

487. *The Alums. Part I. A Study of the Alums by Measurement of their Aqueous Dissociation Pressures.*

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Measurements of equilibrium aqueous dissociation pressures over the temperature range 20—35° (or 40°) have been made, by the transpiration method, for the following (sulphate) alums: sodium, potassium, ammonium, hydroxylamine, and methylamine aluminium alums; potassium and ammonium chrome alums; and ammonium ferric alum. Both the dissociation pressures and the derived heats of dissociation per mole of water (ΔH_{20-40}) are discussed in terms of the crystal structure of the alums. The results support the X-ray crystallographical evidence that there are three distinct alum structures but also extend this knowledge by suggesting reasons why many alums have not so far been and may never be isolated. Results obtained in preliminary experiments with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are also reported.

THIS investigation of the alums by means of their aqueous dissociation pressures was prompted by a crystallographical interest in the nature of the valency forces involved in the linkage of molecules of water of hydration within the crystal lattice. The general problem of the mode of linkage of water molecules in solid hydrate structures is not new; on the one hand there is Werner's co-ordination theory, as developed by Sidgwick, involving direct linkage *via* a co-ordinate link to the cation or involving hydrogen bonds to the oxygen atom of an anion; on the other hand there is the physical electrostatic theory of Fajans (*Deut. physikal. Ges.*, 1919, **21**, 549, 709), Born (*Z. Physik*, 1920, **1**, 45), and others, according to which the forces involved are entirely electrostatic. More recent work, notably by Day, Hughes, Ingold, and Wilson (*J.*, 1934, 1593), tends to support the latter view.

Measurements of equilibrium aqueous vapour pressures at various temperatures enable heats of hydration to be calculated. If these quantities are determined for an isomorphous series of hydrates, then the effect of the crystal structure on the numerical value of the heat of hydration might be expected to be essentially constant from one isomorphous hydrate to the next. Variations found to occur in the values for the heats of hydration would then require explanation in terms of the constituents other than water. In choosing the alums $\text{M}^+\text{M}^{3+}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for investigation it was expected that the heats of hydration might show some well-defined dependence on the nature of the M^+ and/or M^{3+} , which should throw light on the mode of linkage of the water molecules within the crystal structure.

Only the sulphate alums (KAl, NaAl, etc.) were investigated and in all some 700 individual vapour pressure measurements were made within the range of 20—40°. The chrome alums of hydroxylamine and methylamine were prepared, but so far have not been investigated. In some cases, two or more quite distinct series of equilibrium aqueous vapour pressure results were obtained for a given alum and these are discussed in terms of the stages involved in the complete dehydration of the alums. Of general interest, perhaps, is the wide range of vapour pressures found with the alums; thus at 25° NH_4Al gives a value of 1.62 mm. Hg, compared with 20.45 mm. shown by NaAl (cf. water at 25°, 23.7 mm.).

EXPERIMENTAL

The equilibrium aqueous vapour pressures of the alums were determined by the dynamic or transpiration method (see Partington, *J.*, 1911, **99**, 466; 1923, **123**, 160; 1930, 635).

Dry purified air was aspirated through the hydrate column contained in a series of wide-bore U-tubes immersed in a thermostatic bath, and thence *via* weighed phosphoric oxide tubes, etc., to the aspirator. Values for the equilibrium aqueous vapour pressure were then calculated from the volume of air aspirated and the increase in weight of the phosphoric oxide tubes, by using the formula:

$$p_H = \frac{W}{V_0} \left(\frac{273.1 + T_A}{273.1} \right) \left(\frac{760}{0.8039} \right) \left(\frac{P - a - p_H}{P - h - p_w} \right)$$

where W = increase in weight of P_2O_5 tubes, p_H = vapour pressure of the hydrate, T_A = temperature of the air (and water) in the aspirator at the end of the experiment, P = final atmospheric pressure, a and h = readings of the mercury manometers attached to the aspirator and to the hydrate column respectively, p_w = saturation aqueous vapour pressure of the water at temperature T_A , and V_0 is the corrected volume of air aspirated and equals

$$V + \frac{V(P_f - P_i)}{2(P_f - a)}$$

where V is the volume of water in the receiver from the aspirator, and P_i and P_f are the barometric pressures at the beginning and end of the experiments.

The above formula for p_H is the same as that used by Baxter and Lansing (*J. Amer. Chem. Soc.*, 1915, **37**, 309) except that a corrected volume V_0 is used in the present calculations. The means of the vapour pressure values obtained at each temperature were then used to find the best values of the constants A and B in the equation $\log_{10} p = B + A/T_{\text{abs.}}$.

The mean heat of dissociation per mole of water vapour (within the temperature limits of the determination) is then equal to $4.575A$ cals.

Novel features in the experimental lay-out included: complete immersion of the U-tubes (containing the alums) and the delivery tubes below the water level of the thermostatic tank, thereby preventing aqueous condensation and also fluctuations in the temperature of the entraining air in the delivery tubes; direct access of the delivery tubes through the sides of the thermostat (below water level) to the external phosphoric oxide tubes; and arrangement of the transpiration chain to enable the equilibrium aqueous vapour pressures of *three* different hydrates to be determined simultaneously during a single aspiration. The usual precautions were taken to prevent condensation in the delivery tubes outside the thermostatic tank, and the latter was maintained at $T^\circ \pm 0.01^\circ$ by means of a delicate electronic relay. Local variations in air pressure at the beginning and the end of the hydrate columns were measured by means of small mercury manometers.

The general procedure adopted in determining the equilibrium aqueous vapour pressures was as follows. The hydrate crystals (purified by at least one recrystallisation) were ground to small crystals and then stored over concentrated sulphuric acid in a desiccator to initiate efflorescence. The crystals were stirred from time to time with the object of inducing efflorescence in as many crystals as possible. The partially dehydrated crystals were then charged into the appropriate U-tubes (to be placed in the thermostatic tank), and the transpiration chain was assembled and tested for leaks. Air was then aspirated through at a rate of usually 2–4 l. per 24 hours, the approximate duration of each experiment. At best, reproducible results were obtainable from a given hydrate column within a week of commencing the series of experiments, but sometimes about a fortnight was required before reproducible constant values for the aqueous vapour pressure could be obtained. The determinations were then continued until a reliable average result could be determined. The thermostatic bath was then raised to the next temperature and the determinations continued. Weighings were carried out to the fifth decimal place by the method of short swings, with precautions as regards counter-poising, temperature, humidity control, etc.

TABLE 1. $CuSO_4 \cdot 5H_2O \longrightarrow 3H_2O$.

Temp.	V.p. (mm. Hg)	Mean v.p.	Other workers
20°	5.41, 5.44, 5.53, 5.54, 5.48	5.48	—
25	7.83, 7.85, 7.84, 7.79, 7.83, 7.89, 7.80, 7.83, 7.94	7.84	7.71 (1); 7.92 (2); 7.8 (3); 7.82 (4)
30	11.26, 11.41, 11.27, 11.21, 11.31	11.29	11.74 (2), 11.30 (4)
35	16.06, 16.11, 16.06, 16.04, 16.05, 16.06, 16.07	16.06	17.01 (2); 16.14 (4)
40	22.84, 22.81, 22.74, 22.57, 22.60, 22.86	22.74	22.77 (4)

(1) Partington, *J.*, 1911, **99**, 466. (2) Partington, *J.*, 1930, 635. (3) Carpenter and Jetty, *J. Amer. Chem. Soc.*, 1923, **45**, 578. (4) Collins and Menzies, *J. Phys. Chem.*, 1936, **40**, 379.

From the "best-equation" of the form $\log p = B + (A/T)$, *viz.*, $\log_{10} p = 10.4250 - 2840.16/T_{\text{abs.}}$, the value of 12,994 cal. is obtained for the mean heat of dissociation per mole of water vapour in the temperature range 20–40°.

As a control on the method, a redetermination was made of the equilibrium aqueous vapour pressure for the system $CuSO_4 \cdot 5H_2O \longrightarrow 3H_2O$. Our results are shown in Table 1 together with the recorded results. Ours are in excellent agreement with the best recent values, *viz.*, those obtained by Collins and Menzies by the isopiestic method.

RESULTS

The following sections contain the equilibrium aqueous vapour pressure results obtained for the KAl , NH_4Al , NaAl , KCr , NH_4Cr , NH_4Fe , $\text{NH}_2\cdot\text{OHAl}$, and NH_2MeAl (sulphate) alums. These refer to the equilibria of the type $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{KAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} + 6\text{H}_2\text{O}$. Where more than one series of results are quoted, it has been assumed that the lowest series are in each case those appropriate to the above first stage in the hydrate-dissociation reaction: the significance of the various results is briefly considered, but their detailed analysis is deferred to the general discussion.

Potassium Aluminium Alum.—Table 2 below gives the individual and mean aqueous vapour pressure results obtained with recrystallised "AnalaR" $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. They fall into three series as shown in Fig. 1. The best equations for the lowest series of results are:

$$\text{Curve A: } \log_{10} p = 9.9360 - 2859.56/T_{\text{abs.}}$$

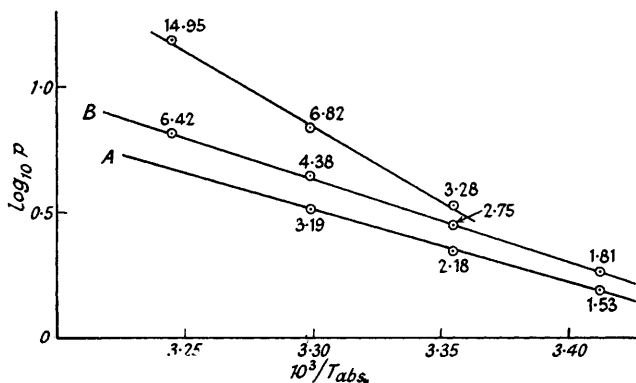
$$\Delta H = 13,082.5 \text{ cal./mole of water.}$$

$$\text{Curve B: } \log_{10} p = 11.6584 - 3342.98/T_{\text{abs.}}$$

$$\Delta H = 15,294.0 \text{ cal./mole of water.}$$

The lowest series of vapour pressure results was obtained on material which had not previously been subjected to a temperature higher than the temperature of the measurement,

FIG. 1.



(Correction: Curve B, second point from right, for 2.75 read 2.74.)

the higher series in general only on material which had previously been subjected to moderate heat (to initiate efflorescence) before the experiments. That preheating of the crystalline material was a contributory cause of the higher equilibrium values was confirmed by the

TABLE 2. $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

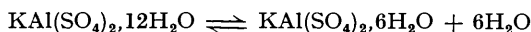
Temp.	Aqueous v.p. (mm. Hg)	Mean
20°	1.81, 1.78, 1.79, 1.83, 1.81, 1.82	1.81
	1.58, 1.66, 1.65, 1.55, 1.41, 1.50, 1.44, 1.43, 1.58, 1.61	1.53
25	3.29, 3.20, 3.41, 3.19, 3.37, 3.19	3.28
	2.78, 2.68, 2.66, 2.73, 2.74, 2.70, 2.88	2.74
30	2.15, 2.10, 2.10, 2.10, 2.25, 2.25, 2.15, 2.36	2.18
	6.94, 6.79, 6.96, 6.66, 6.77	6.82
35	4.37, 4.49, 4.29	4.38
	3.27, 2.93, 3.28, 3.32, 3.34, 3.34, 2.91, 3.11, 3.25	3.19
	6.41, 6.41, 6.40, 6.41, 6.47	6.42
	14.94, 14.38, 14.81, 14.97, 14.93, 15.36, 15.24	14.95

evidence that whenever the determinations were carried out with the same material at a temperature lower than those of the preceding determinations (*e.g.*, 25° after 30°), then the equilibrium vapour pressure value usually belonged to one of the upper series.

It was this multiplicity of equilibrium aqueous vapour pressure values obtained on material differing only in its previous heat treatment that later led to adoption of the room-temperature-efflorescence technique as standard procedure so as to ensure as far as possible that only the lowest series of equilibrium aqueous vapour pressures was measured. Experiments were also carried out at increasing rather than decreasing temperature intervals. This possibly explains

why, in the case of the other alums studied, with the notable exception of NH_4Al alum, only one series of results in each case has been determined in this investigation. In the case of NH_4Al alum, however, three series of results are also reported.

While it is not possible without further evidence to establish conclusively the reason for the three series of results obtained with KAl alum, it has been assumed as mentioned above that the lowest series refer to the normal reaction :



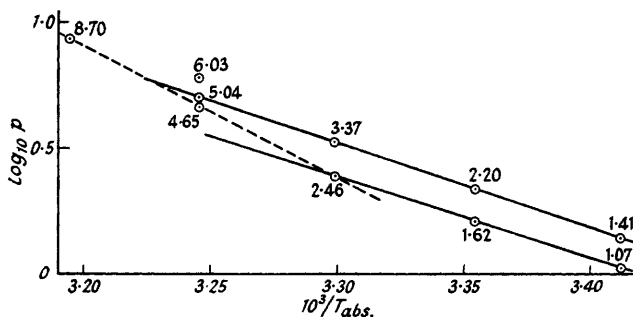
Since the remaining series appear after heat treatment, they may arise from metastable equilibria of the types :



It is then to be supposed that the effect of the heat treatment is to produce nuclei of the lower hydrate and/or of the anhydrous salt, which subsequently initiate dehydration in accordance with the above equilibria.

Ammonium Aluminium Alum.—Table 3 gives the individual and mean equilibrium aqueous vapour pressures obtained with twice recrystallised AnalaR $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. These

FIG. 2.



results, the means of which are plotted in Fig. 2, fall like those of KAl alum into three series. The "best" equation for the two lowest series of results are :

$$\text{Curve A : } \log_{10} p = 11.0089 - 3218.65/T_{\text{abs.}}$$

$$\Delta H = 14,725 \text{ cal./mole of water.}$$

$$\text{Curve B : } \log_{10} p = 11.5350 - 3337.11/T_{\text{abs.}}$$

$$\Delta H = 15,267 \text{ cal./mole of water.}$$

TABLE 3. $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Temp.	Aqueous v.p. (mm. Hg)	Mean
20°	1.15, 1.12, 1.01, 1.05, 1.18, 1.07, 0.99, 0.98	1.07
	1.42, 1.43, 1.43, 1.40, 1.35	1.41
25	1.59, 1.60, 1.61, 1.64, 1.69	1.62
	2.21, 2.14, 2.08, 2.09, 2.05, 2.26, 2.31, 2.28, 2.27, 2.22, 2.13, 2.24, 2.27, 2.24	2.20
30	2.45, 2.46, 2.46, 2.46	2.46
	3.33, 3.44, 3.43, 3.42, 3.25, 3.32, 3.39, 3.43, 3.38, 3.46, 3.29, 3.29, 3.36	3.37
35	5.14, 5.11, 4.99, 5.06, 4.90, 5.02	5.04
	4.78, 4.68, 4.59, 4.80, 4.69, 4.77, 4.60, 4.49, 4.71, 4.47, 4.62	4.65
	5.89, 6.03, 6.01, 6.19, 6.03, 6.20, 5.90, 6.01	6.03
40	8.57, 8.86, 8.57, 8.81	8.70

The lowest series was particularly difficult to determine and indeed no values for this series were obtained for the temperatures above 30°. The difficulty experienced with this alum is attributed to the relatively low numerical values of the equilibrium aqueous vapour pressure coupled with the apparent ease with which other dissociation reactions, probably $12\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{O}$ and $12\text{H}_2\text{O} \rightarrow 0\text{H}_2\text{O}$, appear to occur with increase in temperature in the partly dehydrated crystals. As in the case of KAl alum, discussion of the three series of results is deferred.

Sodium Aluminium Alum.—Table 4 and Fig. 3 give the results for sodium aluminium alum (recrystallised three times). Earlier experiments carried out on coarse crystalline material, as normally sold for laboratory use, gave values (not described) substantially lower than these.

The purer the alum (*i.e.*, the more often it had been recrystallised), the smaller was the tendency to effloresce in air. The results yield:

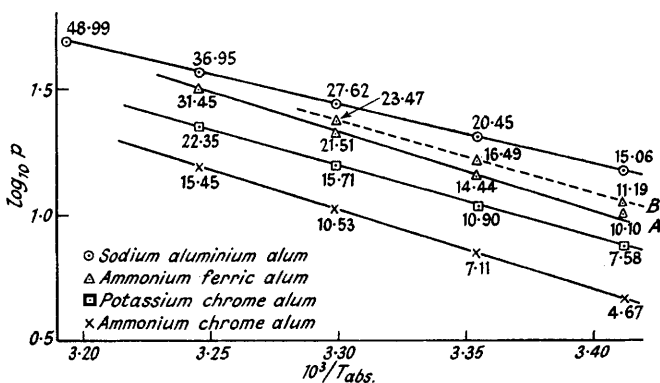
$$\log_{10} p = 9.2032 - 2352.52/T_{\text{abs.}}$$

$$\Delta H = 10,763 \text{ cal./mole of H}_2\text{O.}$$

TABLE 4. NaAl(SO₄)₂·12H₂O.

Temp.	Aqueous v.p. (mm. Hg)	Mean
20°	15.22, 15.08, 15.00, 15.13, 15.15, 15.17, 15.00, 15.12, 14.93, 14.95, 14.72, 15.32, 14.94, 15.02, 14.89, 14.79, 14.92, 15.30, 14.94, 15.18, 15.08, 15.15, 14.93, 15.10, 15.14, 15.32	15.06
25	20.08, 20.02, 20.11, 20.12, 20.12, 20.80, 20.87, 20.92, 20.30, 21.00, 21.29, 20.73, 21.03, 20.93, 20.09, 20.05, 20.13, 20.14, 20.17, 20.08	20.45
30	27.69, 27.61, 27.55, 27.75, 27.44, 27.89, 27.82, 27.10, 27.92, 27.07, 27.95	27.62
35	36.52, 37.09, 37.25, 37.31, 37.16, 36.63, 37.29, 37.02, 37.28, 36.42, 36.70, 37.24, 37.25, 36.24, 36.85	36.95
40	49.01, 49.00, 48.49, 49.45	48.99

FIG. 3.



Potassium Chrome Alum.—Our results are in Table 5 and Fig. 3. Calculation yields:

$$\log_{10} p = 10.5310 - 2829.27/T_{\text{abs.}}$$

$$\Delta H = 12,944 \text{ cal./mole of water.}$$

Measurements on this alum have also been made by Ephraim and Wagner (*Ber.*, 1917, **50**, 1088) and by Cooper and Garner (*Proc. Roy. Soc.*, 1940, *A*, **174**, 487). The latter made their measurements on large single crystals using a static method and it is of interest that their values are approximately 20% greater than those reported above, *viz.*: 9.33 (20°); 13.30 (25°); 17.77 (30°); 24.41 (35°). They state that great care was taken not to subject the crystal to a higher vapour pressure than its dissociation pressure since otherwise the approach to equilibrium could not be attained in several days. According to the present investigation it seems, however, that that is precisely what they did not do. The effect of maintaining a vapour pressure in excess of the equilibrium value would be to produce a saturated solution as a film and, although such a film might well be invisible under the conditions of the experiment, the equilibrium pressure measured would be that of the saturated solution. This explanation is confirmed

TABLE 5. KCr(SO₄)₂·12H₂O.

Temp.	Aqueous v.p. (mm. Hg)	Mean
20°	7.62, 7.47, 7.65, 7.63, 7.54, 7.57	7.58
25	10.89, 10.91, 10.90, 10.89	10.90
30	15.72, 15.70, 15.69, 15.74, 15.70	15.71
35	22.40, 22.60, 22.18, 22.31, 22.20, 22.57	22.38

from the fact that Cooper and Garner's results indicate a value of 10,030 cal. for the heat of dissociation per mole of water of the hydrate, which is similar to that of pure water (10,700 cal.) and to that of a saturated solution of copper sulphate (10,390 cal.). The values for CuSO₄·5H₂O → 3H₂O and for KCr(SO₄)₂·12H₂O → 6H₂O obtained by us are, however, substantially higher, *viz.*, 12,994 and 12,944 cal. respectively.

The only other recent results are those of Spangenberg (*Neues Jahrbuch Min., Geol., Pal.*, 1949, *A*, 99) who used a modified form of the Bremer-Frowein differential tensimeter (*Z. physikal. Chem.*, 1895, **17**, 52). His results appear in general to be only approximate and are in many cases difficult to accept, as indicated, for example, by such results as 17 (25°), 17.5 (30°), 24 (35°), and 34 mm. (40°) for KCr alum.

TABLE 6. $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Temp.	Aqueous v.p. (mm. Hg)	Mean
20°	4.64, 4.69, 4.73, 4.65, 4.81, 4.60, 4.78, 4.62, 4.62, 4.55, 4.57, 4.70, 4.63, 4.79	4.67
25	7.20, 7.19, 7.13, 7.26, 7.09, 7.06, 7.04, 6.94	7.11
30	10.45, 10.31, 10.68, 10.77, 10.72, 10.63, 10.67, 10.42, 10.29, 10.35	10.53
35	15.10, 15.29, 15.35, 15.20, 15.23, 15.50, 15.51, 15.63, 15.75, 15.64, 15.72	15.45

Ammonium Chrome Alum.—See Table 6 and Fig. 3 for results, which lead to :

$$\log_{10} p = 11.3276 - 3123.53/T_{\text{abs.}}$$

$$\Delta H = 14,290 \text{ cal./mole of water.}$$

TABLE 7. $\text{NH}_4\text{Fe}^{\text{III}}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Temp.	Aqueous v.p. (mm. Hg)	Mean
20°	9.63, 10.15, 10.31, 10.26, 10.13 10.66, 10.71, 10.71, 10.67, 10.73, 10.87, 10.76, 10.65, 10.78, 10.87 11.04, 11.10, 11.25, 11.27, 11.23, 11.06, 11.14, 11.18	10.10 10.73 11.19
25	14.46, 14.10, 14.09, 14.22, 14.72, 14.60, 14.48, 14.64, 14.61 16.60, 16.36, 16.43, 16.68, 16.54, 16.44, 16.62, 16.46, 16.47, 16.45	14.44 16.49
30	21.49, 21.47, 21.45, 21.50, 21.45, 21.60 23.62, 23.23, 23.51, 23.41, 23.48, 23.70, 23.73, 23.19, 23.55, 23.27	21.51 23.47
35	29.67, 31.63, 31.75, 31.15, 31.18, 31.70, 31.39, 31.19	31.45

Ferric Ammonium Alum.—The results (Table 7 and Fig. 3) fall into two series and lead to :

$$\text{Curve } A: \log_{10} p = 11.5718 - 3103.79/T_{\text{abs.}}$$

$$\Delta H = 14,200 \text{ cal./mole of water.}$$

$$\text{Curve } B: \log_{10} p = 10.8026 - 2858.39/T_{\text{abs.}}$$

$$\Delta H = 13,077 \text{ cal./mole of water.}$$

The results of curve *A* are considered to be correct for the system $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \rightarrow 6\text{H}_2\text{O}$, leaving the other series to be attributed either to a different dissociation reaction, *e.g.*, $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \rightarrow 3\text{H}_2\text{O}$, or to a limited hydrolysis of the alum crystals. Of the two possibilities, the evidence (drawn very largely from the behaviour of the closely related KFe alum) mainly supports the hydrolysis theory. Thus, KFe alum prepared by crystallisation from the aqueous solution at temperatures of the order of 0° has the same pale violet colour as NH_4Fe alum, but unlike the latter is unstable at ordinary temperatures. Crystals appear to deliquesce at room temperatures, becoming covered with a brown film of ferric hydroxide. Washing the crystals initially with cold sulphuric acid tends to retard this "deliquescence" and suggests that hydrolysis and not deliquescence occurs during the decomposition.

TABLE 8. $(\text{NH}_2\cdot\text{OH})\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Temp.	Aqueous v.p. (mm. Hg)	Mean
20°	8.66, 8.70, 8.60, 8.67, 8.55, 8.63, 8.78	8.66
25	11.85, 12.36, 12.06, 12.31, 12.28, 12.30, 12.20, 11.91	12.16
30	17.06, 16.78, 17.20, 16.95, 16.94, 17.42, 17.19	17.08
35	23.63 25.25, 25.99	23.63 25.62
40	43.26, 42.58, 42.45, 42.85	42.79

Hydroxylamine Aluminium Alum.—Our results (Table 8) lead to :

$$\log_{10} p = 9.8724 - 2619.07/T_{\text{abs.}}$$

(calculated from mean values at 20°, 25°, and 30°)

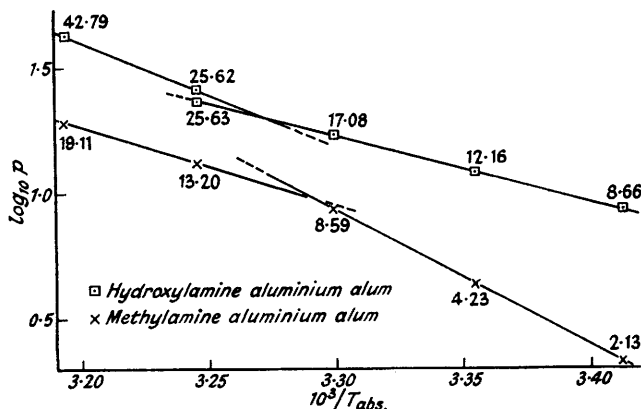
$$\Delta H = 11,982 \text{ cal./mole of water.}$$

The values obtained at 20°, 25°, and 30° are mutually consistent, and Fig. 4 shows that the mean values for these temperatures also conform to the expected linear relation of $\log_{10} p$ to $1/T_{\text{abs.}}$. Results at 35° were not, however, in accordance with expectation. It is true that the

first result obtained at this temperature (*viz.*, 23.63 mm.) was almost exactly that expected from the above "best" equation, but later results were appreciably higher and variable. The temperature was therefore raised to 40°; at this temperature the results agreed very well amongst themselves but were considerably higher than the value extrapolated from results at the three lower temperatures (*viz.*, 42.79 mm.; cf. 32.17 mm.). It thus appears that at or about 35° some change occurs in the material or in the nature of the dissociation reaction.

There appear to be various possible explanations, *viz.*: an increase in the number of mols. of water involved in the dehydration reaction (cf. KAl and NH₄Al alums); a transition or

FIG. 4.



(Correction: upper curve, for 25.63 read 23.63; lower curve, for 4.23 read 4.28.)

morphotropic change from the γ - to α -alum structure (Lipson); hydrolysis or other decomposition of the alum; or various combinations of these. We consider the first explanation to accord most closely with the facts.

TABLE 9. (NH₂Me)Al(SO₄)₂·12H₂O.

Temp	Aqueous v.p. (mm. Hg)	Mean
20°	2.13, 2.11, 2.15	2.13
25	4.26, 4.27, 4.19, 4.41	4.28
30	8.39, 8.54, 8.73, 8.41, 8.90	8.59
35	13.08, 13.01, 13.27, 13.54, 13.11	13.20
40	19.20, 18.89, 19.19, 19.07, 19.05, 19.25	19.11

Methylamine Aluminium Alum.—The results (Table 9) lead to:

$$\log_{10} p = 18.6832 - 5380.27/T_{\text{abs.}}$$

$$\Delta H = 24,615 \text{ cal./mole of water.}$$

Fig. 4 shows that the mean values fall into two series intersecting at 30.9°. Whereas all the other alums examined in this investigation gave results at the higher temperatures which were equal to or greater than those calculated from the "best" equations, these results above 30.9° were lower than expected. Possible explanations are that 30.9° is a true hydrate transition temperature (the 12H₂O hydrate being stable below 30.9°) and that rearrangement occurs within the crystals at this temperature, resulting for example in a change from the β - to the α -alum structure (Lipson). The former explanation, involving release of water could not be substantiated, but there is some evidence in support of the second. Thus, methylamine alum crystallises with the β -alum structure, found also with CsAl alum, where the univalent ion is large in relation to other univalent ions. Although CsAl alum was not examined in this investigation, the fact that the heat of dissociation of methylamine alum determined from the results at 20°, 25°, and 30° (24,615 cal.) is appreciably greater than the corresponding value found for alums having the α -structure (14,000—15,000 cal.) supports the X-ray evidence that this alum does not have the α -structure. Furthermore, Lipson (*Phil. Mag.*, 1935, 19, 887) has found that methylamine alum is dimorphous. It has the same parameters and structure as the CsAl alum (*i.e.*, the β -alum structure) and yet can be deposited from solution on RbAl alum, then having the KAl (α -)alum structure. The heat of dissociation (ΔH) calculated from the

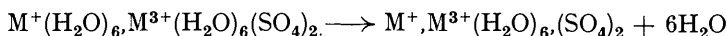
present vapour-pressure values at 35° and 40° is also approximately the same as that determined for those alums known to have the α -alum structure.

It seems very probable therefore that at 30.9° methylamine alum undergoes an internal structural rearrangement from the β - to the α -alum structure. Attempts to establish such a transition by a thermometric method were, however, unsuccessful, but this might well be due to a slow rate of change due to a high activation energy.

DISCUSSION

The X-ray crystal structure analysis by Lipson and his collaborators (Lipson, *Phil. Mag.*, 1935, **7**, 887; Lipson and Beevers, *Proc. Roy. Soc.*, 1935, *A*, **143**, 66) has shown that the alum formula should be written $M^+(H_2O)_6, M^{3+}(H_2O)_6, (SO_4)_2$, since each cation is surrounded by a more or less regular octahedral arrangement of six water molecules as its nearest neighbours. From the additional evidence of the interatomic distances, it appears that the M^{3+} -type water molecules form a much more compact envelope around the central M^{3+} ion than is the case with the corresponding M^+ -water complex. The M^{3+} ion apparently co-ordinates its six water molecules, whereas the M^+ ion appears merely to fill the interstice formed by the enveloping M^+ -type water molecules. The M^+ ion is not, however, without significance in determining the formation of the alum structure, and Lipson has indeed shown from the results of X-ray crystal analysis that there are three slightly different alum structures and that the size of the M^+ ion plays a fundamental role in determining which of these is formed. Of the three, the α -form is obtained with the medium-sized univalent ions (such as K^+ and NH_4^+), the β -structure with the larger univalent ions (such as Cs^+ and NH_2Me^+), and the γ -structure with the smaller univalent ions (such as Na^+).

The present investigation has provided further evidence in favour of the different alum structures and also of the different behaviour of the water molecules surrounding the M^+ and M^{3+} ions. Thus the above conclusion of a less rigid binding of the six M^+ -type water molecules suggests that the primary dissociation reaction involves these, *viz.* :



Direct evidence for this suggestion comes from the heats of dissociation (Table 10).

TABLE 10. *Heats of dissociation (cals.).*

M^+	Structure	Radius (Å)	Al^{3+}	Cr^{3+}	Fe^{3+}
Na^+	γ	0.98	10,763	—	—
NH_3OH^+	γ (<i>a</i> ?)	1.2?	11,982	—	—
K^+	<i>a</i>	1.33	13,083	12,944	—
NH_4^+	<i>a</i>	1.43	14,725	14,290	14,200
$CH_3NH_3^+$	β	2.2	24,615	—	—

Thus, in the ammonium series, replacement of the Al^{3+} by Cr^{3+} or Fe^{3+} causes only a slight change in the heat of dissociation (14,725, 14,290, and 14,200 cals.); on the other hand, in the aluminium series, replacement of Na^+ by $NH_3 \cdot OH^+$, K^+ , etc., leads to considerable increases (10,763, 11,982, 13,083, 14,725, 24,615 cals.).

However, our results appear to reveal also what might be termed a remote field effect due to the strong polarising power of the relatively small M^{3+} ions and support the view that each M^{3+} ion exerts its particular stabilising influence on the alum structure. Thus the smaller the M^{3+} ion, the greater becomes its polarising power. This power might be expected to be transmitted through the $M^{3+}-H_2O$ screen to the structure as a whole and in particular to the M^+ -type water molecules. The resultant tightening-up would then increase the stability of the latter water molecules and hence increase their heat of dissociation. The heats of dissociation should increase slightly with decrease in the radius of the M^{3+} ion. Thus whereas the stability of the alum increases with increase in the radius of the univalent M^+ ion, it increases with decrease in the radius of the trivalent M^{3+} ion.

This inverse relation in the effect of the sizes of the ions is disclosed also in the equilibrium aqueous vapour pressure results, some of which are collected in Table 11. With the exception of the methylamine aluminium alum, it is seen that these values increase with increase in the size of the M^{3+} ion and with decrease in the size of the M^+ ion.

(That the vapour pressure of methylamine alum is greater than that of the NH_4^- and K-alums presumably results from the different (β -)structure of this alum.)

Thus, the stability of the alum appears to be determined by (a) the size of the M^+ ion,

FIG. 5.

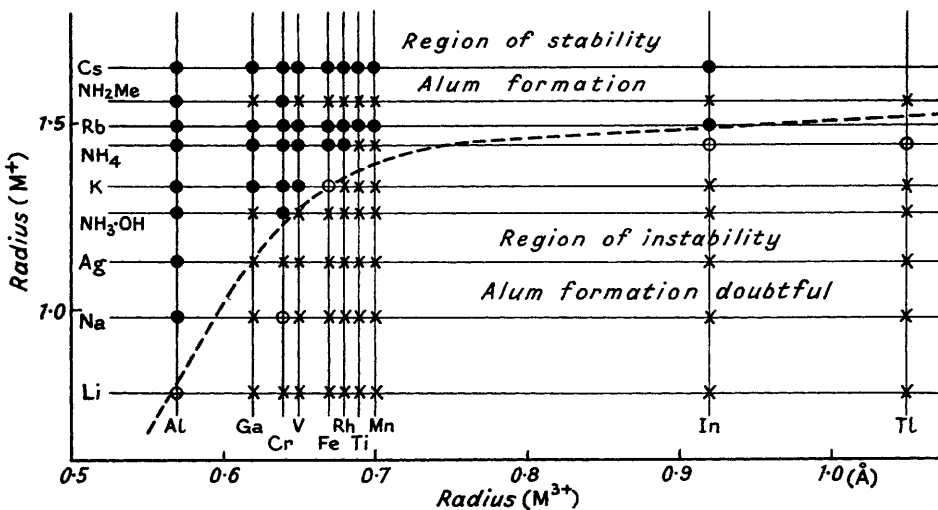
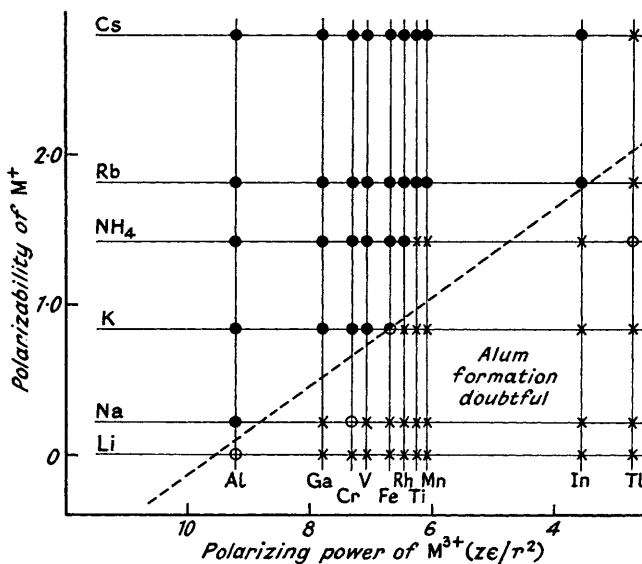


FIG. 6.



(b) the size and hence polarising power of the M^{3+} ion, and (c) the chemical stability of the $\text{M}^{3+}(\text{H}_2\text{O})_6$ complex. Decrease in the size of the M^+ ion has the effect of loosening the

TABLE 11. *V.p.* (mm. Hg) of alums at 25°.

		Increasing radius of M_3^+ →		
		Al (0.57)	Cr (0.64)	Fe (0.67)
Increasing radius of M^+ ↓	Na	20.48	>23.57	>23.57
	$\text{NH}_3\cdot\text{OH}$	12.20	?	?
	K	2.21	10.96	?
	NH_4	1.62	7.07	14.45
	NH_3Me	4.31	?	?

structure and so decreasing the stability of the alums, a tendency which is partly compensated by the change in structure from the β -form, first to the α - and then to the γ -form. The vapour pressures increase and the heats of dissociation decrease. Conversely, increase in the size of the M^{3+} ion causes a similar loosening of the structure as a result of the decreased polarising influence. This results principally in an increase in the vapour pressure and in a (very much smaller) decrease in the heat of dissociation. The latter is thus not uniquely determined by the size of the univalent cation with which the escaping water molecule was associated, but rather by the whole structural environment of that water molecule within the crystal lattice. When the combined effect of both factors would be such as to increase the vapour pressure to a theoretical value in excess of that of water (or, more correctly, of that of a saturated solution of the alum), then it might be expected that such an alum would have no real existence at the temperature in question.

Although one would hesitate to say positively on the evidence adduced in this investigation that certain alums cannot exist, yet it is perhaps significant that in those cases in which the present view suggests non-existence such alums have in fact yet to be reported; in other cases (*e.g.*, NaCr alum), where the theory expresses doubt, the evidence of satisfactory preparation is also indefinite and suspicious.

In Fig. 5, the alums are shown as a function of (increasing) radii of the M^+ and M^{3+} cations. The distribution of the known (and therefore stable) alums provides confirmation of the views expressed above. It is seen that their number increase with both decrease in the size of the M^{3+} cation and increase in that of the M^+ cation. With the exception of the doubtful NaCr alum, all the known alums appear to lie above a boundary line (shown broken in the fig.). A more precise position of this dividing line is obtained (as shown in Fig. 6) by plotting the alums as a function of the polarisability of the M^+ ion and the polarising power of the M^{3+} ion, as suggested by the evidence of this investigation. The present authors suggest that where the "alum" would fall below the "instability line" of Fig. 6 then such an alum does not exist, with reservation as to the precise position of the "instability line."

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