

Chemistry. — “*Equilibria in the system Zinc sulphate-Water*”. By Prof. ERNST COHEN and Dr. A. L. TH. MOESVELD.

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1. In connection with the theory of the so-called “Transition elements” ERNST COHEN, some twenty five years ago, carried out a number of solubility determinations for the system zinc sulphate-water ¹⁾, at temperatures between -5° C. and the transition temperature.

These determinations, mentioned in Table 1, were in good agreement with the experiments carried out by CALLENDAR and BARNES at about the same time ²⁾. The latter also embrace the temperature interval, lying between the transition temperature (39°) and 50° C.

TABLE I.

Temp.	Solubility of $Zn SO_4 \cdot 7 H_2O$.				Solubility of $Zn SO_4 \cdot 6 H_2O$.			
	1st Determ-ination.	2nd Determ-ination.	mean COHEN.	CALLENDAR and BARNES.	1st Determ-ination.	2nd Determ-ination.	mean COHEN.	CALLENDAR and BARNES.
-5°	39.33	39.27	39.30	—	47.08	—	47.08	—
$0^{\circ}.1$	41.94	41.92	41.93	41.85	49.53	49.44	49.48	—
$9^{\circ}.1$	47.11	47.07	47.09	46.96	—	54.20	54.20	—
$15^{\circ}.0$	50.83	50.94	50.88	50.74	57.09	57.20	57.15	—
$25^{\circ}.0$	57.94	57.87	57.90	57.95	63.74	—	63.74	63.74
$30^{\circ}.0$	—	—	—	61.92	65.80	65.84	65.82	65.65
$35^{\circ}.0$	66.59	66.63	66.61	66.61	67.99	—	67.99	67.94
$39^{\circ}.0$	70.00	70.09	70.05	70.05	—	70.08	70.08	70.02

COHEN at the same time, pointed out that the solubility curve of the heptahydrate of zinc sulphate between -5° and 39° C. may be represented by the equation

$$L_1 = 41.80 + 0.522t + 0.00496t^2 \dots \dots \dots (1)$$

while the observations of CALLENDAR and BARNES for the hexahydrate between 39° and 50° C. may be represented by the equation:

$$L_2 = 59.34 + 0.0054t + 0.00695t^2 \dots \dots \dots (2)$$

¹⁾ Zeitschr. f. physik. Chemie **34**, 179 (1900).

²⁾ Proceedings Royal Society London **62**, 117 (1897).

The values in the last column of Table 1 were calculated by means of this equation. In either equation L represents the number of grammes $ZnSO_4$, present at t° in 100 gr. of water. Moreover, COHEN pointed out, that the curve (2) gives a good agreement as regards the solubility of the hexahydrate up to $25^\circ C$.

In an investigation, lately published by CHARLES R. BURY ¹⁾, the study of the equilibrium in the system zinc sulphate-water was again taken up. His results, given in fig. 1, may be summarized as follows:

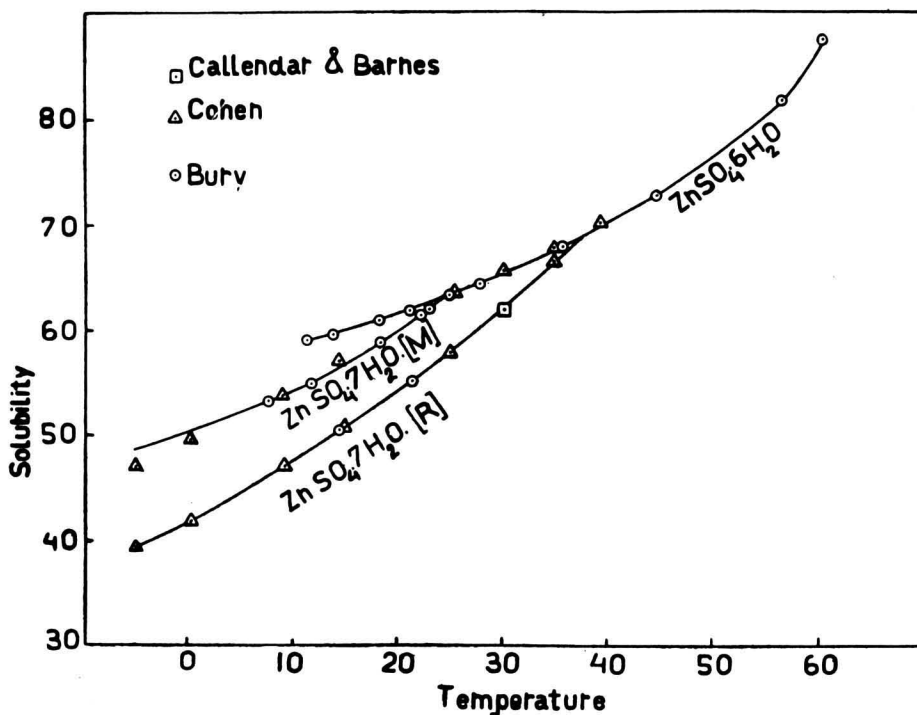


Fig 1.

Between 40° and $50^\circ C$. the agreement with the data of CALLENDAR and BARNES was satisfactory. COHEN's figures between 39° and $25^\circ C$. (meta-stable interval of the hexahydrate) agree with BURY's. Below $25^\circ C$. the values of the solubility of the hexahydrate found by COHEN lie on another curve than those found by BURY for the hexahydrate. They evidently refer to another hydrate.

Below $11^\circ C$. the hexahydrate changes spontaneously and irreversibly into the monoclinic heptahydrate. The latter is most easily obtained by spontaneous crystallisation of supersaturated solutions at about $-10^\circ C$.

¹⁾ Journ. chem. Soc. London **125**, 2538 (1924).

The values found by BURY for the solubility of this monoclinic heptahydrate are, between 7° and 23° C., in very close agreement with those given by COHEN¹⁾ for the hexahydrate in this interval. The monoclinic heptahydrate is metastable at all temperatures with respect to the rhombic heptahydrate. According to BURY the (metastable) monoclinic heptahydrate passes into the metastable hexahydrate at $24^{\circ}.8 \pm 0.3$.

3. We wish to observe here that already SCHROEDER²⁾, and later on LECOQ DE BOISBAUDRAN³⁾ and also STORTENBEKER⁴⁾ have described the monoclinic heptahydrate.

4. In the first place we shall now, by means of another procedure than BURY used, show that his statement, mentioned in 2 (in italics) is perfectly accurate and that therefore COHEN has not determined the solubility of the hexahydrate along the whole range of temperature -5° up to 39° and 50° C., as he thought, but that in a part of this interval (-5° up to 23° C.) another hydrate, probably the metastable monoclinic heptahydrate played the part of solute.

5. This proof, which, as will be shown, can be given very clearly, is drawn from a paper by COHEN: "Eine neue Methode zur Bestimmung von Umwandlungstemperaturen"⁵⁾.

In an apparatus, especially made for that purpose, he determined between -5° and $+50^{\circ}$ C. by means of a dipping electrode (F. KOHL-RAUSCH) the electrical resistance of saturated solutions of zinc sulphate.

In Table 2 as well as in Fig. 2, taken from COHEN's paper, the results of these measurements are given. In Fig. 2 the curves *CB* and *BA'* relate to the hexahydrate, *BA* to the heptahydrate.

The value of the resistance measured (point X) which, at 25° C., according to Table 2 would relate to the (at that temperature) metastable hexahydrate, falls far outside the curve *BA'*, and as this divergence lies far outside the experimental errors, the question arises, whether the points, furnished by the experiments between *A'* and *C*, really belong to one single continuous curve, or whether we have here two curves, to one of which belongs point X.

6. In order to investigate this we proceeded as follows: it appears to be possible to find a curve representing in the temperature interval of 25° — 50° C. the resistances measured as function of the temperature in

1) The italics are C. and M's.

2) Lieb. Ann. **109**, 35 (1859).

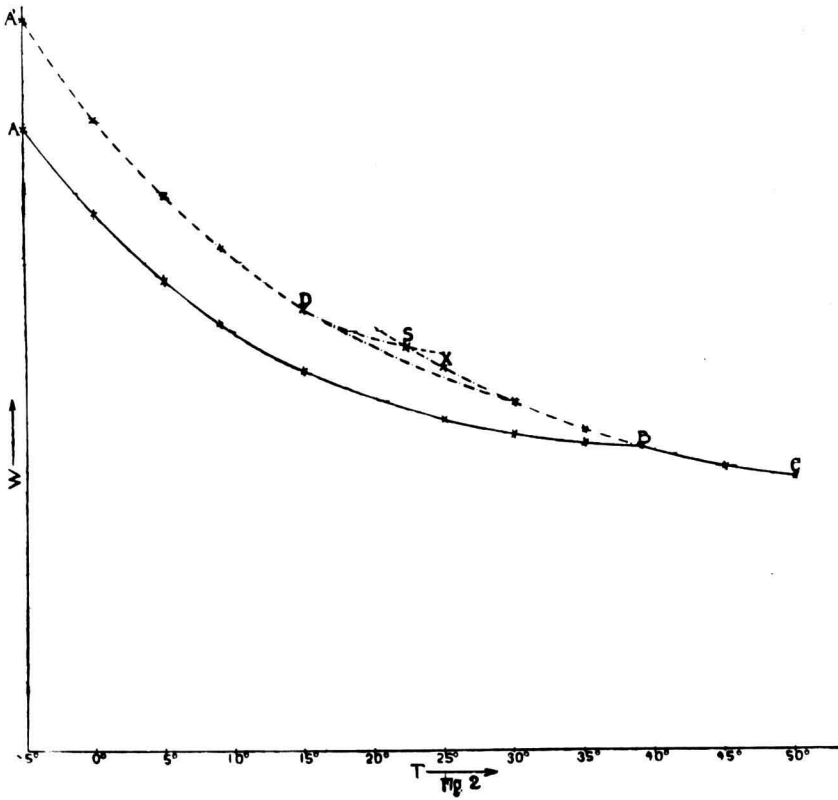
3) Ann. de chim. et de phys. (4) **18**, 266 (1869).

4) Zeitschr. f. physik. Chemie **22**, 60 (1897).

5) Zeitschr. f. physik. Chemie **31**, 164 (1899).

TABLE II.

Temperature.	Resistance of the solution.	
	Saturated with respect to $Zn SO_4 \cdot 7 H_2O$.	Saturated with respect to $Zn SO_4 \cdot 6 H_2O$.
— 5°.0	445.9	524.1
0.0	384.2	452.2
5.0	337.0	396.3
9.0	305.7	360.3
15.0	271.6	315.5
25.0	236.4	274.2
30.0	225.1	248.8
35.0	218.5	228.3
39.0	215.0	215.0
45.0	—	200.1
50.0	—	191.1



solutions in which the presence of the hexahydrate as a solute was supposed. From the values of Table 2, first and third columns we then find by means of the method of least squares the equation:

$$W_2 = 460.0 - 9.51t + 0.0828t^2 \dots \dots \dots (3)$$

From Table 3, fourth column, we see that this equation describes exactly the observations in this interval.

TABLE III.

<i>t.</i>	W_{2found}	$W_{2calc.}$	$W_{2found} - W_{2calc.}$
25°.0	274.2	274.0	- 0.2
30.0	248.8	249.1	+ 0.3
35.0	228.3	228.5	+ 0.2
39.0	215.0	215.0	± 0.0
45.0	200.1	199.7	- 0.4
50.0	191.1	191.4	+ 0.3

As the resistance measurements were made according to KOHLRAUSCH with a bridge wire of 1000 mm., a difference of 1 mm. in reading near the middle of the bridge corresponds with a difference of resistance of 0.4%. As is seen from column 4 of Table 3 this divergence is not reached anywhere.

If, on the contrary, using the values of resistance measured (Table 2, column 3) we try to calculate a curve for the temperature interval -5° to 25° C., in which the point *X* is inserted, divergences appear between the values, given by the curve and the values, which have been experimentally determined, which lie far outside the errors of measurement.

If point *X* is not taken into consideration and with the method of least squares a curve is calculated by means of the figures of Table 2, column 3, between -5° and 15° C. we find for that curve the equation:

$$W_1 = 453.8 - 12.70t + 0.2354t^2 \dots \dots \dots (4)$$

which, as is shown by Table 4 describes the observations most satisfactorily.

TABLE IV.

<i>t.</i>	W_{1found}	$W_{1calc.}$	$W_{1calc.} - W_{1found}$
- 5°.0	524.1	523.2	- 0.9
0.0	452.2	453.8	+ 1.6
5.0	396.3	396.2	- 0.1
9.0	360.3	358.6	- 1.7
15.0	315.5	316.2	+ 0.7

If, by means of (4) the value of the resistance at 25° C. is calculated, we find a value, which considerably differs from the one found experimentally (calc. 282.2; found 274.2).

7. The curves (3) and (4) therefore refer to the saturated solutions of two different substances (solutes). If the temperature of the intersection *S* of curves (3) and (4) is calculated we find for it 22° 5 C.

If we now take into consideration that BURY's values for the solubility of $\text{ZnSO}_4 \cdot 7 \text{ aq.}$ monoclinic between 7° and 23° agree with those given by COHEN for $\text{ZnSO}_4 \cdot 6 \text{ aq.}$ in this temperature interval, and that BURY has found $24^\circ.8 \pm 0.3$ for the temperature of the intersection of the curves, which refer to $\text{ZnSO}_4 \cdot 7 \text{ aq.}$ monoclinic and $\text{ZnSO}_4 \cdot 6 \text{ aq.}$, whereas our curves intersect at 22° 5 C. (curves (3) and (4)), it is highly probable, that curve (4) refers to $\text{ZnSO}_4 \cdot 7 \text{ aq.}$ monoclinic, and is not, as COHEN thought the production of (3) and therefore does not refer to $\text{ZnSO}_4 \cdot 6 \text{ aq.}$

If COHEN had examined in his apparatus the solute which was present at the determinations between -5° and +25° he would undoubtedly have perceived that he had to do with the monoclinic (metastable) hydrate of $\text{ZnSO}_4 \cdot 7 \text{ aq.}$

8. BURY's researches on the one side furnish us with an explanation of the fact that the point *X*, found by COHEN in his resistance determinations falls totally outside the curve of the resistances, while on the other side the present point of view shows, that these resistance and solubility determinations by COHEN are in good agreement with BURY's results, if we apply the figures of the solubility and resistance found by COHEN below 25° C. to the (metastable) monoclinic hydrate $\text{ZnSO}_4 \cdot 7 \text{ aq.}$ instead of to the (metastable) $\text{ZnSO}_4 \cdot 6 \text{ aq.}$

9. The above demonstrates how important it is to mention "discrepant" results, when giving results of an investigation. In the case which we have discussed here, it is the mentioning of point *X*, (Fig. 2) which has facilitated the checking of the results, which have been obtained in a different way.

SUMMARY.

It has been demonstrated that BURY's investigations on the equilibria in the system zinc sulphate-water, made by means of solubility determinations, give a complete explanation of the results, which at the time COHEN obtained by the same method as well as by means of determinations of resistance.

Utrecht, February 1925.

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