XXIII.—*On some Compounds of Calcium Sulphate.*

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CALCIUM sulphate having the character of being a difficultly soluble salt, has not—considering its important place in nature—been much investigated as to its relations to other soluble bodies, and more especially as to its relations to these bodies when passing into the crystalline state, as in the formation of double salts. For a long time the only two double salts known were those having the formulæ $\text{CaNa}_2(\text{SO}_4)_2$ and $\text{CaNa}_4(\text{SO}_4)_3 + \text{H}_2\text{O}$, the one of which was first found naturally formed, afterwards both were formed in the laboratory. It was only lately that the existence was proved of another body having the formula $\text{CaK}_2(\text{SO}_4)_2 + \text{H}_2\text{O}$, containing a potassium instead of a sodium salt; yet it has been formed in tons during the last 50 years in certain manufacturing operations, but has always been mistaken for calcium sulphate.

This body has the peculiarity that, when treated with large quantities of water, it gives up the potassium sulphate which it contains and takes up water to become normal calcium sulphate. If this calcium sulphate be again treated with potassium sulphate it again forms the double compound; in fact, it combines with whichever is in excess. I have found another compound of this double salt with water which is formed under slightly different circumstances. When a strong solution of impure potassium sulphate containing calcium sulphate is evaporated by boiling till a large quantity of granular potassium sulphate has collected, the salt referred to is formed amongst others.

It is obtained by washing away all the soluble salts with water, when a white salt, similar in appearance to steatite, is left. It gave on analysis 7.92 per cent. of water and 40.82 per cent. of CaSO_4 , which agrees pretty well with the formula $2\text{CaK}_2(\text{SO}_4)_2 + 3\text{H}_2\text{O}$, which requires 80.1 per cent. H_2O and 40.35 per cent. CaSO_4 . The principal difference between this salt and that before described is that water does not decompose it, except after long boiling. It is strange that, although it is formed at a higher temperature, it contains more water. The two formulæ might be stated as—

Seeing from these results that calcium sulphate was capable of forming interesting compounds, I considered that in advantageous circumstances it might form many double compounds, the conditions required being that a strong solution of a salt holding CaSO_4 in solution be slowly cooled. I despaired of getting results in the laboratory on a small scale, owing to the difficult solubility of the salt, but I thought that in large manufacturing operations, where solutions of such a character are circulating through the same pipes for months without being disturbed, I might find some of the double salts which I considered were likely to exist. On making an examination, with this view, into layers of crystalline matter deposited upon tubes through which solutions containing simultaneously K_2SO_4 , Na_2SO_4 , CaSO_4 , MgSO_4 , and K_2CrO_4 , of which the last constituted the greater portion, my search was rewarded by finding some interesting double compounds. The temperatures of the liquids varied from 40° to 80° C. Most of the layers consisted of the double salt, $\text{CaK}_2(\text{SO}_4)_2 + \text{H}_2\text{O}$, but amongst the layers I found two remarkable salts, the first of which gave on analysis 38.84 per cent. CaSO_4 , 29.08 CrO_3 , and 5.18 H_2O , which agrees pretty well with the formula $\text{CaSO}_4 + \text{K}_2\text{CrO}_4 + \text{H}_2\text{O}$, or $\text{K}_2\text{CaCrSO}_8 + \text{H}_2\text{O}$, whilst the other gave 25.90 per cent. CaSO_4 , and 74.12 per cent. K_2CrO_4 , which is in close agreement with the formula $\text{CaSO}_4 \cdot 2\text{K}_2\text{CrO}_4$, or $\text{K}_4\text{CaCr}_2\text{SO}_{12}$. These two salts were so similar to each other that they could not be distinguished as separate salts by the eye. They had a bright golden appearance, such as is possessed by iodide of lead crystallised from boiling-water. They were in flat prisms, but too confused and irregular to enable me to determine their crystalline form. When placed in pure water the crystals became white, while the solution became yellow; in fact the whole of the potassium chromate could be dissolved out without the crystal breaking up, although it became quite soft, and was really only a mass of $\text{CaSO}_4 + 2\text{H}_2\text{O}$, having the form of the crystal. Conjoined to the latter of these two salts I found a dull-coloured part, which had no definite crystalline structure, but

looked like an amorphous deposit, but which the microscope showed to be composed of little interlaced needles. Two analyses of different parts of it did not give very accordant results, but the formula seemed to be $\text{CaSO}_4, \text{Na}_2\text{SO}_4, \text{K}_2\text{CrO}_4$, or it may be represented as the second of the two above salts, in which one half of the potassium chromate has been replaced by sodium sulphate. In another tube, where there were large quantities of the salt $\text{CaNa}_2(\text{SO}_4)_2$ deposited, I found a salt similar to the above, but containing water. It occurred as a thick crust, with a crystalline structure radiating from the centre of the tube to the circumference. It gave on analysis as follows:—

	Found.	Calculated for $\text{CaSO}_4, \text{Na}_2\text{SO}_4, \text{K}_2\text{CrO}_4 + \text{H}_2\text{O}$.
Ca.....	8.14	8.17
K and Na.....	25.40	25.32
K.....	16.00	15.94
S.....	12.88	13.05
Cr.....	10.75	10.64
H ₂ O.....	3.62	3.65

As will be seen, these numbers agree with the formula $\text{CaSO}_4 + \text{Na}_2\text{SO}_4 + \text{K}_2\text{CrO}_4 + \text{H}_2\text{O}$. Another set of compounds I examined was that of which the only already-known one was the acid sulphate described by Davy. I had often noticed that when a solution of calcium sulphate is boiled to dryness with hydrochloric acid, the first portions of the acid are not easily expelled, but that two or three per cent. are often retained at 120° to 130° C. On dissolving CaSO_4 in hydrochloric acid, and allowing it to crystallise, nothing of this kind takes place; the crystals only need pressure between bibulous paper and desiccation over oil of vitriol to entirely free them from hydrochloric acid, and leave pure crystals of the compound $\text{CaSO}_4 + 2\text{H}_2\text{O}$. Even when the solution is evaporated over the water-bath, the residue consists of needles of the pure salt. But when evaporated at a higher temperature by active ebullition at the ordinary pressure, or better under a pressure of a few pounds per square inch, the calcium sulphate retains an increasing quantity of hydrochloric acid. I conducted an experiment as follows:—The solution was placed in a bulb, and the neck drawn out to a capillary point, and the bulb heated to 116° , that is placed in a bath maintained at this temperature. The vapour escaped only under some pressure, and the evaporation was continued to dryness, when, before cooling, the residual gas was replaced by air. The substance on analysis gave the following:—On solution in nitric acid and precipitation with silver nitrate it gave 9.86 per cent. of chlorine, and another portion gave on ignition 25.10 of a total loss, while 74.90 of pure calcium sulphate remained. This is in very close

agreement with the numbers required by the formula $2\text{CaSO}_4 + 3\text{H}_2\text{O} + \text{HCl}$, that is the normal salt $2\text{CaSO}_4 + 4\text{H}_2\text{O}$ with one of the water molecules replaced by HCl , a most unexpected result. The numbers for the above formula are 9.79 Cl , 24.96 $\text{H}_2\text{O} + \text{HCl}$, and 75.04 CaSO_4 . I intend, when opportunity offers, to extend this work, and find whether the four separate molecules may be in like manner replaced by varying the pressure and temperature. We already know, from the existence of the compound $2\text{CaSO}_4 + \text{H}_2\text{O}$, that the formula of normal calcium sulphate should be doubled, that is, it should be $2\text{CaSO}_4.4\text{H}_2\text{O}$, and it occurred to me to determine whether this could be further sustained by the isolation of the series of compounds:—

The first and last occur naturally, and are also formed by the evaporation of solutions under different conditions. I found that the evaporation of an aqueous solution of the salt at 100° gave the normal salt, whilst under a pressure of 90 lbs. per square inch, that is, at a temperature of 143° , the last alone is formed. I tried several temperatures between these, but could get no definite results. In one case alone a salt was formed which, on ignition, gave a loss of 13.22 per cent., but as this does not agree with any of the above (the third requires 11.68 per cent., and the second 15.69 per cent.), it was evidently a mixture. This method was then abandoned for the "time method," an account of which is given on page 381.