

MASS SUSCEPTIBILITIES  
OF  
ALKALI SULPHATES AND ALUMS

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T H E S I S  
FOR THE DEGREE OF  
M.Sc  
OF THE  
UNIVERSITY OF LONDON.

PRESENTED BY  
GERTRUDE. T. ODDIE.  
( SISTER M. CECILIA O.P.)

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APRIL 1937.

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MASS SUSCEPTIBILITIES

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ALKALI SULPHATES AND ALUMS

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~~Magnetic~~ **Mass** SUSCEPTIBILITY OF THE ALUMS AND  
ALKALI SULPHATES.

(Abstract)

An investigation of the properties of the alums has shown:-

(1) The existence of lithium alum. (2) That the waters of crystallisation are attached in groups of three. (3) That the anhydrous double sulphates are insoluble.

The magnetic properties of the alums together with those of the hydrated double salts indicate that each group of three molecules of water make equivalent contributions to the molecular susceptibility and therefore must be attached by a similar type of link. Whilst the magnetic properties of the alkali sulphates show that the ions have a quasi independent existence in the crystal, those of the alums suggest that a complex ion formation prevails. It seems probable that the alkali ions are linked to the trivalent ions and three of the sulphate groups by means of the water molecules so that the formula could be written  $(R'_1 R'_1 (SO_4)_3 24H_2O) \cdot SO_4''$ . The insolubility of the anhydrous double salts together with the necessity of heat energy in their formation shows <sup>that</sup> a change in structure takes place, and it is suggested that a chelated compound is formed.

Crystals of the compound  $K_2 SO_4 Al_2 (SO_4)_3 6H_2O 18 D_2O$  were prepared and it was apparent that the substitution of  $18 D_2O$  in place of  $18 H_2O$  had no distorting effect on the crystal structure nor did it produce any peculiar magnetic effects. The value of the molecular susceptibility of  $D_2O$  calculated from these results is in good agreement with the accepted value.

The paramagnetism of the chromic and ferric alums was too great to give any evidence of similarity of links connecting the water

molecules, but they did confirm the idea that the alums have a complex ion structure..

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MASS SUSCEPTIBILITY  
OF  
ALKALI SULPHATES AND ALUMS .

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The results obtained by several workers on magnetic susceptibility show that in many cases the law of additivity appears to break down when the salts measured contain water of crystallisation; the molecular susceptibility of the hydrated salts not being the sum of the susceptibilities of the anhydrous salt and that of the appropriate number of water molecules.

It was therefore determined to investigate the effect of water of crystallisation on molecular susceptibility, and for that purpose the alums were chosen as being the most suitable; firstly on account of their containing a large number of water molecules, and, secondly, because the value of the susceptibility of caesium alum and the anhydrous double salt as given in the International Critical tables showed a divergence from the additivity law of as much as 17%.

It was hoped therefore, in making these experiments, to throw some light on the manner of co-ordination of the water molecules and the general structure of the crystals, and so help in the clearing up of the problem of solvation which up to now, has evaded a satisfactory solution.

## EXPERIMENTAL

The salts investigated were the alums and other double salts formed from the sulphates of lithium, sodium, ammonium potassium, rubidium and caesium with aluminium sulphate; potassium and thallium sulphate with chromium sulphate, and ammonium sulphate with ferric sulphate. A.R. materials were used through out in all preparations.

### Preparation of the materials used.

The literature describes two hydrates of potassium aluminium sulphate containing less water than potassium alum, viz:- The hydrates with six and eight molecules of water of crystallisation respectively. Although repeated efforts were made to procure this latter hydrate, all attempts proved fruitless. It was found, however, that the tendency of the water is to come off in groups of three molecules, and in the case of the series  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot nH_2O$  the complete series was obtained where n is 24, 21, 18, 15, 12, 9 and 6. No trihydrate could be prepared.

An indication was found that a similar series could be obtained for the other alums but time did not permit of a full investigation, representative members only being prepared in each case.



$\text{Li}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$ .

This salt was first described by Kralovansky (1), but its existence was subsequently denied by Rammelsberg (2). Modern literature seems doubtful of its existence.

The salt was prepared from a solution of the component sulphates, which was present in equimolecular proportions. The salts were dissolved in the least possible quantity of distilled water, so that a saturated solution at a temperature well above room temperature was obtained. It was then cooled in a freezing mixture and stirred continuously, when the salt was suddenly thrown out as a very soft, crystalline mass in which the crystal form could hardly be determined.

This was dried on a filter pump and subsequently on a porous plate. Attempts were made to get larger and more perfectly formed crystals, but the salt seems to form good crystals only with great difficulty, and the crystals that come out are so soft that it is difficult to obtain a good specimen.

When a supersaturated solution was cooled in ice without stirring, very small but perfect crystals were formed slowly. They were examined microscopically and found to be isotropic, the crystal form being a combination of octahedron and cube.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken.....	0.2812 gm.....	0.5670 gm
Weight of water found.....	0.1378 gm. ....	0.2778 gm.
% Water .....	<u>49.01%</u> .....	<u>49.00%</u>
Theoretical percentage for the alun .....		<u>48.93%</u>

Li<sub>2</sub>SO<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

This salt was prepared from the fully hydrated salt by heating to a temperature of 200°C. The salt, on heating, showed the characteristic behaviour of the alum, swelling up considerably to a bulky, friable mass. The total sulphate was estimated.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken.....	0.2922 gm.	0.3840 gm.
Weight of BaSO <sub>4</sub> found.....	0.5984 gm.	0.7756 gm.
% SO <sub>4</sub> .....	<u>84.29 %</u>	<u>85.07 %</u>
Theoretical percentage for the anhydrous salt.....	<u>84.96%</u>	

Li<sub>2</sub>SO<sub>4</sub>

This was prepared from the A.R. monohydrate. The salt was recrystallised and then heated at a temperature of 200°C. to convert to the anhydrous condition, and the total sulphate estimated.

RESULTS OF ANALYSIS

	A.	B.
Weight of salt taken.....	0.9560 gm.	0.7168 gm.
Weight of BaSO <sub>4</sub> found.....	2.0209 gm.	1.5205 gm.
% SO <sub>4</sub> .....	<u>87.02 %</u>	<u>87.29 %</u>
Theoretical percentage for the anhydrous salt.....	<u>87.38 %</u>	

Na<sub>2</sub>SO<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·24H<sub>2</sub>O.

The sodium alum was prepared from molecular proportions of the constituent sulphates. These were dissolved in water, the solution concentrated and then cooled in a freezing mixture, being constantly stirred the while. As with the lithium, the alum

was suddenly thrown out as a thick, white mass in which the crystal form could not be distinguished, but it was found that when the mixture of the constituent sulphates was made into a moderately supersaturated solution and then slowly evaporated in air, large characteristic crystals were formed.

The percentage water was estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken.....	0.1860 gm. ....	0.1436 gm
Weight of water found.....	0.0877 gm. ....	0.0674 gm
% Water .....	<u>47.15 %</u> .....	<u>46.95 %</u>
Theoretical percentage for the alum .....		<u>47.20 %</u>

Na<sub>2</sub>SO<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

The anhydrous double salt was prepared from the alum by heating at a temperature of 200 C. The total sulphate was estimated.

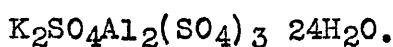
<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken.....	0.3945 gm....	0.5516 gm
Weight of BaSO <sub>4</sub> found .....	0.7624 gm ...	1.0765 gm
% SO <sub>4</sub> .....	<u>79.56 %</u> .....	<u>79.68 %</u>
Theoretical percentage for the anhydrous salt .....		<u>79.62 %</u>

Na<sub>2</sub>SO<sub>4</sub>.

The A.R. anhydrous material was used and the total sulphate estimated.

RESULTS OF ANALYSIS.

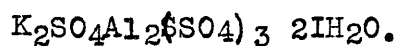
	A.	B.
Weight of salt taken .....	0.6768 gm.	1.2288 gm.
Weight of BaSO <sub>4</sub> found .....	1.1152 gm.	2.0344 gm.
%SO <sub>4</sub> .....	<u>67.81 %</u>	<u>67.97 %</u>
Theoretical percentage for the anhydrous salt .....	<u>67.61%</u>	



Analar material was used, the salt being recrystallised and the percentage water was estimated.

RESULTS OF ANALYSIS.

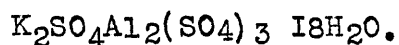
	A.	B.
Weight of salt taken .....	0.4317 gm	0.4370 gm
Weight of water found .....	0.1957 gm	0.1981 gm
% Water .....	<u>45.33 %</u>	<u>45.33 %</u>
Theoretical percentage for the alum .....	<u>45.35%</u>	



The fully hydrated analar salt was recrystallised and then placed in a boiling tube and heated, so that the salt dissolved in its water of crystallisation. The heating was continued over the Bunsen flame till the first sign of solidification appeared. The tube was then tightly corked to prevent any further evaporation to the air, and the heating continued in a beaker of boiling water for about five hours until the salt had set to a hard, crystalline mass.

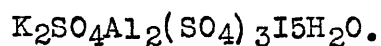
The total percentage water was estimated.

<u>RESULTS OF ANALYSIS</u>	A.	B.
Weight of salt taken .....	0.4556 gm.	0.4883 gm
Weight of water found .....	0.1924 gm.	0.2067 gm
% Water .....	<u>42.23 %</u>	<u>42.34 %</u>
Theoretical percentage for the heneicosihydrate ...	<u>42.27 %</u>	



The recrystallised analar, fully hydrated salt was heated in a boiling tube till the salt had completely dissolved in its water of crystallisation. The tube was then transferred to a beaker of boiling water, but in this case the tube was not corked and the heating was continued for several hours till the salt set to a hard mass. It was seen on cooling that the mass tended to expand so much that the glass of the tube was cracked, and when the pressure was released, by the glass being broken away, the salt expanded visibly.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.8466 gm	0.4677 gm.
Weight of water found .....	0.3258 gm	0.1809 gm.
% Water .....	<u>38.49%</u>	<u>38.68 %</u>
Theoretical percentage for the octodecahydrate ...	<u>38.68 %</u>	

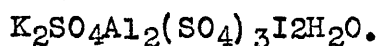


The analar recrystallised alum was heated on a water bath in an evaporating dish for several days. The salt first

Dissolved in its water of crystallisation to a thick, sticky mass which gradually set to an exceedingly hard, rock-like mass, which could be broken up only with considerable difficulty. The percentage water was estimated.

RESULTS OF ANALYSIS

	A.	B.
Weight of salt taken .....	0.4106 gm ....	0.2384 gm.
Weight of water found .....	0.1420 gm....	0.0819 gm.
% Water .....	<u>34.58 %</u> .....	<u>34.36 %</u>
Theoretical percentage for the pentadecahydrate .....	<u>34.35%</u>	

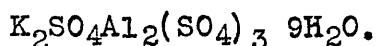


The pentadecahydrate was finely powdered and placed in an evaporating dish on a water bath, and maintained at a temperature of from 60-80°C. for four or five hours.

The percentage water was estimated.

RESULTS OF ANALYSIS.

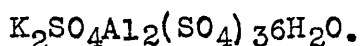
	A.	B.
Weight of salt taken .....	0.3260 gm ....	0.2290 gm
Weight of water found .....	0.0962 gm ....	0.0672 gm
%water .....	<u>29.51 %</u> .....	<u>29.35 %</u>
Theoretical percentage for the dodecahydrate.....	29.49%	



The analar recrystallised alum was finely powdered and then kept at a temperature of 45°C. for several weeks. The total water was estimated.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken .....	0.5116 gm .....	0.3838 gm
Weight of water found .....	0.1220 gm .....	0.0916 gm
% water .....	<u>23.85 %</u> .....	<u>23.86 %</u>
Theoretical percentage for the enneahydrate .....	<u>23.86 %</u>	



The fully hydrated analar salt was finely powdered and then kept for several weeks at a temperature of 61°C. A quicker method of preparation was subsequently found:- The alum is finely powdered and then allowed to fall gently into concentrated sulphuric acid, and the whole allowed to stand for about one hour. The bulk of the acid is then decanted and fresh acid added, and the whole allowed to stand again. The acid is again decanted and then the salt is carefully washed with alcohol and finally with ether. It is then dried at the filter pump.

This compound is of particular importance in that it is the most stable of all the hydrates. It appears that nothing but considerable heat energy (200°C) is capable of removing the last six molecules of water, and when they do come off the whole six are expelled together.

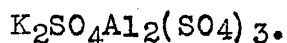
Two further attempts were made to remove the six molecules without undue heating:-

(I) The hydrate was enclosed in a vacuum dessicator over phosphoric anhydride for four weeks, at the end of which time

The vacuum was still very good, but the salt was found to be unchanged and the phosphoric anhydride was still dry and powdery.

(2) The salt was placed in a bulb in connection with a second bulb containing phosphoric anhydride; the whole was evacuated and sealed off at the pump. The bulb containing the alum was now heated at 120°C. for a week. Again the six molecules of water were retained by the salt.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.2843 gm.....	0.3614 gm
Weight of water found ....	0.0494 gm.....	0.0628 gm
% water .....	<u>17.38 %</u> .....	<u>17.38 %</u>
Theoretical percentage for the hexahydrate .....	<u>17.31 %</u>	



This compound was prepared by keeping any of the above hydrates at 200°C., or slightly above, for about two days. When any of the double salts are made anhydrous they at once become only very sparingly soluble in water. They can be induced to go into solution only after continued boiling with water. An attempt was made to make the anhydrous salt to go into solution in a small definite quantity of water by sealing it up in a hard glass tube and heating for several days at 130°C.; only comparatively little dissolved. On filtering and allowing to evaporate, crystals separated out but only in small numbers.

This insolubility was found with all the alums investigated



although all the hydrates, including the hexahydrate, are quite easily soluble.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.4720 gm	0.5840 gm
Weight of BaSO <sub>4</sub> found .....	0.8490 gm	1.0532 gm
%SO <sub>4</sub> .....	<u>74.04 %</u>	<u>74.22 %</u>
Theoretical percentage for the anhydrous double salt	<u>74.13%</u>	

### K<sub>2</sub>SO<sub>4</sub>

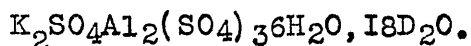
The A.R. material was recrystallised and the total sulphate estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	1.5096 gm	2.0565 gm
Weight of BaSO <sub>4</sub> found .....	2.0046 gm	2.7579 gm
% SO <sub>4</sub> .....	<u>55.01 %</u>	<u>55.20 %</u>
Theoretical percentage for potassium sulphate .....	<u>55.12 %</u>	

### Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

The analar octadecahydrate was used as a starting point and heated at 200°C. for several weeks. The salt became very insoluble when anhydrous. The total sulphate was estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.5905 gm	0.2518 gm
Weight of BaSO <sub>4</sub> found .....	1.1906 gm	0.5344 gm
%SO <sub>4</sub> .....	<u>83.55 %</u>	<u>84.03 %</u>
Theoretical percentage for the anhydrous salt .....	<u>84.26 %</u>	



Owing to the insolubility of the anhydrous double salt it was only possible, with the limited supply of deuterium oxide available, to introduce 18 molecules of 'heavy water' in place of the ordinary water.

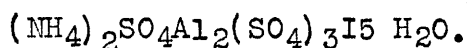
The hexahydrate was prepared by the concentrated sulphuric acid method, and 20 gms of deuterium oxide were used. The hexahydrate was very soluble; it appeared to be more soluble in the 'heavy water' than in ordinary water. A saturated solution in 99.9% deuterium oxide was made, the temperature not being allowed to rise much above 60°C. Very beautiful crystals separated out on cooling; these were removed and more hexahydrate added to the mother liquor. This process was continued till a total of about 8 gms. of the above salt was obtained.

The crystals obtained had the typical 'alum' form; a few almost perfect octahedra were obtained. As far as could be seen by the eye, the introduction of the larger deuterium molecule in place of the water molecules had no distorting effect on the crystal form.

<u>RESULTS OF ANALYSIS</u>	A.	B.
Weight of salt taken .....	0.3669 gm ....	0.3524 gm
Weight of D <sub>2</sub> O + H <sub>2</sub> O found .....	0.1712 gm ....	0.1676 gm
% water + deuterium oxide ..	<u>47.44 %</u> ..	<u>47.56 %</u>
Theoretical percentage for the octadecadeuterate hexahydrate		<u>47.56 %</u>

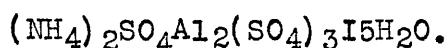
It is of interest to note that both from analysis and susceptibility measurements it is apparent that the six water molecules maintain their position in the molecule and are not

substituted by deuterium oxide.



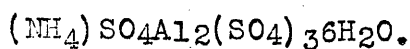
The analar material was recrystallised.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.7416 gm.	0.7274 gm
Weight of water found .....	0.3532 gm	0.3472 gm
% water .....	<u>47.62 %</u>	<u>47.74 %</u>
Theoretical percentage of the alum .....	<u>47.68 %</u>	



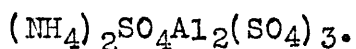
This was obtained when an attempt was made to produce the heneicosihydrate using the same method as was used in the case of the corresponding hydrate in the potassium series, but it was found that whereas in the case of the potassium series the heneicosihydrate separated out from solution after a few hours of heating, in this case it solidified only after the heating had been continued during several days; in fact, until it had lost sufficient water to form the pentadecahydrate. This was at last formed as an exceedingly hard mass which had to be broken out of the tube. The total sulphate was estimated

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.4442 gm.	0.4774 gm
Weight of BaSO <sub>4</sub> found .....	0.5578 gm.	0.5990 gm
% SO <sub>4</sub> .....	<u>51.69 %</u>	<u>51.64 %</u>
Theoretical percentage for the pentadecahydrate.	<u>51.60 %</u>	



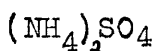
The recrystallised analar alum was heated on a water-bath at a temperature of from 80°-90°C. The salt dissolved in its water of crystallisation and set to a hard mass. This mass was powdered and the heating continued for several days until the salt was finally converted entirely into the hexahydrate

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.6092 gm	0.4674 gm
Weight of BaSO <sub>4</sub> found .....	0.9766 gm	0.7470 gm
%SO <sub>4</sub> .....	<u>66.01 %</u>	<u>65.79 %</u>
Theoretical percentage for the hexahydrate .....		<u>65.95 %</u>



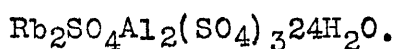
The alum was maintained at a temperature of 200°C. for three days. The total sulphate was estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.3366 gm	0.3968 gm
Weight of BaSO <sub>4</sub> found .....	0.6632 gm	0.7812 gm
%SO <sub>4</sub> .....	<u>81.10 %</u>	<u>81.04 %</u>
Theoretical percentage for the anhydrous double salt ...		<u>80.98 %</u>



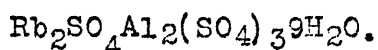
The analar material was used. The percentage sulphate was estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.5086 gm	0.1546 gm
Weight of BaSO <sub>4</sub> found .....	0.9016 gm	0.2738 gm
% SO <sub>4</sub> .....	<u>72.97 %</u>	<u>72.80 %</u>
Theoretical percentage for ammonium sulphate .....	<u>72.73%</u>	



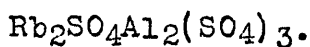
The analar material was used. The percentage water was estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.5298 gm	0.4218 gm.
Weight of water found .....	0.2198 gm	0.1750 gm
% water .....	<u>41.43 %</u>	<u>41.49 %</u>
Theoretical percentage for the alum .....	<u>41.55 %</u>	



The recrystallised alum was ground up and placed in an air oven at a temperature of 120°C. for several days. The salt slowly dissolved in its water of crystallisation and then set to a glassy mass. The percentage water was estimated

<u>RESULTS OF ANALYSIS</u>	A.	B.
Weight of salt taken .....	0.1854 gm	0.2074 gm.
Weight of water found .....	0.0387 gm	0.0438 gm
% water .....	<u>20.98 %</u>	<u>21.12 gm</u>
Theoretical percentage for the enneahydrate.....	<u>21.10 %</u>	

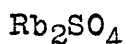


This was obtained by keeping the alum at a temperature of 200°C. for two days.

The percentage rubidium was estimated as the rubidium chloro-platinate. For this purpose the sulphate was converted to the chloride by the addition of the least possible quantity of barium chloride which precipitated out the sulphate. This was filtered through a Gooch crucible, and the total barium sulphate weighed as a check. A calculated quantity in slight excess of platinum chloride in hydrochloric acid was added to the solution that had been previously evaporated to small bulk. The solution was then taken nearly to dryness, the aluminium chloride and excess platinum chloride being washed out with alcohol; the rubidium chloro-platinate being collected in a platinum Gooch crucible and dried in an air oven.

RESULTS OF ANALYSIS

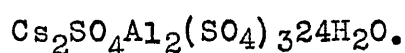
	A.	B.
Weight of salt taken .....	0.3434 gm	0.4174 gm
Weight of $\text{Rb}_2\text{PtCl}_6$ found ...	0.3226 gm	0.3928 gm
% Rubidium .....	<u>27.71 %</u>	<u>27.79 %</u>
Theoretical percentage for rubidium in the anhydrous double salt ..	<u>27.97 %</u>	
Weight of $\text{BaSO}_4$ found .....	0.5260 gm	0.6364 gm
% $\text{SO}_4$ .....	<u>63.02 %</u>	<u>62.77 %</u>
Theoretical percentage for the anhydrous double salt	<u>63.06%</u>	



This was prepared from the alum. The aluminium was precip-

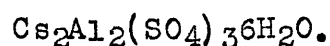
itated as hydroxide with ammonia and filtered off. The remaining liquid, consisting of the mixed rubidium and ammonium sulphate was evaporated to dryness and then heated at a temperature of about 260°C., when the ammonium sulphate decomposed and came off as ammonia, sulphur trioxide and water. The heating was continued until no more vapour was given off; the rubidium sulphate was then dissolved in water, filtered and allowed to crystallise. The total sulphate was estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.4580 gm	0.2304 gm
Weight of BaSO <sub>4</sub> found .....	0.6266 gm	0.3154 gm
% SO <sub>4</sub> .....	<u>56.31 %</u>	<u>56.32 %</u>
Theoretical percentage for the sulphate .....	<u>56.52 %</u>	



The pure A.R. material was used and its percentage water estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.5736 gm	0.5230 gm
Weight of water found .....	0.2176 gm	0.1984 gm
% water .....	<u>37.93 %</u>	<u>37.94 %</u>
Theoretical percentage for the alum. ....	<u>38.06 %</u>	



The recrystallised alum was finely ground and kept over a water-bath at a temperature of 70°-80°C. for several weeks

till no further water was lost. The percentage water was estimated.

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.2920 gm .....	0.2002 gm.
Weight of water found ....	0.0386 gm. ....	0.0268 gm
% Water .....	<u>13.28 %</u> .....	<u>13.39%</u>
Theoretical percentage for the hexahydrate .....	<u>13.31 %</u>	

$Cs_2SO_4Al_2(SO_4)_3$ .

The recrystallised alum was heated at a temperature of 200°C. for two days. The percentage caesium was estimated by the chloroplatinic acid method already described for rubidium

<u>RESULTS OF ANALYSIS.</u>	A.	B.
Weight of salt taken .....	0.3266 gm .....	0.3248 gm
Weight of $Cs_2PtCl_6$ found ...	0.3094 gm.....	0.3098 gm
% ca-esium .....	<u>57.31 %</u> .....	<u>37.68 %</u>
Theoretical percentage for the anhydrous double salt	<u>37.78 %</u>	
Weight of $BaSO_4$ found .....	0.4338 gm.....	0.4320 gm
% $SO_4$ .....	<u>54.68 %</u> .....	<u>54.75 %</u>
Theoretical percentage for the anhydrous salt	<u>54.75 %</u>	

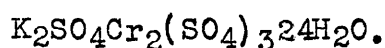
$Cs_2SO_4$

This specimen was kindly lent by Professor E. C. C. Baly, F.R.S. of Liverpool University. The percentage caesium and sulphate were determined as above



RESULTS OF ANALYSIS.

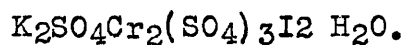
	A.	B.
Weight of salt taken	0.1790 gm	0.1744 gm
Weight of $\text{Cs}_2\text{PtCl}_6$	0.3318 gm	0.3324 gm.
% Caesium	<u>73.19 %</u>	<u>73.13 %</u>
Theoretical percentage for the caesium sulphate	<u>73.48 %</u>	
Weight of $\text{BaSO}_4$ found	0.1162 gm	0.1126 gm
% $\text{SO}_4$	<u>26.73 %</u>	<u>26.58 %</u>
Theoretical percentage for caesium sulphate	<u>26.57 %</u>	



The analar material was used but not recrystallised owing to the difficulty of inducing crystallisation. The percentage water was estimated.

RESULTS OF ANALYSIS.

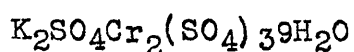
	A.	B.
Weight of salt used	0.5276 gm	0.3408 gm
Weight of water found	0.2274 gm	0.1476 gm
% water	<u>43.14 %</u>	<u>43.32 %</u>
Theoretical percentage for the alum	<u>43.29 %</u>	



The alum was finely powdered and placed in a dessicator over concentrated sulphuric acid for five or six weeks. The percentage water was estimated.

RESULTS OF ANALYSIS.

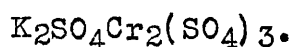
	A.	B.
Weight of salt taken .....	0.3543 gm	0.3900 gm
Weight of water found .....	0.0972 gm	0.1078 gm.
% water .....	<u>27.45 %</u>	<u>27.65 %</u>
Theoretical percentage for the dodecahydrate .....	<u>27.65 %</u>	



The alum was heated until it dissolved in its water of crystallisation and then was maintained at a temperature of 80°-90°C. for several days. The substance first became a thick, viscous, green liquid, and it took several days of heating before finally setting to a solid dry mass that looked almost black, but, on powdering, it appeared as a deep jade green.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken .....	0.1224 gm	0.0283 gm
Weight of water found .....	0.0274 gm	0.0283 gm
% Water .....	<u>22.39 %</u>	<u>22.13 %</u>
Theoretical percentage for the enneahydrate.....	<u>22.13 %</u>	



This was obtained from the alum by heating for two days at 200°C. This compound was found to be not only insoluble in water, as in the aluminium series, but also in acids both dilute and concentrated,

In order to estimate the sulphate present, the compound was fused with sodium carbonate in a platinum crucible until

the soluble chromate was formed. The total sulphate was then estimated, with the precaution of adding concentrated hydrochloric acid to prevent the precipitation of barium chromate and washing the precipitate well with the concentrated acid until no trace of acid remained.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken .....	0.2856 gm .....	0.6190 gm.
Weight of BaSO <sub>4</sub> found .....	0.4722 gm .....	0.0150 gm.
% SO <sub>4</sub> .....	<u>68.06 %</u> .....	<u>67.48 %</u>
Theoretical percentage for the anhydrous double salt ...	<u>67.82</u>	

Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>

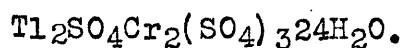
In order to purify the material the sulphate was dissolved in water and the hydroxide precipitated with ammonia. This compound was carefully washed with warm water to free it from all ammonia. It was then cautiously added to hot concentrated sulphuric acid until no more would dissolve. The green solution so formed was then allowed to stand for several weeks, when it gradually turned to a violet colour and deposited deep red crystals of the hydrated salt.

These crystals readily lost water when exposed to the air forming a violet powder. When heated in an air oven, to expel all the water, the compound formed was green and insoluble.

It was analysed by the same method described for the anhydrous double salt.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken .....	0.2898 gm.	0.2198 gm
Weight of BaSO <sub>4</sub> found .....	0.5198 gm	0.3838 gm.
% SO <sub>4</sub> .....	<u>73.84 %</u>	<u>73.18 %</u>
Theoretical percentage for the chromic sulphate .....	<u>73.48</u>	

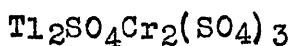


This salt, prepared by reducing thalious chromate in dilute sulphuric acid solution by means of sulphur dioxide, crystallised out slowly from its solution, forming very deep red octahedral crystals. Crystallisation is hastened somewhat by keeping the solution gently evaporating at about 30°C. but care must be taken not to let the temperature rise, otherwise the solution turns green and it will be months, perhaps, before the salt crystallises out.

This alum loses water quickly when exposed to air, forming a violet powder. The percentage water was estimated.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken .....	0.6486 gm	0.7156 gm
Weight of water found .....	0.2094 gm	0.2316 gm.
% Water .....	<u>32.28 %</u>	<u>32.28 %</u>
Theoretical percentage for the alum .....	<u>32.48 %</u>	



This was obtained from the fully hydrated alum by heating at a temperature of 200°C. It is a green powder, very insoluble

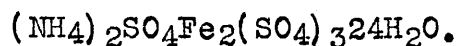
in water and acid. It was estimated by the fusion method.

RESULTS OF ANALYSIS.

	A.	B.
Weight of salt taken .....	0.7126 gm	0.6072 gm.
Weight of BaSO <sub>4</sub> found .....	0.7406 gm	0.6331 gm.
% SO <sub>4</sub> .....	<u>42.78 %</u>	<u>42.92 %</u>

Theoretical percentage for the anhydrous double salt 42.83 %

The method adopted for the preparation of the higher hydrates of the aluminium double salts cannot be used in the case of the chromium, for on heating above 60°C. the violet alum is converted to a thick green fluid which does not solidify until it has lost sufficient water to convert it to the enneahydrate.



The analar material was used; it could <sup>not</sup> be recrystallised owing to hydrolysis. When ground up the specimen released sufficient water of crystallisation to cause slight hydrolysis as could be seen by the yellow colour.

It was analysed by a volumetric method. The ferric solution was reduced to the ferrous state by being passed through a Jones reductor. It was then titrated with potassium dichromate, with diphenylamine as an internal indicator.

Standard Solution of Dichromate.

2.7600 gms. salt made up to 500 c.c. Hence concentration of solution 0.1124 N.

RESULTS OF ANALYSIS.

Weight of salt taken ..... 9.0912 gms.

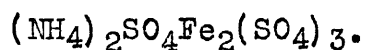
Solution made up to 100 c.c. in dilute sulphuric acid.  
25 c.c. of the ferric alum was reduced in each case and  
titrated with the standard dichromate.

<u>I TITRATION</u>	<u>2 TITRATION</u>	<u>3 TITRATION</u>
41.1 c.c.	40.8 c.c.	40.8 c.c.

Therefore 25 c.c. of ferrous salt oxidised by 40.9 c.c.  
dichromate solution.

Therefore percentage Fe ..... 11.35 %

Theoretical percentage for the alum ..... 11.56 %



This was obtained from the alum by heating at a temperat-  
ure of 200°C. The percentage Fe was estimated as above.

RESULTS OF ANALYSIS.

2.0084 gms. ferric salt was made up to 250 c.c.

25 c.c. of the solution used for each titration and  
reduced.

<u>I. TITRATION</u>	<u>2. TITRATION</u>	<u>3 TITRATION</u>
6.9 c.c.	6.8 c.c.	6.6 c.c.

Therefore 25 c.c. of the ferrous salt oxidised by 6.77 c.c.  
dichromate solution.

Therefore percentage Fe ..... 21.22 %

Theoretical percentage for the anhydrous double salt ..21.21 %

METHOD ADOPTED FOR MAGNETIC MEASUREMENTS

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In making the magnetic measurements the Guoy method was used. Described by Professor S. Sugden (3) and Dr. Trew and Miss Watkins (4).

In this method the material to be measured is in the form of a long uniform cylinder, which hangs symmetrically between the pole-pieces of a powerful electro-magnet in such a way that the lower portion is in the maximum field  $H_1$ . There is, therefore, within the material a field gradient from  $H_1 \rightarrow H_2$ .

If  $F$  is the force per unit volume expressed in dynes,  $\mu_1$  the permeability of the material in a medium of permeability  $\mu_2$ ,  $A$  the area of cross section, and  $l$  the length of cylinder then the force  $F$  is given by the equation:-

$$F = \frac{A(\mu_1 - \mu_2)}{8\pi} \int_{H_2}^{H_1} H \, dH$$

which, on intergrating, gives:-

$$F = \frac{\mu_1 - \mu_2}{8\pi} A (H_1^2 - H_2^2)$$

Substituting  $\mu_1 = 1 + 4\pi k_1$  where  $k_1$  is the volume susceptibility of the material and  $k_2$  that of the medium,

$$F = \frac{1}{2}(k_1 - k_2) A (H_1^2 - H_2^2)$$

The cylinder being taken of such length that the upper end lies

in a region of zero field, i.e.  $H=0$ ,

$$\text{Then } K_1 = \frac{2F}{AH^2} + K_2$$

$$\text{But since } \chi = \frac{K_1}{d} \quad \text{and} \quad d = \frac{w}{Al}$$

$$\chi = \frac{2Fl}{wH^2} + \frac{Alk_2}{w}$$

Since the measurements were made in air,  $k_2 = -0.03 \times 10^{-6}$

$$\text{Therefore } \chi = \frac{2Fl}{wH^2} + \frac{0.03 l A}{w} \times 10^{-6}$$

But  $l$  was a constant length and  $H^2$  was also constant, and therefore  $\frac{l}{H^2}$  is constant =  $\alpha$  (the constant of the balance).

Including these constant values and the factors for the units used ( $F$  in milligrams,  $w$  in grams,  $l$  and  $A$  in cms. and sq.cms. respectively), the equation reduces to :-

$$\chi = \frac{\alpha F}{w} + \frac{0.03 l A}{w}$$

$$\text{where } \alpha = \frac{2 l \times 10^6 \times 981}{H_1^2 \times 1000} \quad \text{in c.g.s. units.}$$

#### Details of Experiment.

A photograph of the balance used is given in Fig. I. The glass tube "t" contains the material to be measured. Great care was taken in the packing of the tube to obtain a uniform cylinder of material and to obliterate, as far as possible, any error that would arise from the presence of air spaces by powdering the material as finely as possible. The tube was



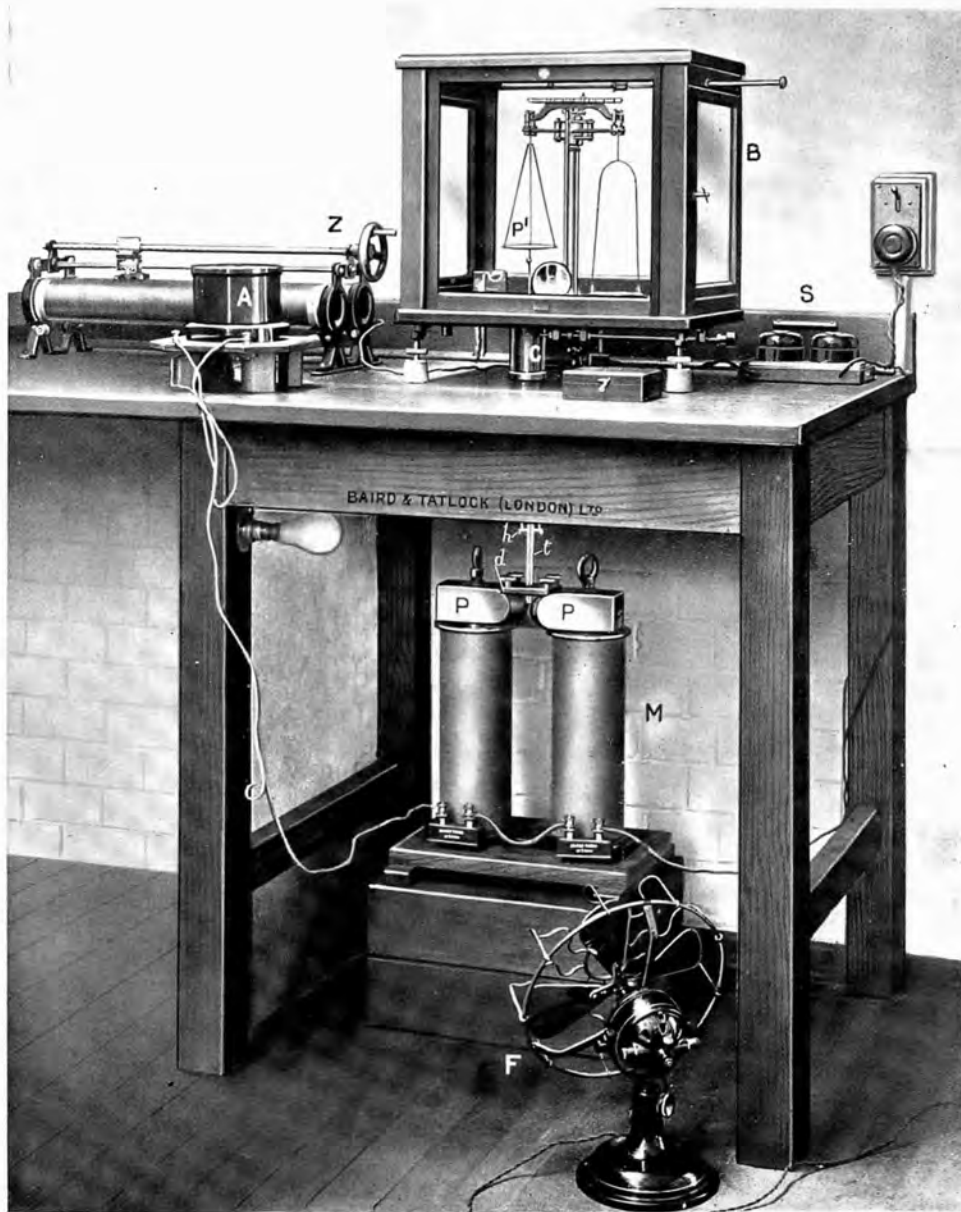


Fig. 1.

packed to a definite mark so that  $l$  should be constant.

The tube was hung on a stirrup and suspended by a platinum wire from the balance pan "P". the bottom of the tube being in line with the axis of the pole pieces. For all the diamagnetic measurements a current of three ampères was used, which was a saturation current for the magnet.

For the paramagnetic substances the exciting current was cut down to 1.5 ampères as the field was too strong.

The current was regulated by the rheostat "Z". The balance had previously been calibrated with a number of highly purified, organic liquids and inorganic salts.

The constant of the balance was first determined. For this purpose re-distilled A.R. benzene was used and the standard value of  $\chi$  for benzene,  $0.716 \times 10^{-6}$ , was taken to calculate. The value obtained was found to be in perfect agreement with a graph drawn from results of observations made by several observers.

The volume was found by first weighing the tube empty and then filled up to the mark with distilled water. Then from the density at the given temperature the volume was calculated.

In making measurements, three or four packings were used in each case and, wherever the quantity of material allowed different samples were used.

For each packing, three separate determinations of the pull were made in each case, the fifth place of decimals being found by the method of weighing by oscillations.

In the case of rubidium sulphate, the material was just not sufficient to pack the tube up to the mark, and in this case the length of the column was measured and the constant calculated from the relation  $\frac{\alpha}{d'} = \frac{1}{l'}$ .

DETERMINATION OF THE CONSTANT OF THE BALANCE FOR 3 AIRRES

Full of the Tube.

<u>Weight Out of Field</u>	<u>Weight in Field</u>	<u>Full</u>
7.41763 gm.	7.41687 gm.	-0.00076 gm.
7.41736	7.41661	-0.00075
7.41702	7.41625	-0.00077
7.41244	7.41169	-0.00075
7.41284	7.41208	-0.00076
	MEAN	-0.00076

Full on Tube and Benzene.

<u>Weight Out of Field</u>	<u>Weight in Field</u>	<u>Full</u>
10.22433 gm.	10.22006 gm.	-0.00429 gm.
10.22566	10.22134	-0.00433
10.22544	10.22102	-0.00442
10.22494	10.22056	-0.00438
10.22500	10.22065	-0.00435
	MEAN	-0.00435

Therefore pull due to benzene = 3.59 milligrammes.

Weight of water = 3.4314 grammes.

Temperature = 20.1°C. Density = 0.9952 gm. c.c.<sup>-1</sup>

Therefore volume of tube = 3.438 c.c.

Weight of benzene = 2.9618 gms.

$$\text{Therefore } -0.716 \times 10^{-6} = \frac{-2 \times 3.59}{2.9618} + \frac{3.438 \times 0.03}{2.9618}$$

$$\text{Therefore } \underline{\underline{\lambda = 0.619}}$$

DETERMINATION OF THE CONSTANT OF THE BALANCE WITH 1.5 AMPÈRESPull on the Tube

<u>Weight without magnet</u>	<u>Weight with magnet</u>	<u>Pull</u>
7.40437 gm.	7.40397 gm.	-0.00040 gm.
7.40440	7.40399	-0.00041
7.40428	7.40388	-0.00043
7.40421	7.40382	-0.00037
	MEAN	-0.00041

Using Benzene as Standard

<u>Weight without magnet</u>	<u>Weight with magnet</u>	<u>Pull</u>
10.41898 gm.	10.41635 gm.	-0.00263 gm.
10.41897	10.41630	-0.00267
10.41877	10.41611	-0.00266
	MEAN	-0.00265

$$\text{Therefore } -0.716 = \frac{\alpha(-2.25)}{3.0114} + \frac{3.438 \times 0.03}{3.0114}$$

$$\alpha = 1.004$$

Using K<sub>2</sub>SO<sub>4</sub> as Standard

<u>Weight without magnet</u>	<u>Weight with magnet</u>	<u>Pull</u>
14.08628 gm.	14.08315 gm.	-0.00313 gm.
14.08630	14.08313	-0.00317
14.08627	14.08313	-0.00314
	MEAN	-0.00315

$$\text{Therefore } -0.403 = \frac{\alpha(-2.74)}{6.6787} + \frac{3.438 \times 0.03}{6.6787}$$

$$\underline{\alpha = 1.020}$$

<u>Weight without magnet</u>	<u>Weight with magnet</u>	<u>Pull</u>
14.21498 gm.	14.21180 gm.	-0.00318 gm.
14.21496	14.21178	-0.00318
14.21493	14.21175	-0.00318
		MEAN -0.00318

$$\text{Therefore } -0.403 = \frac{\alpha(-2.77)}{6.8070} + \frac{3.438 \times 0.03}{6.8070}$$

$$\underline{\alpha = 1.026}$$

Using  $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$  as standard.

<u>Weight without magnet</u>	<u>Weight with magnet</u>	<u>Pull</u>
11.93672 gm.	11.93392 gm.	-0.00280 gm.
11.93675	11.93393	-0.00282
11.93671	11.93387	-0.00284
		MEAN -0.00282

$$\text{Therefore } -0.520 = \frac{\alpha(-2.41)}{4.5292} + \frac{3.478 \times 0.03}{4.5292}$$

$$\underline{\alpha = 1.040}$$

MEAN VALUE OF  $\alpha = 1.022$

The pull of the tube was checked from time to time. During the work the pull fell to -0.00072 for a time after it had been used for several paramagnetic determinations; but it subsequently rose again to -0.00076 gm.

SUSCEPTIBILITY MEASUREMENTS OF SERIES  $\text{Li}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot n \text{H}_2\text{O}$ 

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$	
$\text{Li}_2\text{SO}_4$	4.2072	-3.63	-2.89	-0.400		
		-3.65				
		-3.66				
	4.1870	-3.60	-2.87	-0.399		<u>-43.75</u>
		-3.68				
		-3.61				
	4.2874	-3.60	-2.90	-0.395		
		-3.68				
		-3.69				
			MEAN	<u>-0.398</u>		
$\text{Li}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$	3.2725	-2.72	-2.04	-0.355		
		-2.77				
		-2.80				
	3.1717	-2.67	-1.98	-0.354		<u>-159.6</u>
		-2.70				
		-2.72				
	3.1498	-2.65	-1.95	-0.351		
		-2.65				
		-2.71				
			MEAN	<u>-0.353</u>		
$\text{Li}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	4.3662	-4.75	-4.01	-0.544		
		-4.76				
		-4.67				
	4.0526	-4.40	-3.70	-0.540		<u>-479.7</u>
		-4.42				
		-4.43				
	3.7842	-4.14	-3.46	-0.539		
		-4.42				
		-4.22				
			MEAN	<u>-0.541</u>		



SUSCEPTIBILITY OF SERIES  $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot n \text{H}_2\text{O}$ 

Salt	weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$	
$\text{Na}_2\text{SO}_4$	6.0522	-3.79	-3.03	-0.293		
		-3.75				
		-3.72				
	5.9805	-3.76	-3.06	-0.300		<u>-41.96</u>
		-3.71				
		-3.89				
	6.0110	-3.72	-3.00	-0.293		
		-3.68				
		-3.75				
			MEAN	<u>-0.295</u>		
$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$	4.2935	-3.52	-2.82	-0.383		
		-3.53				
		-3.56				
	4.1655	-3.54	-2.76	-0.384		<u>-184.8</u>
		-3.48				
		-3.55				
	4.1764	-3.43	-2.76	-0.384		
		-3.50				
		-3.50				
			MEAN	<u>-0.384</u>		
$\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$	4.9852	-5.35	-4.63	-0.550		
		-5.35				
		-5.35				
	4.4620	-4.84	-4.13	-0.550		<u>-503.1</u>
		-4.87				
		-4.85				
	4.3824	-4.63	-4.03	-0.546		
		-4.81				
		-4.81				
			MEAN	<u>-0.549</u>		

SUSCEPTIBILITY OF SERIES  $K_2SO_4Al_2(SO_4)_3 \cdot n H_2O$ 

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$
$K_2SO_4$	6.2779	-5.03	-4.27	-0.403	
	6.3428	-5.04	-4.28	-0.403	
	6.7149	-5.30	-4.54	-0.403	
	6.7194	-5.33	-4.57	-0.406	<u>-70.20</u>
	6.5817	-5.19	-4.43	-0.401	
	6.8443	-5.39	-4.63	-0.403	
			MEAN	<u>-0.403</u>	
$Al_2(SO_4)_3$	4.1015	-3.27	-2.50	-0.352	
		-3.27			
		-3.25			
	4.1969	-3.32	-2.54	-0.350	
		-3.29			
		-3.29			
4.0808	-3.22	-2.44	-0.345	<u>-119.1</u>	
	-3.18				
4.2864	-3.30	-2.56	-0.346		
	-3.32				
	-3.33				
			MEAN	<u>-0.348</u>	

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$		
K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	4.0023	-3.28	-2.52	-0.364	<u>-182.3</u>		
		-3.28					
		-3.28					
	4.0989	-3.29	-2.53	-0.357			
		-3.37					
	4.1764	-3.36	-2.67	-0.341			
		-3.55					
		-2.97					
	4.0098	-3.00	-3.05	-0.329			
		-3.17					
-3.50							
4.1871	-3.50	-2.74	-0.374				
			MEAN	<u>-0.353</u>			
K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 6H <sub>2</sub> O	4.8716	-4.29	-3.54	-0.429	<u>-269.2</u>		
		-4.30					
		-4.30					
	4.8413	-4.30	-3.54	-0.431			
		-4.31					
	4.8888	-4.29	-3.58	-0.432			
		-4.32					
		-4.37					
		-4.32		MEAN		<u>-0.432</u>	

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$	
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 9H_2O$	4.9682	-4.59	-3.80	-0.453		
		-4.63				
		-4.56				
	4.8302	-4.43	-3.68	-0.450		
		-4.40				
		-4.48				
	5.0682	-4.67	-3.88	-0.453		<u>-306.0</u>
		-4.64				
		-4.60				
	4.8490	-4.37	-3.68	-0.449		
		-4.50				
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12H_2O$	4.7998	-4.59	-3.83	-0.473		
		-4.61				
		-4.56				
	4.8419	-4.69	-3.92	-0.479		<u>-549.4</u>
		-4.66				
		-4.68				
	4.7789	-4.62	-3.87	-0.479		
		-4.64				
		-4.64				
			MEAN	<u>-0.477</u>		

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\lambda \times 10^{-6}$	$\chi_M \times 10^{-6}$
K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 15H <sub>2</sub> O	4.9391	-4.82 -4.77 -4.76	-4.02	-0.483	
	4.8309	-4.71 -4.73 -4.78	-4.09	-0.488	<u>-383.0</u>
	4.9481	-4.85 -4.87 -4.82	-4.09	-0.490	
			MEAN	<u>-0.487</u>	
K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 18H <sub>2</sub> O	4.4120	-4.40 -4.40 -4.40	-3.64	-0.488	
	4.6612	-4.64 -4.56 -4.66	-3.86	-0.491	<u>-412.0</u>
	4.6393	-4.59 -4.65 -4.58	-3.85	-0.492	
			MEAN	<u>-0.490</u>	

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$
K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 21 H <sub>2</sub> O	4.5479	-4.79	-4.00	-0.521	
		-4.75			
		-4.75			
	4.5229	-4.72	-3.95	-0.517	<u>-461.5</u>
		-4.71			
	4.5426	-4.67	-3.93	-0.513	
		-4.68			
		-4.71			
	4.5182	-4.68	-3.92	-0.516	
		-4.66			
		-4.71			
				MEAN	<u>-0.516</u>
K <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 24H <sub>2</sub> O	4.5395	-4.74	-3.98	-0.520	
		-4.73			
		-4.75			
	4.5810	-4.71	-4.02	-0.521	
		-4.81			
		-4.82			
	4.6195	-4.76	-4.03	-0.518	<u>-493.4</u>
		-4.80			
		-4.80			
	4.5241	-4.64	-3.38	-0.520	
				MEAN	<u>-0.520</u>

SUSCEPTIBILITY OF SERIES  $(\text{NH}_4)_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ 

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$			
$(\text{NH}_4)_2\text{SO}_4$	3.9471	-4.37	-3.60	-0.539				
		-4.35						
		-4.36						
	4.0122	-4.44	-3.67	-0.541		<u>-71.73</u>		
		-4.43						
		-4.41						
	4.0911	-4.39	-3.70	-0.548				
		-4.52						
		-4.47						
				MEAN			-0.543	
	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$	3.6794	-3.37	-2.58			-0.405	
			-3.34					
-3.34								
3.7495		-3.45	-2.62	-0.405				
		-3.36						
		-3.46						
3.8182		-3.47	-2.69	-0.409			<u>-192.2</u>	
		-3.42						
		-3.41						
3.8692		-3.45	-2.67	-0.400				
		-3.45						
				MEAN			-0.405	

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$		
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	4.3106	-4.03	-3.33	-0.454			
		-4.02					
		-4.04					
	4.3683	-4.09	-3.40	-0.458		<u>-255.6</u>	
		-4.11					
		-4.16					
	4.4595	-4.20	-3.46	-0.457			
		-4.15					
		-4.18					
						MEAN	<u>-0.456</u>
	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$	4.1080	-4.29	-3.57		-0.513	
			-4.31				
-4.39							
4.1173		-4.27	-3.55	-0.509	<u>-380.3</u>		
		-4.33					
		-4.34					
4.1294		-4.32	-3.57	-0.510			
		-4.34					
		-4.33					
				MEAN	<u>-0.511</u>		
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$		4.1475	-4.67	-3.93	-0.561		
			-4.67				
	-4.72						
	4.2002	-4.73	-3.99	-0.563	<u>-508.7</u>		
		-4.74					
		-4.73					
	4.1482	-4.66	-3.91	-0.589			
		-4.70					
		-4.65					
					MEAN		<u>-0.561</u>



SUSCEPTIBILITY OF THE SERIES  $\text{Rb}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot n \text{H}_2\text{O}$ 

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$	
$\text{Rb}_2\text{SO}_4$	5.7405 (Length of column of salt = 6.5 cm.). $\alpha = 0.559$	-4.37 -4.35 -4.39	-3.61	-0.333		
	5.7209 (Length of column of salt = 6.3 cm.). $\alpha = 0.559$	-4.31 -4.38 -4.40	-3.60	-0.334	<u>-89.15</u>	
	5.7102 (Length of column of salt = 6.3 cm.). $\alpha = 0.537$	-4.54 -4.50 -4.50	-4.51	-0.334		
			MEAN	-0.334		
	$\text{Rb}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$	4.3306	-2.81 -2.89 -2.88	-2.14	-0.282	
		4.4116	-2.90 -2.90 -2.92	-2.18	-0.283	<u>-172.4</u>
		4.5015	-2.94 -2.96 -2.98	-2.24	-0.285	
				MEAN	-0.283	

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$
Rb <sub>2</sub> SO <sub>4</sub> · Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	3.1387	-4.13	-3.37	-0.386	
		-4.13			
		-4.13			
	5.1590	-4.12	-3.38	-0.385	<u>-296.0</u>
		-4.17			
		-4.19			
	5.2083	-4.13	-3.38	-0.381	
		-4.15			
		-4.14			
			MEAN	<u>-0.384</u>	
Rb <sub>2</sub> SO <sub>4</sub> · Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 24H <sub>2</sub> O	4.6419	-4.11	-3.41	-0.433	
		-4.14			
		-4.14			
	4.7551	-4.23	-3.51	-0.435	<u>-450.9</u>
		-4.23			
		-4.21			
	4.8024	-4.26	-3.52	-0.432	
		-4.21			
		-4.26			
			MEAN	<u>-0.433</u>	

SUSCEPTIBILITY OF SERIES  $\text{Cs}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ 

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$	
$\text{Cs}_2\text{SO}_4$	9.9601	-6.10	-5.37	-0.323		
		-6.13				
		-6.16				
	9.9497	-6.17	-5.43	-0.327	<u>-117.2</u>	
		-6.18				
		-6.24				
	9.9315	-6.09	-5.32	-0.321		
		-6.07				
		-6.08				
				MEAN	<u>-0.324</u>	
	$\text{Cs}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3$	5.3384	-3.74	-3.02	-0.331	
			-3.78			
-3.83						
5.4077		-3.84	-3.12	-0.338	<u>-255.2</u>	
		-3.86				
		-3.94				
5.4002		-3.75	-3.01	-0.334		
		-3.82				
		-3.74				
				MEAN	<u>-0.334</u>	

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$
Cs <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 6H <sub>2</sub> O	4.5011	-3.55	-2.85	-0.369	
		-3.53			
		-3.62			
4.5817	-3.59	-2.87	-0.365	<u>-299.7</u>	
	-3.57				
	-3.60				
4.6823	-3.71	-2.99	-0.374		
	-3.67				
	-3.74				
			MEAN	<u>-0.369</u>	
Cs <sub>2</sub> SO <sub>4</sub> . Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 24H <sub>2</sub> O	4.7886	-4.46	-3.71	-0.458	
		-4.47			
		-4.47			
4.8705	-4.60	-3.82	-0.465	<u>-526.0</u>	
	-4.56				
	-4.59				
4.9385	-4.63	-3.88	-0.465		
	-4.63				
	-4.65				
			MEAN	<u>-0.463</u>	

SUSCEPTIBILITY OF SERIES  $K_2SO_4Cr_2(SO_4)_3 \cdot n H_2O$ 

Salt	weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$
$Cr_2(SO_4)_3$ 28°C.	4.0292	92.2	92.6	23.56	
	4.1544	94.0	94.6	23.30	
	4.2072	97.7	98.3	23.93	
	4.3489	100.0	100.6	23.65	<u>9268</u>
	4.4570	101.9	102.5	23.52	
	4.4956	103.8	104.4	23.81	
				MEAN 23.63	
$K_2SO_4 \cdot Cr_2(SO_4)_3$ 22.7°C.	5.5858	123.1	123.7	22.62	
	5.6581	126.3	126.9	22.95	
	5.5862	123.2	123.8	22.67	<u>12900</u>
	5.6509	126.1	126.7	22.89	
				MEAN 22.78	
$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 9H_2O$ 18°C.	5.0682	91.70	91.76	18.52	
	5.0276	90.30	90.36	18.39	
	5.0884	90.50	90.56	18.19	<u>13340</u>
	5.0457	89.70	89.76	18.18	
				MEAN 18.32	

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$	
K <sub>2</sub> SO <sub>4</sub> . Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 12H <sub>2</sub> O	3.8395	63.1	63.7	16.97		
	3.9577	64.2	64.8	16.75		
	19.5°C.	4.0609	66.0	66.6	16.76	<u>13150</u>
		4.0579	66.2	66.8	16.78	
			MEAN	<u>16.81</u>		
K <sub>2</sub> SO <sub>4</sub> . Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . 24H <sub>2</sub> O	3.7833	48.6	49.2	13.31		
	3.7965	49.0	49.6	13.38		
	21.5°C.	3.8056	49.3	49.9	13.42	<u>13330</u>
		3.7835	49.6	49.2	13.31	
			MEAN	<u>13.35</u>		

SUSCEPTIBILITY OF THE SERIES  $Tl_2SO_4Cr_2(SO_4)_3 \cdot n H_2O$ 

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$
$Tl_2SO_4 \cdot Cr_2(SO_4)_3$ 23.2°C.	8.0297	111.7	112.3	14.29	
	8.3115	115.9	116.5	14.34	
	8.2757	111.7	112.3	13.89	<u>12640</u>
	8.1652	112.5	113.1	14.16	
	8.2622	112.2	112.8	13.97	
			MEAN	14.15	
$Tl_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ 23.8°C.	6.2870	59.9	59.5	9.82	
	6.2797	59.8	60.4	9.82	
	6.2592	57.9	58.3	9.55	<u>12930</u>
	6.2699	59.5	60.1	9.97	
	6.2715	58.4	59.0	9.60	
			MEAN	9.76	

SUSCEPTIBILITY OF SERIES  $(\text{NH}_4)_2\text{SO}_4\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ 

Salt	weight of salt in grams	Full in milligrams	Corr. Full in milligrams	$\kappa \times 10^{-6}$	$\chi_M \times 10^{-6}$
$\text{Fe}_2(\text{SO}_4)_3$ 23°C.	4.2008	256.8	257.4	62.64	
	4.1951	250.5	251.1	61.19	
	4.2391	263.5	264.1	63.70	<u>24950</u>
	4.2516	265.0	265.6	63.85	
	4.3545	257.1	257.7	60.55	
			MEAN	<u>62.38</u>	
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$ 23°C.	4.6394	246.0	246.6	54.33	
	4.6764	259.0	259.6	56.71	
	4.7474	259.0	259.6	55.89	<u>29180</u>
	4.6346	249.0	249.6	53.04	
			MEAN	<u>55.49</u>	
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ 23°C.	4.0993	126.1	126.7	31.58	
	4.0784	124.0	124.6	31.22	
	3.9492	123.2	123.8	32.03	<u>30440</u>
	3.9779	124.5	125.1	32.13	
			MEAN	<u>31.74</u>	



SUSCEPTIBILITY OF  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 18H_2O$ 

Salt	Weight of salt in grams	Pull in milligrams	Corr. Pull in milligrams	$\chi \times 10^{-6}$	$\chi_M \times 10^{-6}$	
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 18H_2O$	4.8406	-4.94	-4.20	-0.5157	<u><u>-507.2</u></u>	
		-4.97				
		-4.97				
	4.8313	-4.94	-4.94	-0.5144		
		-4.89				
		-4.98				
	4.9883	-5.11	-4.33	-0.5167		
		-5.08				
		-5.09				
	4.9203	-5.01	-4.25	-0.5138		
		-5.01				
		-5.01				
			MEAN	-0.515		

## DISCUSSION OF RESULTS

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### Additivity Relationship.

The Langevin equation, deduced from the Larmor precession theorem, gives for the atomic diamagnetic mass susceptibility of a spherically symmetrical atom or ion the expression,

$$\chi_A = \frac{-e^2 L}{6mc} \sum r^{-2}$$

where  $L$  is the number of atoms per gram atom (Avogadro number  $e$ , the electronic charge;  $m$ , the mass;  $c$ , the velocity of light and  $\sum r^{-2}$  the mean square of the radius (on the classical theory).

This equation applies essentially to mononuclear systems

In molecular and polynuclear systems the outer electrons will have their orbits distorted and will move under the influence of more than one centre of force. Consequently the above equation may not be strictly accurate for such systems.

Whilst, therefore, ionic diamagnetic susceptibility should be an additive property of the susceptibilities of the individual ions as long as they maintain their individuality, when they definitely combine into a more complex system, constitutive effects may, and generally do, make their appearance.

Pascal, in an extensive investigation of susceptibilities especially of organic compounds, established the principle of additivity that the molecular susceptibility of a compound

could be represented by the sum of the susceptibilities of the constituent atoms or ions with a corrective factor due to constitution which depends on the type of linking. This he expressed in the equation,  $\chi_M = \sum n_A \chi_A + \lambda$ .

If we apply this to the case of hydrated salts, so long as the type of linking is unaltered, a definite additivity relationship should hold, there being a constant increase in molecular susceptibility for each additional water molecule or groups of molecules.

Mlle. Feytis (5) investigated the effect of water of crystallisation in the case of several sulphates, and found the law of additivity to be applicable in the case of  $\text{CoSO}_4, 7\text{H}_2\text{O}$  :  $\text{CoSO}_4, \text{H}_2\text{O}$  :  $\text{Sm}_2(\text{SO}_4)_3, 8\text{H}_2\text{O}$  : and  $\text{Gd}_2(\text{SO}_4)_3, 8\text{H}_2\text{O}$ .

$\text{NiSO}_4, 6\text{H}_2\text{O}$  and  $\text{CuSO}_4, 5\text{H}_2\text{O}$  showed agreement in respect to the nonhydrates but an appreciable error in respect to the anhydrous salts. From this she concluded that one molecule of water was held in a different form to the others.

Table I shows the results obtained for the diamagnetic series of alums. The experimentally determined susceptibilities are recorded in column three; the fourth column giving values of the salt actually measured (column three) together with  $n$  times the value of the molecular susceptibility of water ( $-12.96$ )  $\times 10^{-6}$ , where  $n$  is 24 - the number of molecules of water present in the salt measured.

In the case of the paramagnetic compounds, the paramagnetic

effect of the chromic and ferric ions almost completely swamps the diamagnetic effect of the rest of the molecule, so that the additivity effect of the additional water does not come within the limit of experimental error.

TABLE I

THE ADDITIVITY RELATIONSHIPS IN THE DIAMAGNETIC ALUMS

Salt	Number of electrons	$\chi_M \times 10^{-6}$	$(\chi_M + \chi_n \text{H}_2\text{O}) \times 10^{-6}$
<u>Lithium</u>			
$\text{Li}_2\text{SO}_4$	51	- 43.75)	- 474.05
$\text{Al}_2(\text{SO}_4)_3$	170	- 119.1 )	
$\text{Li}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3$	221	- 159.6	- 470.8
$\text{Li}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	461	- 479.7	- 479.7
<u>Sodium</u>			
$\text{Na}_2\text{SO}_4$	70	- 41.96)	- 472.2
$\text{Al}_2(\text{SO}_4)_3$	170	- 119.1 )	
$\text{Na}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3$	240	- 184.8	- 496.0
$\text{Na}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	480	- 503.1	- 503.1
<u>Potassium</u>			
$\text{K}_2\text{SO}_4$	86	- 70.20)	- 500.5
$\text{Al}_2(\text{SO}_4)_3$	170	- 119.1 )	
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3$	256	- 182.3	- 493.5
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	316	- 269.2	- 502.6
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	346	- 306.0	- 500.5
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$	376	- 349.4	- 505.0
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$	406	- 383.0	- 499.7
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	436	- 412.0	- 499.8
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 21\text{H}_2\text{O}$	466	- 461.5	- 500.4
$\text{K}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	496	- 493.4	- 493.4

TABLE I (continued)

Salt	Number of electrons	$\chi_M \times 10^{-6}$	$(\chi_M + \chi_{nH_2O}) \times 10^{-6}$
<u>Ammonium</u>			
$(NH_4)_2SO_4$	70	- 71.73)	- 502.03
$Al_2(SO_4)_3$	170	- 119.1 )	
$(NH_4)_2SO_4Al_2(SO_4)_3$	240	- 192.2	- 503.4
$(NH_4)_2SO_4Al_2(SO_4)_3 \cdot 6H_2O$	300	- 265.6	- 499.0
$(NH_4)_2SO_4Al_2(SO_4)_3 \cdot 15H_2O$	390	- 380.3	- 496.7
$(NH_4)_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$	480	- 508.7	- 508.7
<u>Rubidium</u>			
$Rb_2SO_4$	122	- 89.15)	- 519.45
$Al_2(SO_4)_3$	170	- 119.1 )	
$Rb_2SO_4Al_2(SO_4)_3$	292	- 172.4	- 483.6
$Rb_2SO_4Al_2(SO_4)_3 \cdot 9H_2O$	382	- 296.0	- 490.5
$Rb_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$	532	- 450.9	- 490.9
<u>Caesium</u>			
$Cs_2SO_4$	158	- 117.2)	- 547.4
$Al_2(SO_4)_3$	170	- 119.1)	
$Cs_2SO_4Al_2(SO_4)_3$	328	- 235.2	- 546.4
$Cs_2SO_4Al_2(SO_4)_3 \cdot 6H_2O$	388	- 299.7	- 533.1
$Cs_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$	568	- 526.0	- 526.0

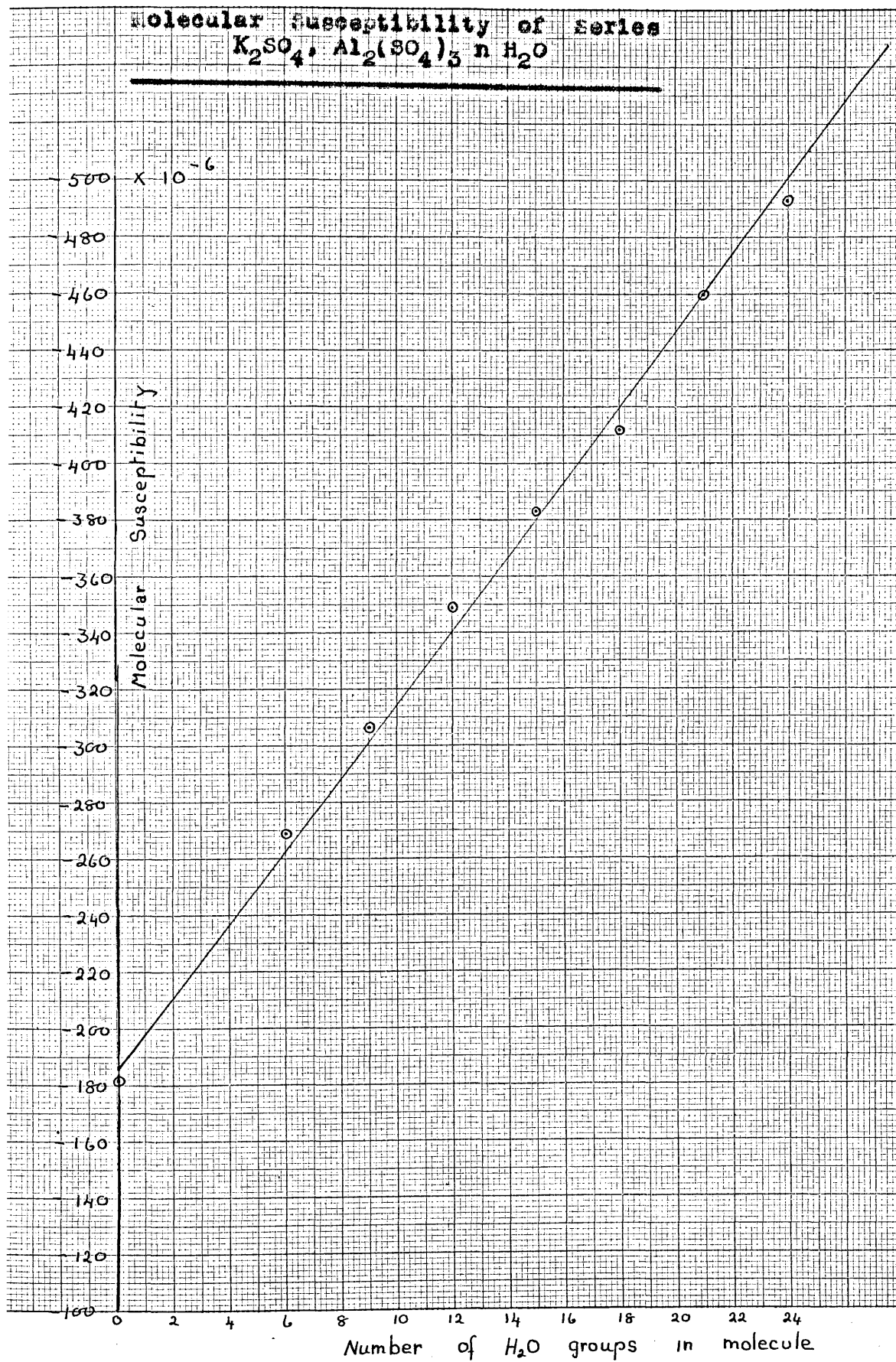
The table shows that the additivity law is obeyed extremely well in the case of the alums of lithium, sodium, potassium and ammonium, but that a slight but definite divergence appears in the case of rubidium and caesium where the fully hydrated salt has rather too low a value. I should like to point out here that the divergence in the case of caesium is very much smaller than that in the I.C.T. values.

This slight departure from additivity found in the case of the heavy monovalent ions may, perhaps, be attributed to the heavy nuclear charge drawing in the orbits of the donated electrons of the co-ordinated water molecules and therefore diminishing the mean square radius on which the susceptibility depends.

On the whole however, the additivity law is obeyed sufficiently to show that all the water molecules are held by similar links.

This additivity relationship is brought out well by graph I where the molecular susceptibility of the members of the complete potassium series are plotted against the number of water molecules. A constant increase for each additional three water molecules is observed.

GRAPH I.





The sum of the molecular susceptibilities of the alkali sulphate and aluminium sulphate is approximately equal to that of the anhydrous double salt except in the cases of sodium and rubidium, which are respectively too low and too high. From the table it also appears that whilst the alkali sulphates increase in susceptibility with increasing atomic number of the cation, the alums remain almost constant and, with the exception of those of lithium and caesium, show a slight decrease as the atomic number of the univalent ion increases.

RELATIONSHIPS BETWEEN THE DIAMAGNETIC SERIES

---

The Langevin equation  $\chi_M = -\frac{e^2 L}{6 m c^2} \sum r^{-2}$ , which holds for mononuclear systems, can also be taken as a first approximation for the polynuclear systems. It shows that the molecular susceptibility depends on the number of electrons and on the mean square radius of the orbits of these electrons.

In Graph II the molecular susceptibility of the members of the complete potassium series is plotted against the number of electrons in the molecule. This shows a linear relationship, that is, a definite increase in molecular susceptibility with additional electrons. The line does not pass through the origin but cuts the molecular susceptibility axes at a point + 128, indicating that the diamagnetism in each case has a smaller value than would be the case if all the electrons were giving their full contribution.

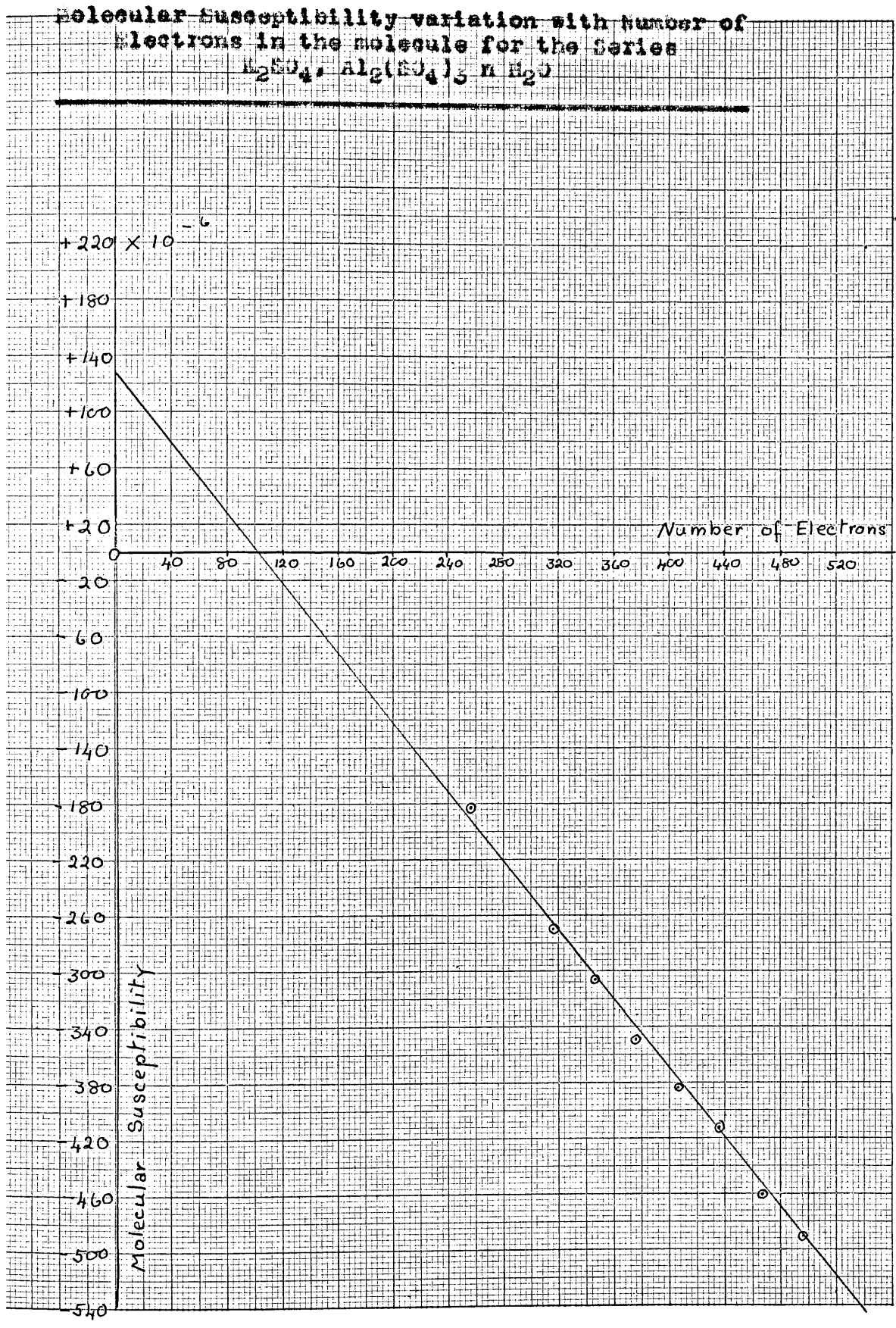
This is probably due to two causes: in the first place it has been shown by Pauling, Hartree and others that the outer electrons have a screening effect which reduces the contribution of the inner levels, so that the outer groups become responsible for almost the whole of the diamagnetic effect.

Secondly, there is the constitutional effect consequent on the interaction of the quite heavily charged ions of which the alum molecule is composed.

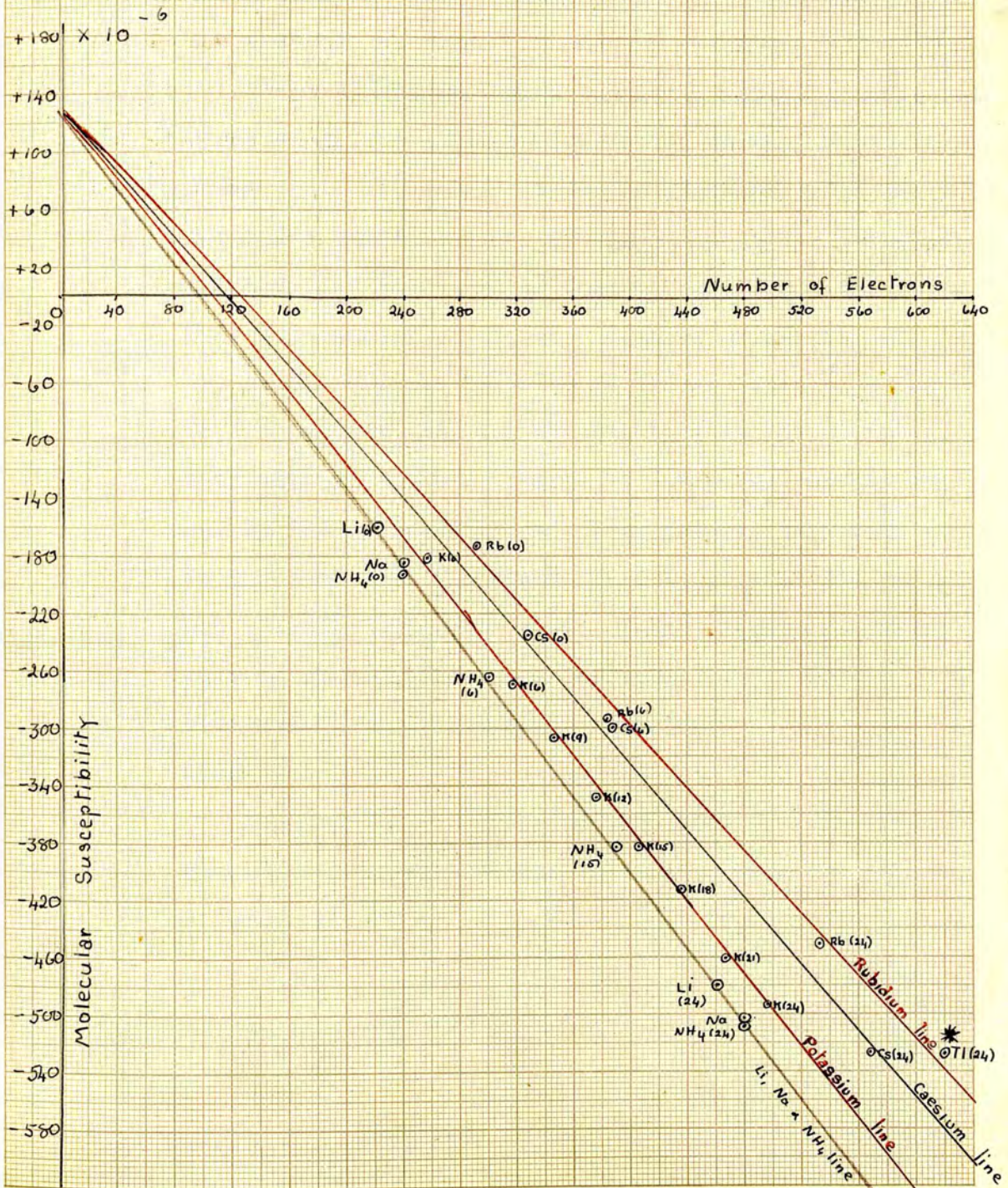
In comparing the diamagnetism of the different series it must be remembered that the only change, apart from any possible change due to modification of constitution, is that of the substitution of one alkali metal by another. In the simple alkali sulphates there is an increase in susceptibility with increasing atomic number of the cation, which is not shown by the alums (see Graph III). It becomes probable that constitutive effects (such as interionic forces change) are influencing the susceptibility.

Since the diamagnetism is due, for the most part, to the outer shell of electrons, there will be two factors at work affecting the mean square radius on which the susceptibility depends. The first is the increase in total radial distance from the nucleus of the outer shell of electrons as we pass from lithium to caesium. This will tend to increase the diamagnetic effect owing to increase of radius of the outer shell of electrons.

GRAPH II.



Variation of Molecular Susceptibility of the Series  $R_2SO_4 \cdot Al_2(SO_4)_3 \cdot n H_2O$  with Number of Electrons.



\* Thallous alum value (Trew. Trans. Far. Soc. 188 xxxii 1937)

The second effect tending to counteract this will be the increase in nuclear charge, tending to draw in the orbital electrons, and hence diminish the radii and therefore the susceptibility.

Graph III shows the variation of molecular susceptibility produced by the substitution of the different alkali ions. It shows that very little change is produced in the value of the molecular susceptibility of the alums of the anhydrous double sulphates in the cases of sodium, potassium, and rubidium. This indicates that the two opposing causes already referred to, namely (a) the increase in radial distance of <sup>the outer</sup> ~~each~~ electrons of the heavier ion, and (b) decrease in the distance, due to a drawing in of these orbits by increased nuclear charge, are, in the above-mentioned alums compensating each other. At the same time the susceptibility of the lithium salts are slightly lower and those of the caesium considerably higher; this is probably due to a difference in structure, which has been established from X-ray measurements. This point is discussed later.

The graph also brings out the fact that in every case where intermediate hydrates have been measured, the linear relationship holds good.

THE EFFECT OF THE INTRODUCTION OF DEUTERIUM OXIDE  
INTO THE ALUM CRYSTAL.

The preparation of the compound  $K_2SO_4Al_2(SO_4)_3 \cdot 18D_2O \cdot 6H_2O$  has already been described.

The additivity law has been well established for the potassium series, and its truth may therefore be assumed to hold in this case also. In this way it becomes possible to obtain a value for  $\chi_m$  for deuterium oxide. At the same time the results can also be used to find if the six water molecules present in the hydrate used as a starting point are still in the crystal, or if a preferential crystallisation has taken place with the substitution of molecules of deuterium oxide in place of the water molecules.

The mean value for the molecular susceptibility for potash alum taken over the whole series of hydrates equals

$$-499.5 \times 10^{-6}$$

$$\text{for } 18 H_2O = -223.5 \times 10^{-6} \quad (\text{assuming } \chi_{H_2O} = -0.72 \times 10^{-6})$$

$$\text{Therefore } K_2SO_4Al_2(SO_4)_3 \cdot 6H_2O = -273.0 \times 10^{-6}$$

$$K_2SO_4Al_2(SO_4)_3 \cdot 18D_2O \cdot 6H_2O = -507.2 \times 10^{-6}$$

$$\begin{aligned} \text{Therefore } 18D_2O &= -507.2 - (-266.0) \\ &= -241.2 \times 10^{-6} \end{aligned}$$

$$\begin{aligned} \text{Therefore } D_2O &= \frac{-241.2}{18 \times 20.027} \\ &= \underline{\underline{-0.641 \times 10^{-6}}} \end{aligned}$$

a result in good agreement with the one found in this laboratory by Trew and Spencer (6), i.e.,  $-0.637 \times 10^{-6}$ .

This shows, therefore, that the accepted value for  $D_{20}$  also holds when it enters the crystal as water of crystallisation and, further, it shows that in this case no substitution has taken place. An important point in view of the suggested structure of the alum crystal which will be discussed later.



THE ALKALI SULPHATES

Table 2 shows the values obtained for the specific and molecular susceptibilities of the alkali sulphates.

Column five gives the values quoted in the International Critical Tables. The two sets of values are, in this case, in very good agreement.

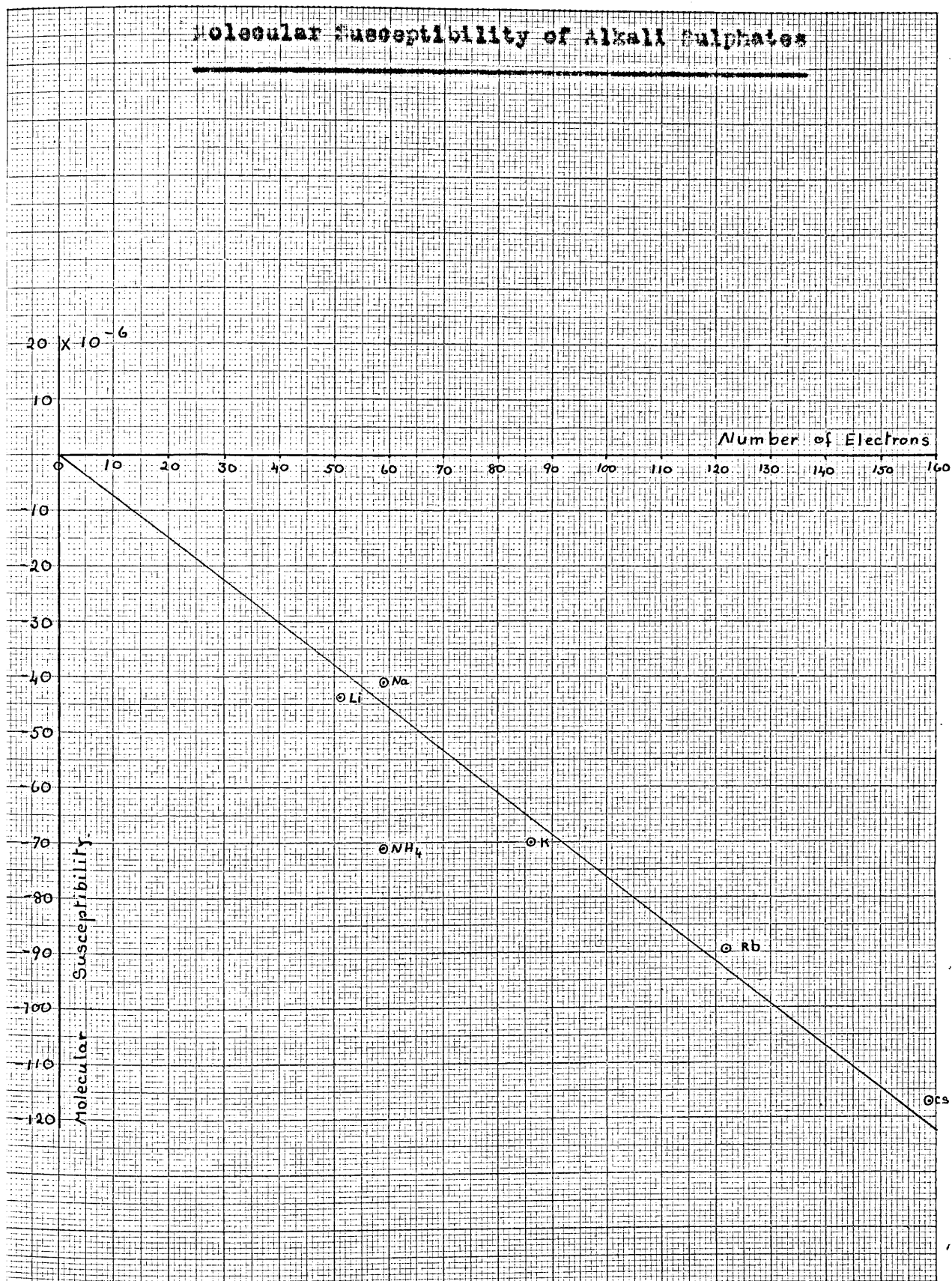
TABLE II.  
THE ALKALI SULPHATES

Salt	$\chi \times 10^{-6}$	$\mu \times 10^{-6}$	Number of electrons	I.C.T. value
$\text{Li}_2\text{SO}_4$	-0.398	-43.75	51	-0.38 Meyer
$\text{Na}_2\text{SO}_4$	-0.295	-41.96	59	-
$\text{K}_2\text{SO}_4$	-0.403	-70.20	86	-0.403 Pascal
$\text{Rb}_2\text{SO}_4$	-0.334	-89.15	122	-0.331 Pascal
$\text{Cs}_2\text{SO}_4$	-0.324	-117.2	158	-0.322 Pascal
$(\text{NH}_4)_2\text{SO}_4$	-0.543	-71.73	59	-

Graph IV shows the molecular susceptibility plotted against the number of electrons. Quite a good linear relationship holds for all the members of the alkali group, there being a definite constant increase of molecular susceptibility with increasing total number of electrons as we pass from lithium to caesium.

There is, however, an important difference in this graph from those of the alums. In this case the line passes through

GRAPH IV.



the origin, showing no constitutional effects and residual paramagnetism.

This is an indication that the Langevin equation which makes the susceptibility a function of the number of electrons is much more closely obeyed than is the case with the alums.

It has already been pointed out that the equation applies essentially to mononuclear systems, and we can therefore conclude that in the sulphates the ions are at least quasi-independent, and so the salt can be treated as the sum of independent mononuclear systems - a condition which does not prevail in the alums.

It is of interest to calculate the gram ionic susceptibilities of the ions of the alkali metals from the experimental values of the sulphate and to see how these values compare with those found by Pascal experimentally and with the calculated value obtained by Brindly and Slater by application of the wave function, and those obtained by Stoner by the application of the Hartree charge distribution.

In calculating the gram ionic susceptibilities of the alkali metal ions we have assumed the sulphate value to be the sum of the values of the separate ions and have taken the Pascal value for  $\text{SO}_4 = -33.6 \times 10^{-6}$ .

Table III gives the results obtained. The table shows that on the whole there is very good agreement between these results and the experimental results of Pascal, although I obtained a considerably lower value for the sodium ion.

TABLE III

## GRAM IONIC SUSCEPTIBILITY

Ion	$\chi_A \times 10^{-6}$	Calculated		Fascal
		S.S.	H.S.	
Li	5.07	0.7	0.7	4.2
Na	4.2	4.1	5.6	9.2
K	18.3	14.2	17.3	18.5
Rb	27.7	25.3	29.5	27.2
Cs	41.8	38.7	-	41.

("Magnetism and Matter" - E. J. Stoner)

Again there is good agreement between experimental results and the calculated, with the important exception of the lithium ion, which is considerably too high in both experimental values to agree with the theoretical.

In the other cases the sodium is in very close agreement with the Brindley-Slater value, but as we come to the larger ions the values found from experiments are somewhat larger than those found by Brindley and Slater, and approximate more closely to the Hartree-Stoner value.

The point of special interest here is that whilst the other alkali metal ions behave normally and are in agreement with theory, lithium, the first member, behaves as if it was a much larger ion. A point of particular importance, when considering

the theoretical possibility of the existence of lithium alum which will be dealt with in a later section.

I may mention here, however, that it has been pointed out by Brindley and Hoare (7) that a large discrepancy between the observed and calculated interatomic distance is to be found in the case of lithium chloride, bromide and iodide, and they offer as explanation the suggestion of Pauling, that the principle forces between the ions of a crystal being Coulomb forces of attraction and repulsion will vary inversely as a high power of the distance separating the ion. Hence, when the positive ion is very small, as is the case with lithium, the surrounding negative ions become close enough together for their intrinsic repulsion to become an important factor, and to produce larger interionic distances than would be theoretically possible where these forces are neglected.

Hence this repulsion of similar ions will allow the small lithium ion to have a larger apparent radius, and so increase its susceptibility.

One more point of interest may be given here as indicative of the general agreement of the alkali metal ions in the sulphate with theoretical requirements, with again the divergent behaviour of lithium the first member of the group.

The radii of the alkali metal ions have been determined experimentally by Goldschmidt (8), who also quotes those obtained theoretically by Pauling.

Table IV gives the square of these values with the gram

ionic susceptibility, whilst Graphs V and VI give the relationships between the susceptibilities and the square of the given values for the radii.

TABLE IV

Ion	$\chi_A$	$\bar{r}^2$ (Goldschmidt)	$\bar{r}^2$ (Pauling)
Li	$-5.0 \times 10^{-6}$	$0.62 \text{ \AA}^0$	$0.36 \text{ \AA}^0$
Na	-4.2	0.96	0.90
K	-18.3	1.76	1.76
Rb	-27.7	2.22	2.19
Cs	-41.8	2.72	2.85
$\text{NH}_4$	-19.0	2.05	--

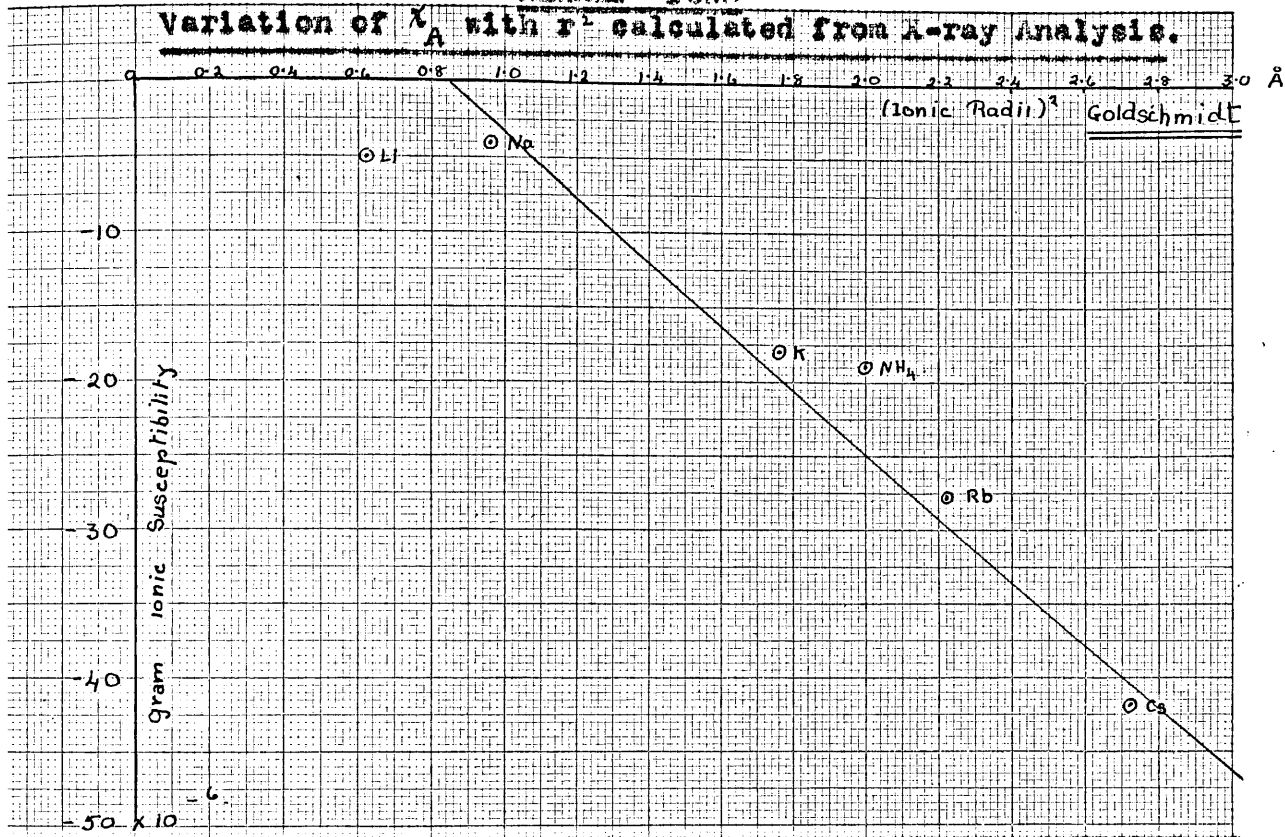
Again a good linear relationship holds for all the alkali metal ions, with the exception of lithium where the susceptibility corresponds to a value of  $r^2 = 0.95$  in place of the calculated values 0.78 and 0.60.

These values of ionic radii squared also gives an explanation for the ammonium sulphate being off the straight line in Graph IV. For although the ammonium ion has the same number of electrons as the sodium ion, according to Goldschmidt the radius is considerably larger, being even slightly larger than the potassium ion. This is in good agreement with the susceptibility which is also slightly larger than the potassium sulphate value.

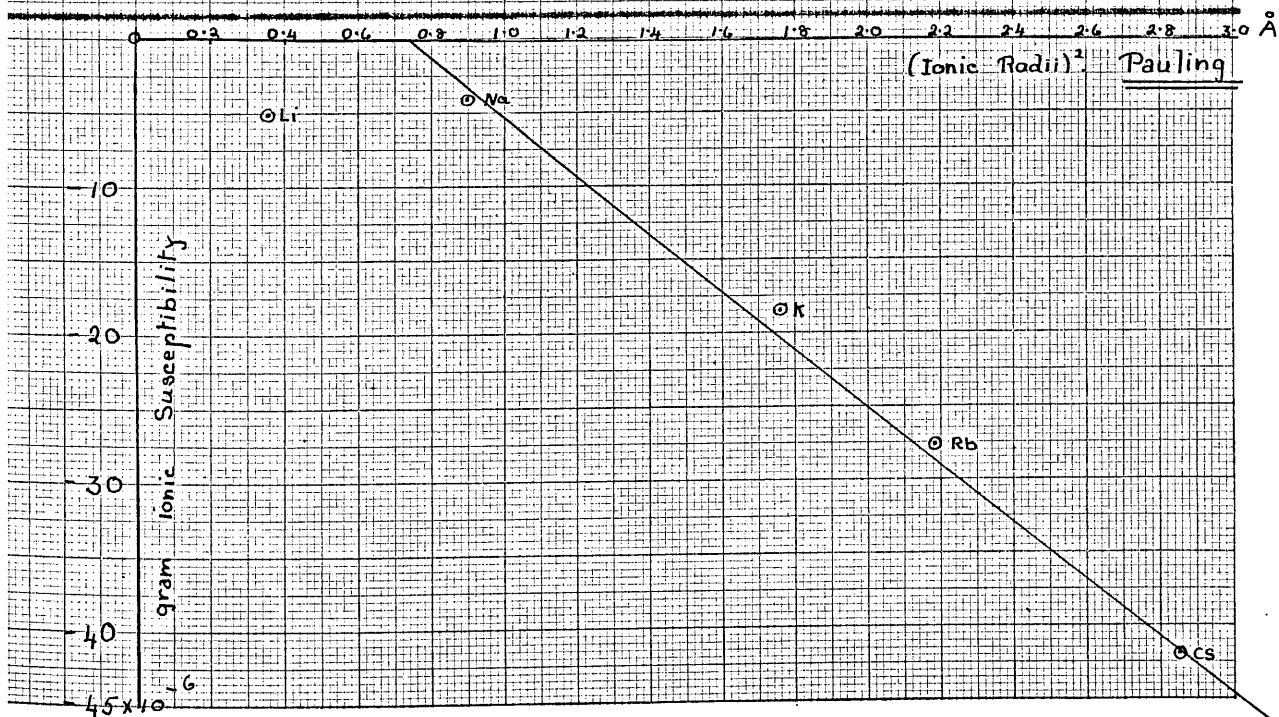
GRAPH V.

ALKALI IONS

Variation of  $\chi_A$  with  $r^2$  calculated from X-ray Analysis.



GRAPH VI.



## THE PARAMAGNETISM OF THE CHROMIUM ALUMS

---

Of the alums with chromium as the trivalent ion only two series were investigated, the potassium chrome alum and the thallium chrome alum.

Owing to the very large numerical results obtained, the investigation is of little value in testing the additivity law for the water of crystallisation, for, in spite of the large number of diamagnetic atoms of which the molecule is composed, the correction for the diamagnetic susceptibility reaches only a very small percentage of the total, not more than could be attributed to experimental error.

But apart from this, the series has proved of interest from the magnetic standpoint.

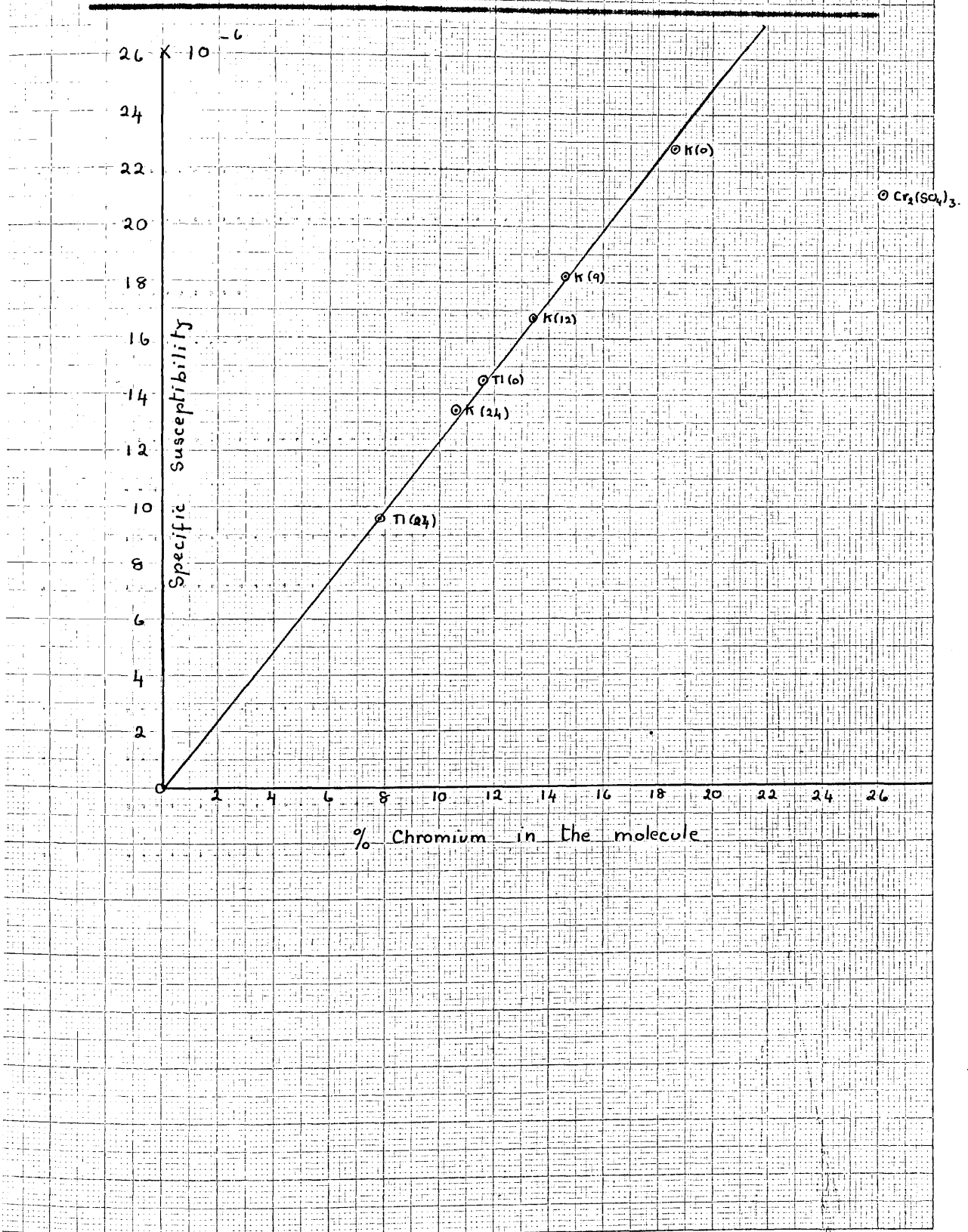
The potassium and thallium alums are co-linear and the straight line passes through the origin, showing that the susceptibility is directly proportional to the percentage of the paramagnetic chromium present.

The susceptibility is therefore due almost entirely to the chromium ion, which must completely swamp the diamagnetic contribution of the large number of the other atoms and ions of which the alum molecules are composed.

It is also of interest to note that the chromic sulphate lies well off the line, pointing again to a difference of structure between the alum and the free chromic sulphate.



Variation of the Specific Susceptibility of Chrome Alums with percentage Chromium in the Molecule.



It would seem at first sight, therefore, that the surrounding ions have little or no effect on the paramagnetism, but if this were so the Hund formula for the effective magnetic moment  $P_B = g\sqrt{j(j+1)}$  (where  $g$  is the Landé splitting factor) would be in agreement with experimental value. This, however, is found not to be the case.

The Hund formula is based on the supposition that the ion is comparatively free and both the angular momentum and spin are effective, a condition which is found to hold in the rare earth ions where the incomplete shell of electrons is shielded from the other ions by a complete shell of higher total quantum number.

In the chromic ions, the incomplete shell is the third and this is the level of the highest quantum number, and is therefore exposed to the interactional effects of the crystal-line fields due to the groups surrounding the chromic ion. The effect of these fields is, in a large measure, to destroy the orbital contribution of the ion's electrons to the magnetic moment which corresponds fairly closely to the resultant spin moment of the electrons.

Bose and Stoner (9) derived an equation for the specific susceptibility, on the assumption that the magnetic moment is due to spin only.

$$\chi = N_p^2 4s(s+1) / 3kT$$

where  $s$  is the resultant spin quantum number equal to  $3/2$  for the chromic ion.  $N$  is Avogadro's number and  $k$  the Bohr magneton

Penner and Schlapp (10) pointed out that the orbital angular momentum is, in most cases, entirely destroyed, the remnant giving rise to a deviation from the above equation. They therefore derived an equation

$$\chi = (15N\beta^2/3kT)(1 - 2\lambda/5D)^2$$

introducing a small correction  $2\lambda/5D$  which would bring the theoretical value for spin only into close agreement with experiment.

The value given by these workers for the chromic ion was  $\lambda = +87\text{cm}^{-1}$  and  $D = 3730$ .

These values were largely based on the agreement they gave with the Leyden data for chrome alum. E. B. Jenes (11) has pointed out, however, that too much reliance should not be placed on the numerical value of  $D$ , since he finds, from his investigation of the compound  $\text{K}_2\text{Cr}(\text{S.O.N})_6\text{H}_2\text{O}$ , a good agreement with experiment is obtained by using  $D = 1480\text{ cm}^{-1}$  when  $kT = 30.10 \times 10^{-6}$ . But  $D = 1720\text{ cm}^{-1}$  when  $kT = 30.30 \times 10^{-6}$ .

It is then of interest to see how these results fit in with the two proposed formulae.

For this purpose the values of the molecular susceptibility have been corrected for the diamagnetic contribution of the atoms other than chromium contained in the molecule, thus obtaining the value for the chromic ion alone.

The value of  $\chi_M$  for the chromic ion was then calculated, and from this value the effective magneton number  $P_B^1$  was calculated from the formula.

$$P'_B = \sqrt{\frac{3R}{5564}} \cdot \sqrt{\chi_{MT}} = 2.84\sqrt{\chi_{MT}}$$

where T is the absolute temperature.

TABLE V.

Salt	Temp.	$\chi_M \times 10^{-6}$	$\chi_{M\text{Cr}_2} \times 10^{-6}$	$\chi_{\text{Cr}^{III}}$	$P'_B \text{Cr}^{III}$
$\text{Cr}_2(\text{SO}_4)_3$	25°C.	9268	9358	$90 \times 10^{-6}$	$3.4 \times 10^{-6}$
$\text{K}_2\text{SO}_4\text{Cr}_2(\text{SO}_4)_3$	22.7	12900	13050	125	3.94
$\text{K}_2\text{SO}_4\text{Cr}_2(\text{SO}_4)_3, 9\text{H}_2\text{O}$	18°C.	13340	13619	130	3.94
$\text{K}_2\text{SO}_4\text{Cr}_2(\text{SO}_4)_3, 12\text{H}_2\text{O}$	19.5	13000	13201	127	3.93
$\text{K}_2\text{SO}_4\text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$	21.5	13330	13796	132	4.03
$\text{Tl}_2\text{SO}_4\text{Cr}_2(\text{SO}_4)_3$	23.2	12640	13140	126	3.94
$\text{Tl}_2\text{SO}_4\text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$	23.8	12930	13430	129	3.98

Mean value of  $P'_B$  for  $\text{Cr}^{III}$  in alum = 3.97

Value including low sulphate = 3.89

Bose and Stoner equation for  $\chi_{\text{Cr}^{III}}$  gives  $P'_B = 3.92$

Penner and Schlapp's equation gives  $P'_B = 3.89$ .

The table of values shows that the mean value for  $P'_B \text{Cr}^{III}$  where the ion is in the particular compound formation of the alums is more in agreement with the Bose and Stoner equation than the corresponding equation of Penner and Schlapp. To bring the latter equation into line with the results would need a negative value for D.

If we take the mean, including the low sulphate value, then the results are in perfect accord with the Penner and Schlapp equation; but this does not seem legitimate treatment as the chromic ion is definitely in a different condition in the sulphate, where the ions are quasi independent, from what it is in the complex alums.

## THE FERRIC ALUM SERIES

---

The ferric alums can receive a similar treatment as the chrome alums, both belonging to the paramagnetic series of compounds.

The ferric ion, however, has a considerably higher paramagnetism than the chromic ions.

As was the case with the chromium, the ferric ion completely swamps the diamagnetic effects on the other ions and atoms of the molecule.

There is a remarkable similarity between the two series in the fact that in both cases the sulphate value is about 20% too low to form an additivity relationship with the alum.

It was suggested, when speaking of the diamagnetic series, that no true additivity relationship held between the component sulphates and the alums. This has been confirmed with strongest evidence in the three paramagnetic series, and we can only suppose that the trivalent ion is in a different condition in the alums from that in the sulphates. In the latter the ions are quasi-independent, whilst in the former a complex condition probably prevails.

This is an important point in view of the suggested structure of the alum crystal, which will be dealt with in the next section.

In this series we may derive a value for the effective magnetic moment of the paramagnetic ion, and compare this with the value given by Stoner (9) for spin only.

Table VI gives the values obtained.

It is seen that the mean value for the ferric ion, when present in the alum, agrees with the value given, presuming that the angular moment has been entirely quenched and the paramagnetism is due to spin only.

TABLE VI.

Salt	Temp.	$\chi_M$	$\chi_M \text{ Fe}_2$	$P_B \text{ Fe}^{+++}$
$\text{Fe}_2(\text{SO}_4)_3$	25°C.	$25000 \times 10^{-6}$	$25100 \times 10^{-6}$	5.43
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$	23°C.	29200	29300	5.90
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$	21°C.	30400	30800	6.02

Mean value  $P_B \text{ Fe}^{+++}$  when in combination in alums = 5.96

Stoner value for spin only = 5.92

Therefore in both cases where the links are those of the alums, whether the paramagnetic ion is chromic or ferric, the effective magnetic moment agrees with the theory if we suppose that the 'spin only' is effective.

Similarly, in both cases, the effective magnetic moment is lowered considerably where the sulphate type of link is substituted for the alum type.

THE STRUCTURE AND FORMATION OF THE ALUMS

Several points of general as well as magnetic chemistry have arisen from this research on the subject of the alums, all of which have to be explained by any theory dealing with the structure and formation of this series of compounds. The chief points may be summarized as follows:-

- (1) The water molecules are linked up in the alum crystal in such a way that they are lost in groups of three.
- (2) Six of these water molecules are held more tenaciously than the other eighteen.
- (3) No trihydrate has been prepared.
- (4) The last six/<sup>water</sup> molecules can be driven off only if a sufficient supply of energy in the form of heat is supplied.
- (5) The anhydrous compound is very insoluble, and the alkali sulphates cannot be dissolved out separately.
- (6) The mass susceptibility shows a constant increase with increase in number of water molecules in the crystal, which implies a similar type of link for all the molecules.
- (7) As has already been pointed out, the magnetic properties further show that the alum is not



behaving as a simple mixture of the component sulphates, but rather as a more complex structure.

Further, there is the work done on the alum structure by the physicists H.Lipson and C.A.Beevers (10). These workers investigated the structure of the alums by the method of X-Ray diffraction, using the two dimensional Fourier analysis of the electron distribution projected on to the cube face. They propose a structure in which there are two sets of water molecules which have essentially different natures. One set form an octahedron group round the aluminium ions, whilst the other set link together the  $\text{SO}_4$  tetrahedron, the  $\text{Al}_6\text{H}_2\text{O}$  octahedron and the univalent ion.

Fig. 2 gives a diagram of a portion of the molecule, showing a little of the very complicated structure they propose.

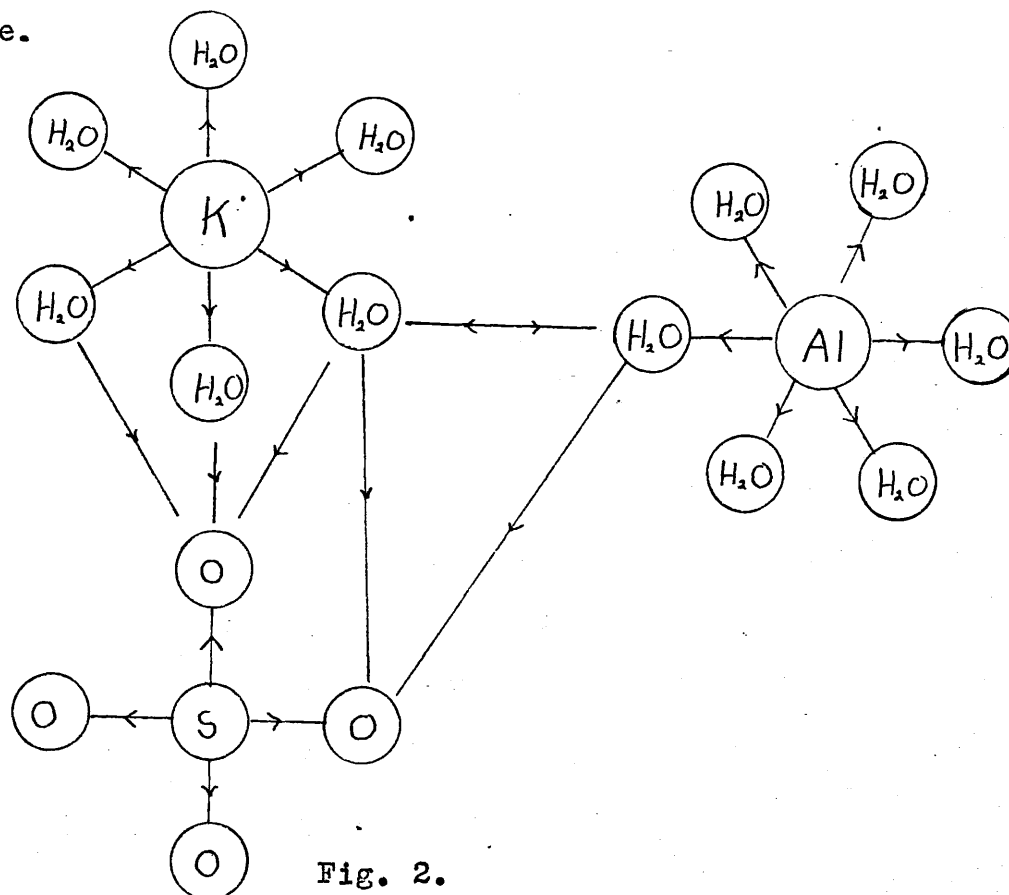


Fig. 2.

They further postulate that the unit cell contains two molecules of alum and that, whilst six of the sulphate groups are linked to the univalent ion through water, the remaining two are not connected by water molecules.

Lastly, they suggest that there are three different structures to be found in the alums, the slight difference in structure to be found in the three types being due to the difference in size of the univalent ion.

These types they call the  $\alpha$ ,  $\beta$  and  $\gamma$  types.

The  $\alpha$  structure is typical of the medium sized ion, the  $\beta$  of the large caesium ion and the  $\gamma$  of the small sodium ion.

The chief difference between the  $\alpha$  and  $\beta$  type is that the caesium ion is so much larger that the slight adjustment of the pushing out of the water molecules by the increasing size of the univalent ion as we pass up the periodic table is no longer sufficient. The caesium ion comes close enough to the  $\text{SO}_4$  group for the mutual attraction to become a governing factor, and a new position of equilibrium becomes necessary.

The  $\gamma$  structure proposes that the  $\text{SO}_4$  groups are oppositely orientated along the triad axes, thus implying that the distance between the univalent ion and the oxygen is much smaller, and that there is a smaller distance between the sodium and the water molecules.

It is then these points that I have tried to correlate to form a chemical theory of the formation and structure of the alum molecule.

THE FORMATION OF THE ALUM CRYSTAL

The normal method of preparation of the alums is from solutions of the component sulphates taken in molecular proportions, care being observed to obtain the most favourable conditions of temperature and concentration.

Aluminium sulphate normally separates out from solution with eighteen molecules of water of crystallisation, and this hydrated salt is very soluble in water, that is, very easily ionised. It is of fundamental importance, in considering the alums, to have some idea of how the water molecules are linked in aluminium sulphate. Aluminium has a co-ordination number six, and it is natural to suppose that each aluminium ion has co-ordinated six water molecules and these latter are arranged octahedrally.

The arrangement of the co-ordination for 6 H<sub>2</sub>O is shown in Fig 3.

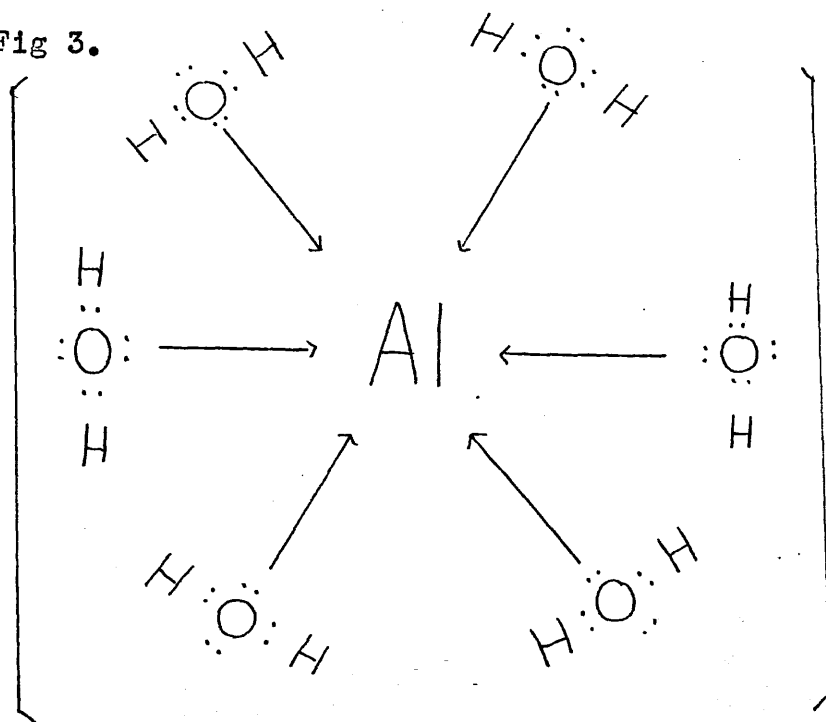
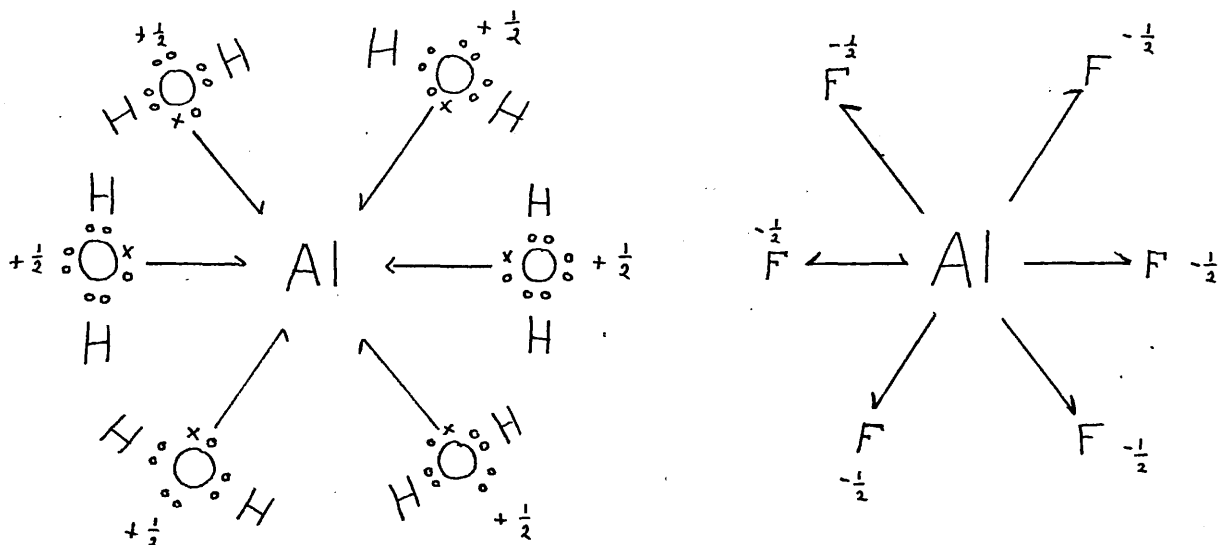


Fig. 3.

The probable existence of the singlet linkages in the cases of co-ordination number six has been pointed out by S. Sugden (13). He suggests that the octet rule is not upset by twelve donated electrons, but rather in these cases it is better to presume singlet linkages, which would give half charges shared amongst peripheral groups. This then ensures that all groups are similarly held and occupy the corners of a regular octahedron. He further gives as an example the complex ion  $\text{AlF}_6^{---}$  in the compound  $\text{Na}_3\text{AlF}_6$ , where he suggests that the fluorine atoms are held by singlet links and thus the triple negative charge is evenly distributed. That the same thing holds for the ion  $\text{Al}_6\text{H}_2\text{O}^{+++}$  I think more than likely, and therefore I have adopted the singlet type of linkage in the following explanations, although, of course, they are not essential to the proposed structure.

The arrangement that I propose for  $\text{Al}_6\text{H}_2\text{O}^{+++}$  is given in Fig. 4.



Distribution of Charge on ion  $\text{AlF}_6^{---}$  according to S. Sugden.

Fig. 4.

In this way twelve of the water molecules are accounted for, and so we may suppose the remaining six to be co-ordinated to the  $\text{SO}_4$  groups, two water molecules to each group.

Again it was found that twelve water molecules could be removed by treating the octadecahydrate with concentrated sulphuric acid, whilst the remaining six were much more firmly held and could be driven off only by heat, after which the anhydrous sulphate was found to be insoluble.

These results could well be accounted for if we suppose the two aluminium ions linked together through six of the co-ordinated water molecules, as in Fig. 5.

It is then apparent that these six water molecules are more firmly bound than the other twelve, and could be removed only by the application of sufficient heat energy to form a covalency bond between these Al ions, which would then result in the insolubility of the anhydrous sulphate.

The general arrangement of the aluminium sulphate can then be drawn out as in Fig. 5.

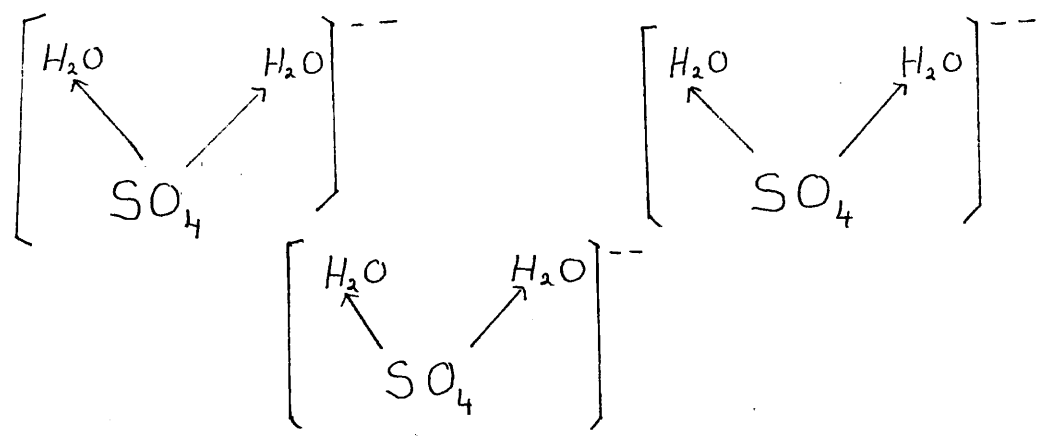
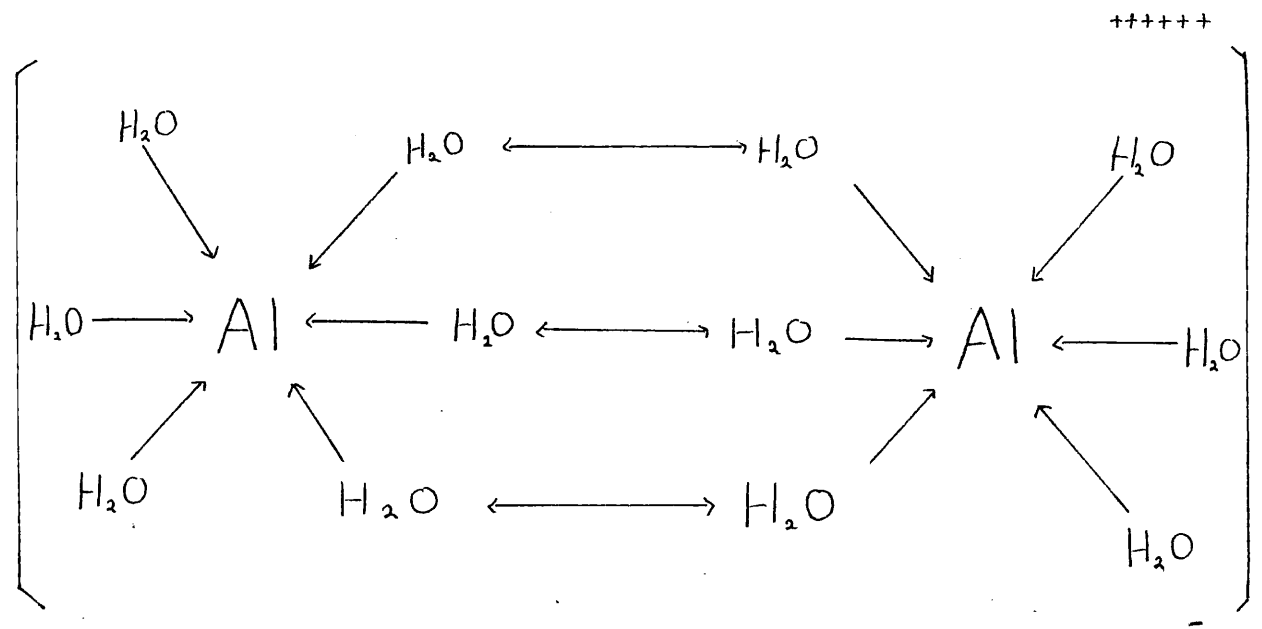


FIG. 5.

The type of link between the water molecules connecting the aluminium ions may be as in Fig. 6.

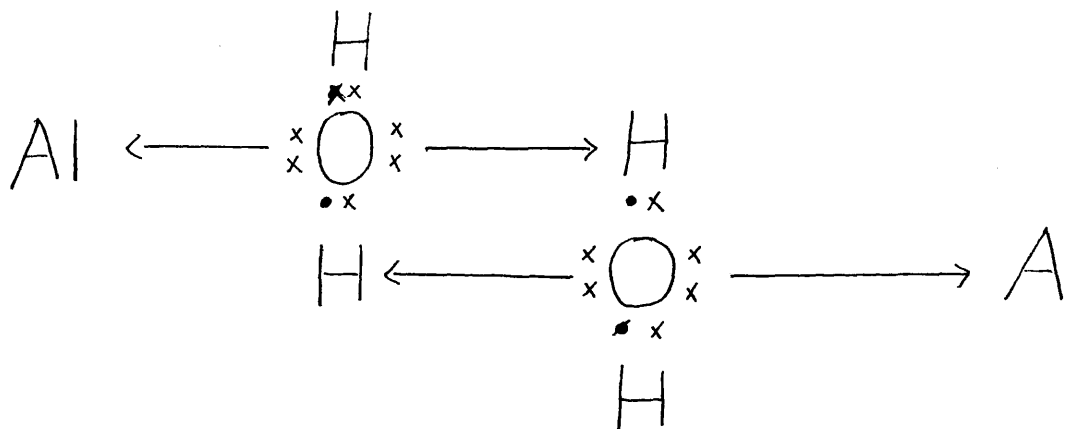
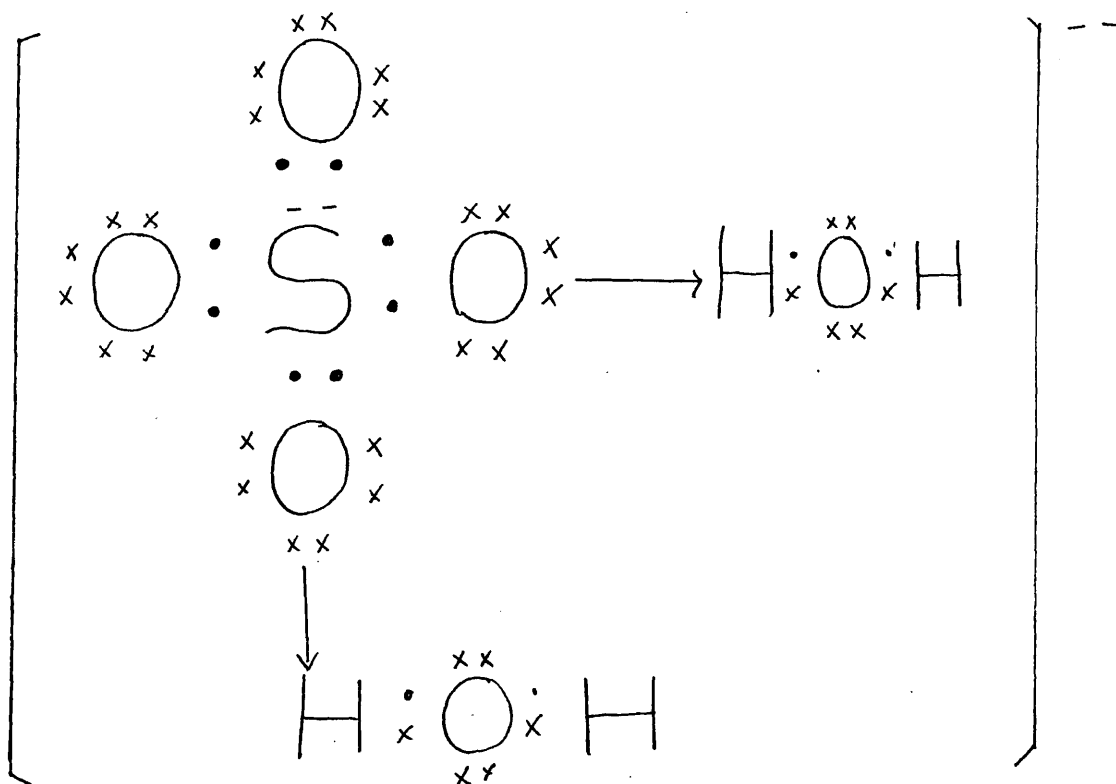
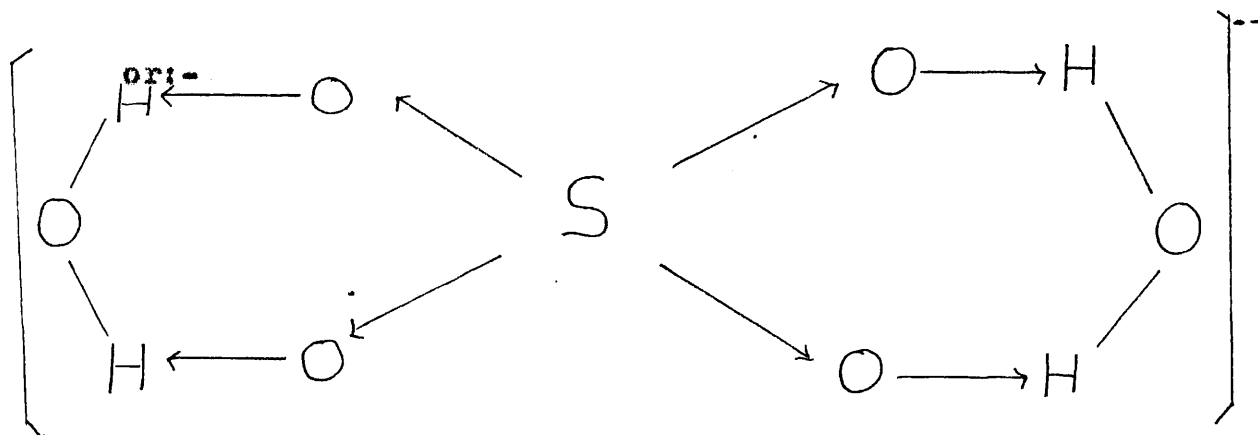


Fig. 6.

whilst the valencies for the  $\text{SO}_4 \cdot 2\text{H}_2\text{O}$  may be satisfied in one of two ways:-

Either:-





We have now to consider what happens when the alum is formed. The aluminium sulphate in solution gives the hydrated ions of Fig. 5.

Molecular proportions of an alkali sulphate - say potassium sulphate - are now added. This solution then contains the non-hydrated potassium and sulphate ions.

The potassium ion, like aluminium, being in the second period, is capable of co-ordinating six water molecules, but it has only a single positive charge and so cannot hold six singlet links on its own; but it can help to hold the water already linked to other atoms or ions.

A very simple process may therefore be considered to occur in the formation of the alum molecule.

Starting therefore with the aluminium sulphate, we can suppose that the potassium ions slip in and connect up the water molecules attached to the three  $\text{SO}_4$  groups. Each of the six outermost water molecules of the aluminium ions, at the



same time, pick up a second water and hold it with the help of the potassium ions, and thus connect up the aluminium with the potassium through the water, a ring structure being thus formed.

At the same time the  $\text{SO}_4$ , which was originally the partner of the potassium ions, is left as an independent ion in the crystal.

The process is best seen by means of Figs. 8 and 9.

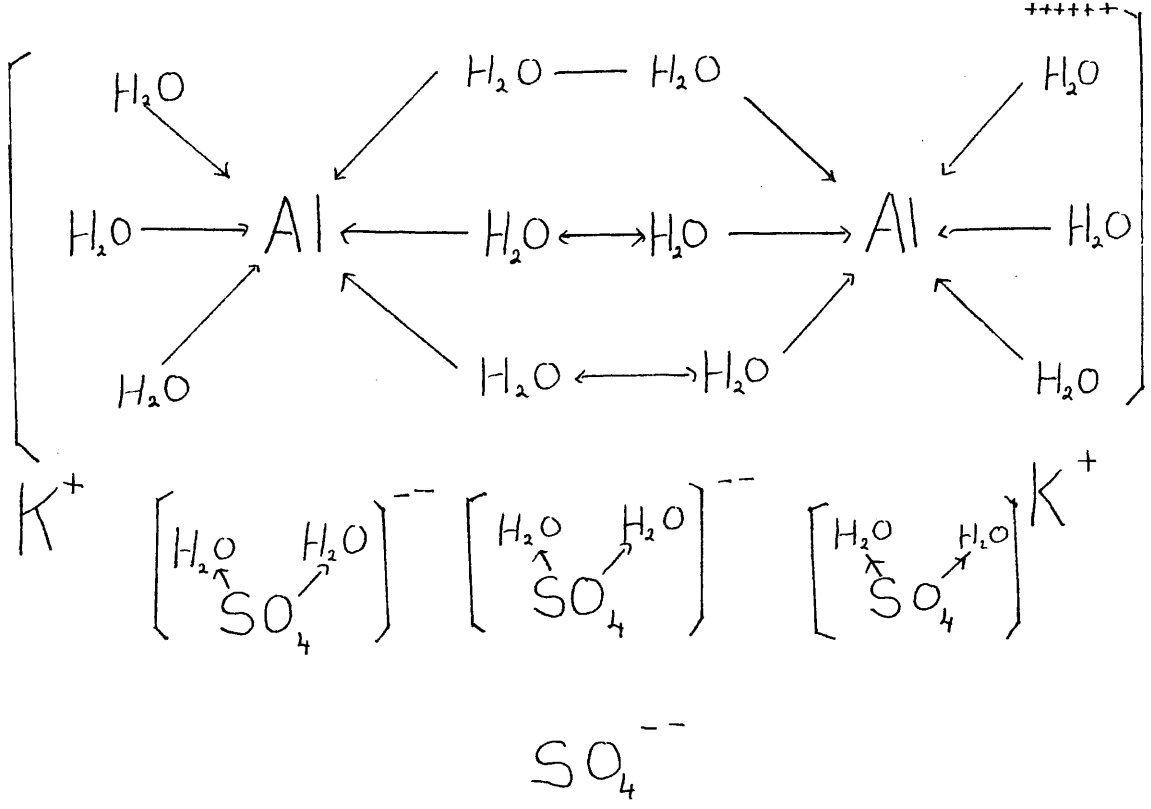


Fig. 8.

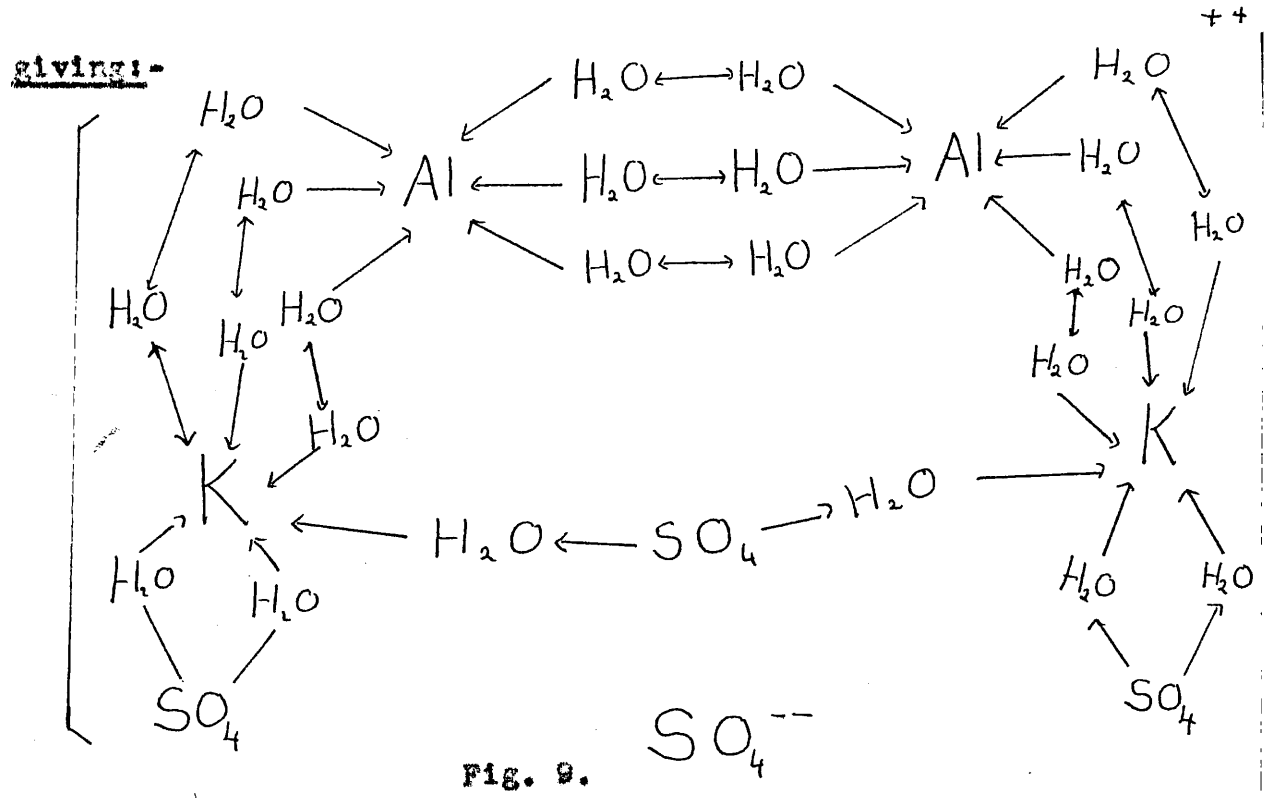


Fig. 9.

It is evident that this type of structure and formation makes the alum into a complex salt. The correct method of writing the formula then becomes  $\{K_2Al_2(SO_4)_3 \cdot 24H_2O\}^{++} SO_4^{--}$ .

The next point to be considered is whether this theory can offer a satisfactory explanation of all the observed experimental data.

In the first place it was seen that the water molecules are lost in groups of three. Now, writing the ring structure in an extended form for the sake of clearness, it is seen that the theory is capable of offering a very satisfactory explanation.

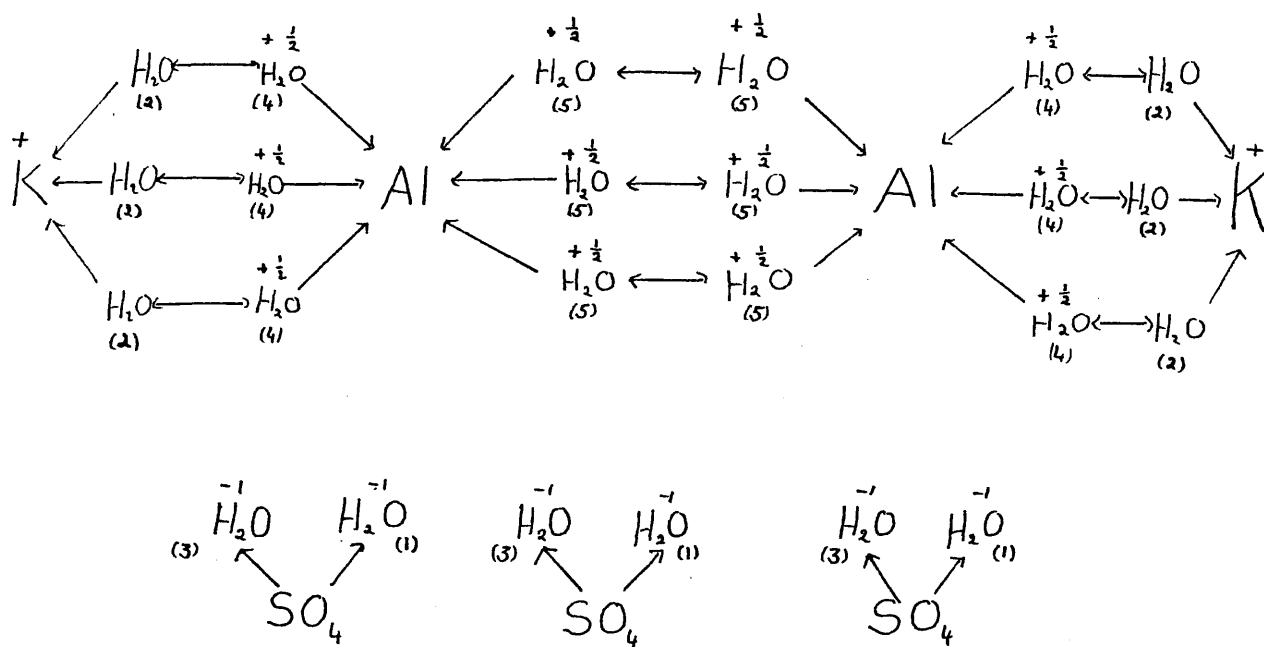


FIG. 10.

To form the heneicosihydrate, each  $\text{SO}_4$  group would lose one water marked I.

Under slightly altered conditions the six water molecules between the potassium and aluminium (marked 2) would come off first, giving the octadecahydrate.

When the molecules marked I and 2 are lost, we have the pentadecahydrate.

If the  $\text{SO}_4$  groups now lose their second water, marked 3, the dodecahydrate will be formed.

Again, if, under altered conditions, the six molecules of water attached to aluminium, marked 4, are lost before the water molecules (2) attached to the  $\text{SO}_4$ , we have the enneahydrate

When the I, 2, 3 and 4 groups of water are lost, it leaves the hexahydrate which, as has been pointed out, is exceedingly stable. It is also clear that the last six molecules of water will be lost together and no trihydrate can exist.

Further, these six water molecules will not come off until a sufficient supply of energy, in the form of heat, has been given, to permit the aluminium ions to form a covalent bond.

From the magnetic standpoint the theory is satisfactory also. All the water molecules have similar links and therefore they will be expected to give a constant contribution to the mass susceptibility, and the susceptibility plotted against the number of water molecules should give a straight line which was the result obtained experimentally.

Further, as has already been pointed out, the magnetic results do not agree with the alums being a mixture of the component sulphates, with quasi-independent ions, but the results give a strong indication of complex ion formation.

Further, the contacts are essentially in agreement with the structure put forward by Lipson and Beevers (12) from physical considerations, but their structure is not complete; they make no reference to any connection between the aluminium ions, and give no reason for six waters being held more firmly.

Furthermore, they imply that the six water molecules belong to the univalent ion, whilst I consider it much more probable that the water molecules are essentially co-ordinated to the  $SO_4$  groups and the aluminium water molecules, the univalent ion serving to hold them in position and to distribute the charges evenly.

In this connection I would like to mention also that the bonds holding this complex ion are weak, and therefore it is highly probable that in dilute solutions this complex breaks down into independent ions. However, an electrolytic investigation of the salt in concentrated solutions might well be expected to give evidence of the complex ion.

The next point to be considered is what happens when the salt becomes anhydrous and why it becomes insoluble.

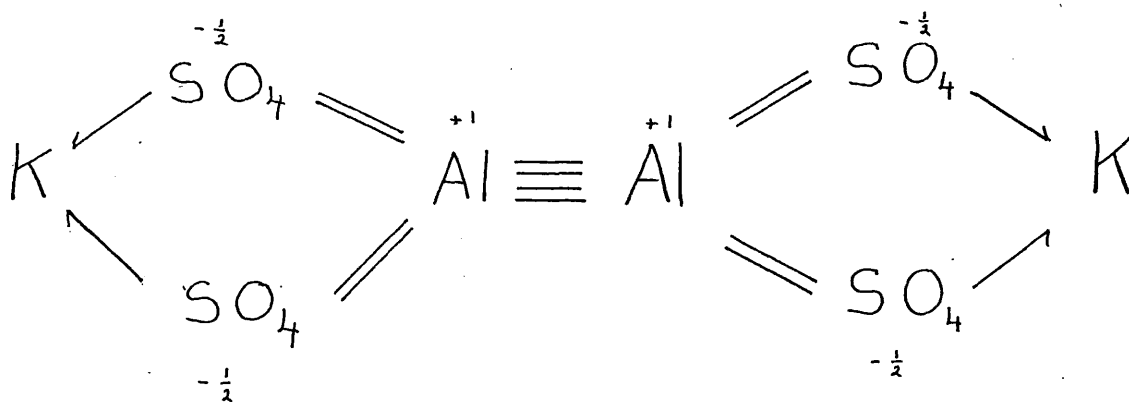
I have only very little evidence here, and the whole subject needs to be thoroughly investigated. I can at most put forward a very tentative suggestion.

It became evident in the course of this research that the anhydrous condition could be obtained only by supplying a considerable quantity of energy in the form of heat. This suggests that some complete change in structure takes place and, as I have already suggested, this may be the formation of a covalent link between the aluminium ions.

At the same time once the salt becomes anhydrous it also becomes very insoluble and, what is more, the alkali sulphate cannot be dissolved out in spite of the independent alkali sulphates always being soluble. Hence we must suppose that in this new structure the alkali sulphate must be involved in some way.

As has been pointed out by Sugden and others, aluminium is capable of forming chelated compounds, as, for example, in aluminium bromide,  $Al_2Br_6$ . Hence it does not seem improbable that such a compound is formed in this case with a covalency double bond between the aluminium ions. This would explain the insolubility, or rather the very slow change of structure when in presence of water and heat energy.

A possible structure is given in Fig II.



The potassium is supposed to be linked by two singlet links, thus becoming neutral, whilst each aluminium ion has its octet.

The solubility difficulty is in this way explained, as it will not be till the covalent bond changes to an electrovalency bond that the compound ionises.

It seems essential to suppose some such structure if we are to explain the experimental results; but the whole subject of insolubility is worthy of an independent piece of research

In making these suggestions as to structure, I have made mention only of the trivalent ion aluminium, but the chromium and iron might be equally well included.

Before leaving this point of the alum structure we must briefly consider the possibility of the three different structures  $\alpha$ ,  $\beta$  and  $\gamma$  as proposed by Lipson (12). The magnetic results certainly point to a difference between the caesium alum and the other members of the series, as can be seen in Graph IV.

Whilst the mass susceptibility of the alums are approximately constant, with a slight decrease as we pass from sodium to rubidium, caesium alum, which should, according to this, have the lowest value, has, on the contrary, a considerably higher value.

This is well in agreement with the suggestion of H. Lipson that the radius of the caesium ion is large enough for interactional effects to take place between the caesium and the sulphates with a consequent readjustment of positions to ensure

equilibrium.

At the same time the magnetic results give no evidence as to sodium alum having a different structure from the others but this, of course, is no evidence against the possible structure, as it is very doubtful if the opposite orientation of the  $\text{SO}_4$  groups, as was suggested, would result in any change in the mass susceptibility.

Another piece of evidence in favour of the complex character of the alum molecule comes from the recent paper on diamagnetic susceptibility of the thallium compounds (14).

In this paper Trew has derived a value for the ionic susceptibility of the thallos ion from the measurement of a large number of compounds.

Assuming the law of additivity to hold, Trew has shown that the ionic susceptibility of the thallos ion varies with the nature of the anion. The values fall into three groups:-

- (1) Univalent anion with a mean value  $-38.4 \times 10^{-6}$
- (2) Divalent and trivalent anions with a mean value  $-37.4 \times 10^{-6}$
- (3) Organic anions with a mean value  $-42.1 \times 10^{-6}$

Thallos alum has been placed in group 2 on account of the divalent nature of the sulphate, and the value of the thallos ion derived by the subtraction of the contribution of the rest of the molecule calculated by the subtraction of the I.C.T. value of potassium ion from my potash alum value. The value  $\chi_A \text{ Ti}$  thus obtained was  $-38.3 \times 10^{-6}$ , which does not fit in very well with its position amongst the divalent ions.



I have already pointed out that the alkali metals are not behaving like independent ions in the alum; hence the contribution of the rest of the molecule cannot be arrived at by subtraction of the accepted value for the alkali ion, these values having been derived, for the most part, from the measurements of electrovalent compounds. At the same time a fairly good approximation to the value of the contribution of the univalent ion in the alum structure could be obtained by this means, but it would be necessary to choose an alum, with a similar structure

Trew's value for thallic alum, as well as its position in the periodic table, shows it to have a similar structure to caesium alum (Graph III).

The following results then follow:-

$$\begin{aligned} \text{Caesium alum } \chi_M &= -526.0 \times 10^{-6} \\ \text{Caesium ion } \chi_A &= -41.0 \times 10^{-6} \text{ ( I.C.T.)} \\ \text{Therefore } \delta &= -444.0 \times 10^{-6} \\ \text{Thallic alum } \chi_M &= -532.1 \times 10^{-6} \text{ ( Trew.)} \\ \text{Thallic ion } \chi_A &= \underline{-44.0 \times 10^{-6}} \end{aligned}$$

This brings the alum into the third group with the organic anions, a result well in agreement with the suggested complex structure and the presence of covalency bonds.

## THE EXISTENCE OF THE LITHIUM ALUM

The existence, and even the possibility of the existence of lithium alum has been repeatedly denied.

Its preparation has already been described, but it is necessary to discuss it from a theoretical point of view and to see how its existence can be reconciled with theory.

It has generally been supposed that the lithium ion is too small to form alums. This supposition rested on the grounds that the alums are mixed sulphates, in which case the ionic distances of interchangeable constituents must not differ more than the order of about 10 %.

The Sidgwick rule for the maximum co-ordination number of an ion makes it dependent on the position in the periodic table giving a limit of four for the first period (Li - F), six for the second and third periods, eight for the elements starting with rubidium.

On this theory it would be impossible for the lithium ion to co-ordinate six water molecules as the alum structure requires.

On the other hand it was shown by Sugden (13) that whilst the rule holds for almost all co-ordination compounds whose constitution has been accurately determined, yet it has its theoretical bases on the Bohr symmetrical sub-division of the electrons in the principal quantum levels. This distribution

has now been abandoned, and it is not easy to find a sound theoretical basis for the rule which has certainly explained many structures.

At the same time Goldschmidt (8) has pointed out that atomic weight is not a determining factor in crystal structure but rather ionic volumes and the ratio of sizes of the neighbouring ions.

Further, it was indicated when dealing with the alkali sulphates that from susceptibility measurements the lithium ion appears to have a radius considerably larger than the calculated value, and the explanation offered by Pauling has already been given.

The real point at issue is: Can the small lithium ion have the co-ordination number six?

Brindley and Hoare (7) and Goldschmidt (8) have drawn attention to the fact that it certainly does in the cases of chloride, bromide, and iodide.

Goldschmidt further gives a table of limiting ratios for the two types of ions concerned, a sudden change of form of crystal structure taking place at a certain limit of the quotient  $R : R$ . The limiting ratio for co-ordination number six being 0.41.

He goes on to point out that in some crystals, especially LiI, morphotropism does not take place at the theoretical limiting ratio 0.41. He explains this by supposing that it is necessary to go to some extent below the geometrical limit before

The electrostatic energy relation can bring about morphotropism. This idea he sums up by saying, "Morphotropism will take place wherever by chemical substitution we exceed the limit "of permissible radii ratios or we introduce those atoms the " properties of which make another arrangement energetically "preferable."

It now remains to see, therefore, if these radii ratios are within the required limits.

In the structure under discussion it has been supposed that the lithium ion is at the centre of an octahedron made up of water molecules, and these latter are linked to the univalent lithium ion through singlet links of the oxygens. Hence we have to consider the ratio of the lithium ion to the Oxygen ion.

Taking the values given by Goldschmidt:-

$$\begin{aligned} \text{Li} &= 0.78 \\ \text{O} &= 1.32 \\ \text{Therefore Li : O} &= \frac{0.78}{1.32} \\ &= \underline{0.58} \end{aligned}$$

On Pauling's calculations:-

$$\begin{aligned} \text{Li} &= 0.60 \\ \text{O} &= 1.69 \\ \text{Therefore Li : O} &= \frac{0.60}{1.69} \\ &= \underline{0.45} \end{aligned}$$

In both cases the ratio has not fallen below the limiting ratio of 0.41.

Hence it seems clear that there can be no kind of a reason for the non-existence of lithium alum on the grounds of the smallness of that ion.

That the compound is not very stable and breaks down when the temperature is raised slightly above the room temperature is due to the low nuclear charge of the lithium ion, which thus finds it difficult to hold the water molecules in position if their state of vibration is augmented in the least. Hence any agitation caused by increasing temperature would enable the water molecules to break free.

Also it is only when the natural vibrations have been decreased by the lowering of the temperature that the lithium ion is capable of forming the links, and so forming the alum.

Hence we may say that the lithium alum has its place in the present theory that has been put forward, and its formation has given a completion to this work on the alums.

There still remains a great deal of work to be done. In fact this present work has but opened up a larger field of research which would bear much fruit to the investigator.

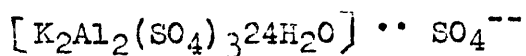
### SUMMARY

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1. The mass susceptibility of the alkali sulphates and alums have been determined, and it is found that the additivity law holds well for the addition of the water of crystallisation.
2. The gram ionic susceptibility of the alkali ions have been determined and found to be in quite good agreement with the values calculated by Brindley, Slater and Hartree, with the exception of lithium.
3. The susceptibility of the alkali ions are shown to be a function of the square of the radii calculated by Pauling and Goldschmidt. Again lithium gave discordant results.
4. A value for the susceptibility of deuterium oxide when in combination was made and found to be in good agreement with the value already obtained for the pure oxide by Trew and Spencer.
5. A value for the magnetic moment of the chromic and ferric ion was obtained from the alum and compared with the theoretical result of Bose and Stoner and Penner and Schlapp. Again a good agreement was found.
6. It was further shown that the water molecules in the alum are lost in groups of three; that six water molecules are

held more tenaciously than the others; and that no trihydrate exists.

7. The anhydrous double sulphates are very insoluble.
8. The formation and structure of the alums have been discussed and a complex ion formation is suggested:-



9. A possible explanation of the insoluble condition of the anhydrous compound was found in the suggestion of a chelated compound being formed.
10. The existence of lithium alum, already prepared in the laboratory, has been discussed from the theoretical standpoint and found to be well in agreement with theoretical expectations.

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