237. *The System Cadmium Sulphate–Cobalt Sulphate–Water.*

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The curious hydrate of cadmium sulphate, $CdSO_4,\frac{8}{3}H_2O$, is one of the best known salts with a fractional water content. No information is available as to the structure of this compound, and no similar hydrate is known for any other sulphate. Experience with zinc and lithium chlorides had shown that ternary aqueous systems containing cobalt chloride could throw light on the nature of hydrates of other chlorides (Bassett and Croucher, J., 1930, 1786; Bassett and Sanderson, J., 1932, 1855). In the hope of obtaining information about the above hydrate, the system $CdSO_4$–$CoSO_4$–H_2O has been studied at 25° and 80°.

Mylius and Funk (*Ber.*, 1897, **30**, 825) found that cadmium sulphate formed a heptahydrate at low temperatures (— 18° to — 5°), which was, however, always metastable towards $CdSO_4,\frac{8}{3}H_2O$. According to these authors, the latter is the stable solid phase in the system $CdSO_4$–H_2O up to 74·8°, where it gives place to the monohydrate. It was found by Benrath and Thönessen (*Z. anorg. Chem.*, 1932, **203**, 405) that the monohydrate exists in two different forms; at 41·5° there is a transition point where $CdSO_4,\frac{8}{3}H_2O$ changes into α-monohydrate which at 74·5° changes into the β-form. When the solubility values are plotted, it is seen that Mylius and Funk actually realised a metastable portion of the $CdSO_4,\frac{8}{3}H_2O$ solubility curve which is normally cut out by the appearance of the α-form of monohydrate; they only obtained the β-form.

Stromeyer (*Schweigger's J.*, 1818, **22**, 369), the discoverer of cadmium, obtained a tetrahydrate $CdSO_4,4H_2O$ in large transparent rectangular crystals. Lescoeur (*Ann. Chim. Phys.*, 1895, **4**, 222), by slow evaporation in a cool place, obtained the same hydrate and found that its dissociation pressure on passing into monohydrate was 12 mm. of mercury at 20°.

In recent literature, it is generally assumed that Stromeyer and Lescoeur were mistaken, and that they were actually dealing with $CdSO_4,\frac{8}{3}H_2O$, but we believe that they probably did have the tetrahydrate. Their analyses and descriptions of the compound are such as would be expected. Our results show that at 80° large proportions of the tetrahydrate can exist in solid solution in cobalt sulphate tetrahydrate, and it is highly probable that the pure tetrahydrate could exist in contact with pure cadmium sulphate solutions at some considerably lower temperature. It would be a metastable form, however, and conditions for its separation are difficult to realise owing to the peculiar solubility conditions in the system $CdSO_4$–H_2O, which make it difficult to prepare, by heating, solutions which will be supersaturated at lower temperatures. Slow evaporation at low temperatures has therefore to be used, with the likelihood that the stable solid phase rather than a metastable one will separate before concentrations have been reached at which inoculation with an isomorphous compound can be used. Mylius and Funk (*loc. cit.*) state that they obtained a solid solution of cadmium sulphate tetrahydrate in the corresponding manganese salt, though unable to get the tetrahydrate itself.

There can now be no reasonable doubt that $CdSO_4,\frac{8}{3}H_2O$ really does have this composition and is not a trihydrate, as thought by Retgers (*Z. physikal. Chem.*, 1895, **16**, 590). There seems to be no sound evidence for the trihydrate.

We find that at 80° $CdSO_4,\frac{8}{3}H_2O$ forms solid solutions with the corresponding cobalt compound. This is important, since it shows that cadmium sulphate is not the only one yielding this type of hydrate. It is possible that the pure cobalt compound might be obtainable at some higher temperature. It would seem from Retgers's results (*loc. cit.*) that similar solid solutions exist containing ferrous and cupric sulphates, although he considered the preparations to be dilute solid solutions of the trihydrates in the cadmium trihydrate. He also obtained $CuSO_4,5H_2O$ containing 1·71% of $CdSO_4,5H_2O$, so the latter compound may be capable of independent existence, though it would be very unstable.

Our experiments at 80° show that the α- and the β-form of cadmium sulphate monohydrate give rise to two independent sets of solid solutions containing cobalt sulphate monohydrate. The latter compound (first prepared by Etard, *Compt. rend.*, 1878, **87**, 602) must therefore be capable of existing in two different modifications.

In the system $CoSO_4$–H_2O, Koppel and Wetzel (*Z. physikal. Chem.*, 1905, **52**, 394) found that transition from hepta- to hexa-hydrate occurred at 40·7°, and Benrath (*Z. anorg. Chem.*, 1931, **202**, 168), who examined the system between 50° and 100°, states that the latter hydrate is stable up to 71°, where it gives way to monohydrate. We cannot understand Benrath's results, according to which, at 80°, the monohydrate is the stable solid phase in equilibrium with a solution containing 35% of anhydrous salt. Our 80° isothermal shows that the tetrahydrate is the stable solid at that temperature in equilibrium with a solution containing 39·94% of anhydrous salt. Pure monohydrate in contact with solution containing only cobalt sulphate would probably be in a highly metastable condition at 80°, the saturated solution containing much more than 40% $CoSO_4$.

EXPERIMENTAL.

The materials used were A.R. $CdSO_4,H_2O$ and iron- and nickel-free $CoSO_4,7H_2O$. Mixtures were made by weight and were designed to give 15—20 g. of solution and about 2 g. of solid phase for the 25° experiments and 5—10 g. and 1—2 g. respectively for those at 80°. Mixtures for the 25° isothermal which contained high proportions of cobalt sulphate could be heated until all solid had dissolved and would then deposit solid on cooling to 25°. This is not the case with mixtures containing much cadmium sulphate because the solubility of its monohydrate decreases with rise of temperature.

In the experiments marked (*a*) in the table, anhydrous cadmium sulphate, obtained by heating the monohydrate at 110—115°, was used in making the mixtures, sufficient cold water being added to dissolve all but about 1 g. of the solid phase. In experiments marked (*b*), all the solid phase was dissolved by adding sufficient cold water. The bottles were then placed in a vacuum desiccator and water evaporated until about 1 g. of solid phase had separated. The mixtures, contained in bottles of hard glass closed by well-waxed corks, were then rotated in the thermostat until equilibrium was reached (about 48 hours).

The procedure followed at 80° was rather different. Sufficient cold water was added to dissolve all the solid phase. The bottles were then suspended in the thermostat and evaporated until about 1 g. of solid phase had separated. The bottles were then closed by corks, which projected above the thermostat liquid, and were shaken frequently by hand. The time required for equilibrium to be reached varied with the nature of the solid which separated; when the solid phase was a metastable form, 1—2 hours sufficed, but when a transition from a metastable to a stable solid phase was involved, the time required was about 12 hours.

At 25° all the mixtures were filtered for analysis in a jacketed filter-tube, but at 80°, the clear supernatant solution was removed with a previously warmed pipette. The tetrahydrate solid phases were then obtained in a moist state for analysis by filtration. The other solid phases separated at 80° in very small crystals which held up large amounts of solution. This made it difficult to interpret experimental results obtained by analysis of the moist solids. It was impossible to be sure of the precise nature of the solid phases, and in particular, to know whether two series of solid solutions based on $CdSO_4,H_2O$ were in question, or whether one of them might be based on some other low hydrate. These solids were therefore filtered off in the jacketed filter-tube, and obtained dry by washing with a small quantity of hot 50% aqueous alcohol, and then with hot absolute alcohol. In some cases very slight dehydration seemed to occur, but the method was satisfactory except when the solid phase was a solid solution of the tetrahydrates. In that case variable results were obtained owing to partial dehydration, but as the tetrahydrate forms much larger crystals than the other hydrates, the separated moist solids were sufficiently free from solution to be suitable for direct analysis.

The tetrahydrate formed fair-sized prisms which were readily distinguished from the three solid solutions found at 80°. These all came out in such minute crystals that a microscopic examination scarcely aided identification. Monohydrate solid solutions could be distinguished from solid solution in $CdSO_4,\frac{8}{3}H_2O$ by means of the pinker colour of the latter, due to the higher content of cobalt sulphate.

Analyses were carried out by the following method which was convenient and reliable. Cobalt was estimated in one portion, being precipitated with α-nitroso-β-naphthol and weighed as Co_3O_4 after strong ignition in an open crucible. Total sulphate was determined in another portion after removal of cadmium as sulphide in presence of hydrochloric acid (5 c.c. of 2*N*-acid in 100 c.c. solution), and expulsion of hydrogen sulphide. Percentages of cobalt and cadmium sulphates were calculated from these two results.

If the cadmium sulphide was precipitated in absence of hydrochloric acid, it carried down a small amount of sulphate. In presence of hydrochloric acid, the precipitate contained no sulphate, but a small amount of chloride. If the barium sulphate was precipitated from solutions containing cadmium, it carried down a small amount of cadmium sulphate and low results were obtained for sulphate.

FIG. 1.

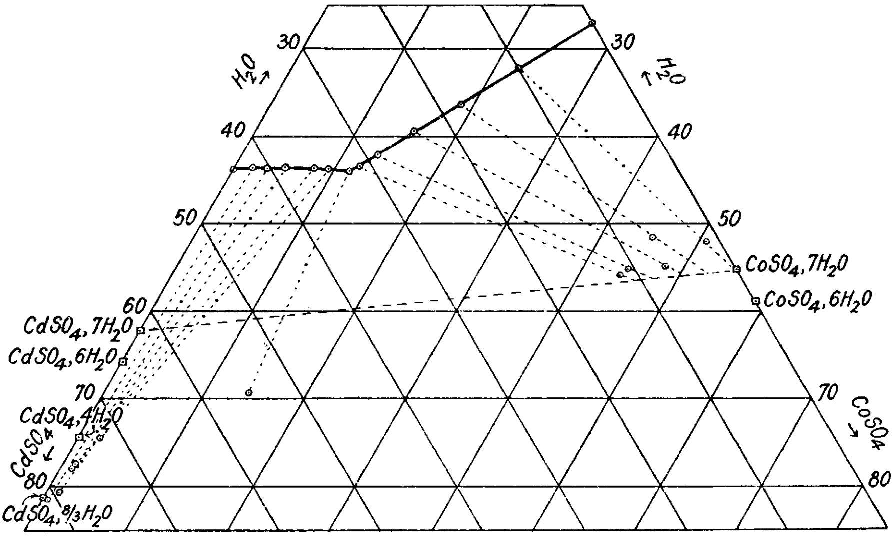
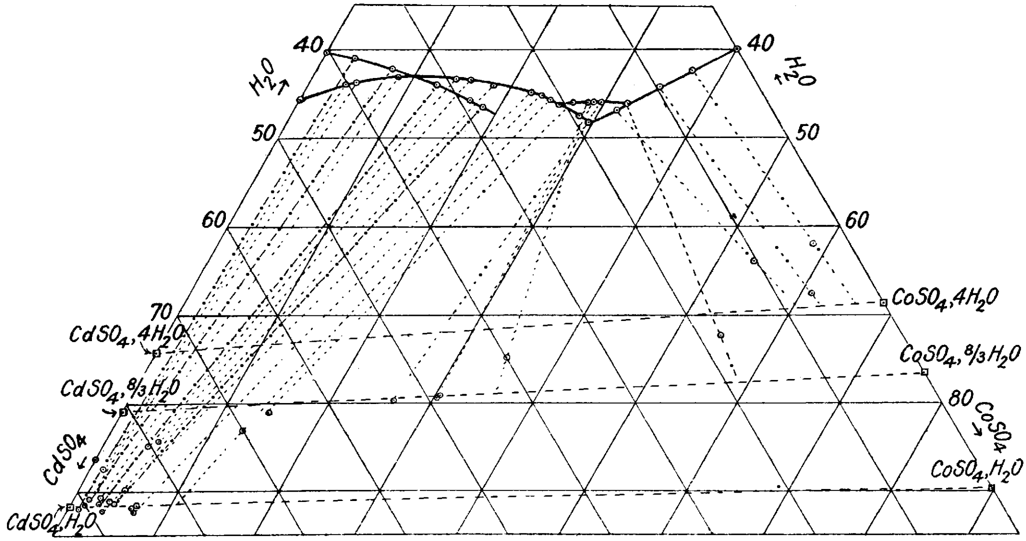


FIG. 2.



The analytical results are given in the tables and are plotted in Figs. 1 and 2, from which it will be seen that all the solid phases found are solid solutions, although the amount of cobalt sulphate in the $CdSO_4,\frac{8}{3}H_2O$ phase at 25° is very small, little greater than the experimental uncertainty.

Solution.		Moist solid.		Solid phase.	Solution.		Moist solid.		Solid phase.
$CoSO_4$.	$CdSO_4$.	$CoSO_4$.	$CdSO_4$.		$CoSO_4$.	$CdSO_4$.	$CoSO_4$.	$CdSO_4$.	
Temp. = 25°.									
27·05	—	—	—	A	9·44	34·52	2·18	72·46	D
22·38	9·97	50·75	1·26	B	8·00	35·85	(*a*) 1·11	76·67	
18·89	17·78	45·18	6·55		5·04	38·84	(*b*) 1·26	79·48	
15·62	23·90	48·18	6·94		3·43	40·46	(*b*) 1·09	76·34	
13·42	28·88	44·64	10·70		1·78	41·84	(*a*) 0·36	81·10	
12·35	31·02	44·19	11·92		—	43·83	—	—	E
11·55	32·64	14·17	55·27	C					

A = $CoSO_4,7H_2O$.
B = Solid solution of $CoSO_4,7H_2O$ and $CdSO_4,7H_2O$.
C = Solid solution (B) and $CdSO_4,\frac{8}{3}H_2O$ (solid solution).
D = $CdSO_4,\frac{8}{3}H_2O$ (solid solution).
E = $CdSO_4,\frac{8}{3}H_2O$.

Solution.		Moist solid.		Solid phase.	Solution.		Moist solid.		Solid phase.
$CoSO_4$.	$CdSO_4$.	$CoSO_4$.	$CdSO_4$.		$CoSO_4$.	$CdSO_4$.	$CoSO_4$.	$CdSO_4$.	
Temp. = 80°.									
39·94	—	—	—	F	22·06	22·83	4·65	85·40	III
36·60	5·94	58·28	3·71	I	18·12	26·08	* 3·54	89·00	
34·30	9·91	60·94	6·72		15·56	27·94	5·30	79·10	
(*m*)31·67	15·35	53·51	10·58		14·13	29·37	4·49	80·66	
32·01	14·08	54·41	17·97	I + II	(*m*) 8·31	34·95	* 2·63	88·25	
(*m*)29·46	18·96	30·50	49·35	I + III	(*m*) 4·66	39·33	* 1·47	89·48	
29·66	16·63	* 26·02	53·96	II	(*m*) 3·63	40·40	1·34	86·14	
28·77	17·30	* 30·56	49·00		(*m*)18·32	28·25	* 4·39	87·34	IV
28·32	17·83	34·92	40·05		(*m*)16·74	29·15	* 3·81	87·64	
26·90	19·31	* 14·83	66·83		(*m*)12·53	31·45	* 2·79	88·88	
(*m*)28·25	19·30	* 6·62	85·17	III	7·26	34·98	* 1·56	90·10	
25·59	20·83	* 6·19	85·91		3·00	38·11	* 1·03	91·30	
24·63	21·24	13·00	70·30		—	40·31	—	—	G
23·32	21·85	* 6·76	85·95		(*m*) —	45·80	—	—	H

* The solid phase was alcohol-washed and air-dried.
(*m*) = metastable region.
F = $CoSO_4,4H_2O$. G = β-$CdSO_4,H_2O$. H = α-$CdSO_4,H_2O$.
I = Solid solution of $CdSO_4,4H_2O$ and $CoSO_4,4H_2O$.
II = „ „ $CdSO_4,\frac{8}{3}H_2O$ and $CoSO_4,\frac{8}{3}H_2O$.
III = „ „ α-$CdSO_4,H_2O$ and α-$CoSO_4,H_2O$.
IV = „ „ β-$CdSO_4,H_2O$ and β-$CoSO_4,H_2O$.
All the above solid solutions, as also the solid solutions of $CdSO_4,7H_2O$ and $CoSO_4,7H_2O$, are red.

DISCUSSION OF RESULTS.

The demonstration that $CdSO_4,\frac{8}{3}H_2O$ can form solid solutions with a corresponding cobalt compound appears to be the most important result of the present investigation. It shows that in forming this peculiar hydrate, cadmium is not so exceptional as is commonly thought. The fact that the hydrate is readily formed in the case of this metal but not of other related metals is to be attributed to the general tendency of cadmium salts to form hydrates of low water content. Any suggestion as to the nature of the cadmium compound must clearly be applicable to other metals as well.

The supposition, commonly accepted, that cadmium has a special facility for autocomplex formation is not altogether justified, for it is mainly based upon the behaviour of the halides, which are frequently exceptional in this respect.

There appears to be a general opinion that in $CdSO_4,\frac{8}{3}H_2O$ some of the metal is contained in a complex anion. There seems to be little, if any, evidence for the existence of complex, as distinct from double, sulphates—at any rate, in the case of bivalent metals. Compounds like ferrous ammonium sulphate are double salts with simple ionic structures, *e.g.*, $[NH_4]_2^{\cdot}[Fe(H_2O)_6]^{\cdot\cdot}[SO_4]_2''$, which have no existence except in the solid state.

If $CdSO_4,\frac{8}{3}H_2O$ really were autocomplex, there are two structures worth consideration, *viz.*, (*a*) $[Cd(H_2O)_8]^{\cdot\cdot}[SO_4CdSO_4CdSO_4]''$ and (*b*) $[Cd(H_2O)_6]^{\cdot\cdot}[H_2OSO_4CdSO_4CdSO_4H_2O]''$ both of which contain chain anions. In our opinion, the fact that the solid solutions containing cobalt are red, disproves both of these structures, for the colour shows that all the cobalt is in the kationic condition (Bassett and Croucher, J., 1930, 1784). This at once rules out structure (*a*), for although cadmium has a maximum co-valency of eight, according to Sidgwick's rule, the maximum for cobalt is six, so it could not replace cadmium in an 8-co-ordinate kation.

Structure (*b*) is also ruled out, however, for the solid solution richest in cobalt sulphate which could be obtained would correspond to complete replacement of $[Cd(H_2O)_6]^{\cdot\cdot}$ by $[Co(H_2O)_6]^{\cdot\cdot}$ and this would contain 21·66% of cobalt sulphate, whereas one of our solid solutions contained 36%. It may be concluded then that, whatever the structure of $CdSO_4,\frac{8}{3}H_2O$, it is one in which the whole of the cadmium is replaceable by cobalt, *i.e.*, one of the constituents of the red solid solutions is actually $CoSO_4,\frac{8}{3}H_2O$.

The hepta-, hexa-, and tetra-hydrates of cobalt sulphate are with good reason regarded as $[Co(H_2O)_6]^{\cdot\cdot}[SO_4{\cdot}H_2O]''$, $[Co(H_2O)_6]^{\cdot\cdot}SO_4''$, and $[Co(H_2O)_4]^{\cdot\cdot}SO_4''$. When a series of hydrated sulphates of any one metal is considered, it would thus seem that, in general, the $[SO_4{\cdot}H_2O]''$ ion tends to lose its water molecule at a relatively low temperature; hence it seems probable that none of the water is attached to the $[SO_4]''$ ion in hydrated sulphates containing less than 4 mols. of water per mol. of MSO_4.

Further discussion is not justified at present, but we believe the only structure for $CdSO_4,\frac{8}{3}H_2O$, worthy of serious consideration, to be

$$[(H_2O)_2Cd(H_2O)_2Cd(H_2O)_2Cd(H_2O)_2]^{VI}[SO_4]_3''.$$

This contains the same type of chain kation, with doubly linked water molecules in which all the metal atoms are 4-co-ordinate, as is present in the hydrated orthophosphates $M_3(PO_4)_2,8H_2O$ (Bassett and Croucher, *loc. cit.*, p. 1803). We also believe that the monohydrates will be found to be $[M(H_2O)_2M]^{IV}[SO_4]_2''$ with a kation $[M_2(H_2O)_2]^{IV}$ analogous to the $[Li_2(H_2O)_2]^{\cdot\cdot}$ ion postulated by Bassett and Sanderson (*loc. cit.*). In this ion both M atoms would be 2-co-ordinate. Both these suggested structures are applications of the principle that the water molecules available in a crystal will usually be distributed in such a way as to allow all the M atoms to have the highest possible even co-ordination numbers. We think that this is an important determining factor in salt hydrate formation.

It seems likely that the α- and the β-form of cadmium and cobalt sulphate monohydrates are only crystallographic varieties containing the same ions, although, of course, the evidence at present available is insufficient to exclude alternative ionic structures such as

$$[Cd]^{\cdot\cdot}[SO_4{\cdot}H_2O]'' \text{ and } [Cd(H_2O)_2]^{\cdot\cdot}Cd^{\cdot\cdot}[SO_4]_2''.$$

SUMMARY.

The system $CdSO_4$–$CoSO_4$–H_2O has been examined at 25° and 80°.

No compound of cadmium sulphate with cobalt sulphate was isolated, but several series of solid solutions were obtained, all of them red. These were solid solutions of $CdSO_4,7H_2O$, $CdSO_4,4H_2O$, $CdSO_4,\frac{8}{3}H_2O$, α-$CdSO_4,H_2O$, and β-$CdSO_4,H_2O$ with the corresponding cobalt compounds. The existence of the last four types of hydration of cobalt sulphate had not previously been suspected.

These results are applied to the interpretation of the nature of $CdSO_4,\frac{8}{3}H_2O$, and structures are suggested for this and for the monohydrate.

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