114. *The Isotherms of Some Ternary Systems of Metal Perchlorates in Aqueous Solution at 30°.*

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A NUMBER of double perchlorates have been reported by Weinland and Ensgraber (*Z. anorg. Chem.*, 1913, **84**, 340), who claim to have obtained the double salts by evaporating in a vacuum over sulphuric acid at room temperature mixed aqueous solutions of the simple salts in equimolecular proportions. In each case the crystals were analysed, but no further investigation was carried out. It seemed desirable, therefore, to investigate these supposed double salts. Moreover, since perchlorate and sulphate ions resemble each other in structure but differ in valency, an analogy might be sought between the double perchlorates and double sulphates. Weinland and Ensgraber, indeed, attribute to sodium aluminium perchlorate a formula analogous to that of the corresponding alum.

EXPERIMENTAL.

The thermostatic, stirring, and sampling arrangements have been previously described (Caven, J., 1932, 2417). The various mixtures of salts and water were usually agitated for 3 or 4 days before being allowed to settle; portions were then taken for analysis. The bottle was sealed again, and rotated for a further day or two before another sample was taken to prove equilibrium.

System NH_4ClO_4–$Al(ClO_4)_3$–H_2O.—The ammonium perchlorate was prepared from synthetic ammonia and A.R. perchloric acid, recrystallised from water, dried, and analysed (Found: NH_3, 14·43. Calc.: NH_3, 14·49%). The aluminium salt was prepared by dissolving 12·2 g. of $AlCl_3,6H_2O$ in 93 g. of 19% perchloric acid, and heating the mixture on the water-bath until free from chloride. The solution gave long, rectangular crystals on evaporation in a vacuum over sulphuric acid. These were filtered off with suction, washed with a very little water, and dried on a porous plate in a vacuum over sulphuric acid. Samples were taken for analysis after twelve days (Found: $ClO_4 : Al = 11·00$. Calc.: 11·06).

[Since the molecular proportion of water in this salt, and in the cupric perchlorate described later, is well known, no attempt was made to obtain these salts definitely hydrated.]

Analysis. The aluminium was precipitated by ammonia with methyl-red as indicator, and weighed as oxide, after ignition in platinum over a blast lamp. The total perchlorate was estimated in dilute solution by titration with sodium hydroxide at the boiling point, with phenolphthalein as indicator, a method similar to that first used for aluminium sulphate by Schmatolla (*Ber.*, 1905, **38**, 987), and improved by Britton (J., 1922, **121**, 982). Ammonium perchlorate was estimated by distilling with alkali and collecting displaced ammonia in standard acid.

System $NaClO_4$–$Al(ClO_4)_3$–H_2O.—Analysis of dehydrated sodium salt: Found, Na, 18·91 (Calc.: Na, 18·77%). As before, the aluminium in the liquid phase was determined as oxide. After the method had been proved valid, the sodium was precipitated directly in presence of aluminium as sodium magnesium uranyl acetate (Caley and Foulk, *J. Amer. Chem. Soc.*, 1929, **51**, 1664; Caley and Sickman, *ibid.*, 1930, **52**, 4247). The precipitate was washed with a measured volume of alcohol, dried for 30—40 mins. at 105°, and weighed.

System $KClO_4$–$Al(ClO_4)_3$–H_2O.—A sample of potassium perchlorate was obtained which was proved free from chloride and chlorate. Before use, however, it was thrice recrystallised from water. For analysis of the liquid phase a sample was evaporated to dryness on the water-bath, a suitable volume of alcoholic perchloric acid (1 c.c. of 19% acid to 100 c.c. of 95% alcohol) was added, and the crystals thoroughly stirred with the liquid. After some time the residue of potassium perchlorate was collected on a tared Gooch crucible, washed with alcohol, dried at 120°, and weighed. The filtrate, containing the aluminium, was evaporated to dryness on the water-bath, the residue dissolved in water, and the aluminium in a portion of the solution estimated as oxide.

System NH_4ClO_4–$Cu(ClO_4)_2$–H_2O.—Electrolytic copper foil was dissolved in the minimum quantity of nitric acid, and copper perchlorate formed by repeated evaporation with 60% perchloric acid. The deep blue salt was finally crystallised from 1% perchloric acid, washed with a very little cold water, dried after crushing on a porous plate, and analysed (Found: $ClO_4 : Cu = 3{\cdot}139$. Calc.: 3·128).

The copper was estimated iodometrically, and the perchlorate determined by precipitating the copper by hydrogen sulphide, filtering off the sulphide, and titrating the acid in the filtrate. In the liquid phases ammonium perchlorate was estimated by distilling ammonia into excess of standard acid, and copper iodometrically.

The point at which the solid phase contained ammonium perchlorate and copper perchlorate hexahydrate was found by adding ammonium perchlorate crystals to saturated copper perchlorate solution in presence of excess of the solid salt, until no more would dissolve. The solid phase was examined and found to be a mixture.

Thorium Perchlorate.—Pure thoria was prepared from the hydrated sulphate through the iodate, since direct precipitation with ammonia gave a product contaminated with sulphate. The thoria was dissolved in an equivalent of 19% perchloric acid, and the solution evaporated in a vacuum over sulphuric acid. A thick syrup resulted, which after a long time yielded striated crystals, and not the soapy mass reported by Cleve (*Bull. Soc. chim.*, 1878, **29**, 492). The salt was extremely deliquescent. No system was investigated as in the previous cases; but it was shown that ammonium perchlorate crystallises when mixed solutions containing ammonium and thorium perchlorates in various proportions are evaporated in a vacuum over sulphuric acid at room temperature.

Results, expressed as g. of anhydrous salt per 100 g. of water.

System NH_4ClO_4–$Al(ClO_4)_3$–H_2O *at* 30° (Fig. 1).

NH_4ClO_4.	$Al(ClO_4)_3$.	Solid phase.
28·00	—	NH_4ClO_4
25·03	3·13	
23·10	5·25	
18·66	9·77	
15·12	14·09	
13·15	17·47	
10·47	22·90	
8·59	26·19	
2·36	55·69	
0·91	107·7	NH_4ClO_4 and $Al(ClO_4)_3$ aq.
—	110·1	$Al(ClO_4)_3$ aq.

System $NaClO_4$–$Al(ClO_4)_3$–H_2O *at* 30° (Fig. 2).

$NaClO_4$.	$Al(ClO_4)_3$.	Solid phase.
215·0	—	$NaClO_4,H_2O$
135·4	27·76	
116·6	37·30	
100·7	45·59	
50·64	72·46	
43·84	76·26	$NaClO_4,H_2O$ and $Al(ClO_4)_3$ aq.
30·02	83·87	$Al(ClO_4)_3$ aq.
—	110·1	

System $KClO_4$–$Al(ClO_4)_3$–H_2O *at* 30° (Fig. 3).

$KClO_4$.	$Al(ClO_4)_3$.	$KClO_4$.	$Al(ClO_4)_3$.
2·528	—	1·028	4·956
1·462	2·652	0·7041	8·158
1·357	3·043	0·2115	34·56

Solid phase : $KClO_4$ throughout.

Calculated solubility products for the system $KClO_4$–$Al(ClO_4)_3$–H_2O *at* 30° (Fig. 3).

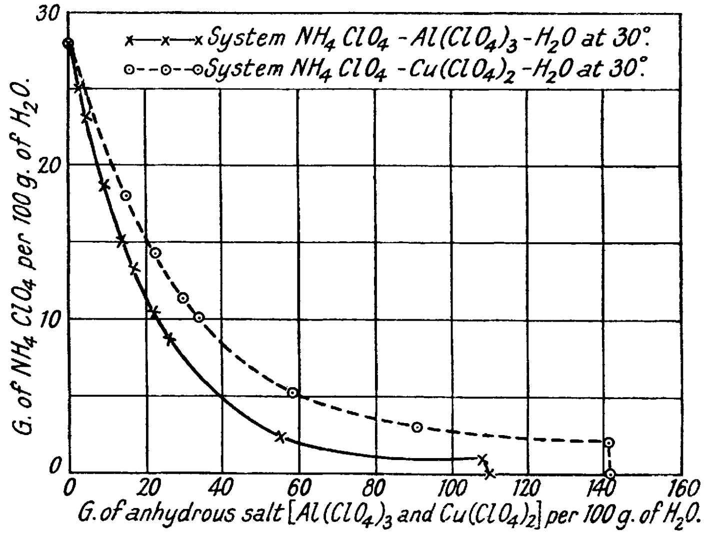
$KClO_4$.	$Al(ClO_4)_3$.	$KClO_4$.	$Al(ClO_4)_3$.
2·528	—	0·500	9·610
2·000	0·936	0·200	24·86
1·300	2·830	0·100	49·94
1·000	4·220		

Solid phase : $KClO_4$ throughout.

System NH_4ClO_4–$Cu(ClO_4)_2$–H_2O *at* 30° (Fig. 1).

NH_4ClO_4.	$Cu(ClO_4)_2$.	Solid phase.
28·00	—	NH_4ClO_4
17·99	14·89	
14·28	22·51	
11·42	30·00	
10·13	34·04	
5·322	58·12	
3·059	90·93	
2·075	141·0	NH_4ClO_4 and $Cu(ClO_4)_2,6H_2O$
—	141·6	$Cu(ClO_4)_2,6H_2O$

FIG. 1.



Conclusions.—In none of the cases examined does the isotherm show a double-salt curve. In each case, when aluminium or copper perchlorate is added to saturated alkali perchlorate solution at 30° the alkali perchlorate is precipitated. Ammonium and potassium perchlorates are but slightly soluble in concentrated aluminium or copper perchlorate solution; but, as might be expected, sodium perchlorate is somewhat more soluble. The curves have been plotted for 30°, but their nature is such as to make double-salt formation unlikely over a range of temperature on either side of 30°. In the case of the system potassium and aluminium perchlorates a theoretical solubility curve is shown for comparison with that obtained experimentally. The value $[K^{\cdot}][ClO_4{}']$ in presence of aluminium perchlorate has been calculated from the value found for the solubility of potassium perchlorate at 30°, complete ionic dissociation of both salts being assumed. Notwithstanding the solubilities of the salts concerned, and the influence of interionic attraction, the theoretical and the experimental curve are fairly close over a considerable range, and this shows the antithesis of double-salt formation.

In a double perchlorate, twice as many perchlorate groups would be required as the corresponding sulphate would require sulphate groups. Thus, lack of space, even with the quadrivalent thorium ion, may account for the non-formation of double perchlorates, while so many double sulphates are known.

SUMMARY.

The isotherms for the systems $NH_4(Na,K)ClO_4$–$Al(ClO_4)_3$–H_2O and NH_4ClO_4–$Cu(ClO_4)_2$–H_2O at 30° have been obtained. There is no evidence of Weinland and Ensgraber's double perchlorates, and no double-salt formation has been observed in the case of ammonium and cupric perchlorates at this temperature, or ammonium and thorium perchlorates at room temperature. It appears probable, therefore, that no double perchlorates are formed by alkali perchlorates and the perchlorates of bi-, ter-, and quadri-valent metals.

FIG. 2.
System $NaClO_4$–$Al(ClO_4)_3$–H_2O *at* 30°.

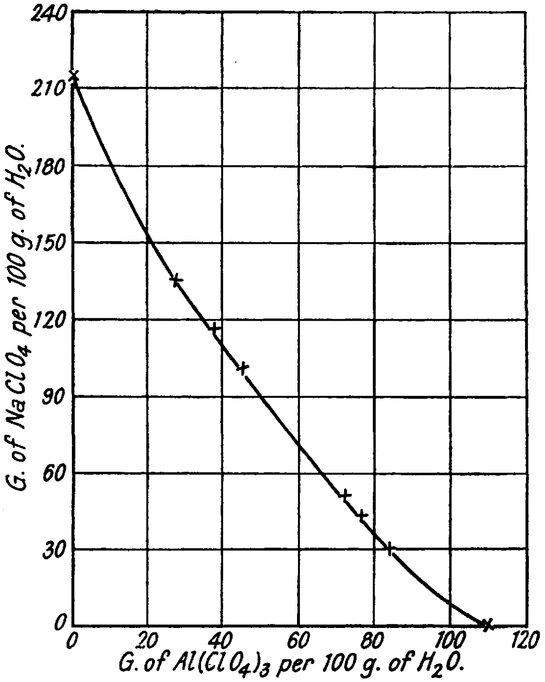
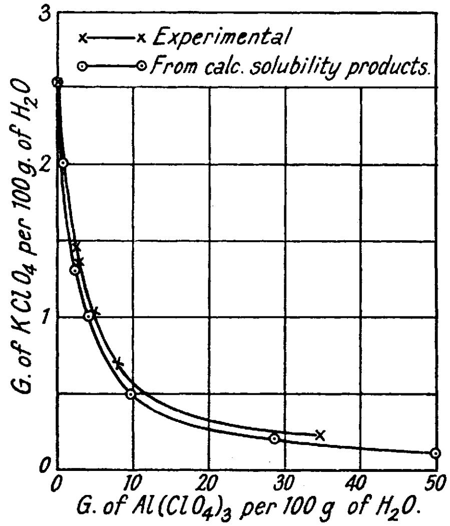


FIG. 3.
System $KClO_4$–$Al(ClO_4)_3$ *at* 30°.



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