THESIS

BY

C.P.FINLAYSON

ON

DOUBLE SULPHATES OF COPPER AND CADMIUM.

APRIL I3 I9I6.

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The object of this work was to investigate the possibility of a double sulphate of cppper and cadmium, and to obtain such, a solution of each was mixed with the other in different ratios and allowed to evaporate spontaneously, with the crystallization of some salt.

A 5E solution of cadmium sulphate was used in which there were 627.5 grams to a liter, while a 2E solution of copper sulphate was used, there being 249.66 grams to a liter of water. The molecular ratio of these solutions was about I $CuSO_4$ to 2.5 $CdSO_4$. The solutions from which the crystals were crystallized were all of the same volume, 20 c.c. but varied in the per cent of volume of the two solutions. The composition of each is given below,

Number	I.	I8 c.c.	$CuSO_4.5H_2O$	and	2c.c.	$CdSO_4.8/3\ H_2O$.	
"	II	I6 c.c.	"	"	4c.c.	"	"
"	III	I4 c.c.	"	"	6c.c.	"	"
"	IV	I2c.c.	"	"	8c.c.	"	"
"	V	I0 c.c.	"	"	I0 c.c.	"	"
"	VI	8 c.c.	"	"	I2 c.c.	"	"
"	VII	6 c.c.	"	"	I4 c.c.	"	"
"	VIII	4 c.c.	"	"	I6 c.c.	"	"
"	IX	2 c.c.	"	"	I8 c.c.	"	"

It is seen that each crystallizing solution is stronger in $CdSO_4$ and weaker in $CuSO_4$ than the one preceding.

These solutions were placed in a room of almost constant temperature and there allowed to stand uncovered, but protected from dust and dirt, until crystals began to form. These were removed from the mother-liquor and placed on a filter paper and

there washed with a small amount of water to remove any of the mother-liquor adhering to them. They were dried by the use of filter papers and put in cork tubes. None but homeogenous crystals were saved, while the others were redissolved in the original solvent and allowed to recrystallize. All second crops of crystals were keep separate from the first. In order to get the most regular crystals it was found best to remove them as soon as formed.

In the analysis of the samples the most difficult problem was to separate the copper from the cadmium quantitatively, and it was not until several methods were tried that one suitable was found. This was as follows- A .5 gram sample of the crystals was weighed out and dissolved in water and treated with NH_4OH until the precipitate formed dissolved giving the solution that deep blue copper color. This color was destroyed by adding sufficient KCN to convert all copper present into the double salt of cuprous cyanide and potassium cyanide, the corresponding salt of cadmium also being formed. The later is decomposed by H_2S while the former is not, and the separation of the copper and cadmium depends on this fact. The solution was saturated with H_2S, the cadmium being precipitated as the yellow CdS. This precipitate was filtered off and dissolved in hot dilute HCL, gm precipitate was dissolved in hot dilute HCL from a filter paper and allowed to run in a porcelain crucible. To it was added a little concentrated H_2SO_4 and the whole slowly evaporated, by which process the cadmium was converted into $CdSO_4$ and was weighed as such after being heated to a red hot heat.

The filtrate after the removal of the CdS was treated with HNO_3, which broke up the double cyanide, and was then evaporated almost to dryness, by which operation the cyanide and H_2S were almost completely destroyed leaving the copper

as copper nitrate. Water was added and the solution treated with NaOH, to neutralize any acid present, until a permanent precipitate was formed. The excess of alkali was neutralized with acetic acid the result being a clear pale green solution. The copper is now in such a condition that it can be determined by the Iodine and Sodium-thio sulphate method.

In this method the solution containing the copper is treated with KI, CuI_2 being formed, which immediately breakes up into CuI and free I. The liberated I is determined by Na_2S2O_3 using starch as and indicator. The same amount of I is liberated as remains combined with the copper, thus the amount of copper present is determined by the amount of free I.

It seems evident that the cadmium present in the crystals does not effect their character as to its system of crystallization. Crystals of I, II, III, IV, V, VI, are in general outline of the same make-up as the pure $CuSO_4.5H_2O$ crystals. VII, VIII and IX which are pure $CdSO_4.8/3H_2O$ belong to the monoclinic system.

The reactions which take place in all of the above work are represented by the following equations-

(I) $CdSO_4 + 2CuSO_4 + 6KCN = 3K_2SO_4 + 2Cu(CN)_2 + Cd(CN)_2$

(2) $2Cu(CN)_2 \rightarrow 2CuCN + C_2N_2$

(3) $2CuCN + 6KCN = 2K_3Cu(CN)_4$

(4) $Cd(CN)_2 + 2KCN = K_2Cd(CN)_4$

(5) $K_2Cd(CN)_4 + H_2S = CdS + 2KCN + 2HCN.$

(6) $3CuCN + 7HNO_3 = 3Cu(NO_3)_2 + 3HCN + NO + 2H_2O$

(7) $3KCN + 2HNO_3 = 3KCNO + 2NO + H_2O$ or

(8) $K_3Cu(CN)_4 + 9HNO_3 = 3Cu(NO_3)_2 + 3HCN + 3NO + 3KCNO + 3H_2O.$

(9) $3HCN + 2HNO_3 = 3HCNO + 2NO + H_2O.$

(IO) $Cu(NO_3)_2 + 2KI = CuI_2 + 2KNO_3$

(II) $CuI_2 \rightarrow CuI + I$

(I2) $2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$.

Below are the results of the analyses -

	Sample	Copper	Cadmium sulphate
I			
	A. .4498gm.	.I026gm.	.0096gm.
	B. .4335gm.	.0997gm.	.0089gm.
II			
	A. .4355gm.	.I0082gm.	.0I68gm.
	.4404gm	.I0354gm.	.0I33gm.
III			
	A. .4348gm.	.I0062gm.	.03I5gm.
	B. .4338gm.	.0995gm.	.0330gm.
IV			
	A. .4650gm.	.I029gm.	.0288gm.
	B. .4848gm.	.I076gm.	.0352gm.
V			
	A. .2446gm.	.5063gm.	.025Igm.
	B. .2502gm.	.5228gm.	.027Igm.
VI			
	A. .I960gm.	.0386gm.	.027Igm.
	B. .2003gm.	.0399gm.	.0280gm.
VII	No Copper.		
VIII	No Copper.		
IX	No Copper.		

The ratio of cadmium sulphate to copper sulphate and copper sulphate to cadmium sulphate in each sample was found by analysis to be-

	$CdSO_4$		$CuSO_4$	.	$CuSO_4$		$CdSO_4$.
I.	I	:	35.0		I	:	.0285
II.	I	::	I0.90		I	:	.09I7
III.	I	:	I0.I6		I	:	.0985
IV.	I	:	9.2I		I	::	.I095
V.	I	:	6.50		I	::	.I540
VI.	I	:	4.60		I	:	.2I80

Futher data in regard to formula is given below: The water of

crystallization is not distributed between the two sulphates but is given in its molecular ratio.

I.

$CuSO_4$.	57.22%
$CdSO_4$.	2.I3%
H_2O .	40.65%
	I00.00% total.

Formula- $35CuSO_4.CdSO_4.225.5H_2O$.

I. By analysis.

$CuSO_4$.	57.22%
$CdSO_4$.	2.I3%
H_2O.	42,87%
	I02.22%

Formula- $35CuSO_4.CdSO_4.236H_2O$.

II.

$CuSO_4$.	58.95%
$CdSO_4$.	8.0I%
H_2O.	33.04%
	I00.00%

Formula- $I0.9CuSO_4CdSO_4.42.5H_2O$.

II. By analysis.

$CuSO_4$.	58.95%
$CdSO_4$.	8.0I%
H_2O .	37.70%
	I04.66%

Formula- $I0.9CuSO_4.CdSO_4.6I.6H_2O$

III.

$CuSO_4$.	57.83%
$CdSO_4$.	7.42%
H_2O .	34.75%
	I00.00%

Formula- $I0.I6CuSO_4.CdSO_4.59.9H_2O$.

IV.

$CuSO_4$.	55,5I%
$CdSO_4$.	6.75%
H_2O .	37.74%
	I00.00%

Formula- $9.2ICuSO_4.CdSO_4.62.7H_2O$

V.

$CuSO_4$.	52.I5%
$CdSO_4$.	I0.46%
H_2O .	37.44%
	I00.00%

Formula- $6.5CuSO_4.CdSO_4.39.5H_2O$.

VI.

$CuSO_4$	49.46%
$CdSO_4$	I3.8I%
H_2O	36.73%
	I00.00%

Formula- $4.6CuSO_4.CdSO_4.30.3H_2O$.

VII. Formula- $CdSO_4.8/3H_2O$.

VIII. " " .

IX. " " .

The work as awhole is not satisfactory but it seems that one fact has been proven , and that is that cadmium sulphate is soluble in copper sulphate while copper sulphate is not soluble in cadmium sulphate. Without a doubt the crystals recovered from the solutions were cases of solid solutions in which copper sulphate was the solvent and cadmium sulphate the solute. This solubility seems to increase with the increase of the concentration of the solute and its range is between zero and .217 molecules to one molecule of the solvent.

The constitution of the crystals in reference to the water of crystallization varied greatly and it appears that this water increases when the salt is the case of a solid solution, but no definite law can be seen or worked out without very acurate analyses. But it does look as if the cadmium sulphate is forced to crystallize with 5 molecules of water instead of 8/3 molecules.