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Distribution of Isomorphous Salts Between Liquid and Solid Phases In Ternary Systems

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In our work two isomorphous salts , $CusO_4.5H_2O$ - $ZnSO_4 .7H_2O$ were taken. They were allowed to crystallize after dissolving them in water at various ratios. Then the crystals were analyzed by titrometry technique. Many equations suggested for co-crystallization of salts, in equilibrium and non-equilibrium conditions, were tested. Finally it is found that our system obeys the laws applicable for non-equilibrium condition. Further is also found that in the crystallization of mixed salt , the mixed crystals contain the same number of water of hydration molecules in both salts as the number of molecules salt which in greater amount . for example in our case when the amount of copper sulphate is greater , then the mixed crystal Zinc sulphate also contains 5 water molecules and vice versa. This finding of our work will be very useful in future to prepare a salt with a number of water molecules different from that of its usual number of water molecules.

Key words: co-crystallization , non-equilibrium , equilibrium , to crystallize , molecules .

INTRODUCTION

when a pair of isomorphous salts is crystallized together from an aqueous solution ,a solid of homogenous composition results. In such a ternary system the compositions of both the aqueous and solid phases are continuously changing during the course of crystallisation. A study of the distribution of the salts between crystallisation the aqueous and solid phases is of considerable importance both from theoretical and practical aspects of fractional crystallisation. Further two types of system – equilibrium and non-equilibrium are encountered during fractional crystallisation. Crystallization carried out rapidly and stopped at the end of a short period (a few hours) always leads to a system in a state of non-equilibrium , ie., no equilibrium is attained between solid and aqueous phases with respect to the composition of salts in the two phases , though the process of crystallization itself is complete.if the non-euilibrium system is kept in an isothermal condition for sufficiently long periods, recrystallisation begins.This finally gives rise to a system in equilibrium in which the composition of aqueous and solid phases do not change even if the two phases are in contact with each other for any length of time.

Several theories have been putforth to explain the distribution of salts between aqueous and solid phases during crystallization , resulting in equilibrium and non-equilibrium ternary systems. Since it is presently envisaged to compare the merits of those theories , it is become necessary to examine the laws relating to these two types of systems . Van't Hoff[1] and Roozeboom[2] said that the gas laws apply to dilute solid solutions. Berthelot - Nernst law[3] governs the distribution of impurities in micro level between the solid and liquid phases similar to the distribution laws. Berthelot-Nernst law for cocrystallisation of Radium with Barium nitrate is given by,

$$C_{S}/C_{L} = K_{N} \qquad \text{-----------} [1]$$

Where C_S and C_L represent the concentration of Radium ion in solid and liquid phases in micro levels ; K_N represents the Distribution constant. Khlopin[4-12] has written the equation in the following form

$$X \rho_S / m_S = K_{N\ (1-x)} \rho_{L} / m_L \qquad \text{----------} [2]$$

where x is the fraction of the micro-component in the solid phase. ρ_S and ρ_L are the dencities of the solid and liquid phases respectively. m_S and m_L are the amounts of the solid and liquid phases respectively. Henderson and Kracek has written the equation in the following form

$$X / Y = D (a - x) / (b - y) \qquad \text{---------} [3]$$

Where X and Y are the amounts of the solid and liquid phases respectively.a and b are respectively the initial amounts of the micro and macro components in solution; D is the Distribution constant. D and K are related by the equation,

$$D = K_{N\ (1-mx)} \rho_{L} / m_L$$

Where $(1 - mx) \rho L / m L$ is the concentration of the macro component expressed in gm/ml of the solution. Doerner and Hoskins gave a different equation for coprecipitation of Radium ion and Barium sulphate. Each layer in a crystal should satisfy the following equation

$$dy/dx = \lambda * y/n \quad - \qquad \text{-------------} [4]$$

the logarithmic equation of Doerner and Hoskins :

$$\ln Y /a = \lambda \ \ln n / b \qquad \text{-------------} [5]$$

where n and y are the concentrations of Barium and Radium ions respectively in solutions at any instant. dy

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***Corresponding author:** nadippiii@yahoo.com and dn are the amounts of radium and barium ions respectively precipitated as sulphates at this instant. λ is a constant known as Distribution Constant of the impurity. Doerner and Hoskins law does not assume a true equilibrium between crystals and the solution at the end of crystallization , but postulates a uniform layer like distribution of impurities in the solid phase, with a momentary equilibrium between the crystallizing layer and the solution. These laws have been thoroughly checked with experimental data. Using different methods , Kholpin has evaluated for several systems the values of D and K_N are constantthus Kholpin has shown that true equilibrium has been attained in these systems and the value on $K_{N\ is}$ independent of the way in which equilibrium was reached. A similar conclusion has been reached by Hahn , who investigated radium chloride and Barium chloride. His results have confirmed that the Berthelot – Nernst law is applicable to the distribution of an electrolyte between crystalline and liquid phases. Dis sensitive to variation in temperature of the system

Roozeboom has classified systems of two isomorphous salts A & B , varying in respect of only one ion , which constitute ternary systems with water , forming continuous solid solutions.The classification is based on the relative distribution of salts between liquid and solid phases. In type I , the mole fraction of one of the salts , say A , is always greater in the liquid than in the solid phase, over the entire range of concentration of the system .ie., Y is always greater than X. In type II , Y is greater at lower concentrations of A and then becomes smaller than X for the range of concentrations approaching pur A. Type III is just the reverse of type II, ie., Y is smaller than X at low concentrations of A and becomes larger than X at larger concentrations of A .

Abu Elamayem's Equation

Abu Elamayem has proposed the following equations to explain the fractional crystallization of alums and Picromerites

$$- dy/dw$$
$$= 1/W[1/1+MB/MA\ [\ 1/k\ (\ 1- w / a - w\ y\ ) -1]\ MB/MA\ ]^{1/m} - y$$
$$y^2\ w\ (\ k - 1) - y\ [\ (\ w + a\ )\ (\ k -1\ ) + 1\ ]\ _+\ k_a\ _= 0$$

Where W = fraction by weights of the original
mixture that has separated as crystals.
Y = fraction by weight of the less soluble salt
in the crystals
a =fraction by weight of the less soluble salt
in initial mixture.

M_A and M_B are the molecular weights of the two salts;
k and m are the constants. The differential equation [1] is applicable to systems in non – equilibrium conditios encountered in rapid crystallization and is based on the following assumptions :

1] The solid phase formed during fractional crystallization is built up layer by layer , each layer having a composition different from that of the preceding one.

2] The solid solution in each layer is momentarily in equilibrium with th aqueous phase from which it has separated and its composition is determined by that of the liquid phase at the moment of its formation.

Equation [2] is applicable to systems in equilibrium.

FRACTIONAL CRYSTALLISATION STUDIES AT
DIFFERENT 'a' VALUES.

Object and Scope of The Present Studies

The object of the present investigation is to study ther validity of Berthelot - Nernst , Doerner – Hoskin 's distribution laws and Abu Elamayem's equation for non – equilibrium systems encountered during the fractional crystallization of ternary systems consisting of a pair isomorphous salts and water. The system chosen is as follows :-

Copper Sulphate-Zinc sulphate - Water

The time of crystallization is Six hours . It is also proposed to determine the water of crystallization of the mixed crystal in each and every experiment and to see whether the same can throw any light on the crystallization process .ie., to see whether the system can form a continuous solid solution or not.

Fractional Crystallisation Studies at Different 'a' Values.

The pair of isomorphous salts selected for the study of fractional crystallization is Copper Sulphate - Zinc sulphate

All the experiments were carried out at 28° c . It was found to be convenient to express the ratio of weights of the two isomorphous salts in the system in terms of a parameter of equation [1].Since 'a'represents the fraction by weight of less soluble salt in the initial mixture , the values of 'a' chosen in the present study is directly represent the fraction by weight of $CuSO_4 . 5H_2O$

Experiment

Zinc Sulphate and Copper Sulphate were of BDH AR grade and used without any further purification and distilled water was used in all the experiments. Experiments on fractional crystallization were designed to obtain different values of 'w' (fraction by weight of the crystals separating from the solution) for a given ratio of the two salts in the initial mixture. This was done by preparing mixtures of the two salts corresponding to , a = 0.9 , 0.75 , 0.66 , 0.5 , 0.25 , 0.1 crystallizing the mixtures from solutions containing different amounts of water. In all experiments crystallization was allowed to proceed only for 6 hours which ensured the non – equilibrium state of systems.

The general experimental procedure adopted was as follows:

A clean and dry Pyrex flask (about 100 ml capacity) fitted with a good ground glass stopper was weighed. Suitable amount of the two salts (5 gm of less soluble salt and 5 gm of the more soluble salt) to correspond to , a =0.500 were weghed accurately and added into the flask. An appropriate amount of water was added and the flask was weighed again. The flask was gently heated with the stopper on to dissolve the salts completely. It was then kept in the bath maintained at 28° c .± 0.5 °c . Crystallization was generally found to occur within 15 minutes : when it not occur spontaneously , the solution was seeded with a tiny crystal of the less soluble salt. The flask was kept in the thermostat for 6 hours. At the end of six hours , the flask was removed from the thermostat and the outer surface was quckly wiped dry with filter papers. The mother liquor was rapidly but carefully decanted into a weighed conical flask. The conical flask was reweighed and the weight of mother liquor was noted. The moist crystals were transferred to a previously weighed Silica Crucible and the same was ignited in an electric Bunsen for about one hour and the weight of water lost was found out.The weighings were repeated for the concordant weight was noted. From these weights the weight of water of crystallization was found for the crystals formed in this experiment. The mother liquor was made upto a known volume (usually 250 ml) . An aliquot of this made up solution was used for estimating the amount of Copper Sulphate and Zinc Sulphate .The entire experiment was repeated with the same initial amounts of salts but varying amounts of water. Similarly the experiment was repeated for different ‘a’ values.

Analytical Techniques

It was essential to adopt suitable analytical techniques for the analysis of mixtures of the systems. The primary concern here was that the methods of analysis should be quick and accurate. Hence the following were the procedures adopted for the chosen system.

Titration I

For the analysis of total amounts of copper Sulphate and Zinc Sulphate , a known aliquot of the solution (obtained from moist crystals or mother liquor) was pipette out into a clean 250 ml conical flask. It is diluted to about 100 ml. Solid hexamine was added to maintain the pH at about 5 to 6. It was titrated against standard EDTA using PAN indicator. At the end point the colour changed to green from blue. This gives the titre value corresponding to total amounts of Copper and Zinc present in the aliquot taken.

Titration II

The amount of Copper salt alone was determined iodometrically from second aliquot as follows :

The aliquot was pipette out into a conical flask and the mineral acid present was neutralized with ammonium hydroxide drop wise until a slight precipitate of Cupric hydroxide is formed. Then 1:1 acetic acid was added just to dissolve the precipitate of Cupric hydroxide and then 4 to 5 drops in excess. The solution was diluted to 50 ml and 20 ml of 20 % Potassium Iodide solution was added. The liberated iodine was titrated immediately with standard Thiosulphate solution using 1% starch solution as indicator towards the end of the titration. The end point is the disappearance of the blue colour and the appearance of creamy white precipitate. This gives the titre value corresponding to the amount of Copper salt alone in the aliquot taken. By subtracting this value from the total amount , the amount of Zinc Sulphate in the aliquot taken was obtained. Titrations were repeated for concordant values. The quantities determined during the course of the experiments are:

1. Weight of Salt A taken = W_1 gm
2. Weight of Salt B taken = W_2 gm
3. Weight of water taken = W_3 gm
4. Weight of mother liquor = W_4 gm
5. Weight of moist crystals = W_5 gm
6. Weight of Salt A in moist crystals = W_6 gm
7. Weight of Salt B in moist crystals = W_7 gm

In order to calculate D and λ and w and y of equation [1] , it is necessary to know the composition of both solid and the liquid phases. The analysis of moist crystals yields the amount of the two salts in the solid phase but this also includes the amount of salts present in the adhering mother liquor. Obviously a correction has to be made for tha amounts of salt A and B present in the adhering mother liquor. The method employed here is identical with Schreinmaker’s method. The weight of water present in the moist crystals and the amount of salts held by this water were calculated from the weight of mother liquor and the amounts of salts present in it. The calculations were carried out as follows :

Weight of salt A in mother liquor = $w_1 - w_6 = w_8$

Weight of salt B in mother liquor = $w_2 - w_7 = w_8$

Weight of salt A in mother liquor = $w_4 - (w_8 + w_9) = w_{10}$

Weight of water present in the mother
Liquor adhering to moist crystals = $w_3 - w_{10} = w_{11}$

Weight of salt A present in w_{11} gm of water = $w_8 X w_{11}/w_{10} = \partial M_A$

Weight of salt B present in w_{11} gm of water = $w_9 X w_{11}/w_{10} = \partial M_B$

Corrected weight of salt A in crystals = $w_6 - \partial M_A = w_{14}$

Corrected weight of salt B in crystals = $w_7 - \partial M_B = w_{15}$

Corrected weight of W crystals = $w_{14} + w_{15}$

The values of λ and D are calculated as follows :

$$\lambda = \frac{\log \dfrac{(\text{Amt.A})_{\text{initial}}}{(\text{Amt.A})_{\text{final}}}}{\log \dfrac{(\text{Amt.A})_{\text{initial}}}{(\text{Amt.A})_{\text{final}}}} = \frac{\log \dfrac{w_1}{w_1 - w_{14}}}{\log \dfrac{w_2}{w_2 - w_{15}}} \qquad \text{Where}$$

$(\text{Amt.A})_{\text{initial}}$ = weight of A in solution
before crystallization = w_1

$(\text{Amt.A})_{\text{final}}$ = weight of B in solution
before crystallization = $W_1 - W_{14}$

$(\text{Amt.B})_{\text{initial}}$ = weight of B in solution
before crystallization = w_2

$(\text{Amt.B})_{\text{final}}$ = weight of B in solution

D is given by the expression :

$$D = \frac{(\text{Amt.A in crystals})}{(\text{Amt A in solution})_{\text{final}}} \text{ X } \frac{(\text{Amt.B in solution})_{\text{final}}}{(\text{Amt.B in crystals})}$$

$$= \frac{w_{14}}{w_{15}} \text{ X } \frac{(w_2 - w_{15})}{(w_2 - w_{15})}$$

(Amt.A in crystals) = Weight of A in solid phase $= w_{14}$

(Amt.B in crystals) = Weight of B in solid phase $= w_{15}$

(Amt A in solution) $_{\text{final}}$ = weight of A in solution after crystallization $= w_1 - w_{14}$

(Amt B in solution) $_{\text{final}}$ = weight of B in solution after crystallization $= w_2 - w_{15}$

When m = 1,

$$q_0 = - 0.5 y^2_0 \; [1/k (1 – a)] \text{ X } (y_0 – a) / a(1 – a)$$
$$= - 0.5 y^2_0 \; (y_0 - a) / k.a^2)$$

Thus for a given system and a given ‘a’ values , the values of $\mathbf{q_0}$ and y_0 depend upon the constants k and m. The value of w and y can be calculated by modified Euler’s method as follows :

Initial condition of $y = y_0$, $- dy / dw = q_0$ when **w = 0**
Let a quantity Δw crystallises out. Then $w = \mathbf{w_1} = \Delta w$ and the first approximation of y is given as ${}^1y_1 = \mathbf{y_0} + \mathbf{q_0} \Delta w$
The first approximation of q is calculated as ,

$${}^{1q}{}_1 = 1/w [1/ 1+ [1/k (1- w / a – w\, {}^1y_1) – 1] - {}^1y_1]$$

Second approximation of y1 = 2y1 = y0 (q0 +1q1/ 2) Δw
Second approximation of q_1 ,

$$\mathbf{{}^{2q}{}_1 = 1/w [1/ 1+ [1/k (1- w / a – w\, {}^2y_1) – 1] - {}^2y_1]}$$

This is carried out till successive approximation of y have the same values nearly .Now the initial condition for the second step is $y = y_1$; $q = q_1$ when $w = w_1$ again let w crystallize out ; then $w = w_{1} + \Delta w = w_{2} + \Delta w = \mathbf{w_2}$
First approximation q

$${}^{1q}{}_2 = 1/w [1/ 1+ [1/k (1- w / a – w\, {}^1y_2) – 1] - {}^1y_2] \text{ etc.,}$$

till concordant values are obtained for y2 . the calculations were continued for successive values of W = 0.1 , 0.15 , 0.2 , 0.25 etc.,

Calculation of w and y from equation

The differential equation can only be solved by numerical methods of integration. Modified Euler’s method of successive approximation can be employed. The initial conditions required for these calculations were obtained as follows : Equation can be written as ,

$$y = - dy/dw$$
$$= 1_/1+M_{B/}M_A [1/k (1- w / a – w y) –1] \; M_{B/}M_A]^{1/m}$$

When m = 1

$${}^q{}_{0 =} \; {}_{1 / 1 +} [1/k (1 –a / a)]$$

writing ${}^q{}_{0 \text{ for the initial slope} – dy / dx , \; w = 0}$

$${}^q{}_{0 = -} -0.5 y^2_0 \; M_{B/}M_A *1/m[1/k (1 –a / a)]^{1/m} \text{ X } (y_0 – a) / a(1-a)$$

a typical calculation is given below for the system , Zinc Sulphate - Copper Sulphate – Water

a = 0.75 ; k = 4.72 and m = 1

Likewise Y_{Theory} was calculated for each and every experimental ‘w’ and approximately placed in the tabular columns.

RESULTS AND DISCSSION

Results

The results are presented in tables 1 to 14. The table 1 to 6 contain the results for the system $CuSO_4$ - $ZnSO_4$ - Water in the form required to verify equations (3) , (6) , and (16) . Table 7 gives the comparison of ‘λ’ and ‘D’ values of k chosen for every experiment. Tables 9 to 14 gives the percentage of water molecules present in the mixed crystal for every ‘a’ value.

Discussion

We can devide the discussion into two parts:

PART I: We can consider the verification of equation [3] and [6] in this part. If at all we want to verify the equation [3] and [6] , we should prove that the values of λ should be constant and the values of D should also be a constant. If we consider the Table [7], we come to know that the values of λ and D are not constants. The non – constancy can be attributed to the non – equilibrium nature of the system. T true equilibrium will be attainable only if the system is kept in isothermal conditions for a minimum perid of four days or a maximum period of seven days. So non – equilibrium kinetic model would be more appropriate. In this model λ was related to the rate of precipitation. The λ values are tending towards D. in the system a =0.1 , [micro component is 2 gms and macro component is 18 gms.] the amount of less soluble salt is 10% and more soluble salt is 90%. So in the crystal lattice a constant amount of less soluble salt may be present when we consider the terms of probability. Therefore variation of λ and D can be attributed to a variation in the rate of crytallisation and to the non – equilibrium nature of the system.

PART II: now we can consider the applicability of equation [16]. It is of practical importance. This predicts the amount of less soluble salt that will be present in crystal that are growing. In all experiment the value of k is same as to λ values. In our case $CusO_4.5H_2O$ - $ZnSO_4 .7H_2O$ - H_2O , THE number of molecules of water of hydration plays an important role. When the amount of $CusO_4.5H_2O$ is higher during the mixed crystal formation , the mixed crystal that will be formed after 6 hours also has only 5 water molecules each. Even though $ZnSO_4$ has 7 water molecules, as water of crystallization , during the mixed crystal formation ,it has only five molecules of water of hydration. When the amount of $ZnSO_4 .7H_2O$ is more , the mixed crystal formed will be having 7 water molecules as the water of hydration. That is $CusO_4.5H_2O$ - $ZnSO_4 .5H_2O$ – water and $CusO_4.7H_2O$ - $ZnSO_4 .7H_2O$ - water as

Table 1.

W	Y_{Theory}	
0.00	Y_0	0.9340
0.05	Y_1	0.9324
0.10	Y_2	0.9307
0.15	Y_3	0.9289
0.20	Y_4	0.9270
0.25	Y_5	0.9248
0.30	Y_6	0.9225

a = 0.999 temperature : 28 ^{0} c

W_1 = Initial weight of Copper Sulphate = 18 gm

W_2 = Initial weight of Zinc Sulphate = 2 gm

Table 2.

Expt. No.	Wt. of water W_3	Corrected Salts in$CuSO_4$ W_{14}	Wt.of Crystals Zn SO_4 W_{15}	Correctd Wt. of crystals $W_{14} + W_{15}$	λ	D	$W_{Expt.}$	$y_{Expt.}$	Y_{Theory}	k
1.	15.44	12.331	0.537	12.868	3.71	5.94	0.6434	0.958	0.959	3.76
2.	15.03	12.140	0.517	12.657	3.75	5.94	.6329	0.959	0.959	3.76
3.	14.01	12.469	0.557	13.026	3.72	5.98	0.6513	0.959	0.959	3.76
4.	13.04	12.611	0.553	13.164	3.73	6.12	0.6582	0.958	0.958	3.76
5.	11.99	12.874	0.567	13.441	3.76	6.35	0.6721	0.958	0.958	3.76
Average					3.76	6.07				

a = 0.750 temperature : 28 ^{0} c

W_1 = Initial weight of Copper Sulphate = 15 gm

W_2 = Initial weight of Zinc Sulphate = 5 gm

Table 3.

Expt. No.	Wt. of water W_3	Corrected Salts in$CuSO_4$ W_{14}	Wt.of Crystals Zn SO_4 W_{15}	Correctd Wt. of crystals $W_{14} + W_{15}$	λ	D	$W_{Expt.}$	$y_{Expt.}$	Y_{Theory}	k
1.	16.88	8.694	0.822	9.516	4.82	7.02	0.4758	0.914	0.913	4.90
2.	16.35	8.657	0.792	9.449	5.00	7.25	0.4725	0.916	0.914	4.90
3.	14.00	9.364	0.892	10.256	4.98	7.65	0.5128	0.913	0.916	4.90
4.	13.18	9.704	0.941	10.645	4.99	7.90	0.5328	0.912	0.909	4.90
5.	12.03	10.226	1.077	11.203	4.72	7.78	0.5652	0.905	0.906	4.90
Average					4.90	7.52				

a = 0.666 temperature : 28 ^{0} c

W_1 = Initial weight of Copper Sulphate = 15 gm

W_2 = Initial weight of Zinc Sulphate = 7. 5 gm

Table 4.

Expt. No.	Wt. of water W_3	Corrected Salts in$CuSO_4$ W_{14}	Wt.of Crystals Zn SO_4 W_{15}	Correctd Wt. of crystals $W_{14} + W_{15}$	λ	D	$W_{Expt.}$	$y_{Expt.}$	Y_{Theory}	k
1.	16.03	8.921	1.920	10.841	3.06	4.27	0.4818	0.823	0.823	3.08
2.	15.01	9.335	2.016	11.351	3.11	4.48	0.5044	0.822	0.821	3.08
3.	14.01	10.254	2.423	12.677	2.95	4.53	0.5634	0.809	0.813	3.08
4.	14.10	10.254	2.574	13.258	2.96	4.74	0.5892	0.806	0.809	3.08
5.	12.00	11.122	2.516	13.638	3.31	5.68	0.6061	0.816	0.807	3.08
Average					3.08	4.74				

a = 0.5 temperature : 28 ^{0} c

W_1 = Initial weight of Copper Sulphate = 10 gm

W_2 = Initial weight of Zinc Sulphate = 10 gm

Table 5.

Expt. No.	Wt. of water W_3	Corrected Salts in$CuSO_4$ W_{14}	Wt.of Crystals Zn SO_4 W_{15}	Correctd Wt. of crystals $W_{14} + W_{15}$	λ	D	$W_{Expt.}$	$y_{Expt.}$	Y_{Theory}	k
1.	11.70	1.269	1.091	2.360	3.88	4.35	0.1180	0.538	0.535	3.83
2.	11.20	1.401	1.231	2.632	3.84	4.48	0.1316	0.532	0.532	3.83
3.	10.50	1.725	1.599	3.324	3.75	4.41	0.1662	0.519	0.523	3.83
4.	10.00	1.852	1.708	3.560	3.83	4.58	0.1780	0.520	0.520	3.83
Average					3.83	4.54				

a = 0.333 temperature : 28 ^{0} c

W_1 = Initial weight of Copper Sulphate = 7.5 gm

W_2 = Initial weight of Zinc Sulphate = 15 gm

Table 6.

‘a’values	‘λ’ values for Expt.					‘D’ values for Expt				
	1	2	3	4	Average	1	2	3	4	Average
0.900	3.71	3.75	3.72	3.73	3.76	5.94	5.94	5.98	6.12	6.07
0.750	4.82	5.00	4.98	4.99	4.90	7.02	7.25	7.65	7.90	7.52
0.666	3.06	3.11	2.95	2.96	3.08	4.27	4.48	4.53	4.74	4.74
0.500	4.46	4065	3.88	4.17	4.29	5.13	5.64	4.82	5.68	5.32
0.333	3.75	3.53	3.99	3.40	3.63	4.06	4.03	4.73	4.20	4.30
0.250	3.88	3.84	3.75	3.83	3.83	4.35	4.48	4.41	4.58	4.54
AVERAGE					3.40	AVERAGE				4.68

a = 0.250 temperature : 28^{0} c

W_1 = Initial weight of Copper Sulphate = 5 gm

W_2 = Initial weight of Zinc Sulphate = 15 gm

Table 7. comparison of ‘λ’ and ‘D’at different ‘a’ values

‘a’values	1	2	3	4	5
0.900	3.76	3.76	3.76	3.76	3.76
0.750	4.90	4.90	4.90	4.90	4.90
0.666	3.08	3.08	3.08	3.08	3.08
0.500	4.46	4.46	4.46	4.46	-
0.333	3.63	3.63	3.63	3.63	3.63
0.250	3.83	3.83	3.83	3.83	3.83

Table 8. The values of ‘k’ chosen every experiment

Expt. No.	Wt. of water W_3	Corrected Salts in$CuSO_4$ W_{14}	Wt.of Crystals Zn SO_4 W_{15}	Correctd Wt. of crystals $W_{14} + W_{15}$	λ	D	$W_{Expt.}$	$y_{Expt.}$	Y_{Theory}	k
1.	17.02	2.948	0.754	3.702	4.46	5.13	0.1851	0.796	0.796	4.46
2.	16.02	3.743	0.959	4.702	4.65	5.64	0.2351	0.796	0.790	4.46
3.	15.00	4.244	1.326	5.570	3.88	4.82	0.2785	0.762	0.768	4.06
4.	14.02	5.129	1.586	6.715	4.17	5.68	0.3358	0.764	0.770	4.46
Average					4.29	5.32				

Table 9.

Expt. No.	Wt. of water W_3	Corrected Salts in$CuSO_4$ W_{14}	Wt.of Crystals Zn SO_4 W_{15}	Correctd Wt. of crystals $W_{14} + W_{15}$	λ	D	$W_{Expt.}$	$y_{Expt.}$	Y_{Theory}	k
1.	16.01	1.458	0.841	2.299	3.75	4.06	0.1022	0.634	0.627	3.63
2.	15.02	2.245	1.439	3.684	3.53	4.03	0.1637	0.639	0.608	3.63
3.	14.01	2.637	1.544	4.181	3.99	4.73	0.1858	0.631	0.610	3.63
4.	13.00	3.248	2.296	5.534	3.40	4.20	0.2460	0.585	0.587	3.63
Average					3.63	4.30				

weight of Copper Sulphate = 18 gm

weight of Zinc Sulphate = 2 gm

a = 0.900

Table 10.

	1	2	3	4	5
Wt. crucible +mixed crystal	43.329	39.923	41.990	38.485	40.804
Wt. of crucible	32.863	30.220	32.863	30.221	32.862
Wt. of mixed crystal initially	10.466	9.703	9.127	8.264	7.942
Wt. cruicible + mixed crystal after heating	39.351	36.141	38.527	35.292	37.791
Wt.. of mixed crystal finally	6.488	5.921	5.664	5.071	4.929
Wt. of water lost	3.978	3.782	3.463	3.193	3.013
% of water lost	38.01	38.96	37.95	38.64	37.94
Average % of water lost	38.23				

weight of Copper Sulphate = 15 gm

weight of Zinc Sulphate = 5gm

a = 0.75

Table 11

	1	2	3	4	5
Wt. crucible +mixed crystal	43.548	40.785	42.896	39.378	41.508
Wt. of crucible	42.863	30.221	32.863	30.221	32.863
Wt. of mixed crystal initially	10.685	10.564	10.033	9.157	8.645
Wt. cruicible + mixed crystal after heating	39.552	36.934	39.119	35.904	38.353
Wt.. of mixed crystal finally	6.689	6.713	6.256	5.683	5.490
Wt. of water lost	3.996	3.851	3.777	3.474	3.155
% of water lost	37.84	36.46	36.87	37.94	36.50
Average % of water lost	37.12				

weight of Copper Sulphate = 15 gm

weight of Zinc Sulphate = 7.5 gm

a = 0.666

Table 12.

	1	2	3	4	5
Wt. crucible +mixed crystal	42.682	44.905	41.763	43.139	40.085
Wt. of crucible	30.221	32.863	30.221	32.863	30.221
Wt. of mixed crystal initially	12.461	12.042	11.542	10.276	9.864
Wt. cruicible + mixed crystal after heating	37.714	40.211	37.256	39.168	36.845
Wt.. of mixed crystal finally	7.493	7.348	7.035	6.305	6.624
Wt. of water lost	4.968	4.694	4.507	3.971	3.924
% of water lost	39.87	38.98	39.05	38.64	39.78
Average % of water lost	39.26				

weight of Copper Sulphate = 10 gm
weight of Zinc Sulphate = 10 gm
a = 0.500

Table 13.

	1	2	3	4	5
Wt. crucible +mixed crystal	39.475	35.649	37.495	33.738	35.341
Wt. of crucible	32.863	30.221	32.863	30.221	32.863
Wt. of mixed crystal initially	6.612	5.428	4.632	3.517	2.478
Wt. cruicible + mixed crystal after heating	36.683	33.671	35.519	32.231	34.281
Wt.. of mixed crystal finally	3.820	3.150	2.656	2.010	1.418
Wt. of water lost	2.792	2.278	1.976	1.507	1.060
% of water lost	42.24	41.98	42.65	42.84	42.78
Average % of water lost	42.50				

weight of Copper Sulphate = 7.5 gm
weight of Zinc Sulphate = 15 gm
a = 0.333

Table 14.

	1	2	3	4	5
Wt. crucible +mixed crystal	35.620	37.138	33.462	35.394	31.381
Wt. of crucible	30.221	32.862	30.220	32.863	30.221
Wt. of mixed crystal initially	5.399	4.276	3.242	2.531	1.160
Wt. cruicible + mixed crystal after heating	33.225	35.257	32.019	34.284	30.858
Wt.. of mixed crystal finally	3.004	2.395	1.799	1.421	0.637
Wt. of water lost	2.395	1.881	1.443	1.110	0.523
% of water lost	44.36	43.98	44.52	43.87	44.86
Average % of water lost	44.32				

weight of Copper Sulphate = 2 gm
weight of Zinc Sulphate = 18 gm
a = 0.100

crystallization process. This information is base on calculation of number of water molecules lost from the mixed crystals formed. Thus our object of specifying the k and λ values. For the system is fulfilled , and we have also seen that the Henderson – Kracek equation and Doerner – Hoskin's equation could not be verified because the system is an out and out non – equilibrium system.

Abstract

In our work two isomorphous salts , $CusO_4.5H_2O$ - $ZnSO_4.$ $7H_2O$ were taken. They were allowed to crystallize after dissolving them in water at various ratios. Then the crystals were analyzed by titrometry technique. Many equations suggested for co-crystallization of salts, in equilibrium and non-equilibrium conditions, were tested. Finally it is found that our system obeys the laws applicable for non-equilibrium condition. Further is also found that in the crystallization of mixed salt , the mixed crystals contain the same number of water of hydration molecules in both salts as the number of molecules salt which in greater amount . for example in our case when the amount of copper sulphate is greater , then the mixed crystal Zinc sulphate also contains 5 water molecules and vice versa. This finding of our work will be very useful in future to prepare a salt with a number of water molecules Different from that of its usual number of water molecules.

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