Hydrogen Isotope Fractionation in the Water of Hydration of Crystals

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Hydrogen Isotope Fractionation in the Water of Hydration of Crystals

Hydrogen isotope fractionation in the water of hydration of several crystals was studied. Dehydration of $CuSO_4 \cdot 5H_2O$ in stages shows that in general water containing deuterium is preferentially retained in the crystal. Some variations from this general trend are observed at the composition of $CuSO_4 \cdot 3H_2O$ and $CuSO_4 \cdot H_2O$. These variations can be explained as being due to a change in the manner in which the water coming off was held in the crystal. Similar behavior is observed for $ZnSO_4 \cdot 7H_2O$. Rehydration of anhydrous $CuSO_4$ with distilled water indicates that heavy water is preferentially incorporated into the hydrated crystals. Experiments circulating water vapor over $CuSO_4 \cdot 5H_2O$ crystals indicate that isotopic equilibrium is obtained only very slowly. The time at room temperature is probably well over 68 hours for vapor that started with about 30% less heavy water than the expected equilibrium value. Water samples were analyzed by passing the vapor over hot uranium metal to reduce the hydrogen in the water to hydrogen gas and using a mass spectrometer to obtain the D/H ratios relative to a standard sample.

Hydrogen isotope fractionation has been studied for many types of waters, but the fractionations in the water of hydration of crystals has been largely ignored. In work that has been done density methods have been use to measure the isotope ratios. These methods are much less precise than the ±1 per mil precision obtainable with high precision mass spectrometry used in the experiments described here.[1] Some work has been done by Peinelt, Maass, and Heuber[2] on oxygen exchange reactions in inorganic hydrates, again using density methods, but no descriptions of previous high precision work on hydrogen exchange in inorganic hydrates could be found.

In the experiments described here samples of copper sulfate pentahydrate, zinc sulfate heptahydrate, and sodium sulfate decahydrate were dehydrated in stages. The hydrogen isotope fractionation was determined for each aliquot of water removed. Fractionation was then plotted against the percent of water removed at that stage.

Several attempts were made to partially rehydrate the anhydrous copper sulfate that resulted from the dehydration with water of known hydrogen isotope composition. Attempts were also made to equilibrate copper sulfate pentahydrate with water of known composition in a system that circulated the

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[1] Taylor, Trans. Amer. Geophys. Un., Vol. 47, No. 1, p. 287 (Mar., 1966).

[2] Peinelt, Maass, and Hueber, Abh. Deut. Akad. Wiss. Berlin, Kl. Chem., Geol., Biol. 1964(7), 765-7. (Pub. 1965).

water as vapor over and through the salt.

Experimental

All salts used were analytical reagents in the fine crystal form.

Figure 1 is a sketch of the apparatus used for the dehydration of the copper sulfate pentahydrate. Bulb B contained the copper sulfate sample and Bulb A was used to give the system enough volume to allow sufficient water to be in the vapor phase at one time to provide a sample large enough for the mass spectrometer. The total volume of the system to the right of stopcock E was approx. 1200 ml. The salt sample was weighed into Bulb B, and Bulb B was then attached to the system and immersed in liquid nitrogen to freeze the water in the sample. All stopcocks were opened to evacuate the system. A mechanical pump and a mercury diffusion pump were used as the source of the vacuum. Stopcock F was then closed, the sample in Bulb B briefly thawed, refrozen, and again pumped on by reopening stopcock F. Stopcock E was closed, the liquid nitrogen removed, and water left the crystals going into the system as vapor. The system was allowed to stand at room temperature until the pressure over the crystals reached equilibrium. The pressure was considered to be at equilibrium when the mercury manometer showed no change in pressure over a period of about an hour. After the pressure reached equilibrium stopcocks F and G were closed, stopcocks E and I were

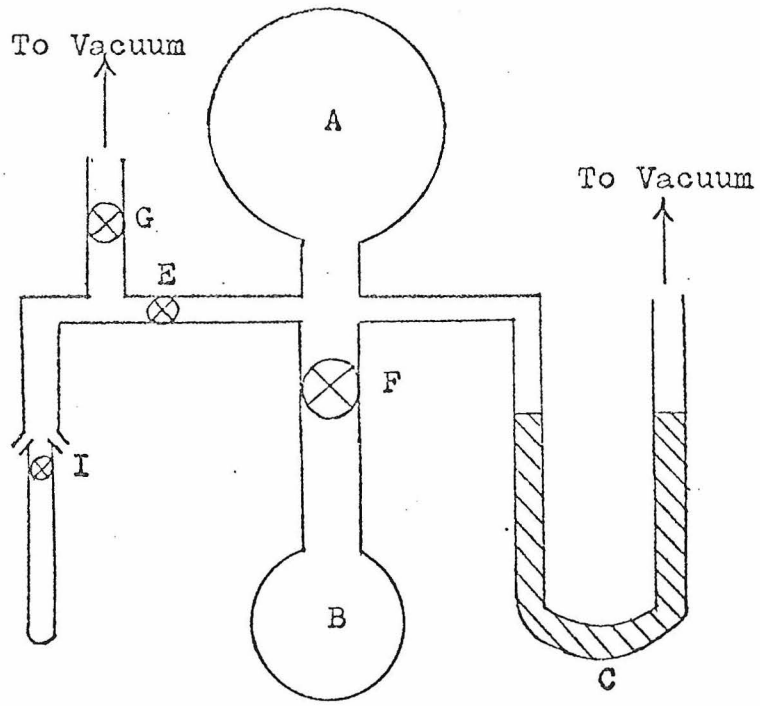

Figure 1

Apparatus for $CuSO_4 \cdot 5H_2O$ Dehydration

A- 1 liter bulb
B- Approx. 20 ml. bulb for $CuSO_4 \cdot 5H_2O$ Sample
C- Mercury manometer
D- Sample tube into which water samples were frozen
E,F,G,I- Stopcocks

opened and the water vapor frozen with liquid nitrogen into sample tube D. From the pressure before freezing, the volume of the system, and the temperature of the vapor before freezing, the amount of water collected in the sample tube could be calculated. The first sample of copper sulfate pentahydrate consisted of 1.4547 grams. Four sample tubes of water (RB 1-RB 4) were collected from this sample. Each tube had several aliquots of water vapor frozen into it and the total amount of water in each tube was calculated. Only about 20% of the total water in the sample was removed in these four tubes. After taking the four samples it became apparent that the sample was too large to allow for complete dehydration in a reasonable length of time. The partially dehydrated copper sulfate sample was replaced by a smaller 0.3573 gram sample of copper sulfate pentahydrate. A complete dehydration was done on this sample and water samples RB 6 to RB 20 were collected. RB 6 to RB 9 were collected in the same way described for RB 1 to RB 4. For RB 10 the copper sulfate was heated by immersing the bulb containing it in a hot water bath to get the water vapor pressure up. The pressure was then allowed to equilibrate as previous samples had before being frozen out. Samples RB 11 to RB 17 were heated with the gas-air flame of a hand torch to get the pressure up before equilibrating and freezing. RB 18 to RB 20 were heated with the hand torch but the pressure was not allowed to equilibrate before freezing. RB 20 was heated hard to make sure all water was driven off. Due to what looked like contamination of RB 20 with sulfur compounds,

RB 20 was not processed any further except for determining the weight of the water. Some of the very first water to come off this sample was lost. The amount lost was assumed to be the difference between the total amount of water collected and the total amount of water calculated to be in the sample.

The hydrogen in the water samples was collected by passing the water as vapor over hot uranium metal in the apparatus shown in Fig. 2. The sample tube containing the water was put into the system at A and the system was evacuated. The water was then frozen with liquid nitrogen into the side arm B and any non-condensable gases were pumped out. The water was then frozen into the trap at C and the system again pumped on to remove any non-condensable vapors that had been previously trapped in the ice. As the water in C was allowed to thaw its own vapor pressure carried it over the hot (600-700°C) uranium metal at D where the hydrogen in the water was reduced to hydrogen gas. Toepler pump (F) pumped the hydrogen gas to sample tube G. The amount of gas collected from each sample was measured first by trapping the hydrogen gas below stopcocks I and K and raising the mercury level above the pump to the level of M. The difference in mercury height between M and the mercury level in tube N was used with the previously determined volume of the system between M and I and K and the temperature to calculate the amount of hydrogen collected. The hydrogen was then allowed to go into sample tube G. This method was used to determine the amount of water given off at each stage of dehydration for all samples except RB 1 to RB 4.

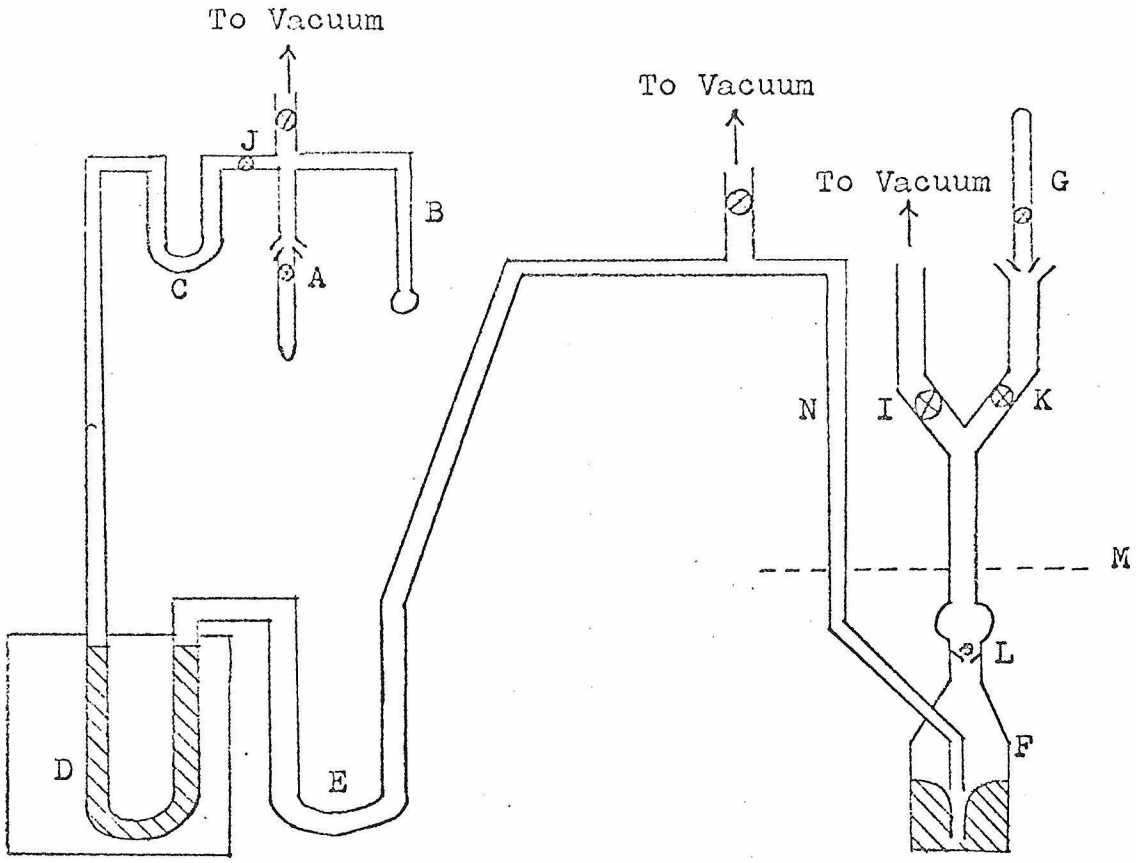

Figure 2

Uranium Line for Freeing Hydrogen from Water Samples

A- Water containing sample tube
B- Side arm into which water is first frozen
C- Trap into which water is refrozen
D- Uranium metal in U-tube in oven
E- Cold trap
F- Toepler pump
G- Sample tube for hydrogen gas
I,J,K- Stopcocks
L- Ball valve
M- Manometer reference level

The hydrogen gas samples were then run through the mass spectrometer which gave the deviation of the D/H ratio in the hydrogen sample from the D/H ratio in a standard. The deviations are reported as δ values.

$$\delta = \left[\frac{(D/H)_{sample}}{(D/H)_{Standard}} - 1\right] 100$$

This differs from the standard definition for δ[3]

$$\delta = \left[\frac{R_{Sample}}{R_{Standard}} - 1\right] 1000$$

where R is an isotope ratio

only in changing the factor 1000 to 100. This results in the δ's in this paper being in units of per cent rather than per mil. Thus δ=+1 implies that the sample is 1% richer in D than is the standard. Table I summarizes the results of RB 1 to RB 4 and RB 6 to RB 20, and Fig. 3 is a plot of δ vs. % of water removed from the copper sulfate pentahydrate.

A zinc sulfate heptahydrate sample was dehydrated. The system used was the same as that shown in Fig. 1 except that the 1 liter bulb (A) was replaced with a small cap. The method of dehydration used for the zinc sulfate was different than the method used for the copper sulfate in that the vapor was frozen immediately into the sample tube without letting the pressure first equilibrate. After enough water for a mass spectrometer run had been accumulated in the sample tube, stopcocks E and I were closed, the sample tube

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[3]Epstein, "Variations of the O^{18}/O^{16} Ratio in Nature and Some Geologic Implications," in Researches in Geochemistry, ed. by P.H. Abelson, New York, John Wiely & Sons, 223, 1959.

Table I

$CuSO_4 \cdot H_2O$ Dehydration

Weight of Samples:
For RB 1 to RB 4 1.4547 gm.
For RB 6 to RB 20 0.3573 gm.

Sample #	Moles hydrogen	% Total water in sample	% Total water off at this pt.	δ(%)	Notes
RB 1	.00201	6.94	6.94	0.14	
RB 2	.00146	4.69	11.9	0.78	
RB 3	.00178	6.2	18.1	1.16	
RB 4	.000565	1.9	20.0	1.98	
RB 6	.000738	10.32	21.92	1.72	First 11.6% of water lost.
RB 7	.000640	8.93	30.85	2.62	
RB 8	.000450	6.29	37.14	3.43	
RB 9	.000370	5.19	42.33	2.06	
RB 10	.000315	4.39	46.72	2.15	Hot water heated
RB 11	.000532	7.48	54.20	3.05	1st torch heated
RB 12	.000567	7.90	62.10	4.01	
RB 13	.000462	6.50	68.60	3.39	
RB 14	.000434	6.00	74.6	4.08	
RB 15	.000384	5.4	80.0	5.03	
RB 16	.000194	2.7	82.7	5.72	
RB 17	.000210	2.9	85.6	5.76	Two aliquots
RB 18	.000405	5.7	91.3	7.53	1st not allowed to pressure equilibrate
RB 19	.000455	6.5	97.8	6.73	
RB 20	.000161	2.2	100.0	----	Only amount of hydrogen determined

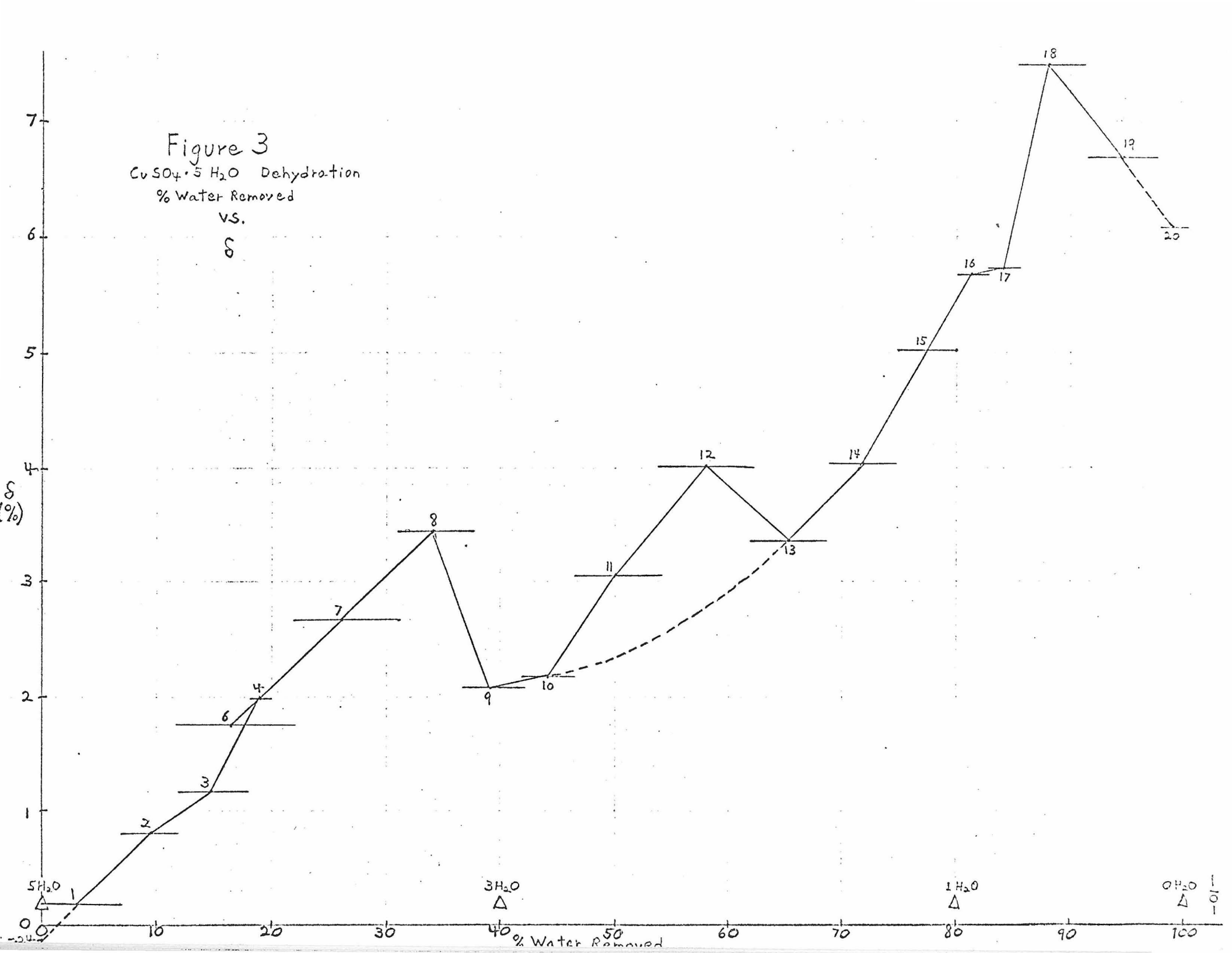


Figure 3
CuSO4·5 H2O Dehydration
% Water Removed
vs.
δ
δ (%)
% Water Removed
5H2O
3H2O
1H2O
0H2O
1
2
3
4
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

was removed, a new sample tube put in place and evacuated, stopcocks E and I opened, and the next sample was frozen out. Zn 1 to Zn 8 came off at room temperature while to get Zn 9 and Zn 10 the zinc sulfate had to be heated with the gas-air flame of the hand torch. Zn 10 was heated hard to be sure all the water came off. The water samples were treated identically with the water samples obtained from the copper sulfate. Table II shows the results of the zinc sulfate dehydration and Fig. 4 is a plot of δ vs. % of water out of the zinc sulfate.

A 0.2325 gram sample of sodium sulfate decahydrate was prepared and dehydrated the same way as the zinc sulfate sample. The salt was exposed to the atmosphere for about 10 minutes between the time the stock bottle was opened and the time the sample was frozen. Samples Na 1 to Na 5 came off at room temperature. A sixth sample could not be obtained even with hard heating from the gas-air flame of a hand torch. Table III shows the results of this dehydration and Fig. 5 is a plot of δ vs. % of total water removed. The total amount of water removed consisted of only 40.65% of the theoretical amount.

The anhydrous copper sulfate left after the pentahydrate was dehydrated was partially rehydrated. A capillary containing a known amount of distilled water was put in the system and the system evacuated. The capillary was then broken and the water entered the system. The system was given about 24 hours to equilibrate and the sample was frozen out and run through the uranium line and mass spectrometer. Several samples of the same distilled

Table II

$ZnSO_4 \cdot 7H_2O$ Dehydration

Weight of sample = 0.2197 grams

Sample #	Moles Hydrogen	% Total Water in Sample	% Total Water off at this Pt.	δ (%)	Notes
Zn 1	.000508	9.50	9.50	-0.820	
Zn 2	.000525	9.81	19.31	0.881	
Zn 3	.000525	8.70	28.01	1.389	
Zn 4	.000495	9.25	37.26	1.940	
Zn 5	.000563	10.52	47.78	2.131	
Zn 6	.000475	8.88	56.66	3.922	
Zn 7	.000980	18.32	74.98	4.265	
Zn 8	.000342	6.39	81.37	5.873	
Zn 9	.000255	4.77	86.14	8.738	1st torch heated
Zn 10	.000590	11.03	97.17	6.971	
					Other 2.83% of water not recovered.

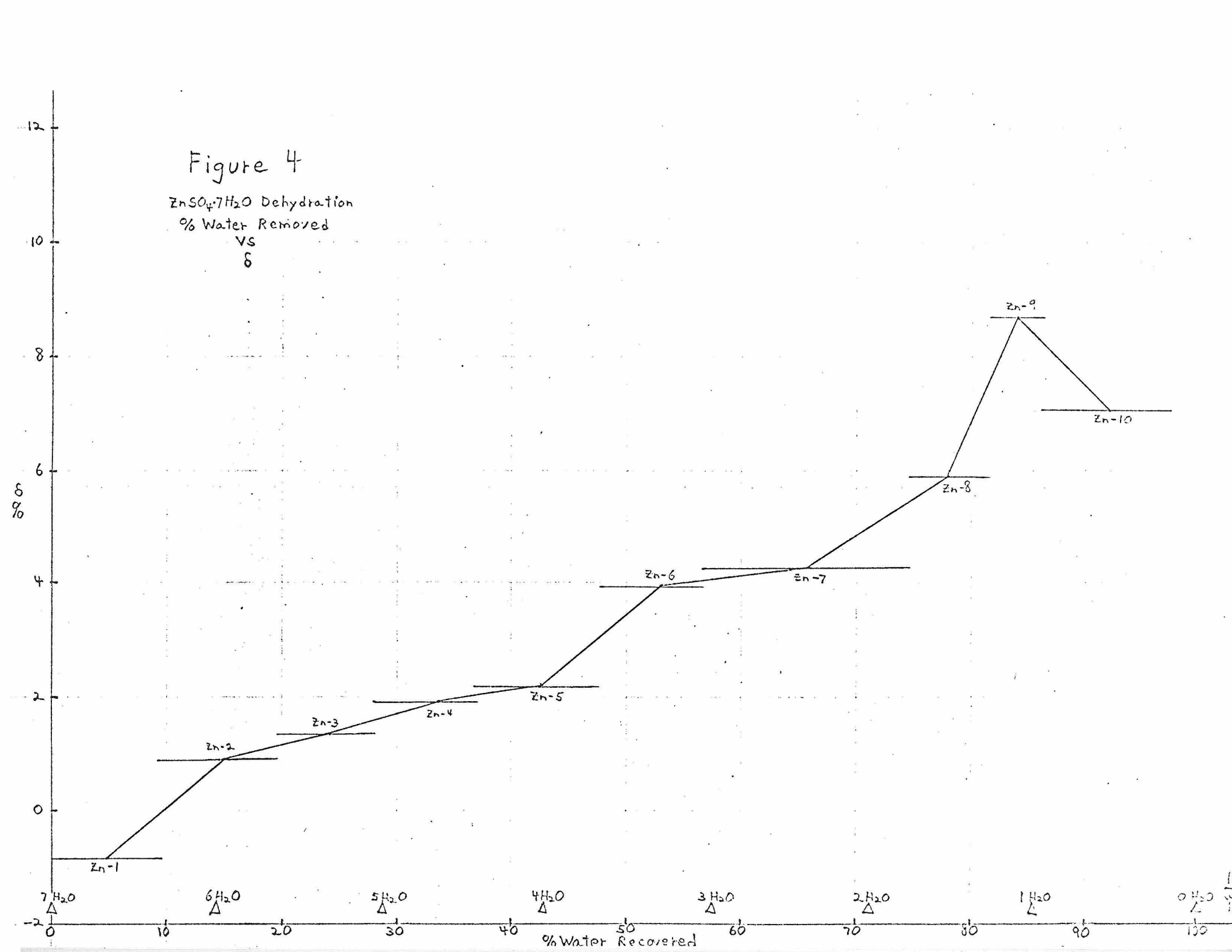


Figure 4
ZnSO4·7H2O Dehydration
% Water Removed
vs
δ
δ %
12
10
8
6
4
2
0
-2
Zn-1
Zn-2
Zn-3
Zn-4
Zn-5
Zn-6
Zn-7
Zn-8
Zn-9
Zn-10
7 H2O
6 H2O
5 H2O
4 H2O
3 H2O
2 H2O
1 H2O
0 H2O
0
10
20
30
40
50
60
70
80
90
100
% Water Recovered

Table III

$Na_2SO_4 \cdot 10H_2O$ Dehydration
Weight of Sample = 0.2325 grams

Sample #	Moles Hydrogen	% Total Water in Samole	% Total Water off at this Pt.	δ (%)	Notes
Na 1	.000362	5.01	64.36	6.162	1st 59.35% of water assumed lost
Na 2	.001038	14.37	78.73	5.267	
Na 3	.000592	8.20	86.93	6.447 6.541	Na 3 repeated
Na 4	.000544	7.53	94.46	6.244	
Na 5	.0004000	5.54	100.0	7.615	

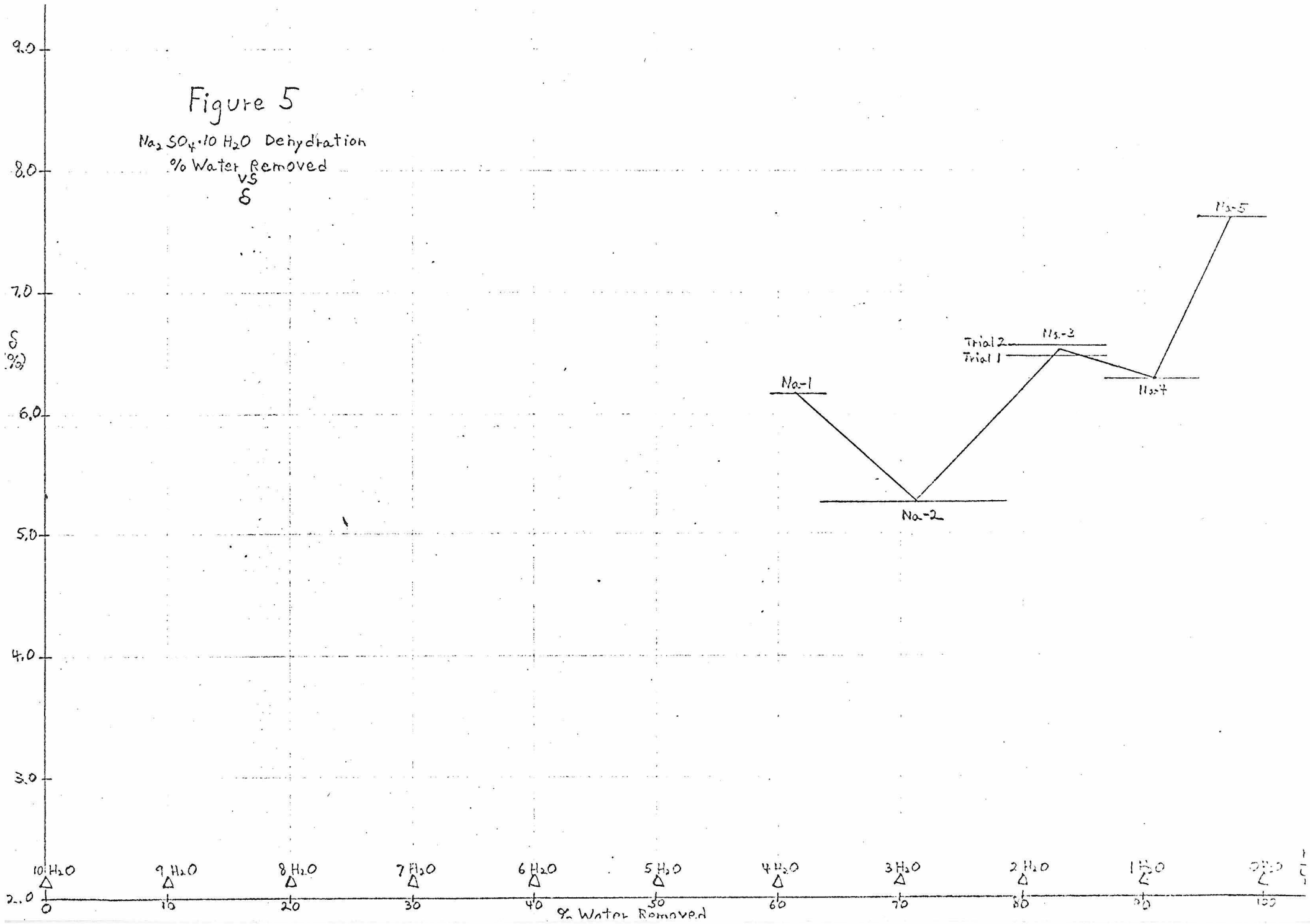
Figure 5

$Na_2SO_4 \cdot 10\,H_2O$ Dehydration

% Water Removed

VS

δ



water were run directly through the uranium line and mass spectrometer to determine the isotopic composition of the water added to the anhydrous copper sulfate. The copper sulfate was heated to dehydrate it between additions of water. Table IV shows the results of these rehydrations.

The apparatus shown in Fig. 6 was constructed and used for circulating water vapor over a sample of copper sulfate. The circulation was attempted in order to allow all the vapor to equilibrate with the water in the crystals. The U-tube (D in Fig. 6) contained 35.50 grams of copper sulfate pentahydrate when it was sealed into the system. This sample was large enough that experiments done on it would make only an insignificant change in the total isotopic composition of the water in the crystals. A dewar of liquid nitrogen was placed around the U-tube, the copper sulfate frozen, and the system evacuated. The internal volume of the system was 924.9 ml. and the volume of the part of the system from M to I to G to F was 168 ml. Samples of vapor were removed by freezing the vapor into a sample tube at B. Capillaries of water of known isotopic conposition were put in the side arm C, the system evacuated, and the capillaries broken to introduce the water into the system. Stopcocks F and G were kept closed when capillaries were inserted and sample tubes changed. This prevented the copper sulfate from being contaminated by the atmosphere. The Toepler pump (A) circulated the vapor through the system and U-tube of copper sulfate. Four samples of copper sulfate were sealed in weighing bottles at the same time the U-tube was filled. These (CC 1, CC 2, CC 5, and CC 10 in Table V) were competely dehydrated

Table IV

Anhydrous $CuSO_4$ Rehydration

Sample #	Wt. Water Added (gm)	μMoles Added	Temp °C	δ (%)	Notes
RB 21	.0882	845	33.7	-1.943	3.7 moles water per mole of salt
RB 22			32.9	-0.266	To determine composition of water added in RB 21
RB 23			33.3	-0.238	Same as RB 22
RB 26	.1274	1108	34.3	-2.47	3.46 moles water per mole salt
RB 24			33.9	-0.165	To determine composition of water added in RB 26
RB 25			34.2	-0.414	Same as RB 24
RB 27				-0.249	Same as RB 24

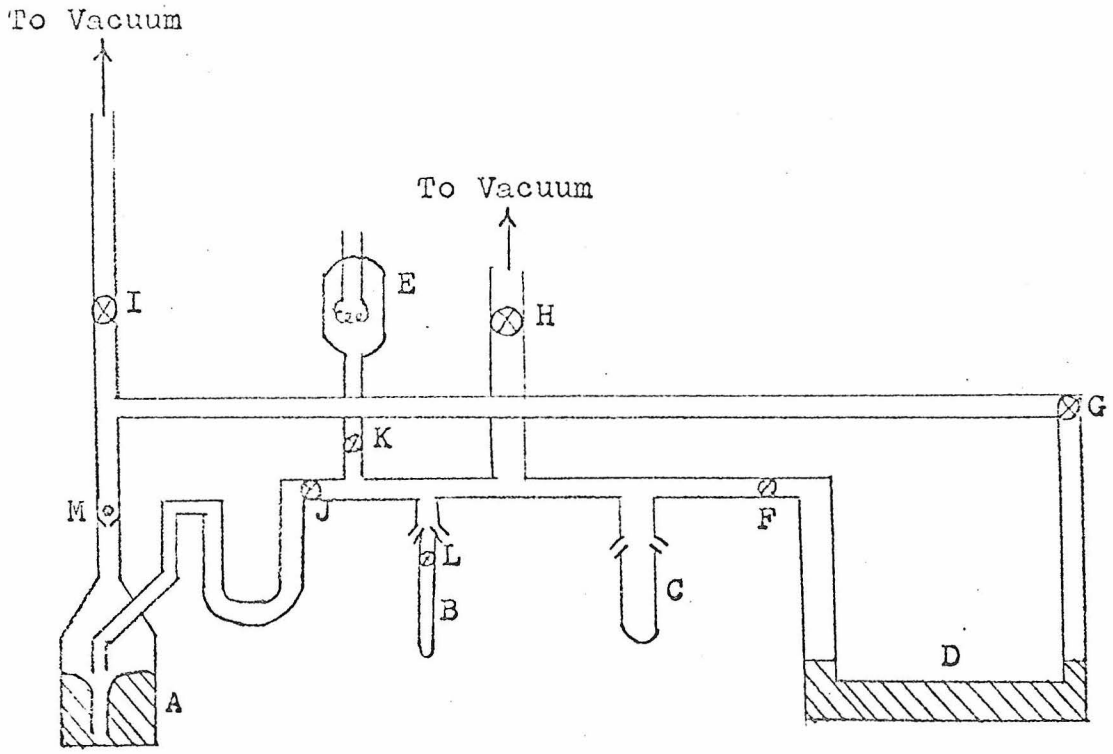


Figure 6

System for Circulating Water Vapor

A- Teopler pump for circulation vapor
B- Sample Tube
C- Side arm where water containing capillaries were inserted and broken
D- U-tube containing $CuSO_4 \cdot 5H_2O$ sample
E- Vacuum gauge
F to L- Stopcocks
M- Ball valve

Volume of system below I and H = 924.9 ml.

Volume of system along M,I,G,F = 168 ml.

Volume of system along M,A,J,L,C,F = 756.9 ml.

Table V

Circulated Samples

Complete Dehydrations of $CuSO_4 \cdot 5H_2O$ Samples

Sample #	μmoles of water out	δ (%)
CC 1	568	2.25
CC 2	786	2.86
CC 5	745	3.41
CC 10	345	0.764

Additions of δ=+8.92% water samples

Sample #	Circulation time (hrs)	Temp. C	Hydrogen μmoles out n_1	μmoles water added	δ(%)	Effective δ of added water (δ_e) (%)
CC 4	3	32.0	674	1318	2.81	8.12
CC 6	.833	32.0	1264	1829	4.68	8.46
CC 13	20	31.9	1293	1688	-3.155	6.98
CC 14	100 1/3	33.7	1015	1949	-0.567	7.37
	Additions of δ=-29.34% water samples					
CC 8	1	31.2	1064	1208	-11.852	-24.00
CC 9	3	~31.0	980	1069	-17.573	-26.15
CC 11	14	30.4	1167	1974	-20.016	-28.12
CC 12	68	30.1	1020	2620	-15,209	-28.55
	Addition of δ= ~0.0% water sample					
CC 7	3 to 15	31.7	1114	1405	1.747	0.784
	First water to come off sample naturally					
CC 3	12 to 24	30.7	620	---	0.318	---

to determine the overall isotopic composition of the water in the copper sulfate. CC 3 was composed of the first water that came off the copper sulfate in the U-tube when circulation was started. In CC 4, CC 6, CC 13, and CC 14 the water added in the capillary had a δ of +8.92‰. In CC 8, CC 9, CC 11, and CC 12 the water added had a δ of -29.34‰. In CC 7 the water added had a δ of about 0.0‰. These samples were circulated for various periods of time. Since when a vapor sample was frozen out into a sample tube stopcocks F and G were closed and since vapor could not get past ball valve M when the pump was off, vapor was left in the volume from M to I to G to F. When the next capillary was added the vapor of the water in the capillary was added to the vapor left in the system and the effective isotopic composition of the vapor added was not that of the water in the capillary but a combination of the vapor left behind from the previous experiment and the water added. This mixing was corrected for in tabulating the results of these experiments. From the volume of the part of the system from which the sample was frozen (756.9 ml $=V_1$), the number of moles of hydrogen obtained (hence the number of moles of water frozen out, n_1), and the temperature (T) at the time just before the freezing started, the pressure (P) of the water vapor in the entire system was calculated.

$$P = \frac{n_1 RT}{V_1} \qquad R = \text{gas constant}$$

From this pressure, the temperature, and the volume in which vapor was left behind (168 ml. = V_2) the number of moles of vapor left behind was calculated.

$$n_2 = \frac{PV_2}{RT}$$

The composition of the vapor left behind was known since it was identical to the vapor taken as the sample (δ). The effective composition (δ_e) of the water added then was the average of the composition of the water added in the capillary (δ_c) and the vapor left from the previous experiment weighted by the number of moles of water from each source.

$$\delta_e = \frac{\delta_c n_a + \delta_p n_{2p}}{n_a + n_{2p}}$$

p ⇒ previous sample
n_a = # moles added by capillary

The results are tabulated in Table V. Fig. 7 is a plot showing the change in δ from its initial value to its end value plotted against the time of the circulation for each trial.

Results and Conclusions

It would be expected that the isotopic composition of the vapor circulated over the copper sulfate pentahydrate would eventually reach the composition of the first water to come off the salt (CC 3). In the times allowed for the circulation in these experiments it does not appear that equilibrium was reached. In all trials the composition of the vapor removed was closer to the composition of CC 3 than was the composition of the water added. Instead of approaching the composition of CC 3 closer with increasing time of circulation, CC 8, CC 9, and CC 11 showed the opposite trend. CC 12 however, which had the longest circulating time of any of the trials where light water was added, approached the value of CC 3 more closely than either CC 9 or CC 11. Except for CC 13 which ended up lighter than CC 3 by 3.47% the trials that started with heavy water samples approached the value of CC 3 fairly well. CC 14 after 100 1/3 hours was only 0.894% different from CC 3. The results

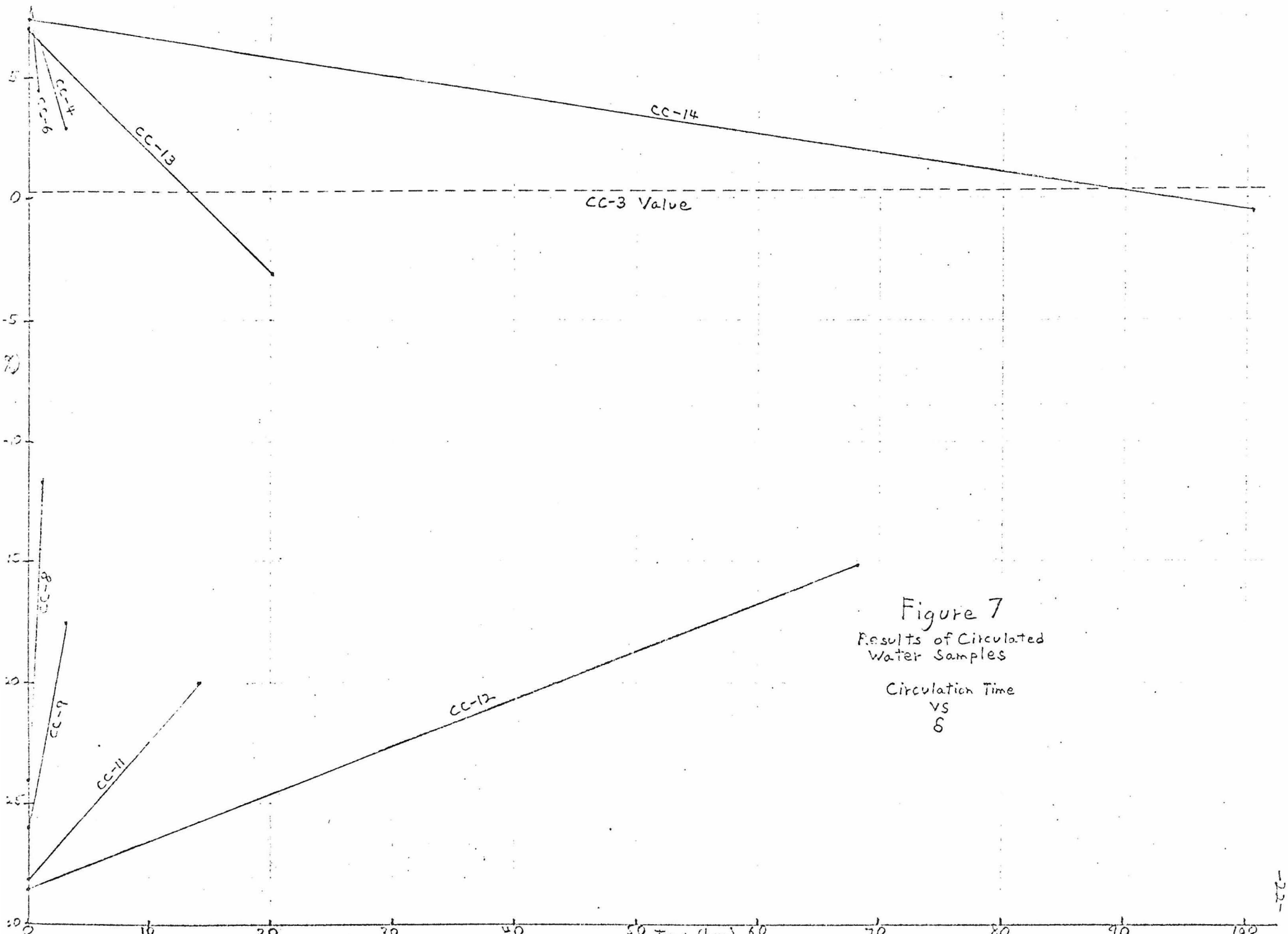


Figure 7
Results of Circulated Water Samples

Circulation Time
vs
δ

of these experiments indicate that it takes a long time for the hydrogen isotope fractionation between copper sulfate pentahydrate and water vapor to equilibrate at room temperature. One hundred hours, and possibly less, may be sufficient when the vapor starts with about 9% more heavy water than the expected value, but 68 hours is not nearly enough when the vapor starts with nearly 30% less heavy water. A salt with water held less tightly such as sodium sulfate decahydrate might equilibrate faster and be a suitable subject for further experiments.

The experiments which involved partially rehydrating anhydrous copper sulfate show that heavy water is preferentially incorporated into the hydrated crystal. The vapor left after the rehydration was a good bit lighter than the overall composition of the water added. In light of the long time indicated previously for isotope equilibration, the values obtained probably are not equilibrium values.

The dehydration curve for copper sulfate pentahydrate shows that in general heavy water is preferentially retained in the crystal. The jump in the curve between RB 12, RB 13, and RB 14 was probably caused by the heating used first on RB 11 to drive off water to get the pressure up. The increased temperature would have driven off a greater than normal amount of heavy water and the long equilibration time for the isotopes prevented equilibrium at room temperature from being reached before the sample was taken. The curve should probably follow close to the dotted line between RB 10 and RB 12. The assumption that the 11.6% of the water lost from the copper sulfate that was completely dehydrated was all lost

at the beginning was verified by the accuracy with which RB 1, RB 2, RB 3, and RB 4 matched up with RB 6 to RB 20 when both sets of points were plotted on the same graph (Fig. 3) with RB 6 starting at 11.6%. Stable copper sulfate hydrates are the penta, tri, and mono hydrates.[4] The dip in the curve between RB 8, RB 9, and RB 10 corresponds to 40% of the original water being gone or to the composition of the trihydrate.. The jog at RB 16 and 17 corresponds closely to 80% of the water being gone or to the composition of the monohydrate. The crystal structure of copper sulfate pentahydrate[5] is such that each Cu has 4 waters around it in a square and 2 sulfate oxygens around it to form an octahedron with the waters. The fifth water is bound tetrahedrally to 2 sulfate oxygens and to 2 other waters. This fifth water molecule is held tighter than the others. The 4 waters around the Cu are in two slightly different environments and thus two are held tighter than the other two. Upon dehydrating, first the two least tightly bound waters around the Cu come off. The lighter water molecules come off preferentially since they need slightly less energy to break the bonds holding them in the crystal than do molecules of heavy water. After these first molecules of water all come off the composition of the crystals is that of the trihydrate. Next the other two water molecules around the Cu come off, again with the lightest tending to leave first, leaving the composition of the monohydrate. Finally the tetrahedrally bound water comes off with the addition of more energy. The greater

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[4] Logan, J. Phys. Chem., 36, 1035, 1936.

[5] Proc. Roy. Soc., A 146, 570(1934).

energy needed to break bonds holding heavy water than light water tends to concentrate the heavy water into positions with the strongest bonds. The jumps in the copper sulfate dehydration curve occur because heavy water in the less strongly bound positions need less energy to come off than the light water in the more strongly bound positions.

The dehydration curve for zinc sulfate also shows heavy water to be preferentially retained in the crystals. Stable hydrates have been observed for the compositions of the hepta, hexa, penta, and mono hydrates.[6,7] Others may also exist. The transitions between these states do not show up in the curve (Fig. 4) as clearly as the transitions did in the case of copper sulfate.

In both the copper sulfate and zinc sulfate there is a lightening observed in the last water to come out. It is known that in clays where water is present as hydroxyl groups light water is preferentially retained.[8] Whether the lightening observed in the hydrates is due to a similar situation as occurs in clays or is due to some other reason is not clear from these experiments.

The results of the dehydration of the sodium sulfate decahydrate are not particularly meaningful since about 60% of the water was not recovered. This was probably lost to the atmosphere

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[6] Foote, and Scholes, J. Am. Chem. Soc., 33, 1309(1911).

[7] Bonnell and Burridge, Trans. Faraday Soc., 31, 473-8(1935).

[8] Dr. Samuel Epstein, Personal communication , Pasadena, Calif., July, 1967.

while the salt was still in the stock bottle. The plot (Fig. 5) was made assuming all the water was lost before the first sample was taken. The curve does show a slight trend for heavy water to be retained.

Much further work can be done in this general field. Many other hydrates with different cations and anions and with different means of bonding water could be studied. For example while copper sulfate has waters associated directly with either the Cu or the sulfate in the crystal, the water of hydration in alums is not associated directly with a cation or anion but instead occupies a definite spot in the crystal lattice.[9] More work could also be done on a method to assure isotope equilibrium between vapor and a hydrate. The best way to do this might be to use a circulating system similar to the one used here, and to try to find salts that equilibrate more rapidly than copper sulfate. Higher temperatures could be investigated along with this. The work could be further expanded to include oxygen isotope fractionation in addition to hydrogen.

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[9] E. Eugene Weaver, "Hydrates," in McGraw-Hill Encyclopedia of Science and Technology, Vol. 6, Dallas, p. 524, 1960.