agree within their own rather large experimental uncertainty with the recent precise isotonic measurements of Scatchard, Hamer and Wood. The results calculated from freezing points show smaller but systematic deviations, which apparently are considerably beyond the experimental error of the thermal measurements.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

# The System Magnesium Sulfate, Cadmium Sulfate and Water at 25 and 40°

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In the study of modified Weston cells[1] some difficulty was experienced in the preparation of a double salt of magnesium and cadmium sulfates. Schiff[2] prepared a double salt with the composition $MgSO_4 \cdot CdSO_4 \cdot 14H_2O$ in 1857, but no mention of later work on this compound has been found. Attempts to make the double salt by slow evaporation at room temperature of a solution containing the two component salts failed, and it was apparent that further study of the system magnesium sulfate, cadmium sulfate and water was desirable.

Mixtures were prepared of carefully weighed quantities of recrystallized magnesium and cadmium sulfates and water and brought to equilibrium in closed tubes which were rotated in an air-bath at 25 ± 0.1°. The time allowed for equilibrium varied considerably, but in only a few cases was it less than forty-eight hours. Often it was much longer than this, and the consistency of the data is an indication that equilibrium was attained in the time allowed.

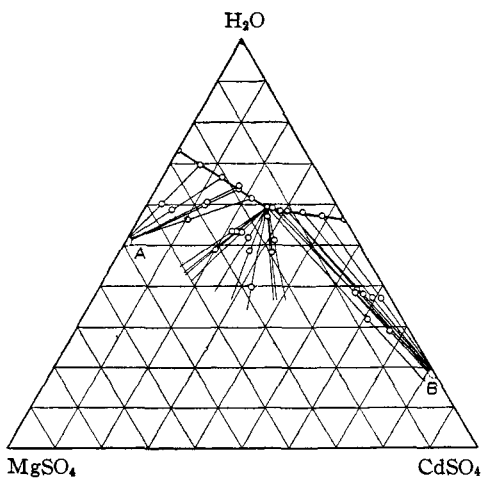


Fig. 1.—The system magnesium sulfate, cadmium sulfate and water at 25°. Points A and B represent the calculated compositions, in weight percentage, of hydrated magnesium and cadmium sulfates, respectively.

After sufficient rotation, the saturated solution was drawn off through a glass-wool filter, this operation being carried out within the air-bath. The solution was weighed, diluted to a known volume and aliquot portions taken for analysis. Total solids were determined by evaporation to dryness and ignition in a muffle at 500°. Other samples were acidified with sulfuric acid, the cadmium was precipitated as sulfide, and the magnesium sulfate determined in the filtrate by evaporation, ignition at 500° and weighing. The cadmium sulfide was dissolved by hydrochloric acid, and the solution evaporated to dryness after addition of an excess of sulfuric acid. The cadmium sulfate was ignited at 500° and weighed.

TABLE I

COMPOSITIONS OF SATURATED SOLUTIONS AND ORIGINAL MIXTURES AT 25°

| Saturated solutions | | Original mixtures | |
|---|---|---|---|
| $CdSO_4$, wt. % | $MgSO_4$, wt. % | $CdSO_4$, wt. % | $MgSO_4$, wt. % |
| 6.5 | 23.8 | 3.1 | 36.8 |
| 12.5 | 20.9 | 5.9 | 35.4 |
| 17.2 | 18.3 | 12.2 | 26.9 |
| 17.4 | 18.9 | 12.3 | 27.8 |
| 21.7 | 17.0 | 10.3 | 33.2 |
| 25.5 | 15.2 | 27.1 | 16.3 |
| 25.7 | 14.9 | 20.0 | 31.1 |
| 25.8 | 15.4 | 32.4 | 19.4 |
| 26.0 | 15.0 | 21.2 | 25.5 |
| 26.1 | 15.0 | 31.3 | 17.6 |
| 26.2 | 15.3 | 22.2 | 24.4 |
| 26.2 | 15.1 | 25.5 | 22.6 |
| 26.4 | 15.0 | 32.3 | 28.1 |
| 26.4 | 15.2 | 23.4 | 23.4 |
| 26.4 | 15.2 | 27.6 | 21.9 |
| 26.9 | 14.9 | 60.9 | 7.2 |
| 27.0 | 13.9 | 55.0 | 6.6 |
| 29.1 | 12.5 | 54.9 | 5.9 |
| 30.5 | 11.2 | 56.8 | 5.1 |
| 30.5 | 11.0 | 67.0 | 3.9 |
| 34.0 | 8.0 | 59.3 | 3.6 |
| 38.6 | 4.3 | 61.3 | 1.9 |

(1) Vosburgh, Derr, Cooper and Pettengill, THIS JOURNAL, **61**, 2687 (1939).

(2) Schiff, *Ann.*, **104**, 327 (1857); **107**, 73 (1858).

The compositions of the original mixtures and saturated solutions are given in Table I and plotted in Fig. 1.

It is apparent from Fig. 1 that no double salt was formed at 25°. Consequently, some experiments were carried out to see whether a transition temperature could be detected, since the temperature range within which the double salt of Schiff[2] is capable of existence might not include 25°. Two modified Weston cells[1] were constructed with an electrolyte saturated with magnesium and cadmium sulfates and with an excess of both hydrated solids present. On measurement of the electromotive force at several temperatures between 20 and 40° it was found that the temperature coefficient ($\Delta E/\Delta T$) changed abruptly and considerably at about 30°. The reproducibility and constancy of the cells were not good, and the error might amount to a few tenths of a degree. Following this, equimolecular quantities of magnesium and cadmium sulfates and a little water were rotated together for several days at 40° and a cooling curve for the mixture determined. It gave clear evidence of an evolution of heat at about 30.2°.

TABLE II

COMPOSITIONS OF SATURATED SOLUTIONS AND ORIGINAL MIXTURES AT 40°

| Saturated solutions | | Original mixtures | |
|---|---|---|---|
| $CdSO_4$, wt. % | $MgSO_4$, wt. % | $CdSO_4$, wt. % | $MgSO_4$, wt. % |
| 2.6 | 29.6 | 2.0 | 36.0 |
| 5.0 | 28.8 | 3.2 | 36.5 |
| 7.6 | 27.8 | 5.1 | 35.1 |
| 9.2 | 28.0 | 8.5 | 34.9 |
| 9.6 | 27.8 | 12.3 | 31.1 |
| 10.2 | 27.5 | 14.5 | 28.9 |
| 9.6 | 28.3 | 13.2 | 31.0 |
| 12.1 | 24.4 | 24.0 | 23.2 |
| 17.2 | 20.0 | 25.6 | 20.4 |
| 14.5 | 22.4 | 27.3 | 22.0 |
| 20.0 | 17.6 | 31.4 | 20.4 |
| 20.9 | 17.1 | 31.7 | 19.3 |
| 24.2 | 14.3 | 32.4 | 18.8 |
| 28.2 | 12.2 | 32.4 | 16.4 |
| 33.5 | 10.4 | 34.4 | 14.5 |
| 38.8 | 9.2 | 37.7 | 13.2 |
| 39.6 | 9.2 | 40.3 | 14.8 |
| 40.1 | 8.8 | 44.7 | 13.8 |
| 40.9 | 7.7 | 57.1 | 4.7 |
| 42.7 | 4.5 | 59.4 | 2.5 |

The solubilities were determined again at a temperature of 40 ± 0.2°, and the data in Table II (shown graphically in Fig. 2) obtained. It is clear that a double salt can exist at 40° in equilibrium with solutions of a wide range of compositions. Point C in Fig. 2 represents the calculated composition of the compound $MgSO_4 \cdot CdSO_4 \cdot 14H_2O$ while D represents that of a double salt with twelve molecules of water. Points A and B represent $MgSO_4 \cdot 7H_2O$ and $3CdSO_4 \cdot 8H_2O$, respectively, in both Figs. 1 and 2. The solubilities of these salts in water were taken from "International Critical Tables."

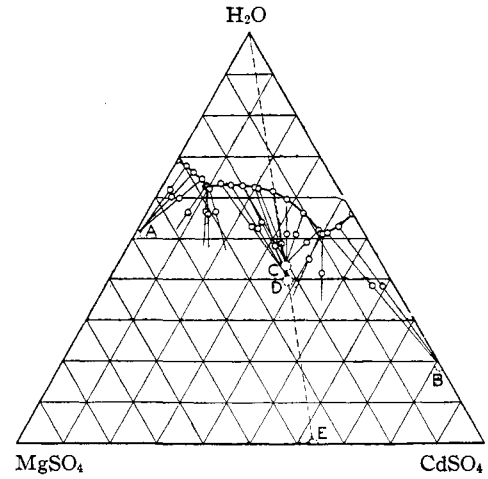


Fig. 2.—The system magnesium sulfate, cadmium sulfate and water at 40°. Points A and B are the same as in Fig. 1. Point C represents the calculated composition of the compound $MgSO_4 \cdot CdSO_4 \cdot 14H_2O$, point D a double salt with twelve molecules of water and point E the anhydrous double salt.

As a further check on Schiff's formula for the double salt, samples of the salt were prepared by rotation of equimolecular mixtures of hydrated magnesium and cadmium sulfates with some excess water at 40° and filtering and drying in the air-bath at the same temperature. Determination of water lost at 500° and of magnesium and cadmium sulfates gave the following results for three different preparations of the double salt.

| | Calcd. for $CdSO_4 \cdot MgSO_4 \cdot 14H_2O$ | Observed | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| $MgSO_4$, % | 20.72 | 20.74 | 20.76 | 20.83 |
| $CdSO_4$, % | 35.88 | 35.85 | 35.83 | 35.87 |
| $H_2O$, % | 43.41 | 43.41 | 43.39 | 43.40 |

## Summary

A double salt of magnesium and cadmium sulfates, $MgSO_4 \cdot CdSO_4 \cdot 14H_2O$, can exist in equilibrium with saturated solutions at 40°, but not at 25°. A transition point for the system was found at about 30.2°.

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