

*Citation:*

Holsboer, H.B., On heats of solution in general, that of  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$  in particular, in:  
KNAW, Proceedings, 3, 1900-1901, Amsterdam, 1901, pp. 467-469

the *i*-form than in the antipodes. It may, therefore, be suspected that at that higher temperature the solubility of the *i*-form in different solvents will be greater than that of the active forms.

The line obtained with benzoin as third substance shows that the racemic compound still exists at  $97^{\circ}.2$ ; the zone is, however, very restricted. Finally, at a still higher temperature the racemic compound has disappeared; the investigation with anthracene as third substance gave a continuous curve with a minimum at 50 percent *d.*—50 percent *l.* At  $105^{\circ}.6$  the *i*-oxime must, therefore, be regarded as a mixed crystal of equal quantities of the active oximes.

This is quite in concordance with my previous investigations on camphoroxime, the results of which have been communicated in the report of the meeting of June 24, 1899.

**Chemistry.** — Professor BAKHUIS ROOZEBOOM presents the dissertation of Dr. H. B. HOLSBOER: "*On heats of solution in general, that of  $CdSO_4, \frac{8}{3} H_2O$  in particular*" making the following communication regarding it.

Since 1884 it has been recognised that the calculation of the course of the solubility curves of solid substances in liquids as functions of temperature requires a knowledge of the so-called theoretical heat of solution, that is the heat of solution of the solid substance in its saturated solution. In 1885 I discovered a graphic construction by means of which this quantity, which cannot be determined experimentally, may be obtained from the curve of the heats of solution in different quantities of solvent. Later on VAN DEVENTER and STACKELBERG devised methods of calculating the same quantity from such determinations.

For salts whose saturated solutions are very dilute, the theoretical heat of solution differs but little from that in pure water; for salts with large solubility the sign may even differ. With some salts a minimum of solubility is shown at a definite temperature, the solubility, therefore, first decreases with an increase of temperature and then increases when past the minimum. On the first part of the curve the theoretical heat of solution must, therefore, be positive, on the second part negative and *nil* at the temperature of the minimum.

Up to the present, this change of sign of the evolution of heat has not been accurately proved to occur in any such case. Dr. HOLSBOER has investigated cadmium sulphate with  $\frac{8}{3}$  mol. of  $H_2O$

which shows a minimum of solubility at 15°. He determined accurately the heat of solution of this hydrate in much water at 15° and also the heats of dilution of all kinds of solutions beginning with the greatest possible concentration. He further determined the specific heats of a series of solutions and of the solid salt, so that the heats of solution of solid salt in varying quantities of water at different temperatures could be calculated from the values at 15°. He obtained the following results.

Heat of solution of  $\text{Cd SO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$  in  $(x - \frac{8}{3}) \text{H}_2\text{O}$ .

$x$	5°	10°	15°	20°	25°
400	2075	2303	2530	2758	2985
200	2194	2306	2418	2530	2642
100	2118	2203	2288	2373	2458
50.6	2013	2065	2118	2170	2223
30.6	1835	1876	1918	1959	2001
20.6	1657	1645	1633	1621	1609
15.6	1405	1332	1258	1185	1111
13.6	1061	966	870	775	679

The saturated solutions contain, at the temperatures given: 15.03, 15.10, 15.17, 15.10, 15.03  $\text{H}_2\text{O}$ .

The determinations of the heats of solution go beyond these concentrations. It was, therefore, easy to deduce the theoretical heat of solution from the course of the curves for the ordinary solutions in the immediate neighbourhood of the point corresponding to the saturated solution.

The following results were obtained:

Theoretical heat of solution.

5°	+ 219 cal.
10°	+ 165 »
15°	+ 3 »
20°	- 620 »
25°	- 1221 »

The agreement between the signs of the heats of solution and the course of the curve of solubility and the position of the minimum is very good.

The influence of temperature on the heat of solution is also very considerable.

It appears also from the table of the ordinary heats of solution that with dilute solutions the heat evolved increases with the temperature, owing to the fact that the specific heat of the solution is smaller than the sum of the values for solid salt and water. With concentrated solutions the reverse is the case. From this it follows that there must be a concentration where the heat of solution is independent of the temperature because the specific heat of this solution is equal to those of solid salt + water.

This appears to be the case with a solution with 22.5 H<sub>2</sub>O.

In the graphic representation all the heat of solution curves intersect each other at the point corresponding to this concentration. For want of investigation of concentrated solutions, this peculiarity, which no doubt occurs with many substances, has up to the present escaped notice.

**Chemistry.** — Dr. ERNST COHEN: "*The Enantiotropy of Tin*" (VI)  
(Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

*Contributions to the history of grey Tin.*

1. In the journal *Prometheus*<sup>1)</sup> E. KRAUSE referring to my previous investigations on the Enantiotropy of Tin<sup>2)</sup> makes the following communication: "Schon die Alten wussten, dass dieses weiche Metall, welches „schreit“, wenn man es biegt, seine Mucken habe und der Verfasser eines mit Recht oder Unrecht dem ARISTOTELES zugeschriebenen Buches (*de Mirabilibus Auscultationibus* Cap. 51<sup>1</sup> Edit. BECKMANN) sagt: das keltische Zinn habe unter anderen merkwürdigen Eigenschaften auch die, nicht bloss (wie die anderen Metalle) in der Wärme zu schmelzen, sondern auch eintretender Frost bewirke dasselbe.

Auch PLUTARCH in den *Tischreden* (VI, 8) berichtet von in strengen

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<sup>1)</sup> Jahrgang XI, 44, S. 701 (1900).

<sup>2)</sup> These Proceedings 1899 and 1900 also Zeitschrift für phys. Chemie 30, 601 (1899) 33, 57 (1900) 33, 588 (1900).