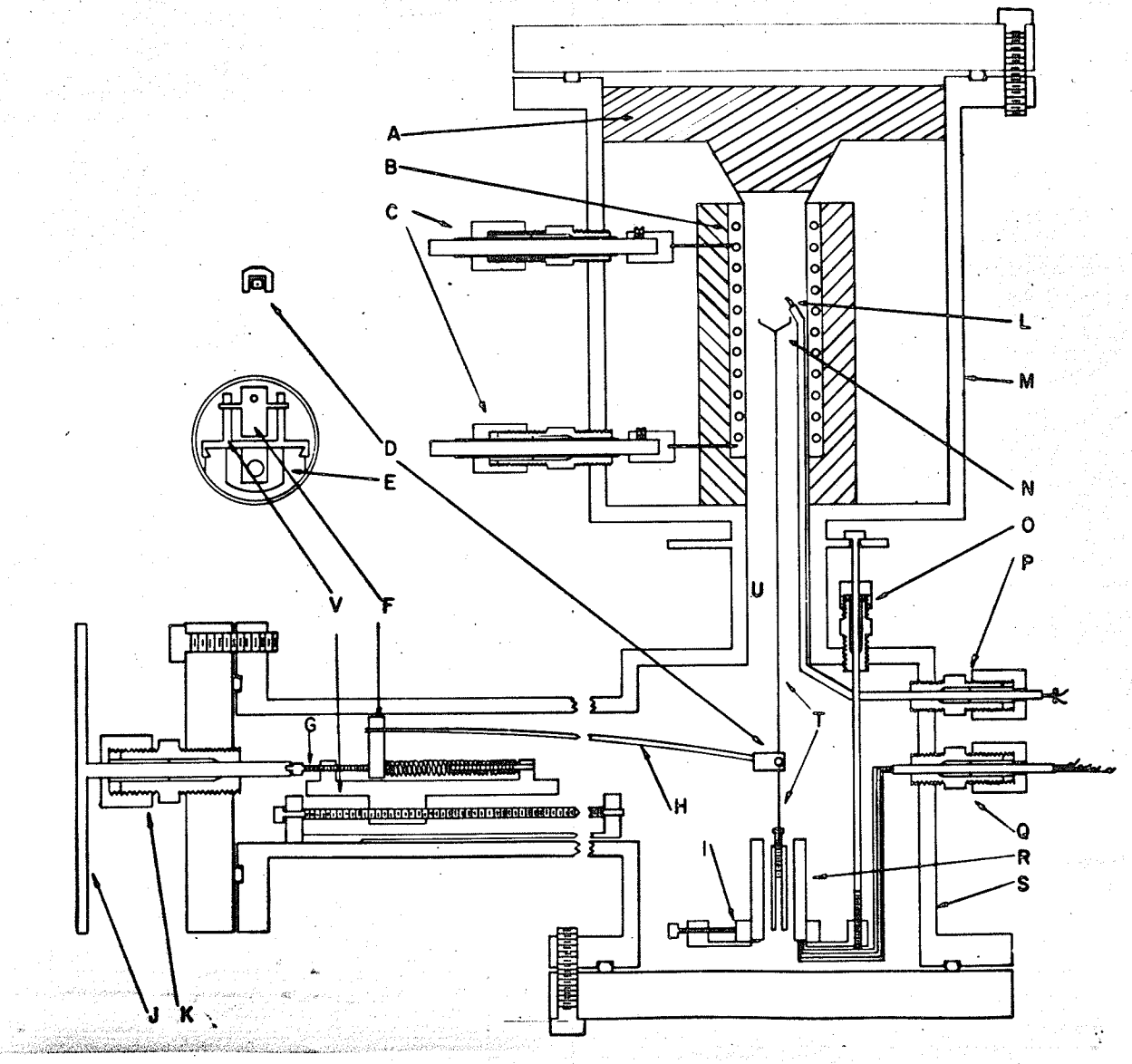
The pressure vessel consists of three cylindrical chambers. An upper chamber M, with a removable top plate, houses the furnace and sample. Communicating with the upper chamber through a tube is the transducer chamber S, from the side of which projects the third cylindrical chamber, housing the cantilever rod and its associated adjustment mechanisms. A removable bottom plate and a removable end plate permit access to these latter chambers. The entire construction was from type 304 stainless steel, employing wall thickness of 0.25 inch for the chambers, 0.50 inch for the flanges welded onto the open ends of the chambers, and 0.75 inch for the access plates. These plates were secured by hardened steel cap screws, and gas-tight closure was effected with Teflon "O" rings.

Instead of using flat plates on the ends of the pressure chambers, they could alternately be machined to spherical segments which would permit the same pressures to be contained with thinner walls. It would also be better practice to use radius cuts on the terminations and joinings of the chambers rather than the right-hand cuts which are shown on the drawing.

A tripod support, not shown on the drawing, holds the pressure vessel about 6 inches off the vibration pad on

Figure 30

Mechanical construction of the thermobalance.


A
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which it rests, permitting adjustments to be made through the lower access port, using a mirror for vision. The vibration pad consists of several layers of lead and cork, sandwiched between plywood, and mounted onto a concrete block wall by rigid brackets and was originally intended to support an analytical balance.

Calculations indicate that the pressure vessel should safely hold a pressure of about 1500 p.s.i., and it has been tested up to 1100 p.s.i. by applying oxygen from a cylinder.

A vertical quartz rod T supports the dish-shaped platinum foil sample pan on a tripod support N in the center of an electrically heated furnace. Fixed on the bottom of the quartz rod is the core of a Schaevitz Type 175 ES-L LVDT. This particular LVDT was chosen because we had anticipated more vibration background than was actually experienced; the amount of deflection needed is much less than the linear range of this unit. A much shorter range LVDT can therefore be substituted.

Immediately above the core, the quartz rod is supported by the cantilever rod H, a jewel-bearing supported pivot D allowing the quartz rod to remain vertical as the angle between it and the cantilever rod changes as a result of displacement. As displacements of only a few thousandths of an inch are used, this assembly is essentially

a strain gauge. Originally it had been planned to use a quartz rod for the cantilever, but experience showed that a rod thin enough to give adequate sensitivity was subject to frequent breakage. A 10-inch length of alloy steel drill rod (3/32-inch diameter) was then substituted and it has proved to be highly satisfactory both as regards mechanical strength and retention of calibration.

The furnace in the upper chamber was wound with Kanthal A-1 wire, backed with Alundum cement to give a rigid, cylindrical heating element B, which surrounds the sample. Asbestos fibers were packed in the space between the heating element and the wall of the pressure vessel. Closure of the top was effected with a lid A, fabricated from an insulating firebrick, which sits on the packed asbestos fibers. When the furnace is operated at 1000°C, very little heating of the outer vessel takes place. Two platinum foil radiation shields, in the vicinity of U in Figure 30 minimize heat transfer to the lower sections of the pressure vessel.

Electrical connection to the heating element was made by slipping a cover of Teflon tubing over brass rods and then leading them through the wall of the pressure vessel with Conax sealants (Conax Corporation, Buffalo, N.Y.) with Teflon seals, as shown at C on Figure 30.

Temperature in the vicinity of the sample is

measured by means of a conventional high-temperature thermocouple L, led in through a Conax sealant P and having an exposed platinum, platinum-rhodium junction for low thermal lag. A similar thermocouple employing a chromel-alumel junction has also been employed. Placement of the thermocouple in different positions gives no change in the temperatures at which mass changes occur, indicating that no important thermal gradients exist in the vicinity of the sample pan.

The LVDT R in the lower compartment was mounted on a triangular brass plate, supported near each corner by an adjusting screw, one of which is shown at O, permitting leveling and approximate vertical positioning of the transducer body. Conax pressure sealants with neoprene seals were used to pass the adjusting screws through the wall of the pressure vessel. Three adjusting screws, one of which is shown at I, were used to center the transducer case about the core. Once the transducer case has been positioned, it requires no further adjustment between runs, vertical adjustment of the core for zeroing being done with the cantilever rod adjustment.

The fixed end of the cantilever rod H is anchored in a small brass plate, shown in both side and front view as F, which is in turn supported on a pivot which can rotate in ball bearing assemblies fixed to the carriage V. The

angular position of this small plate is fixed by the end of the threaded rod G, against which it is pressed by a firm coil spring. This rod can be moved horizontally by rotation, being threaded through a block on the end of the carriage (40 threads/inch). A conax sealant, with a neoprene seal, passes this adjusting rod through the end plate with a gas-tight seal, and permits it to be turned with the 3-inch handwheel J after pressure buildup. This very simple system permits surprisingly precise adjustments of core position with no difficulty whatever.

The entire carriage assembly can be moved horizontally along the dovetail track E by means of a drive screw. This adjustment was intended to allow coarse adjustments of sensitivity by changing the length of the cantilever rod. Thus far it has been superfluous, the linear range of the LVDT being sufficiently long, and the stability and sensitivity of the other components sufficiently high that a change in range is more easily accomplished by taking greater or lesser fractions of the demodulator output.

DEMODULATOR

Although the output of the LVDT is greater than would be required for full-scale deflection of a 10-mv recorder, the output signal is put through an amplifier stage before rectification to circumvent the difficulty of

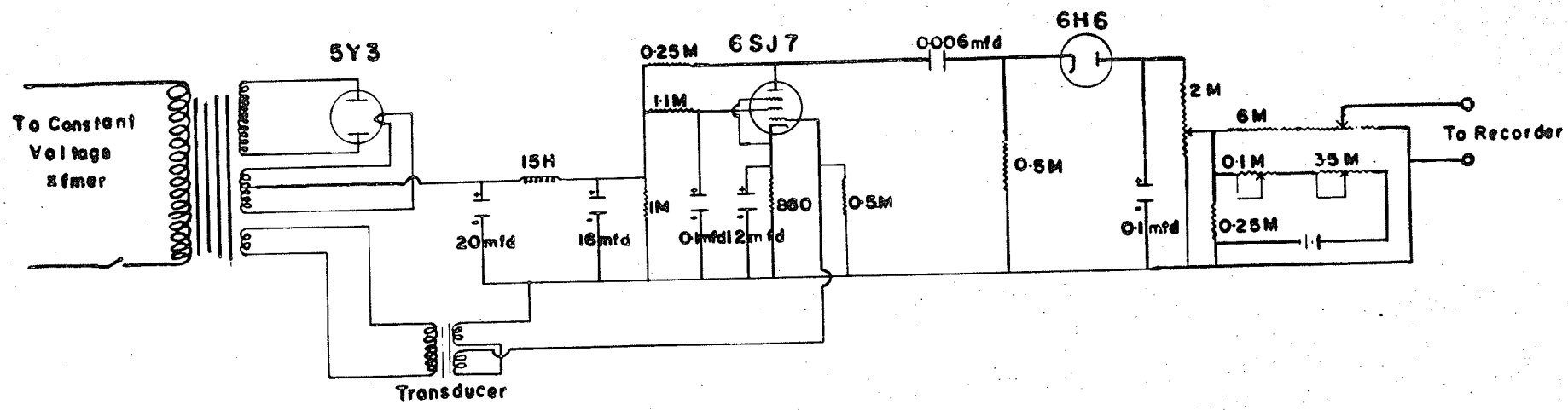
finding a rectifier with linear characteristics at low voltages. Following half-wave rectification of the amplified signal, a portion, usually 1/12, is selected by a variable potential divider network for feeding to a 10-mv recorder. The demodulator circuit is shown as Figure 31. It will be noticed that the recorder output voltage fed to the recorder is opposed by a variable voltage taken from a mercury cell. This is a convenient way of setting the recorder to zero when beginning a run with the transducer slightly removed from its null point to get into a more linear region, and also to eliminate the effects of any constant inductive effects before the rectifier.

This demodulator is probably more complex than required. In principle, as there is adequate voltage from an LVDT in this situation to drive a recorder directly, it should only be necessary to follow the rectifier, even though non-linear, with an RC circuit having a time constant several times as long as the duration of a cycle in the LVDT output. We have not yet explained our failure to achieve satisfactory operation with the simpler circuit.

The recorder used was a two-pen, 10 mv/channel ServoRiter recording potentiometer (Texas Instrument Company, Houston, Texas) which permitted simultaneous recording of the LVDT and thermocouple outputs with 10-inch deflections on a common time axis.

Figure 31

Demodulator circuit.


To Constant Voltage Xfmer
5Y3
15H
20mfd
16mfd
0·25M
6SJ7
1·1M
1M
0·1mfd
2mfd
860
0·5M
0·006mfd
6H6
0·5M
0·1mfd
2M
6M
0·1M
3·5M
0·25M
To Recorder
Transducer

TEMPERATURE PROGRAMMER

When the power supplied to the furnace was varied by linear variation of the voltage across the heater with time, the resulting time - temperature plots showed only moderate changes of slope. As this curvature was not great enough to be a handicap in any work we have in mind, a relatively simple motor and gear box drive was used to turn a variable autotransformer, with a limit switch at the end of its range. This was fed by a second variable auto-transformer, much in the manner used by Reisman.[19] By selecting suitable gear combinations a wide range of heating rates can be selected.

PERFORMANCE OF THE THERMOBALANCE

OPERATION

With the bottom plate removed, the transducer case is centered coaxially about the core in the vicinity of the null point by manipulation of the six adjusting screws which determine its position. As mentioned previously, this adjustment seldom needs to be repeated.

As the demodulator is not phase sensitive, deflections on either side of the null point are not distinguishable by the recorder. It is, therefore, easy to locate the null point by moving the cantilever rod with the handwheel until minimum deflection of the recorder is noted. Because an LVDT is generally non-linear in the immediate vicinity of its null point, it is most convenient to displace the core downward sufficiently to come into a linear region, the displacement with this apparatus being equivalent to about 40 mg in the sample pan. The region of linearity of the LVDT, in this apparatus, extends over a sample mass in excess of 1 g and the voltage developed across the 2-meg potential divider in the 6H6 plate circuit is about 1.0 mv/mg load in the sample pan. Since the recorder used gave full-scale deflection with 10-mv input, it was found convenient in most cases to use 1/12 of the demodulator output and to choose samples of such size that the mass change would be of the order of 0.1 g.

When set up as above, calibration was done directly by the addition of a succession of fractional weights, and the resultant sensitivity was 1.23 mg/chart division (0.1 inch), linear within the uncertainty of interpolating between chart markings. Greater or lesser sensitivity can be obtained, if experimentally convenient, by using a different fraction of the demodulator output. Zeroing of the recorder at different positions within the linear range is accomplished by applying a counter voltage in series with the demodulator output. The magnitude of the counter voltage, obtained from a mercury cell, is determined by the settings of the 3.5- and 0.1-meg potentiometers functioning as variable resistors and giving a coarse and fine control, respectively.

With the transducer core positioned at the beginning of the linear region, an appropriate-sized sample is then placed on the sample pan. If mass is to be lost, the recorder is set near full-scale deflection, and where mass is to be gained by reaction with the atmosphere within the pressure vessel, the recorder is set near zero deflection. While it would be possible to record the absolute mass of the sample, greater use is made of the sensitivity of the apparatus by weighing the sample on a balance and, using the above method of setting the recorder and an appropriate setting of the sensitivity selector, recording only the loss

or gain in mass.

RESULTS

Typical plots of mass and temperature as functions of time were traced from the recorder charts of the apparatus described above, and are reproduced as Figures 32, 33 and 34. The temperature curve is easily distinguished from the loss of weight curve by the absence of inflection points. Calibration of the thermocouples by conventional calibration at invariant points served to fix the temperature axis.

Figure 32 shows the pyrolysis of a 0.2-g sample of calcium oxalate. The first plateau, representing completion of drying, begins at a temperature of 230°C, and the third plateau, completion of conversion to calcium oxide, occurs at 860°C, both temperatures being in substantial agreement with Newkirk.[46] The center plateau, formation of calcium carbonate by the loss of carbon monoxide, is apparently reached at 435°C, substantially lower than Newkirk's value, but the irregularity in the temperature curve in this vicinity suggests that oxidation of the carbon monoxide is probably responsible for the rise in sample temperature, and served to underline the stress laid by Newkirk and by Garn and Kessler[55] on the effect of atmosphere and venting on the shape of the thermogram.

Figure 32

Thermogram obtained by heating calcium oxalate.

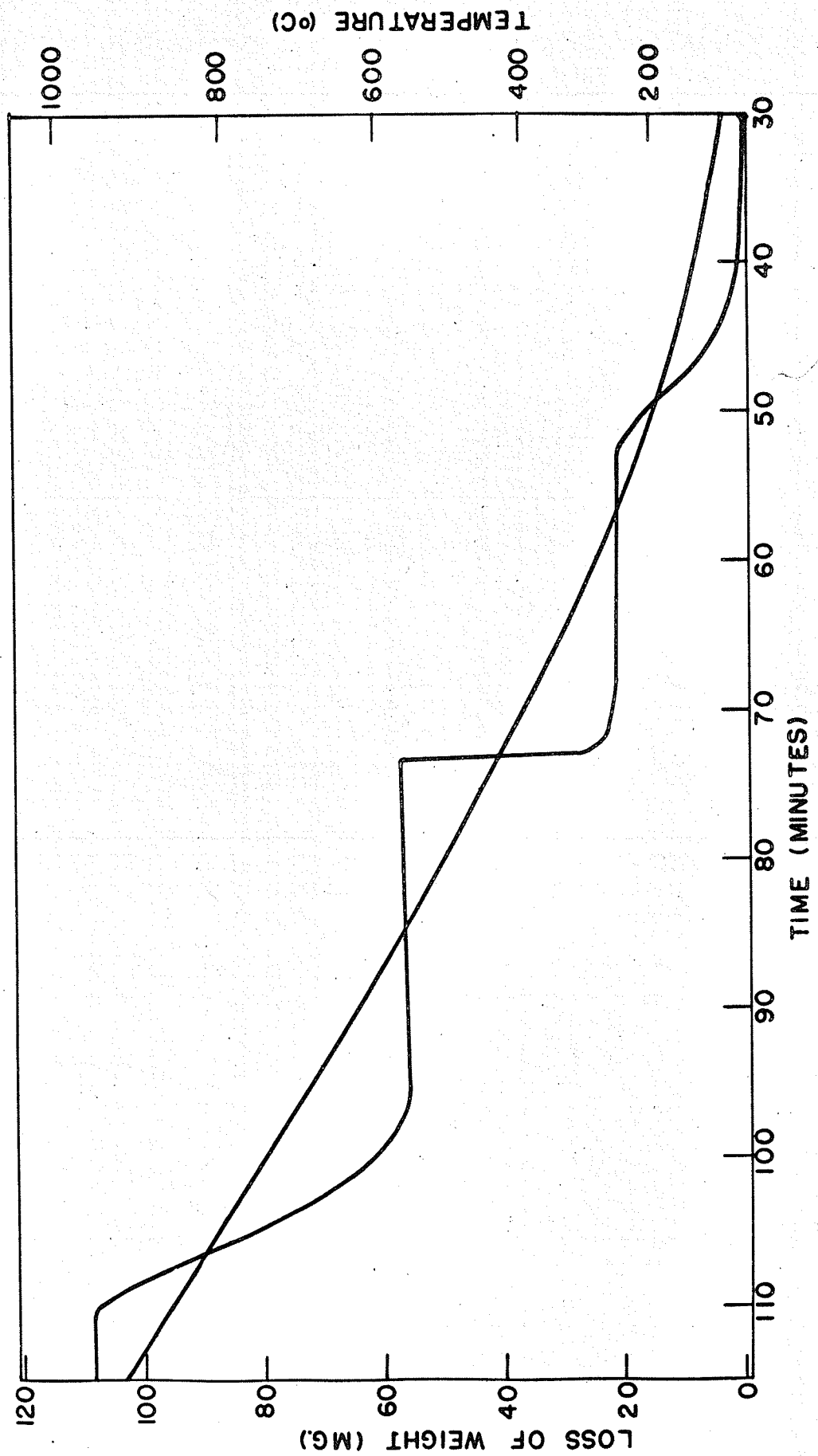

TEMPERATURE (°C)
1000
800
600
400
200
30
40
50
60
70
80
90
100
110
TIME (MINUTES)
0
20
40
60
80
100
120
LOSS OF WEIGHT (MG.)

Figure 33

Thermogram for heating chromium (VI) oxide under oxygen pressure of 200 p.s.i.

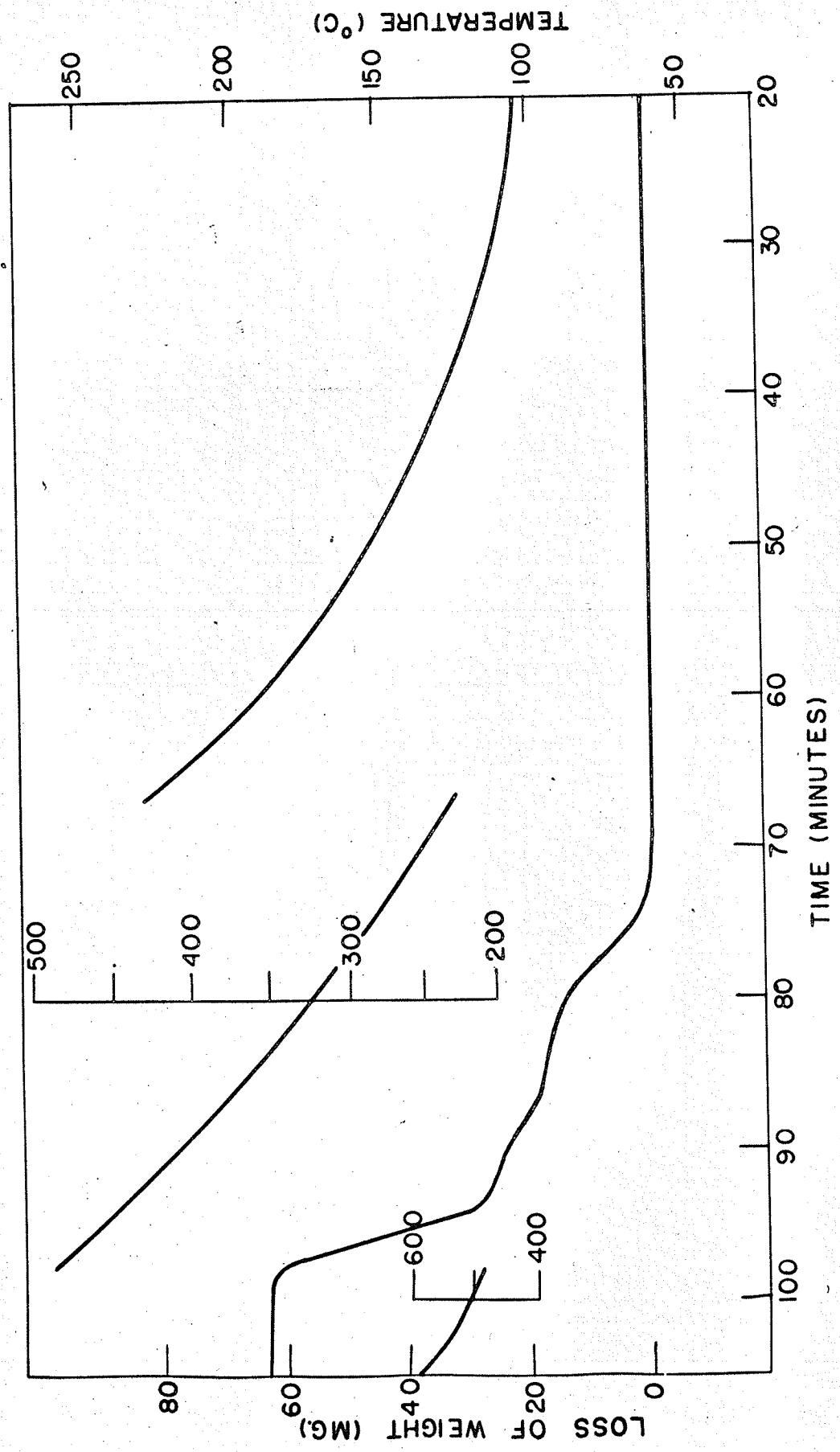

TEMPERATURE (°C)
250
200
150
100
50
20
30
40
50
60
70
80
90
100
TIME (MINUTES)
500
400
300
200
600
400
80
60
40
20
0
LOSS OF WEIGHT (MG.)

Figure 34

Thermogram obtained on heating Mohr's salt.

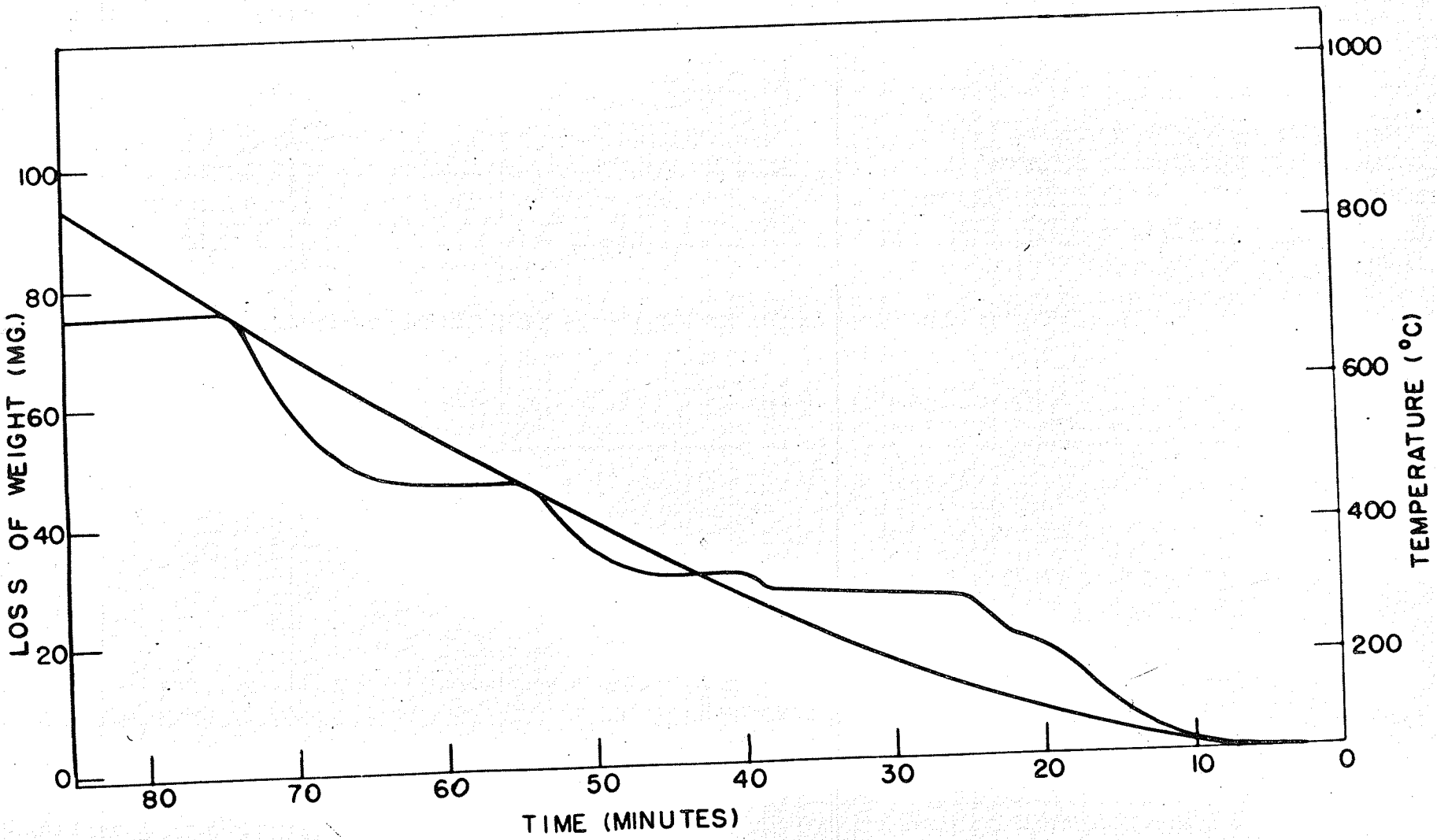

LOSS OF WEIGHT (MG.)
100
80
60
40
20
0
80
70
60
50
40
30
20
10
0
TIME (MINUTES)
1000
800
600
400
200
TEMPERATURE (°C)

Figure 33 is a thermogram for the pyrolysis of chromium (VI) oxide under an oxygen atmosphere of 200 p.s.i. A precision potential divider allowed all, half, or one fifth of the chromel-alumel thermocouple output to be fed into the recorder. Thus leading to the three temperature axes shown on this thermogram. Oxygen is lost in three steps, the weight losses in these steps being in the ratio 4.10:1.97:9.00, which agrees with the successive formation of Cr_5O_{13}, Cr_5O_{12}, and Cr_2O_3, as reported by Mellor.[12] The 258.2-mg sample gave a residue of 194.8 mg, compared to the theoretical value of 196.1 mg.

Figure 34 is a pyrolysis curve for Mohr's salt. This thermogram can be tentatively interpreted by postulating a decomposition in the following steps:

(1) a loss of 4, and subsequently 2 more, moles of water per mole of Mohr's salt, with the loss of mass being 34.68% of the sample weight (34.58% theoretical);

(2) a loss of 1 mole of ammonia and 1/2 mole of hydrogen simultaneously, the loss of mass being 5.64% (5.69% theoretical);

(3) the simultaneous loss of 1 mole of ammonia and 1/2 mole of sulphuric acid, the mass loss being 21.29% (21.19% theoretical);

(4) the loss of 1 1/2 moles of sulphur trioxide, corresponding to a mass loss of 38.39% (38.42% theoretical).

APPENDIX 2

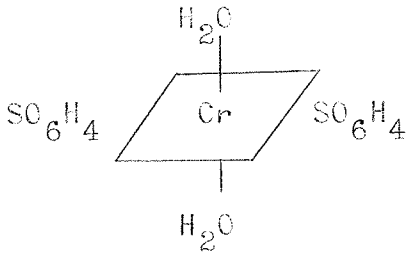
REVIEW OF HARMELIN'S THESIS AND COMPARISON TO THIS WORK.

REVIEW OF HARMELIN'S THESIS AND COMPARISON TO THIS WORK

This section is added as an appendix because the publication by Harmelin[56] appeared only after this thesis was essentially completed.

Harmelin and Duval[31] have investigated potassium chromealum using the techniques of thermogravimetry, infrared absorption spectral analysis, and conductance measurements. Harmelin[30] reports a similar study on the hydrates of chromium (III) sulphate. Conductance measurements in dilute and concentrated solutions of the chrom alum led to the conclusion that, in dilute solutions, the alum gave rise to four or more ions, whereas in concentrated solutions the alum behaved as a binary electrolyte. Migration experiments showed that the potassium ions and small amounts of cationic chromium migrated to the cathode, whereas, most of the chromium and the sulphate ions were found at the anode. These observations, alone, led to the conclusion that the alum is, therefore, better represented by the formula $K[Cr(SO_4)_2]$ 12 H_2O, indicating complex formation. Thermogravimetric analysis of the alum shows that 6 molecules of water are lost readily and are, therefore, assigned to ''water of crystallization''. The last 6 molecules of water are lost in two separate stages, first 4 molecules, then 2 molecules of water. The four molecules of water are assumed to be bonded to the metasulphate ion

$SO_4^{=}$, thus becoming derivatives of orthosulphuric acid $H_4SO_6^{=}$. The two molecules of water form part of the complex to maintain octahedral coordination for the chromium (III) ions. Their conclusion is that the potassium chromealum should be formulated as $K[Cr(SO_6H_4)_2(H_2O)_2]$ 6 H_2O, and that it will contain the complex anion.



The trans configuration was preferred to the cis configuration because the trans structure would be more compatible with the cubic structure of alum.

Harmelin[30] finds that the hydrates of chromium (III) sulphate, with n values between 16 and 18, lose ''water of crystallization'' or ''water of wetting'' between 35-80°C, upon pyrolysis, to give the hydrate with an n value of 14. These 14 molecules of ''water of crystallization'' are lost between 115-540°C. A change in slope at 170°C is observed after 10 of these have been lost, the last four are then lost slowly. The thermograms show a stable plateau between 540 and 570°C, corresponding to the anhydrous chromium (III) sulphate. Her conclusion is that 6 molecules of water are attached in the form of 3 $H_4SO_6^{=}$ ions, another 4 are weakly bound to the 2 chromium (III) ions, and upon pyrolysis these

10 are lost simultaneously. The other 4 are strongly bonded to the chromium (III) ions and are lost only at high temperatures.

The two infrared absorption bands at 2500 cm^{-1} and 3000 cm^{-1} are taken as evidence for the existence of OH groups in the orthosulphate ion $H_4SO_6^{=}$. The influence of the water molecules on the symmetry of the sulphate ion in the orthosulphate ion is evident in that they notice a change in the number and the position of the absorption bands from that observed for the metasulphate ion. Thus, v_1 and v_2 become active (986 and 467 cm^{-1} respectively) while v_3 is displaced to a lower frequency (1092 cm^{-1}), whereas v_4 is found in its usual place (610 cm^{-1}). An examination of Table 6 on page 94 shows that if v_1 and v_2 become infrared active, then v_3 and v_4 must split into several absorption bands. In a recent paper brought to the author's attention, subsequent to the completion of this thesis, Harmelin gives a more detailed description of her studies on the hydrates of chromium (III) sulphate.[56] The conclusions from this publication are reproduced here for the convenience of the reader. In this last publication, the author reports that if one takes careful account of the construction of the absorption cell, one can obtain evidence for the appearance of shoulders at 1135, 1108, 1092, 1075, and 1060 cm^{-1} on the main absorption band. These bands,

however, find no assignment in the publication.

Harmelin, in this latter publication,[56] concludes that the hydrates of chromium (III) sulphate would be more correctly formulated as $[Cr_2(SO_4)_3\ 14\ H_2O]\ X\ H_2O$, where X would have values between 0 and 4, but generally between 2 and 3. The sulphate group is not bonded directly to the chromium (III) ion, instead, the chromium (III) ion is assumed to possess a regular octahedron of water molecules in its coordination sphere. Eight of these twelve water molecules are strongly hydrogen bonded to the sulphate ligands and are lost readily upon pyrolysis, whereas the other four of the twelve molecules, bound only to the chromium (III) ions, are lost only at higher temperatures. Another two water molecules which complete the fourteen molecules of constitutional water are not assigned any definite positions. Thus the structure shown in Figure 36 is assumed to exist in the hydrate.

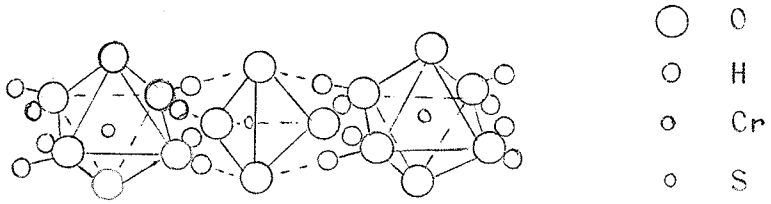


Figure 36

or one may consider this hydrate to contain the anion $H_8SO_8^{=}$ shown in Figure 37

Figure 35

Reproduction of Harmelin's ''Resme et conclusions generales''.

RÉSUMÉ ET CONCLUSIONS GÉNÉRALES

Les résultats personnels les plus importants obtenus au cours de ce travail peuvent se résumer ainsi :

1° *Une étude détaillée des méthodes de préparation du sulfate* violet *de chrome-III montre que l'on ne peut pas lui attribuer un nombre de molécules d'eau défini. L'état d'hydratation le plus fréquent, auquel aboutissent les différents procédés de préparation se trouve compris entre 16 et 17. Le sulfate violet se présente comme un complexe renfermant de l'eau de constitution et de l'eau d'insertion. Il semble plus correct de le représenter par la formule globale* $[Cr_2(SO_4)_3\ 14\ H_2O] + x\ H_2O$, *x étant un nombre variable d'une préparation à l'autre, généralement compris entre 2 et 3, avec les valeurs extrêmes zéro et 4.* Les 14 molécules d'eau de constitution ne sont pas identiques entre elles. *Elles se répartissent en deux groupes, l'un de dix, l'autre de quatre, correspondant à deux sortes de liaisons au moins. La disposition octaédrique des molécules d'eau autour de l'atome de chrome se trouve conservée. Le groupe de quatre occupe les positions* trans *et, dans le groupe de dix, huit sont disposées dans le plan moyen des atomes de chrome, situés au centre de l'octaèdre, et présentent, en même temps, des liaisons par « pont d'hydrogène » avec les radicaux sulfuriques, de sorte que l'on peut observer les vibrations des groupes apparents* $SO_8H_8^{--}$ *ou* $SO_6H_4^{--}$ *(bandes de 2 950, 2 500 et 1 090 cm⁻¹). Deux molécules d'eau restent encore sans position privilégiée. Elles peuvent se trouver à l'état d'insertion dans le composé, ou bien servir de ponts entre deux ou plusieurs autres molécules de sulfate dans la maille dont la configuration reste encore inconnue.*

2° *Les sulfates* verts *de chrome-III contiennent également de l'eau en quantité variable, 11 à 3 molécules, et les spectres d'absorption infrarouge ne permettent pas de leur attribuer un rôle privilégié et déterminé. L'allure de la courbe thermogravimétrique et la présence de deux maximums sur la bande large de 3 000-3 400 cm⁻¹ semblent indiquer la présence d'eau liée et d'eau plus libre, comme on le trouve chez certaines zéolites. Il résulte de la comparaison des différents types de spectres d'absorption infrarouge que la répartition des molécules d'eau chez le sulfate vert provenant de la déshydratation du sel violet correspond à un arrangement plus ordonné que chez les sulfates verts, préparés directement par voie chimique. La présence de deux bandes à 1 210 et 1 075 cm⁻¹, liée à la dissimulation totale des ions sulfuriques et chromiques vis-à-vis de leurs réactifs dans les solutions recemment préparées, laisse présumer que* tous les groupes SO_4 participent à l'édifice du sulfate vert sous forme de ponts *reliant les atomes de chrome entre eux.*

3° *Nous avons etendu ces résultats à l'étude des* acides chrome-III polysulfuriques. *La présence, sur les spectres d'absorption infrarouge de ces corps, de deux bandes à 1 200 et 1 055 cm⁻¹, jointe à l'absorption intense de 2 900-3 000 cm⁻¹, est compatible avec l'existence de* groupes hydrogénosulfates HSO_4^-. *L'augmentation de la teneur en acide sulfurique, quand on passe de l'acide chrome-III monosulfurique à l'acide chrome-III hexasulfurique, ne provoque pas de modifications brutales des spectres. On observe, au contraire, un passage progressif d'un type de spectre à l'autre. Il semblerait que le squelette constitutif de ces acides soit « l'hydrate sulfochromique » de Recoura, que nous formulons* $SO_4 = Cr - (HSO_4)$ *et qui fait apparaître sur ses spectres d'absorption les bandes principales des acides chrome-III polysulfuriques (2 900, 1 055, 660, 574, 455 et 370 cm⁻¹).*

4° *L'étude des* solutions aqueuses *nous a permis de confirmer certains résultats obtenus sur le solide : forces d'association entre les ions chromiques et sulfuriques par l'intermédiaire des molécules d'eau formant pont entre les deux édifices, formules polymérisées chez les sulfates verts se traduisant par une dissimulation totale des ions chromiques et sulfuriques vis-à-vis de leurs réactifs.*

Les deux techniques mises en œuvre pour l'étude du solide — thermogravimétrie et spectrographie d'absorption infrarouge — nous ont permis d'améliorer nos connaissances dans ce domaine de la chimie ; mais le problème de la structure des deux variétés de sulfate de chrome pose encore des énigmes. Certaines pourront être levées, lorsqu'un chercheur aura réussi à jeter les bases de la structure, par analyse aux rayons X, diffraction de neutrons et résonance magnétique nucléaire (pour cette dernière méthode, le paramagnétisme du chrome soulèvera d'ailleurs des difficultés). Nous avons été arrêtée aussi par le comportement colloïdal de certaines de nos solutions. Là encore, un ou plusieurs chercheurs spécialistes de cet état de la matière pourront trouver de nouveaux sujets de recherches.

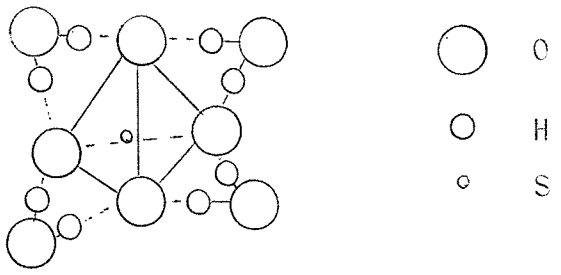


Figure 37

Harmelin also suggests that the interpretation advanced for the potassium chrom alum should be modified to be compatible with this interpretation, thus giving both the potassium chrom alum and the 16-18 hydrates of chromium (III) sulphate similar structures in keeping with their similar infrared absorption spectra. The 2457 cm^{-1}, assigned to the OH stretching vibration in the anion $H_8SO_8^{=}$, disappears for the 4 hydrate whereas the 2940 cm^{-1}, assigned to the stretching frequency v_1 and v_3 of coordinated water shifts to a higher frequency 3225 cm^{-1} for the 4 hydrate. The 1630 cm^{-1} band, assigned to the deformation mode of water v_2, slowly disappears upon complete dehydration. These observations are essentially identical to those reported in this thesis. Furthermore, the assignment of these bands is essentially identical to those in this thesis.

Harmelin[56] again reports the presence of an

absorption band at 940 cm^{-1} in the 16 hydrate and assigns this band to the hindered rotation of a coordinated water molecule. The experimental results outlined in this thesis show the appearance of this band at 940 cm^{-1} only for the partially dehydrated forms of the normal violet chromium (III) sulphate and in the impure products obtained in preparing the hexadecahydrate of chromium (III) sulphate as discussed in the main body of this thesis.

The bands at 1092, 610 cm^{-1} are assigned to the v_3 and v_4 vibration of the sulphate group and the bands at 986 and 467 cm^{-1} to the vibrations v_1 and v_2 respectively, which, theoretically, are infrared active. The infrared activity of the latter two bands is attributed either to coupling between the sulphate groups or to an important change in the symmetry of the sulphate group due to distortion as might be provided by the water molecules in the lattice. The structure in Figure 37 for the ion $H_8SO_8^{=}$ shows the sulphate group, possessing a high degree of symmetry, which according to Harmelin, explains the small number of bands found for the sulphate group in the 16 hydrate. These conclusions are not consistent. First, if the sulphate group does possess a high degree of symmetry, then the bands at 986 and 467 cm^{-1} should be infrared inactive unless allowed due to a reduction in symmetry because of lattice requirements. This is possible only if the sulphate group

having all four oxygens equivalently bonded, lies along a symmetry axis of the crystal, giving the sulphate group a site symmetry lower than that observed for the isolated group. The selection rules outlined by Winston and Halford[48] and presented in this thesis state that a vibration assigned infrared inactivity under site analysis will still be infrared inactive under the more rigorous rules of factor group analysis. This means that if two bands at 986 and 467 cm^{-1} are allowed due to lattice requirements, the symmetry of the sulphate site is lower than T_d, presumably C_{3v}, since only one band is observed for the v_2 vibration. If the site symmetry is C_{3v}, then the absorption due to the v_3 vibration should split into two absorption bands. However, only one band 1092 cm^{-1} is assigned to the v_3 vibration. Secondly, if the sulphate ligand does possess a lower symmetry, as indicated by the presence of the two bands at 986 and 467 cm^{-1}, then the absorption bands for v_3 and v_4 should be split into several components depending on the symmetry of the sulphate ligand. Some of the unresolved and unassigned bands reported by Harmelin can easily be assigned to these latter two vibrations, thus obtaining agreement with theoretical predictions and experimental results.

The second type of spectra obtained by Harmelin, corresponding to the hydrates with n values between 4 and 5, are characterized by the appearance of two very broad

bands, whose maxima appear to be at 1060 and 1210 cm^{-1}. The first has a very strong, and the second, a medium intensity. The latter is assigned to the first harmonic of v_2 which is 2 X 610 = 1220 cm^{-1}, whereas the 1060 cm^{-1} band is assigned either to a combination band of v_2 and v_4 = 467 + 610 = 1077 cm^{-1} or to the v_1 vibration of the sulphate group. No assignment is made for the v_3 vibration of the sulphate ligand except to note that the modification of the spectra in the 1000 - 1200 cm^{-1} region represents some change in the bonding of the sulphate group.

The bands in the third type of spectra observed for the anhydrous chromium (III) sulphate are assigned as follows: the three bands at 1105, 1122, and 1135 cm^{-1} to the triply degenerate v_3 vibration; three bands at 600, 630, 690 cm^{-1} to that of v_4; two bands at 443 and 475 cm^{-1} to v_2. A band at 378 cm^{-1} is assigned to the valence vibration of Cr - S, and a band at 1240 cm^{-1} to the harmonic 2 v_4. The band at 1070 cm^{-1} received an assignment either to the combination band of $v_2 + v_4$, or to the v_1 vibration. Three bands at 338, 499, and 690 cm^{-1}, receive no assignment.

The second type of spectra given by Harmelin for the hydrate with an n value between 4 and 5 does not correspond to those described in this thesis for similar n values, whereas the bands observed for the anhydrous chromium (III) sulphate show close correspondence. However, in subsequent

discussion of the spectra of various green salts of chromium (III) sulphate, Harmelin describes the spectra observed for commercial green chromium (III) sulphate and the green salt produced by evaporating a solution of the normal violet salt to dryness on a water bath, which are essentially identical to those reported in this research for the green hydrates of chromium (III) sulphate with n values greater than 4. Harmelin concludes that since the four bands in the region of 1000 - 1200 cm^{-1} are essentially identical to those observed by J.P. Mathieu et al[*] for the bridging sulphate in μ ammino μ sulphato octammine dicobalt (III) chloride the sulphate groups in the green chromium (III) sulphate act as bridging sulphate ligands. The four bands have the values of 1200 - 1115 - 1040 - 990 cm^{-1}. However, some ambiguity exists in terms of assignment of the first three bands. Harmelin assigns the 990 cm^{-1} band to the v_1 vibration of the sulphate group and suggests that the other bands indicate a strong perturbation on the tetrahedral symmetry of the sulphate group. In the conclusions, she states - "La présence de deux bandes à 1210 et 1075 cm^{-1} liée à la dissimulation totale des ions sulfuriques et chromiques vis-á-vis de leurs réactifs dans les solutions recement préparées laisse présumer que tous les groupes SO_4 participent à l'édifice du sulfate vert sous forme de

ponts reliant les atomes de chrome entre eux.'' The bridging sulphate groups would have C_{2v} symmetry and should, according to the selection rules given in Table 6, give rise to three infrared absorption bands as the degeneracy of the v_3 vibration is removed completely. The spectra recorded by Harmelin is in complete accord with the theoretical predictions but it is not certain that Harmelin appreciates this fact.

Harmelin[56] reports as well the experimental data obtained on the ''chromipolysulphuric acids.'' These are the water soluble products obtained by heating solutions of chromium (III) sulphate and sulphuric acid on a water bath until they are dry. According to her description, these are identical to the starting materials used by this author in the second method of preparing the hydrogen salts of sulphatopolychromate (III) anions as outlined on page 37. The results obtained by Harmelin essentially confirm the observations made by this author. It may be recalled that baking these materials for prolonged periods of time caused crystallization of these products except for the first acid in this series ''chromimonosulphuric acid''. The others all crystallized to give a product containing a sulphate to chromium ratio near two.

Thermogravimetric analysis of the ''chromipoly-sulphuric acids'' leads Harmelin to the conclusion that

these acids all lose a variable amount of water below 115°C: the amount of water lost depends primarily on the length of time they are dried on the water bath. The mono and di acids show a continuous loss in weight between 110 and 550°C, due to the simultaneous loss of water and sulphuric acid: an increase in the rate between 270 and 320°C is evident as the last sulphuric acid is lost. All of the other ''chromipolysulphuric acids'' lose water below 100°C followed by loss of water and sulphuric acid for the ''chromitrisulphuric acid'' and loss of only sulphuric acid for the tetra, penta and hexa acids, below 290°C. These acids all lose one mole of sulphuric acid per mole of chromium (III) sulphate between 350 and 550°C. These latter acids lose water in the temperature interval of 350 to 550°C corresponding to 0.7 ± 0.3, 1.2 ± 0.3, 1.4 ± 0.3 and 2.1 ± 0.3 for the tri, tetra, penta and hexa acids respectively per mole of sulphuric acid lost above 290°C or per mole of chromium (III) sulphate.

The infrared absorption spectrum of the mono acid shows a strong band at 1060 cm^{-1} and a shoulder at 1200 cm^{-1}, both being poorly defined. A slow modification of the spectra starts with the di acid; this spectrum shows better resolution and the appearance of new bands at 990 and 885 cm^{-1}. For the tri, tetra, penta and hexa acids the spectra are well defined and show absorption bands at 1232, 1200,

1155, 1057 and 910-860 cm^{-1}. Heating these latter acids at a temperature of 175°C for 4 or 5 hours causes no change in the absorption spectra and no loss in weight. The spectra of the pyrolysis products of these acids obtained at 290°C are all identical and correspond to ''1'hydrate sulfochromique''; this corresponds to the compound Recoura[10] designated as ''the isomeric form of chromitetrasulphuric acid''. The spectrum for ''1'hydrate sulfochromique'' shows two absorption bands at 1215 and 1055 cm^{-1}.

Harmelin concludes that, since all of these acids show infrared absorption bands characteristic of ''1'hydrate sulfochromique'' and since only the weak bands disappear in going from one compound to the other, the basic structure of ''1'hydrate sulfochromique'' exists already in the ''chromipolysulphuric acids''. These weaker bands presumably are the bands evident in the ''chromipolysulphuric acids'' which disappear upon heating to 290°C where ''1'hydrate sulfochromique'' is produced. Furthermore, since all of these acids except the first two, lose all but one mole of sulphuric acid when heated to 290°C, and since this last mole is then lost between 350 and 550°C, Harmelin suggests that this excess sulphuric acid present in these acids does not belong to the structure of the ''1'hydrate sulfochromique''. The basic structure for the latter compound exists for all of the ''chromipolysulphuric acids''

except the first two, and the 3, 4 or 5 molecules of sulphuric acid which are liberated after precipitation of these acids by metal salts from their solutions, are already separated in these compounds. However, Harmelin's conductance measurements on the solutions of these acids would seem to negate this conclusion because she reports that the conductance of these solutions justifies formulation of these acids as $H_2(Cr_2(SO_4)_4]$, $H_4[Cr_2(SO_4)_5]$, etc.

Since the thermogravimetric and infrared spectral analysis of the ''chromipolysulphuric acids'' suggest that the accumulation of sulphuric acid in these acids does not alter the basic structure of these acids, and since they all show the infrared absorption bands of ''l'hydrate sulfochromique'' one is tempted to concur with Harmelin, that these acids are simply mixtures of sulphuric acid and a sulphato complex of chromium (III) which has a sulphate to chromium ratio of two. This, however, does not mean that sulphato complexes with sulphate to chromium ratios greater than two do not form, because the above results may be interpreted as arising from a mixture of various complexes with different sulphate to chromium ratios. The complexes with ratios greater than two may all decompose upon heating to produce the more stable complex with a ratio of two. This interpretation would then be substantiated by the results obtained from conductance

measurements which apparently give evidence that these acids are coordination compounds.

The results obtained by Harmelin, thus support the conclusion, obtained by this author, that the most stable hydrogen salt formed by digesting chromium (III) sulphate with sulphuric acid, has a chromium to sulphate ratio of two. These results again suggest that Recoura's "chromipolysulphuric acids" may be individual chemical species but no contribution has been made to an interpretation of their structure and composition, beyond that which has previously been described in the literature. As suggested in this thesis, a detailed investigation of these acids employing anion exchange columns to separate the various anionic species formed in the digestion may be very useful in further characterization of these acids.

The assignment of the two bands observed at 1200 and 1055 cm^{-1} to infrared absorption by the bisulphate group, HSO_4^-, for "l'hydrate sulfochromique" is not in accord with the assignment made in this thesis, if the latter is identical to the products such as P and R described in this thesis. One must conclude that they are identical because they contain the same sulphate to chromium ratios of two and because they contain coordinated water molecules which are lost only after the sulphuric acid has been expelled.

Harmelin assigns the bands at 875 or 860 cm^{-1}, 1055 and 1200 cm^{-1} to absorption by HSO_4^- and the bands at 910 and 1155 cm^{-1}, particularly in the last two acids in the series, to absorption by H_2SO_4. These assignments are readily justified because as may be seen in Figure 27 and Table 8, sulphuric acid does have strong absorption bands in these various regions. However, the strongest absorption band observed for sulphuric acid is centered near 1165 cm^{-1} with two strong bands at 850 and 875 cm^{-1}. The latter two bands are evident in the spectra for potassium and sodium bisulphate.[33] Since ''l'hydrate sulfochromique'' does not show these latter bands and since the two bands at 1055 and 1200 cm^{-1} are the main absorption bands in these compounds and do not show the same relative intensities as observed in the spectrum of sulphuric acid or potassium and sodium bisulphate, one may question the validity of assigning the 1055 and 1200 cm^{-1} bands to absorption by HSO_4^- groups. Coordination of the bisulphate groups will produce changes in the absorption frequencies for these groups, but one would expect that coordination of these groups should result in a lower force constant for the OH bond and result, therefore, in a shift of the absorption band to lower frequencies.

Having established that the spectrum for ''l'hydrate sulfochromique'' is due to bisulphate groups and having

established that the sulphate to chromium ratio is two, Harmelin proposes that this compound may be formulated as $H[Cr(SO_4)_2]$ and may have the following structure ...-Cr=SO_4...H-SO_4Cr=SO_4...H-SO_4Cr=... in which the chain is held together by hydrogen bonding between the components of the chain. This structure does not show the presence of any coordinated water molecules in the structure; these must be present because ''l'hydrate sulfochromique'' loses water which must be coordinated water between 350 and 550°C, according to Harmelin and this author.

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