

XIII.—*The Solubility Curves of the Hydrates of Nickel Sulphate.*

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THE experiments recorded in this paper were undertaken with the object of determining the conditions of equilibrium and the composition of the phases in the two component system, nickel sulphate—water.

Hydrates of nickel sulphate have been described containing 1, 2, 6, and 7 molecules of water. The heptahydrate, which is found in nature as the mineral moresonite, may be obtained by crystallisation at the ordinary temperature from neutral solutions of the salt. It occurs in the form of pale green, rhombic crystals isomorphous with heptahydrated magnesium sulphate, and on prolonged exposure to the atmosphere becomes changed into aggregates of blue crystals having the composition $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. This change has, for a long time, been regarded as being brought about by the action of sunlight (Phillips and Cooper, *Poggendorf's Annalen*, 1879, 6, 194), but Dobrosserdoff (*J. Russ. Phys. Chem. Soc.*, 1900, 32, 300) has recently shown that this is not the case, since sunlight has no effect on the heptahydrate, provided that the crystals are contained in a space saturated with water vapour and maintained at a low temperature; accordingly the

114 STEELE AND JOHNSON: THE SOLUBILITY CURVES OF

reaction in question is a simple case of efflorescence. The same hexahydrate was obtained by Brooke and Phillips (*loc. cit.*) and by Pierre (*Ann. Chim. Phys.*, 1846, [iii], 16, 252) in the form of blue, tetragonal crystals by crystallisation at the ordinary temperature from a solution containing sulphuric acid, and by Marignac and Mitscherlich from neutral solutions at about 40°.

Isothermal crystallisation of neutral solutions at temperatures between 60° and 70° yields a bright green, monoclinic salt which also contains 6 molecules of water.

The dihydrate is described by Étard (*Compt. rend.*, 1878, 87, 602) as being formed by the action of strong sulphuric acid on the hexa- or hepta-hydrates, and Lesœur (*Chem. Centr.*, 1895, i, 525) states that by adding concentrated sulphuric acid to a solution of nickel sulphate, a precipitate of the monohydrate is obtained.

The study of the solubility curves of nickel sulphate between -5° and 100° has not indicated the existence of any hydrate containing less than 6 molecules of water of crystallisation. Solubility determinations have not been made at temperatures above 100°, but from the curves of Étard and Engel (*Compt. rend.*, 1888, 106, 206) there appears to be a transition point at about 118°, and on analysing the solid phase separating at 131°, we found it to be the dihydrate, $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$.

The solubility of nickel sulphate has been determined at various temperatures by Töbler (*Annalen*, 1855, 95, 193). His results, however, differ considerably from ours, and are not sufficiently numerous to indicate the position of the various transition points.

Preparation of the Hydrates.

The heptahydrate was prepared by twice recrystallising the ordinary salt and shown to be pure by analysis. The salt used in estimating the solubilities at a few temperatures was prepared by precipitating a saturated aqueous solution with alcohol, and was thus obtained in the form of very small, green, granular crystals containing 21.12 per cent. of nickel, the calculated value being 20.91.

The foregoing salt, when left in contact with its saturated solution for some hours at any temperature between 32° and 53°, is converted into the blue hexahydrate, which was analysed with the following result: Found Ni = (1) 22.54; (2) 22.41.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ requires Ni = 22.23 per cent.

The blue hexahydrate, employed in the experiments made between 32° and 53°, was prepared by the slow evaporation at the ordinary temperature of solutions containing 30 per cent. of sulphuric acid.

The large crystals thus obtained were powdered and thoroughly washed with a saturated solution of nickel sulphate in order to remove sulphuric acid.

If the heptahydrate or the blue hexahydrate is left in contact with the saturated solution at temperature above 54° , it very rapidly becomes converted into the bright green, monoclinic salt which, on analysis, was found to have the same composition as the blue tetragonal hydrate.

Found, Ni = (1) 22.55 ; (2) 22.50.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ requires Ni = 22.23 per cent.

In order to determine the composition of the solid phase, which is present at temperatures above 118° , a quantity of the dry hexahydrate was sealed up in a thick walled glass tube and heated for some hours at 131° . A little below this temperature, the substance partially melted with the formation of a clear green solution and a dull yellowish-green, amorphous solid, for the separation of which the following method was adopted. The tube containing the mixture was carefully inverted, so that the greater part of the liquid drained away from the powder. After cooling in this position, it was cut into two parts, and the solid, placed on pieces of porous tile, was sealed up in another tube and again heated at 131° . The adherent liquid portion, which had solidified on cooling, again liquefied and was absorbed by the porous tile, leaving the new salt practically dry and pure, as indicated by the following analysis :

Found, Ni = (1) 30.8 ; (2) 30.87.

$\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$ requires Ni = 30.87 per cent.

Solubility Determinations.

The solubilities were determined by enclosing the salt, with the requisite amount of distilled water, in tubes provided with well-fitting india-rubber stoppers. The tubes were attached to a shaking apparatus driven by a Henrici hot-air motor, and immersed in a thermostat provided with a toluene gas regulator, by means of which the temperature could be kept constant to a tenth of a degree. Preliminary experiments having shown that equilibrium was reached in about 12 hours, the tubes were shaken for twice that time to ensure saturation.

The solutions were filtered within the thermostat in the following manner. The india-rubber stopper in the solubility tube contained a hole, which was closed with a glass rod during the shaking. When it was desired to filter the solution, the rod was withdrawn, and in its place was inserted a piece of glass tubing with a small bulb blown in

the centre, this bulb being packed with asbestos to serve as a filter. The other end of the tube passed through an india-rubber stopper, which fitted into a weighing bottle, and through which passed a glass tube long enough to reach out of the thermostat. The solubility tube was thus attached to a weighing bottle by a filtering tube, and by inverting the two and applying suction to the projecting tube, the solution was filtered without having been for an instant removed from the bath. The filtrate in the weighing bottle was weighed and diluted to 500 c.c., a convenient portion of this solution being taken for analysis.

The nickel was estimated electrolytically, using a current density of 0.5 ampere, 8 to 10 hours being required for the electrolysis, which was carried out in a solution containing ammonium sulphate and excess of ammonia.

All the solubility results (with the exception of those at 0° and -5°) are the mean values of at least two closely concordant determinations carried out in different vessels.

Of the experiments recorded in Table I, the first was carried out in

TABLE I.*

(1) The solubility curve of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.

Salt used.	Temperature.	Concentration.	Salt remaining.
1. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	-5°	25.74	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
2. —	0	27.22	—
3. —	9	31.55	—
4. —	15	34.19	—
5. —	22.6	37.90	—
6. —	22.8	38.88	—
7. —	30.0	42.46	—
8. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	30.0	42.47	—
9. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	32.3	44.02	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
10. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	32.3	43.57	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
11. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	33.0	45.74	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
12. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	33.0	43.35	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
13. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	34.0	45.5	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
14. ' ,	34.0	43.84	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
15. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	34.0	43.82	—

* In this and the other tables in the paper, concentrations are expressed as parts by weight dissolved in 100 grams of water.

a bath of brine surrounded by a mixture of powdered ice and salt, and maintained at a constant temperature by allowing a very slow current of warm brine to circulate through the bath. The second experiment was carried out in a bath of melting ice. For temperatures

below 30°, the heptahydrate only was used in determining the solubilities. For temperatures between 30° and 34°, a number of experiments were made, using both the heptahydrate and the blue hexahydrate in the hope that a portion of each curve extending beyond the transition point might be realised. This has been done for the heptahydrate, the metastable portion of the curve being represented by experiments 9, 11, and 14, in Table I, which give solubilities of the heptahydrate at temperatures close to the point of transition of this hydrate into the hexahydrate.

In experiment 8, in which the solid phase was originally the blue hexahydrate, transformation rapidly took place into the green heptahydrate, and although many attempts were made, it was not found possible to obtain the metastable portion of the curve for the hexahydrate.

In the accompanying diagram (p. 118), the experiments from this table are represented by the curve ABC.

TABLE II.

Solubility curve of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue tetragonal).

Salt used.	Temperature.	Concentration.	Salt remaining.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	32·3°	43·57	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)
"	33·0	43·35	—
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	34·0	43·84	—
"	35·6	43·79	—
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	44·7	48·05	—
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	44·7	47·97	—
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	50·0	50·15	—
—	51·0	50·66	—
—	52·0	52·34	—
—	53·0	52·34	—
—	54·5	52·5	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (green)

On plotting the results collected in Tables I and II, the two curves are found to intersect between 31° and 32°. The transition point corresponding with the change $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{NiSO}_4 \cdot 6\text{H}_2\text{O} + \text{saturated solution}$ therefore lies very near to 31·5°. In order to confirm this point and in the hope of determining it with greater accuracy, experiments were carried out with a dilatometer, which assumed the usual form of a large thermometer with a graduated stem partially filled with a mixture of the heptahydrate, the blue tetragonal hexahydrate, and a certain amount of *m*-xylene. The vessel, being exhausted to remove air bubbles from the salt, was then filled to the

required position with more of the hydrocarbon and placed in a bath at 30°. The temperature was now allowed to rise very slowly; a steady increase of volume occurred up to 31.4°, when there was a sudden break followed by a much smaller increase as the temperature was raised still further. The transition point may therefore be taken as lying between 31.4° and 31.6°.

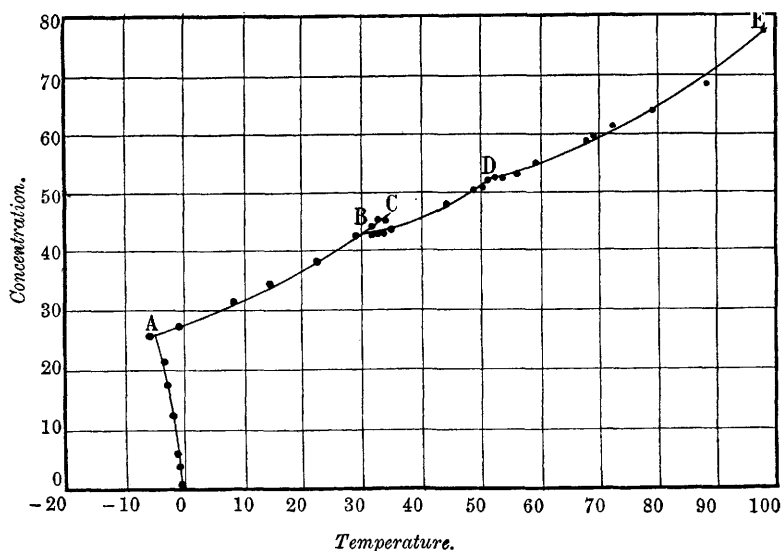


TABLE III.

Solubility curve of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (green monoclinic).

Salt used.	Temperature.	Concentration.	Salt used.	Temperature.	Concentration.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	54.5°	52.50	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	70.0°	59.44
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ "	57.0	53.40	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	73.0	60.72
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue)	60.0	54.84	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ "	80.0	63.17
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	69.0	58.38	"	89.0	67.90
"			"	99.0	76.71

Throughout the series of determinations indicated in Table III, the remaining salt is the green, monoclinic hexahydrate.

The solubility data obtained in the neighbourhood of 52° indicate a

break in the curve, due to a second transition point. This inflexion, which is very slight and might be easily overlooked, is confirmed by the appearance of the residual solid phase after equilibrium is established. If we start with the blue, tetragonal hexahydrate, at temperatures above 53° a very rapid change takes place, the blue substance giving place to a bright green solid having the same composition. On the other hand, this green salt is rapidly converted at temperatures slightly below 53° into the blue modification, and on plotting, on a large scale, the results given in Tables II and III, the two curves are found to cut each other very close to 53° . In order to confirm this conclusion, experiments were made with a dilatometer containing initially the blue hexahydrate mixed with a small quantity of the green salt. No indication of a break could be detected until the mixture was heated for some time at 70° , when the salt was seen to have changed into the green modification. The dilatometer was then placed in a bath at 56° and allowed to cool slowly, when there was a steady contraction down to 54.0° , then little or no contraction until 53.3° , and then a steady contraction, but less than the original diminution. A duplicate experiment confirmed this result and also failed to detect any break on slowly raising the temperature from a point below 53° . According to this result, the temperature corresponding with the change $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue tetragonal) \rightleftharpoons $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (green monoclinic) lies between 53.3° and 54° . The solubilities give this temperature as lying near 53° , and 53.3° is probably not far from the true transition point.

Since the solubility curves of the three salts, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (blue), and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (green), lie so nearly in a straight line, it was thought that possibly a break in the curve between 55° and 100° might have been overlooked.

In order to test this, analyses of the undissolved salt were made at 60° , 70° , and 89° , and in all cases the salt was found to be the hexahydrate. Moreover, the solid phase at all temperatures between the above limits has the bright green colour characteristic of the monoclinic hexahydrate. In the analysis of the solutions at 89° and 99° , the saturated solution was separated from the undissolved salt by the method of decantation in a bent tube employed by Étard and Engel (*loc. cit.*).

Ice Curve and Cryohydrate Point.

The ice curve was determined by measuring the temperature at which ice began to separate from solutions of nickel sulphate of known concentration, the measurements being carried out in a Beckmann freezing point apparatus.

120 SOLUBILITY CURVES OF THE HYDRATES OF NICKEL SULPHATE.

The temperatures and concentrations from which the curve has been plotted are as follows :

Temperature.....	- 0.47°	- 0.72°	- 1.46°	- 2.15°	- 2.85°
Concentration	3.35	5.53	11.97	17.23	21.18

The cryohydrate point was fixed in the following manner. A solution containing about 30 parts of the anhydrous sulphate, NiSO_4 , to 100 parts of water was placed in the inner tube of the Beckmann apparatus, which was surrounded with a freezing mixture maintained at about -5° , and the steady temperature at which ice and nickel sulphate separated was found to be -4.15° .

Summary.

The following is a summary of the results obtained with the system, nickel sulphate—water.

(1) *Quadruple Points.*

A. Cryohydrate point of the heptahydrate [-4.15°].

B. Transition point: heptahydrate \rightleftharpoons hexahydrate (blue) + saturated solution [31.5°].

D. Transition point: hexahydrate (blue) \rightleftharpoons hexahydrate (green) [53.3°].

Transition point: hexahydrate (green) \rightleftharpoons dihydrate + saturated solution (not accurately determined).

(2) *The Equilibrium Curves.*

The curves OA, ABC, BD, and DE in the diagram correspond with the solid phases: ice; the heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; the blue hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$; and the green monoclinic hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, respectively.

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