action, this is offset by decomposition of the hydrogen peroxide initially formed.

3. The mercury vapor lamp gives the most resonance radiation (λ 2536.7 Å.) with a mercury pressure of about 0.01 mm.

4. The rate of reaction is roughly proportional to the arc current, suggesting that the rate varies as the first power of the light intensity.

5. The temperature coefficient of the reaction is 1.04.

6. The product of reaction is predominantly hydrogen peroxide, the maximum rate of formation observed being two grams per hour.

SCHENECTADY, NEW YORK

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# THE SYSTEM $MgSO_4$-$H_2O$ FROM 68 TO 240°[1]

BY HOMER LOUIS ROBSON

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Five hydrates of magnesium sulfate may exist in contact with aqueous solutions of the salt near their boiling points. These are the monoclinic or ordinary hexahydrate, the penta-, tetra-, five-fourths and monohydrates.[2] Of these, the hexahydrate is the stable phase from 48.4[3] to 68° and may be followed up to 100°. The transition point of the hexahydrate to the monohydrate was found by Van't Hoff, Meyerhoffer and Smith[4] to be 68°, and the monohydrate is the stable phase from this temperature up to 240°. They also found the transition of the hexahydrate into the five-fourths hydrate to lie between 68 and 72°[5] and that of the pentahydrate into the tetrahydrate to lie close to 77.5°. The transition

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[1] Part of a thesis submitted to the Faculty of the Graduate Division of the University of California in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Other hydrates of magnesium sulfate are the dodecahydrate prepared by Fritsche (a) (Fritsche, *Pogg. Ann.*, **42**, 577 (1842), see also observations by F. G. Cottrell, mentioned by Van't Hoff, Meyerhoffer and Smith, *Sitzb. preuss. Akad. Wiss.*, **1901**, 1035), the rhombic heptahydrate or epsom salt (b) (for properties see E. S. Larsen, "The Microscopic Identification of the Non-Opaque Minerals," Bulletin 679, U. S. Geol. Survey, **1921**, and Groth, "Chemische Krystallographie," Part 2, **1908**, p. 429), the tetragonal hexahydrate prepared by L. de Boisbaudran (c) (de Boisbaudran, *Ann. chim. phys.*, (4) **18**, 260 (1869)), the monoclinic heptahydrate prepared by Loewel (d) (Loewel, *Ann. chim. phys.*, (3) **43**, 405 (1855); Groth, ref. 2 b, p. 431), and the dihydrate.

[3] Carpenter and Jette, THIS JOURNAL, **45**, 578 (1923). The rhombic heptahydrate is the stable phase below this temperature.

[4] Van't Hoff, Meyerhoffer and Smith, *Sitzb. preuss. Akad. Wiss.*, **1901**, 1034.

[5] The nearness of this point to that found for the hexahydrate—monohydrate transition caused them to doubt the identity of the five-fourths hydrate (ref. 4, footnote to page 1037).

point of the hexahydrate into the pentahydrate was found by T. Estreicher-Rozbiersky to be 77.5°.[4,6]

The transition of the tetrahydrate into the hexahydrate occurs fairly rapidly. A mixture of the tetrahydrate and a solution saturated with respect to it was cooled one degree per hour while being stirred; at 77° lumps which were found to contain the hexahydrate formed in the mixture. The hexahydrate may form alone if the solution is slowly evaporated at its boiling point. If the evaporation is rapid, or if the solution is agitated, the penta- and tetrahydrates form along with the hexahydrate. The tetrahydrate is the more stable of the three and solutions in equilibrium with it may be stirred for several days at 100° without the formation of lower hydrates. The five-fourths, and possibly the monohydrate also, may be induced to form by violent boiling or by inoculation from crusts formed on the sides of the vessel during evaporation. The solution comes to equilibrium with these slowly.

## Preparation of Hydrates

Crystals of the penta- and tetrahydrates were first obtained by Wyrouboff[7] by evaporation of a solution of magnesium sulfate acidified with sulfuric acid at 50°. They have also been obtained by Van't Hoff and Estreicher-Rozbiersky[8] by the evaporation of solutions of magnesium sulfate containing magnesium chloride at 25°. Playfair[9] and Thorpe and Watts[10] claimed to have prepared the pentahydrate by drying the heptahydrate to constant weight over sulfuric acid and, according to Millon,[11] the pentahydrate may be prepared by heating the heptahydrate to 40° in moist air.

Van't Hoff and Dawson[12] found that above 40° the tetrahydrate was replaced by the dihydrate when in contact with solutions of magnesium sulfate also saturated with respect to $MgCl_2.6H_2O$. This hydrate was unstable and at 65° was replaced by the five-fourths hydrate, which apparently was the stable phase in these solutions down to 20°. Both the

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[6] Wiedemann, *Pogg. Ann.*, **17**, 571 (1882), from dilatometric observations, concluded that there were two forms of the hexahydrate with a transition point under 92°. To test this, solutions in equilibrium with the monoclinic hexahydrate at 95° and containing a very little of the solid in suspension were inoculated with crystals of tetragonal nickel sulfate hexahydrate, which L. de Boisbaudran[2c] had found to be isomorphous with tetragonal magnesium sulfate hexahydrate. This did not cause the formation of a tetragonal (optically uniaxial) hydrate of magnesium sulfate, so that it does not seem probable that the tetragonal hexahydrate is formed at this temperature. No other hexahydrate of magnesium sulfate is known. Van't Hoff, Meyerhoffer and Smith[4] suggest that he observed the change of the pentahydate to the tetrahydrate.

[7] Wyrouboff, *Bull. soc. franç. minéral.*, **12**, 75, 366 (1889).

[8] Van't Hoff and Estreicher-Rozbiersky, *Sitzb. preuss. Akad. Wiss.*, **1898**, 487.

[9] Described by Thorpe and Watts, Ref. 10.

[10] Thorpe and Watts, *J. Chem. Soc.*, **37**, 102 (1880).

[11] Millon, *Ann. chim. phys.*, (3) **13**, 134 (1845).

[12] Van't Hoff and Dawson, *Sitzb. preuss. Akad. Wiss.*, **1899**, 340.

dihydrate and the five-fourths hydrate are unstable with respect to the monohydrate above about 25°[13] in contact with solid $MgCl_2.6H_2O$, but the monohydrate ordinarily does not form spontaneously under 75–85°.

Playfair,[9] Hannay[14] and Millon[15] observed that the dihydrate was formed on drying the heptahydrate in air at 100°. Hannay stated that his data favored the existence of a trihydrate but an examination of his curves does not warrant this. Millon obtained evidence in favor of a hydrate intermediate between the di- and monohydrates at 115° and this was confirmed by Van't Hoff and Dawson,[12] who found that the rate of water loss drops to one-tenth after the composition $MgSO_4.5/4H_2O$ has been reached. The dihydrate is best prepared in this way by allowing crystals of the heptahydrate to effloresce in air at 50–60° and then heating the powder at 100° for two hours. The product was found to contain crystals of the tetrahydrate and some monohydrate as a very fine powder. After drying in an oven at 95° for one day, the moisture content of a 3 mm. layer of the salt was found to be 17.5%, after two days, 15.6% and after three days 14.4%, showing a slowing up at the composition of the five-fourths hydrate, which has 15.7% of water. The dehydration can be continued to the monohydrate at this temperature. If the crystals of the heptahydrate are allowed to melt and then dried at 100°, a cake is formed containing the monohydrate.

Playfair[9] prepared the dihydrate by the action of boiling absolute alcohol on the heptahydrate. This is not a satisfactory method for the preparation of this salt. The heptahydrate is rapidly converted into the tetrahydrate by this treatment. If the tetrahydrate is boiled with three to four times its weight of absolute alcohol for twelve hours, most of it is converted into the dihydrate, but considerable five-fourths hydrate and finely divided monohydrate are formed with it. On further boiling the dihydrate and five-fourths hydrate may be converted into the monohydrate.

The monohydrate occurs in nature and is called kieserite. It may be prepared by heating the higher hydrates to 140–180° for several days.[9,10] Kieserite loses its water slowly at 250° and rapidly at 350°. Water may be determined readily by heating to 500° in an open crucible. The decomposition of anhydrous magnesium sulfate was found to be inappreciable at 750° but rapid above 850°.[16]

[13] Van't Hoff and Meyerhoffer, *Sitzb. preuss. Akad. Wiss.*, **1904,** 1418, inferred that the monohydrate was formed in contact with $MgCl_2.6H_2O$ above 18° but did not actually determine the transition point. Their conclusion was not confirmed by W. C. Blasdale, *J. Ind. Eng. Chem.*, **12,** 164 (1920), who found that the monohydrate was apparently unstable at 25°.

[14] Hannay, *J. Chem. Soc.*, (2) **32,** 381 (1877).

[15] Millon, ref. 11. He also states that the dihydrate may be prepared by keeping the heptahydrate in contact with very dry air at 35° for one month. The product probably contains considerable monohydrate.

[16] Cf. Marchali, *J. chim. phys.*, **22,** 325 (1925).

## Solubility Relations

A search was made for the solubility curve of the dihydrate between 70° and the boiling point, but it was not found. Solutions in equilibrium with the hexahydrate or tetrahydrate slowly came to equilibrium with the monohydrate when inoculated with preparations of the dihydrate, most of which had close to the theoretical water content, but contained some monohydrate.

The curve of the five-fourths hydrate was not determined, but from similar experiments it would appear to lie very slightly above the curve for the monohydrate at 95°.

Wyrouboff[17] observed that the solubility curves of the penta- and tetrahydrates were close together in sulfuric acid solutions at 50°. They are apparently close together in aqueous solutions at 100°. Both hydrates are formed in the boiling solution but on stirring at 95° the pentahydrate slowly disappears and the solubility drops slightly, from which it is assumed that the pentahydrate curve lies slightly above that of the tetrahydrate, as indicated in Fig. 1.

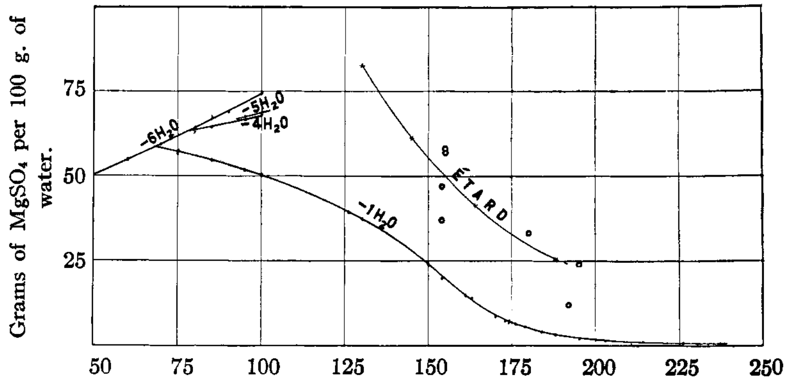

Fig. 1.—The system $MgSO_4$-$H_2O$ from 68 to 240°.

Geiger[18] gave for the solubility at 83°, 67.2 g. of $MgSO_4$ per 100 g. of water, but the solid phase present with his solutions was probably the hexahydrate. Smith[18] gave the concentration of a solution in equilibrium with kieserite at 80° as 62.8 g. of $MgSO_4$ per 100 g. of water and Meyerhoffer[18] obtained 68.5 at 99.4°. These points fall on the tetrahydrate curve as determined in this investigation, so that the solid phase was probably the tetrahydrate and not kieserite. Mayeda[19] gave 51.2 g. per 100 g. of water at 105°, a value slightly above the curve for the mono-

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[17] Ref. 7, p. 369.

[18] From Landolt-Börnstein Tabellen, **1923** ed.

[19] Mayeda, *J. Chem. Ind. (Japan)*, **23**, 573 (1920).

hydrate given in this paper. Étard[20] gave for the solubility of magnesium sulfate the following values.

| | | | | |
|---|---|---|---|---|
| Temperature, °C. | 130 | 145 | 164 | 188 |
| Per cent. $MgSO_4$, liquid phase | 45.3 | 38.0 | 29.3 | 20.4 |
| G. of $MgSO_4$ per 100 g. of water (calcd.) | 82.8 | 61.3 | 41.4 | 25.6 |

Étard enclosed his solutions in sealed tubes divided into two equal chambers by a constriction in the middle. The salt and solution were placed in one chamber and the tube was sealed off; the tube was then placed in a thermostat and after shaking a few times the liquid phase was poured into the empty chamber through the constriction, which acted as a filter. The tube was then cooled and the contents analyzed. He does not state the time given for the solutions to come to equilibrium. Suspensions of kieserite in solutions in equilibrium with it require several hours or even days to settle and Étard's liquid phase probably contained some finely divided kieserite. The salt may be more granular when formed from a supersaturated solution with comparatively little agitation.

Étard's results may give the composition of solutions on the supersolubility curve of kieserite. On this assumption, solutions lying below the curve could be agitated without depositing the salt, while those above it would deposit kieserite by spontaneous crystallization upon agitation.[21]

The data given in the following table are in agreement with this interpretation of Étard's data.

Table I

| Temp., °C. | Hours stirred | Liquid phase[a] Before stirring | After stirring | Salt formed | Remarks |
|---|---|---|---|---|---|
| 154 | 4 | 37 | same | none | below Étard's curve |
| 154 | 1 1/2 | 47 | same | none | below Étard's curve |
| 192 | 1 | 12 | same | none | below Étard's curve |
| 155 | 1 1/2 | 57 | 37 | kieserite | above Étard's curve |
| 155 | 1 1/2 | 58 | 32 | kieserite | above Étard's curve |
| 195 | 3 | 24 | 4.6 | kieserite | above Étard's curve |

[a] Liquid phase given in g. of $MgSO_4$ per 100 g. of water.

The trials in this table were not inoculated with kieserite. They are represented by circles in Fig. 1, while Étard's measurements are represented by crosses. Étard observed that a solution containing 33.3 g. of magnesium sulfate per 100 g. of water crystallized spontaneously at 180°.

When a solution exceeds the supersolubility curve, crystallization occurs spontaneously upon agitation, with the formation of many very small crystals. As the crystal surface exposed by these very fine crystals is large, the formation of a small quantity of them would be expected to be

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[20] Étard, *Ann. chim. phys.*, (7) **2**, 503 (1894).

[21] Blasdale, "Equilibria in Saturated Salt Solutions," A. C. S. Monograph Series, No. 31, **1927**, p. 66.

more effective in reducing the supersaturation of the solution than the presence of several times as much of the salt in a coarser crystalline form. Trials which became inoculated through exceeding the supersolubility curve came to equilibrium more rapidly than those which were inoculated with 5 or 10% of kieserite by weight.

The solubility curve of kieserite is given by Landolt-Börnstein, **1923** ed., as passing through the values given by Smith and Meyerhoffer and the last two values given by Étard.

## Identification of Hydrates

The hydrates of magnesium sulfate occurring near the boiling point may be identified with the aid of the petrographic microscope. After a portion of the liquid phase had been taken for analysis, the suspended hydrates were allowed to settle for a few minutes and a small quantity was removed with a glass or perforated platinum spoon. When the hexahydrate, pentahydrate or tetrahydrate was present, this was rubbed dry on warmed filter paper or pressed on a porous plate warmed to 80°. These hydrates are partially decomposed by pressing dry on a porous plate warmed to 100°, which treatment was required to dry the monohydrate. Some hexahydrate formed by cooling of the adhering liquor while pressing the solids dry between filter paper. The absorbent cotton rolls used by dentists were found of value in drying the samples. Some of the samples were washed with alcohol, but this is objectionable as the addition of absolute alcohol to a saturated solution of magnesium sulfate at 80–90° usually precipitates some tetrahydrate.

The optical properties of the hydrates are given in the following table.[22]

TABLE II

THE OPTICAL PROPERTIES OF THE HYDRATES

| Hydrate | $\alpha$ | $\beta$ | $\gamma$ | $2V$ sign disp. | Orientation | System |
|---|---|---|---|---|---|---|
| Hexa- | 1.438 | 1.463 | 1.465 | $29° - \rho > v$ | $Y = b, X_{\wedge}c - 25°$ | Monoclinic |
| Penta- | 1.482 | 1.492 | 1.493 | $45° - \rho < v$ | $X$ near $b$ | Triclinic |
| Tetra- | 1.490 | 1.491 | 1.497 | $50° + \rho > v$ | $Z = b, X_{\wedge}c\ 81°$ | Monoclinic |
| Di- | | 1.493 | radiate clusters of very fine needles | | | |
| Five-fourths | 1.512 | 1.530 | indices of diamond-shaped crystals | | | |
| Mono- | 1.523 | 1.535 | 1.586 | $57° + \rho > v$ | $Y = b, Z_{\wedge}c\ 76^1/_2°$ | Monoclinic |

The monoclinic hexahydrate may be recognized by its indices of refraction and small optic angle. The penta- and tetrahydrates may be distinguished by their difference in sign. When prepared from solutions containing magnesium chloride, the tetrahydrate appears in six-sided

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[22] The nomenclature is that employed by Larsen, ref. 2 b. The optical orientation of the hexa-, penta- and tetrahydrates, with their optic angles and dispersion, is given by Wyrouboff, ref. 7. The indices of refraction given in this table are probably accurate to ±0.003. The optical properties of the monohydrate are given by Larsen, ref. 2b, p. 211.

plates, showing the forms *m*(110) and *b*(010).[23] The angle $m_\wedge m$ is 48° 40′ and frequently this angle may be measured to within 1° under the microscope. No dome or pyramid faces were observed. Cleavage was observed parallel to *a*(100) and *b*(010). The pentahydrate and hexahydrate are elongated in the direction of the *c* axis, and do not show cleavage. Crushed fragments of the three hydrates look very similar when placed between crossed nicols with parallel light.

The needles of the dihydrate show varying extinction angles and elongation and were too fine for the observation of their optical properties. Single crystals of the five-fourths hydrate were not observed. The diamond-shaped crystals show crossed twinning, with the opposite quadrants extinguishing at 5° to the symmetry plane of the diamond. The twinning is often imperfect.

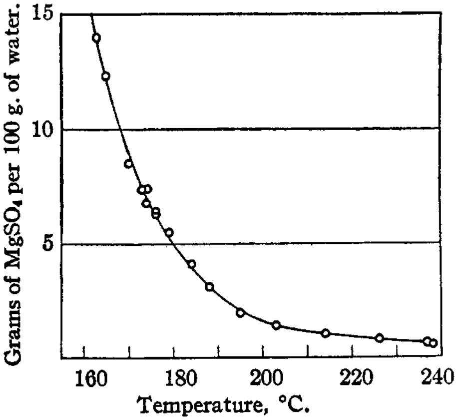

Fig. 2.—The system $MgSO_4$-$H_2O$ from 160 to 240°.

In all the trials except those above 200° kieserite occurred in aggregates of very small grains, which were too small for the observation of crystal structure or optical character. It may be recognized by its high index of refraction and fine-grained structure. Solutions inoculated with preparations of kieserite and allowed to come to equilibrium with it had minimum contents of magnesium sulfate. After trials at 226, 240 and 246° had been sampled, the valve of the solubility bomb (see below) was left open until all of the liquid phase had passed out. The bomb was then quickly opened and the solid phase found to be granular and quite dry. On analysis it gave 1.00, 0.99 and 0.98 molecules of water per molecule of magnesium sulfate, respectively. Some of the grains were large enough so that interference figures could be obtained. As there is no break in the solubility curve, this was taken as evidence that the solid phase present in the trials between 100 and 240° and which fell on the "monohydrate" curve was in reality the monohydrate.

## Description of Apparatus

In the experiments under 100°, the solutions in contact with the solid phase were stirred in 4 × 30 cm. tubes immersed in an oil-bath kept constant to within half a degree. The tube was closed off with a rubber stopper where it projected above the level of the

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[23] Indices assigned by Groth, ref. 2 b, p. 413.

oil, the stirring screw coming through a glass tubing which passed through this stopper. After sufficient stirring, about 30 g. of the solution was filtered through a dried alundum thimble[24] into a weight pipet and analyzed.

The trials above 100° were made with a gold-plated bomb of Monel metal, shown in Fig. 3. This consisted of a cylindrical vessel A, 9 cm. long by 3.25 cm. inside diameter, and a head-piece B which carried the filtering apparatus and the needle valve. The upper part of the cylinder was 4 cm. in diameter and was threaded to receive the head, which screwed into it against a flat gold washer C resting on a 3mm. shoulder. The gold washer was $^1/_{50}$ inch thick and the volume of the cylinder up to the shoulder was 70 cc. This arrangement gave a joint that was satisfactory for the pressures encountered up to 240° but which did not hold well at higher temperatures.

The head was hollowed out to a depth of 1 cm. to give a flat surface 3.5 cm. in diameter, and the filtering apparatus was mounted in this recession. This consisted of an alundum disk D, 1 × $^1/_8$ inche, with a beveled edge, the composition being given by the Norton Co. as RA98. This was held against the flat surface of the head by four prongs attached to an expansion ring E. Under the alundum disk was an asbestos pad, then a flat gold washer F which was 3 cm. in diameter and $^1/_{100}$ inch thick, with a 6mm. hole in the center. Under this washer was another asbestos pad. The asbestos pads were prepared by suspending carefully selected, long fiber asbestos in water and then slowly evaporating off the water. They could be compressed to a thickness of $^1/_{500}$ of an inch.

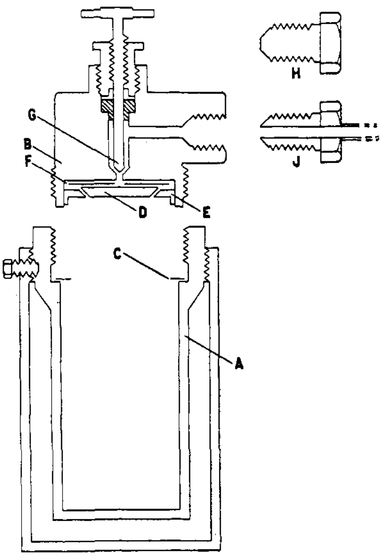

Fig. 3.—Solubility bomb.

The hole in the washer gave an empty space of negligible volume directly over the needle valve G. After the salt and water mixture had been stirred the required length of time, the bomb was removed from the bath and clamped head downwards. When the needle valve was opened, the liquid phase was forced through the alundum disk into the valve chamber under its own vapor pressure and through an opening in the side of this chamber into the delivery tube J. The delivery tube was a short piece of $^1/_8$-inch copper tubing attached to a brass piece which screwed into the opening in the head. While the bomb was in the oil-bath, the opening was closed with a plug H. The delivery tube was connected to the condenser, which was a U-shaped copper tube $^3/_4$ inch in diameter and two feet long, weighing 125 g. During sampling this was partially immersed in ice water. The end not connected to the delivery tube was open to the atmosphere. No water vapor was observed to come out of this end.

After about 30 g. of liquid had been drawn off, the valve was closed and the contents of the condenser analyzed. With trials run above 160° this quantity of liquid was obtained in about thirty seconds, depending upon the amount of solid salt inside the

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[24] The thimbles were supplied by the Norton Company. Those most satisfactory were of mix RA98. The solutions filtered through thimbles of this composition rapidly, carrying a negligible quantity of kieserite into the sample where it was present in the tubes. Thimbles of composition RA225 gave clear solutions, but the liquid phase passed through them very slowly.

bomb. At lower temperatures a longer time was required, the trial at 126° taking two and one-half minutes. The time taken for the liquid phase to pass the filter did not seem to affect the results.

The bomb had an outer brass shell to prevent rapid loss of heat after it had been taken from the bath. After charging, the bomb was fastened to a stirring device and rotated at 60 r.p.m. in a bath of meprolene kept at constant temperature within half a degree. The bath was thoroughly stirred and the temperature taken with two calibrated thermometers. When stirred a sufficient length of time, the bomb was taken from the bath, clamped to a stand, the delivery tube and condenser were attached and the valve was opened, this taking about one minute. From preliminary experiments with ice it was estimated that the contents of the bomb were within one degree of the temperature of the bath after twenty-five minutes of stirring.

This apparatus was designed to measure equilibrium in ternary salt-water systems, but with most of the salt solutions experimented with crystals formed in the valve chamber during sampling. With magnesium sulfate, the negative slope of the solubility curve with temperature, and its tendency to supersaturate, prevented error from this source.

An attempt was made to employ a filter outside the bomb. This consisted of a male brass piece which screwed into the opening in the head of the bomb, and also into a 1″ brass sleeve, which was closed at one end except for an eighth-inch delivery tube going to the condenser as in other experiments. An alundum disk was placed between two lead washers in the sleeve and the male piece screwed tightly against the outer washer. On opening the valve, the liquid was forced out through the valve chamber and the alundum disc into the discharge tube and so to the condenser.

This arrangement was unsatisfactory, chiefly because the liquid phase cooled after passing through the needle valve, due to the release of pressure and consequent evaporation, and so was filtered from any solid salt it carried along with it at a lower temperature than it had before leaving the bomb. With kieserite the solubility increased with falling temperature and this apparatus gave high results. As there is a drop in pressure across the filter, any filter which the liquid phase might pass after leaving the needle valve would become cooled by the evaporation of some of the water and so introduce an error. To avoid this the filter must be placed inside the bomb.

## Results

Solutions came to equilibrium with the hexahydrate in a few minutes, and to equilibrium with the penta- and tetrahydrates fairly rapidly. Three to seven days were required for solutions to come to equilibrium with kieserite under 100°, unless an abundance of solid phase was present. Equilibrium was not obtained in less than twenty-four hours' stirring under 160° nor with less than four hours' stirring under 190°, but was obtained after stirring for one-half hour at 238°. Many trials, well inoculated, which were stirred for shorter periods gave high results.

There appears to be a relation between the degree of crystallographic perfection exhibited by a salt and the rapidity with which it comes to equilibrium with its aqueous solution. Thus kieserite is poorly crystallized under 200° and comes to equilibrium slowly. Above this temperature it is granular and comes to equilibrium rapidly. The dihydrate would be expected to come to equilibrium slowly. Salts such as sodium chloride, potassium chloride and potassium sulfate, which are well crystallized, formed crystals in the valve chamber in experiments at 150° even when no delivery tube was employed, while sodium sulfate and sodium carbonate, which are less well crystallized, could be filtered with the external filter, but the solutions altered in composition in passing through the apparatus.

The trials made with the bomb fall on a definite line, as may be seen from Fig. 2, in which the values from 160 to 240° are plotted on a larger scale. All the trials which fulfilled the requirements of adequate inoculation, duration of stirring and proper filtering fell within one degree of this curve. The samples were analyzed by precipitating an aliquot part with barium chloride, the method being accurate to 0.1% by trials against pure sodium sulfate.

Table III gives the results of experiments which are considered satisfactory. Three values of Mulder[18] and those of Smith and Meyerhoffer previously mentioned are included. The values are plotted in Fig. 1.

TABLE III

COMPOSITION OF SOLUTIONS SATURATED WITH $MgSO_4$

| Temp., °C. | Liquid phase, g. of $MgSO_4$ per 10 g. of water | Hours stirred | Remarks |
|---|---|---|---|
| 70 | 59.4 | | By Mulder, hexahydrate |
| 75 | 56.5 | 150 | Kieserite |
| 75 | 57.4 | 150 | Kieserite |
| 80 | 64.2 | | By Mulder, hexahydrate |
| 80 | 62.8 | | By Smith |
| 85 | 67.1 | 2 | Hexahydrate |
| 85 | 67.6 | $1^1/_4$ | Hexahydrate |
| 85 | 64.3 | 8 | Penta- and tetrahydrates |
| 85 | 64.6 | 5 | Penta- and tetrahydrates |
| 85 | 64.7 | 24 | Penta- and tetrahydrates |
| 85 | 64.1 | 24 | Tetrahydrate |
| 85 | 64.3 | 48 | Tetrahydrate |
| 85 | 54.75 | 150 | Kieserite |
| 85 | 54.75 | 150 | Kieserite |
| 85 | 55.05 | 150 | Kieserite |
| 90 | 69.0 | | By Mulder, hexahydrate |
| 95 | 67.7 | 1 | Penta- and tetrahydrates |
| 95 | 67.2 | 4 | Penta- and tetrahydrates |
| 95 | 66.6 | 24 | Tetrahydrate |
| 95 | 66.2 | 30 | Tetrahydrate |
| 95 | 52.0 | 150 | Kieserite |

TABLE III (*Concluded*)

| Temp., °C. | Liquid phase, g. of $MgSO_4$ per 10 g. of water | Hours stirred | Remarks |
|---|---|---|---|
| 95 | 52.1 | 150 | Kieserite |
| 95 | 51.6 | 150 | Kieserite |
| 95 | 51.6 | 100 | Kieserite |
| 95 | 51.6 | 96 | Kieserite |
| 99.4 | 68.5 | | By Meyerhoffer |
| 100 | 74.6 | 2 minutes after concentration by boiling | Hexahydrate |
| 100 | 68.1 | $^1/_2$ | Penta- and tetrahydrates |
| 100 | 67.7 | $1^1/_2$ | Penta- and tetrahydrates |
| 100 | 50.4 | 40 | Kieserite |
| 126 | 39.3 | 96 | Kieserite |
| 130 | 37.2 | 65 | Kieserite |
| 150 | 23.9 | 24 | Kieserite |
| 154 | 19.8 | 48 | Kieserite |
| 161 | 14.8 | 24 | Kieserite |
| 163 | 14.0 | 24 | Kieserite |
| 165 | 12.3 | 12 | Kieserite |
| 170 | 8.5 | 18 | Kieserite |
| 173 | 7.4 | 24 | Kieserite |
| 174 | 7.4 | 48 | Kieserite |
| 174 | 6.8 | 24 | Kieserite |
| 176 | 6.3 | 5 | Kieserite |
| 176 | 6.4 | 18 | Kieserite |
| 179 | 5.5 | 5 | Kieserite |
| 184 | 4.1 | 12 | Kieserite |
| 188 | 3.1 | 4 | Kieserite |
| 195 | 1.9 | 18 | Kieserite |
| 203 | 1.4 | 36 | Kieserite |
| 214 | 1.05 | 34 | Kieserite |
| 226 | .78 | $1^1/_2$ | Kieserite |
| 237 | .64 | 12 | Kieserite |
| 238 | .56 | $^1/_2$ | Kieserite |

In conclusion, the author wishes to express his thanks to Professor W. C. Blasdale for his valuable assistance during this research.

## Summary

1. An apparatus has been described with which solubility determinations have been made up to 240°, with magnesium sulfate monohydrate as the solid phase.

2. The solubility curve of magnesium sulfate monohydrate was found to fall off rapidly with increase of temperature from 68 to 200°, and then to decrease slowly at least to 238°. Equilibrium was obtained very slowly under 200° and more rapidly above that temperature.

3. It has been suggested that the solubility measurements of Étard on this salt give the position of the supersolubility curve, and observations in agreement with this have been tabulated.

4. The solubility curves of magnesium sulfate hexa-, penta- and tetrahydrate have been studied at 85, 95 and 100°.

5. The preparation of the hexa-, penta-, tetra-, di-, five-fourths and monohydrates of magnesium sulfate has been discussed, together with their identification with the aid of the petrographic microscope, and new optical data for the hexa-, penta-, tetra-, di- and five-fourths hydrates have been given.

6. It has been suggested that there is a relation between the degree of crystallographic perfection exhibited by a salt and the rate at which it comes to equilibrium with its aqueous solution.

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# THE CATALYTIC ACTIVITY AND ADSORPTIVE POWER OF SUPPORTED IRON, COBALT, NICKEL, COPPER AND SILVER

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This paper records the results of experiments on the activities of similarly prepared, supported iron, cobalt, nickel, copper and silver catalysts in the hydrogenation of ethylene. The experiments were undertaken with the view to determine the true relative activities of these metals as hydrogenation catalysts and to obtaining preliminary results on reaction kinetics.

The specific activity of a contact catalyst depends ultimately on its chemical nature. In addition, however, the catalytic effect as experimentally determined is conditioned by the area of surface exposed per unit volume of reactants and by its submicroscopic form, and these vary from one sample to the next. If a comparison of two substances as catalysts is desired, therefore, some standardization relative to surface characteristics is required. Bulk catalysts are out of the question, because the utmost care in preparation cannot ensure similarity of surface. Supported catalysts are of greater promise. The surface of a porous refractory will not change with any ordinary treatment and a film of the substance to be examined spread over the surface should assume the form of the latter. Consequently, if the catalysts to be compared are supported on average samples of the same refractory material, it may fairly be assumed that differences in activity are chiefly due to the specific properties of the substances under investigation.

We have prepared a uniform supply of crushed diatomite brick and have impregnated samples with such quantities of solutions of the nitrates of the metals as would correspond to 1 gram atom of metal per 1000 g. of dry brick. These samples were then dried slowly, calcined and reduced. The amount of the metal is admittedly arbitrary. It is approximately