means of equation (8) and are given in Table IV. The corresponding values of $\Delta\varphi(\varphi_{\text{exptl.}} - \varphi_{\text{D}})$ have also been calculated and are included in the same table (III). For some of the salts $\Delta\varphi$ has been plotted against $m$ in Fig. 6. Cerium, praseodymium and neodymium chlorides were omitted from the plot because the values of $\Delta\varphi$ for these salts were so close to lanthanum chloride which has been included.

The values of $\Delta\varphi$ representing the deviation from Scatchard's equation are not proportionately large when compared to those given by him for the higher valence sulfates measured by Robinson and Jones.[14] In fact, the actual values of $\Delta\varphi$ found in this investigation are less than those for the sulfates.

(14) Robinson and Jones, THIS JOURNAL, **58**, 959 (1936).

I am indebted to Professor Scatchard and Dr. Wood for the use of their data for the osmotic coefficients of potassium and sodium chlorides prior to publication and for several suggestions regarding the use of equation (8). For these courtesies I wish to express thanks.

### Summary

1. The osmotic coefficients of aluminum, scandium, yttrium, lanthanum, cerium, praseodymium and neodymium chlorides have been determined in aqueous solution at 25° by the isotonic method of Robinson and Sinclair.[2]

2. The activity coefficients of these salts have been computed from the osmotic coefficients.

3. The data obtained in both 1 and 2 have been compared with theory.

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## Ternary Systems. XXIV. Calcium Sulfate, Sodium Sulfate and Water

BY ARTHUR E. HILL AND JOHN H. WILLS[1]

Early study of this system by Fritsche[2] disclosed the existence of two double salts, glauberite ($CaSO_4 \cdot Na_2SO_4$) and a salt of the composition $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$, which has been variously known as syngenite, from a mistaken reading of its composition, and as the labile double salt, from its metastable relationship to other double salts. Isotherms of the system have been studied at 22° by Cameron and Seidell,[3] and at 25° by Cameron and Breazeale,[4] in both cases without inclusion of double salts. Barre[5] compiled the concentrations of isothermally invariant solutions saturated with two salts, glauberite and each of the components of the system and the labile salt with each of the components, giving an outlined polytherm of the system from room temperature to 100°. D'Ans and Schreiner[6] discussed the two double salts and added a point of saturation by glauberite and gypsum at 60°. Van't Hoff[7] determined the invariant points of saturation by each of these

(1) This paper is an abridgment of the thesis presented by Mr. Wills in partial fulfilment of the requirements for the degree of Ph.D. at New York University, June, 1935.
(2) Fritsche, J. prakt. Chem., **72**, 291 (1857). Glauberite had been prepared previously only in the dry way.
(3) Cameron and Seidell, J. Phys. Chem., **5**, 643 (1901).
(4) Cameron and Breazeale, ibid., **8**, 335 (1904).
(5) Barre, Ann. chim. phys., [8] **24**, 145 (1911).
(6) D'Ans and Schreiner, Z. anorg. Chem., **62**, 129 (1909).
(7) Van't Hoff, Z. physik. Chem., **45**, 257 (1903).

double salts with gypsum and mirabilite (Glauber's salt) as 30.2° for the transition involving the labile double salt and 29° for that involving glauberite. The present research contains a repetition of the 25° isotherm and additional isotherms at 35, 50 and 75°, including in addition to the previously known double salts, anhydrite at the higher temperatures and a new double salt, sodium pentacalcium sulfate; these data permit the construction of a fuller polytherm than was previously possible.

In carrying out work in this system in which there occur so many degrees of metastability at any given temperature, much use has been made of van't Hoff's[8] generalization that the retardation of salts in coming to equilibrium with their solutions is related to the mean valence, calculated by dividing the total valence representing all the ions in the formula by the total number of such ions, giving each water molecule in a hydrate an arbitrary mean valence of 4/3; this rule guided us in this research, as in other related researches,[9] in deciding upon appropriate time of contact for

(8) Van't Hoff. "Zur Bildung der ozeanischen Salzablagerungen." F. Vieweg und Sohn, Braunschweig, 1905; Vol. I, p. 32; Vol. II, p. 17.
(9) Hill, THIS JOURNAL. **56**, 1071 (1934); Hill and Yanick, ibid., **57**, 645 (1935).

the different salts, for which periods as short as one or two minutes may sometimes not be exceeded without change, while in other cases weeks or months are necessary. The entire list of salts now known in this system, with the mean valence for each, is as follows:

| Name | Formula | Mean valence |
|---|---|---|
| Mirabilite | $Na_2SO_4 \cdot 10H_2O$ | 1.33 |
| (Unnamed) | $(Na_2SO_4 \cdot 7H_2O)$ | (1.33) |
| Thenardite | $Na_2SO_4$ | 1.33 |
| Labile salt | $2Na_2SO_4 \cdot CaSO_4 \cdot 2H_2O$ | 1.43 |
| Gypsum | $CaSO_4 \cdot 2H_2O$ | 1.50 |
| Glauberite | $Na_2SO_4 \cdot CaSO_4$ | 1.60 |
| Pentasulfate | $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ | 1.64 |
| (Hemihydrate) | $(CaSO_4 \cdot 0.5H_2O)$ | (1.71) |
| Anhydrite | $CaSO_4$ | 2.00 |

Of this series, the second and the eighth, sodium sulfate heptahydrate and calcium sulfate hemihydrate, did not appear spontaneously in any of our experiments, and were omitted from consideration; the others have been considered in the appropriate isotherms. Special attention was paid to the labile salt, concerning which a number of points have apparently remained unsettled in the eighty years since its discovery and of course special attention was likewise given to the new pentasalt after it had appeared in one of the isotherms.

**The Labile Salt, Sodium Hemicalcium Sulfate.**—The composition of this salt as proposed by Fritsche and its condition as metastable with respect to glauberite as held by van't Hoff were disputed by Cameron, Bell and Robinson,[10] who believed the formula to be $2CaSO_4 \cdot 3Na_2SO_4$ (anhydrous) on the basis of indirect determination of composition in a sodium chloride solution, and also believed that their dilatometric experiments showed it to be stable. Experimental answer to this view appears in the four isotherms presented in this paper, which show by solubility curves that the labile salt is metastable with respect to glauberite between 25 and 75°, in accord with van't Hoff's conclusion based upon the transition temperatures. The matter of the composition of the salt was gone into by D'Ans and Schreiner,[6] who were able to obtain samples sufficiently freed from mother liquor, by use of a hydraulic press, to permit analyses, which agreed well with the formula $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$. It is worth noting that each of the methods which led to the conflicting results is accompanied by unusual difficulties in the case of this salt, which forms from

gypsum in sodium sulfate solution in the form of a network of fine spicules so knitted together that a weight of approximately 2% of the salt will hold the mass in suspension so rigidly that there is no movement upon inversion of the vessel. This condition obviously retards the attainment of equilibrium and may leave a considerable portion of gypsum unchanged, which is probably the cause of Cameron, Bell and Robinson's error. This network retains a large proportion of mother liquor even upon centrifuging at 1800 r. p. m., so that a direct analysis such as D'Ans and Schreiner made is not always possible. We are able, however, to confirm their findings, by the use of both methods; algebraic extrapolation of the tie lines for the labile salt in Table I gave (assuming the water content of the salt correct) agreement with the original formula of Fritsche with an average deviation of 0.75% for the six cases there tabulated, with a maximum deviation of 1.30%, in experiments in which the amounts of solid phase were usually less than 1% of the weight of the system. A sample was also prepared by washing out the mother liquor with alcohol–water mixtures, which was found to contain 29.75% $CaSO_4$ (theory 29.83), 61.57% $Na_2SO_4$ (theory 62.27), and 8.68% $H_2O$ (theory 7.90), in agreement with the formula $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$.

With respect to the metastability of the salt, our findings are in agreement with those of Barre and of D'Ans and Schreiner that the salt can be held unchanged for long periods of time in contact with its solutions at lower temperatures (25° e. g.), and that only at 75° and above does the change toward glauberite begin at once. The action of the salt when treated at 25° with pure water instead of a sodium sulfate solution with which it is in equilibrium (30–34%) is noteworthy; the decomposition cannot be better described than as explosive, both because of the astonishing speed at which the solid disappears, and also because of the unexpected concentration attained. A sample was treated with cold water and immediately filtered from a small residue of calcium sulfate; the solution was analyzed and found to contain 1.01% calcium sulfate. At 25° the solubility of gypsum is 0.208% and that of anhydrite[11] is 0.274%; the solubility of hemihydrate from the curve of Chassevent[12] is about 0.8%, all figures being considerably less than the value found.

(10) Cameron, Bell and Robinson, J. Phys. Chem., 11, 409 (1907).

(11) Hill, THIS JOURNAL, 59, 2242 (1937).

(12) Chassevent, Ann. chim. phys., [10] 6, 244 (1926).

This seems to be evidence that the mechanism by which the salt decomposes on treatment with water cannot be a simple change into dissolved sodium sulfate and solid calcium sulfate in one of the three forms noted, since a solution cannot supersaturate itself from a given solid phase; either a fourth solid calcium sulfate is formed (an amorphous body, perhaps, which may be the condition of the oft-quoted "soluble anhydrite") or else the primary change is into dissolved material which only later precipitates. Investigation of this phenomenon of decomposition is being continued.

Microscopic identification of the labile hemisalt is comparatively easy, by two of its properties: first, the unusual slimness of the long needles, which run quite uniformly between 1 and 2 $\mu$ in breadth, whatever be the length, and by their refractive index $\gamma = 1.510$ ($\pm 0.003$), which is sufficiently different from that of glauberite as given by Larsen[13] ($\gamma = 1.536$) as well as that of the pentasalt given later in this paper. The refractive indices in the other directions could not be determined accurately enough.

**Sodium Pentacalcium Sulfate.**—The new salt, resembling the pentacalcium sulfates found in the potash series and the ammonia series except as to extent of hydration, was first found at 75° when solutions of about 14% sodium sulfate content were treated with gypsum; in general, it may be prepared easily at temperatures of 60 to 75° in solutions of 10 to 14% sodium sulfate upon addition of gypsum, or more rapidly by introduction of gypsum and glauberite in proportions corresponding to the reaction $4(CaSO_4 \cdot 2H_2O) + CaSO_4 \cdot Na_2SO_4 \rightarrow 5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O + 5H_2O$. The reaction is completed in four days or less; if the concentration of the solution is such that the salt is metastable only with respect to anhydrite (see Fig. 4), subsequent change to that solid is very slow and need hardly be taken into consideration, but operation in the concentration where the pentasalt is metastable with respect to glauberite will result in fairly rapid and eventually complete change into that salt. Samples of the pentasalt may be washed free of mother liquor without appreciable decomposition, and are found upon analysis to be in close agreement with the formula given; a sample gave $CaSO_4$ 77.59% (theory 77.63), $Na_2SO_4$ 16.21 (theory 16.20),

H2O 6.20 (theory 6.17). This water content, which was confirmed by a number of analyses giving 6.2% of water or a few tenths higher, corresponds to a trihydrate, whereas the corresponding potassium and ammonium salts have been found by all investigators to be monohydrates.

The salt crystallizes in rather fine needles of an average diameter of about 7 $\mu$, which under the microscope are seen to be prisms (or pinacoid faces) with pyramidal ends. They show oblique extinction; $Z \wedge c$ is 11° ($\pm 2$), which is quite close to that found for the corresponding potassium and ammonium salts by Gabriel;[14] the refractive indices found were $\alpha = 1.5557$ ($\pm 0.003$), $\gamma = 1.567$ ($\pm 0.003$).

### Experimental Procedure

The materials used were precipitated gypsum and analyzed anhydrous sodium sulfate. Where salts were expected to form by reaction of these components, they were weighed accurately with weighed quantities of water, to give a known original complex as one of the points to be used in extrapolations for the composition of the solid phases. The materials were rotated in stoppered bottles in thermostats for appropriate times. For analysis, solution was filtered off and a part evaporated to constant weight, first at 100° and finally for a day at 200°; in the remainder of the solution, the calcium was precipitated as oxalate and weighed as oxide. It was found that the precipitated calcium oxalate occluded sodium sulfate in weighable amount, whereas occlusion of potassium sulfate did not occur in our previous work;[9] the most effective method of elimination was found to be the volatilization of the sodium salt from the bottom of the platinum crucible to the lid, which occurred at temperatures reached by a Meker burner or blast lamp, and subsequent volatilization from the lid by heating it in the open; failure to do this would leave the results one per cent. or more too high in calcium.

**The 25° Isotherm.**—The results at 25° are given in Table I and shown in Fig. 1.

The solubility curve for gypsum passes through a minimum at a concentration of about 1.5% of sodium sulfate, and through a maximum at about 20%. The figures of Cameron and Breazeale[4] are distinctly higher than found by us; the isothermally invariant point for gypsum and mirabilite

(13) Larsen. "The Microscopic Determination of the Nonopaque Minerals," U. S. Govt. Printing Office, Washington, D. C., 1934, p. 156.

(14) Gabriel, THIS JOURNAL, **57**, 686 (1935).

## TABLE I
### CaSO₄-Na₂SO₄-H₂O AT 25°

| Original complex Wt. % | | Saturated solution Wt. % | | |
|---|---|---|---|---|
| Na₂SO₄ | CaSO₄ | Na₂SO₄ | CaSO₄ | Solid phases |
| —— | —— | —— | 0.209 | Gypsum |
| 0.573 | 3.773 | 0.595 | .148 | Gypsum |
| 1.529 | 3.789 | 1.601 | .139 | Gypsum |
| 3.109 | 2.561 | 3.200 | .144 | Gypsum |
| 5.964 | 3.805 | 6.251 | .161 | Gypsum |
| 10.80 | 1.176 | 10.93 | .181 | Gypsum |
| 14.63 | 3.304 | 15.23 | .194 | Gypsum |
| 17.89 | 1.093 | 18.09 | .197 | Gypsum |
| 19.24 | 3.803 | 20.15 | .198 | Gypsum |
| 24.21 | 1.276 | 21.75 | .197 | Gypsum + mirabilite |
| —— | —— | 25.87 | .188 | Gypsum(m) + glauberite |
| ·— | —— | 27.98 | .180 | Gypsum(m) |
| 29.84 | 0.325 | 29.78 | .174 | Gypsum(m) + labile salt |
| —— | —— | 33.85 | .155 | Gypsum(m) + thenardite |
| —— | —— | 21.70 | —— | Mirabilite |
| 22.29 | 1.138 | 21.72 | .120 | Mirabilite |
| ·—· | —— | 33.91 | .049 | Glauberite + thenardite |
| —— | —— | 32.61 | .065 | Glauberite |
| —— | —— | 29.31 | .113 | Glauberite |
| —— | —— | 26.60 | .175 | Glauberite |
| 36.37 | 0.358 | 34.13 | .055 | Labile salt + thenardite |
| 33.31 | .700 | 32.72 | .070 | ·Labile salt |
| 32.84 | .426 | 32.49 | .073 | Labile salt |
| 31.74 | .427 | 31.41 | .094 | Labile salt |
| 31.60 | .693 | 31.05 | .123 | Labile salt |
| 30.69 | .317 | 30.47 | .115 | Labile salt |
| 31.01 | .744 | 30.34 | .141 | Labile salt |
| | | 34.00 | .00 | Thenardite |

shows very little change in the solubility of mirabilite caused by the small amount of calcium sulfate present. It is not easy to explain Cameron and Breazeale's view that the solubility of mirabilite is considerably depressed. We have con-
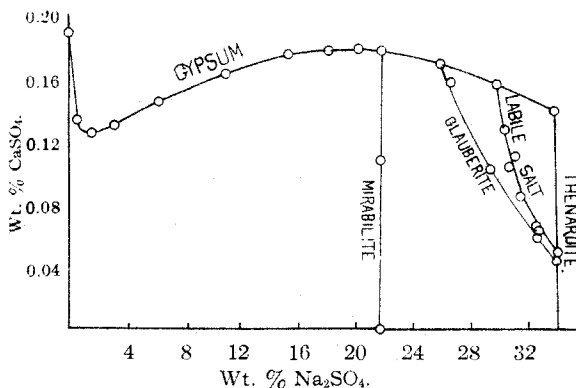


Fig. 1.—CaSO₄-Na₂SO₄-H₂O at 25°.

tinued the measurements in the region of supersaturation with respect to mirabilite, which was accomplished by warming the systems above the transition temperature of mirabilite (32.4°) before immersion in the thermostat at 25°. The points on the curve for the labile salt were obtained by allowing the compound to form from gypsum, after seeding with the labile salt; the reaction required one to two weeks for completion, except where excess solid thenardite was present, in which case the change of gypsum to labile salt is quite rapid. Glauberite, however, did not seem to form at all at this temperature; the measurements were made, therefore, by addition of glauberite prepared at higher temperatures; equilibrium was reached in one day. Anhydrite was not included in the work at this temperature, because of the extreme difficulty in obtaining

## TABLE II
### CaSO₄-Na₂SO₄-H₂O AT 35°

| Original complex Wt. % | | Saturated solution Wt. % | | |
|---|---|---|---|---|
| Na₂SO₄ | CaSO₄ | Na₂SO₄ | CaSO₄ | Solid phases |
| —— | —— | —— | 0.214 | Gypsum |
| 0.489 | 1.023 | 0.503 | .150 | Gypsum |
| .984 | 0.974 | .988 | .142 | Gypsum |
| 1.937 | .983 | 1.896 | .142 | Gypsum |
| 5.916 | .978 | 5.968 | .164 | Gypsum |
| 13.85 | 1.064 | 13.97 | .198 | Gypsum |
| —— | —— | 25.16 | .204 | Gypsum |
| 27.70 | 0.819 | 27.93 | .199 | Gypsum |
| 29.51 | 1.216 | 29.89 | .190 | Gypsum |
| 33.54 | 0.700 | 32.85 | .178 | Gypsum + thenardite |
| —— | —— | 32.90 | —— | Thenardite |
| 35.21 | .560 | 32.87 | .046 | Thenardite + glauberite |
| 29.67 | .962 | 29.31 | .084 | Glauberite |
| 28.70 | .993 | 28.34 | .099 | Glauberite |
| 25.73 | 1.169 | 25.17 | .146 | Glauberite |
| 23.68 | 1.219 | 23.06 | .199 | Glauberite |
| 22.96 | 2.103 | 22.65 | .206 | Glauberite + gypsum |
| 33.79 | 0.734 | 32.85 | .065 | Thenardite + labile salt |
| 33.79 | 2.498 | 31.66 | .078 | Labile salt |
| 31.73 | 0.751 | 31.18 | .088 | Labile salt |
| 31.73 | 1.583 | 30.48 | .102 | Labile salt |
| —— | —— | 27.25 | .176 | Labile salt |
| —— | —— | 26.70 | .200 | Labile salt + gypsum |
| —— | —— | 27.93 | .217 | Pentasalt |
| —— | —— | 30.06 | .189 | Pentasalt + gypsum |
| —— | —— | 31.01 | .179 | Pentasalt |
| —— | —— | 31.4 | .166 | Pentasalt |
| —— | —— | 32.5 | .144 | Pentasalt |
| —— | —— | 32.88 | .135 | Pentasalt + thenardite |

equilibrium with that salt at low temperatures;[9,11] it is unquestionably metastable with respect to gypsum in water, with a solubility curve which crosses that for gypsum at a high concentration of sodium sulfate. The new pentacalcium sulfate was also omitted, since the isotherms at higher temperatures make it reasonably sure that it is metastable at 25° with respect to all other salts in the system.

**The 35° Isotherm.**—The isotherm at 35° was chosen to illustrate conditions just above the temperature at which mirabilite has disappeared. The results are shown in Table II and Fig. 2.
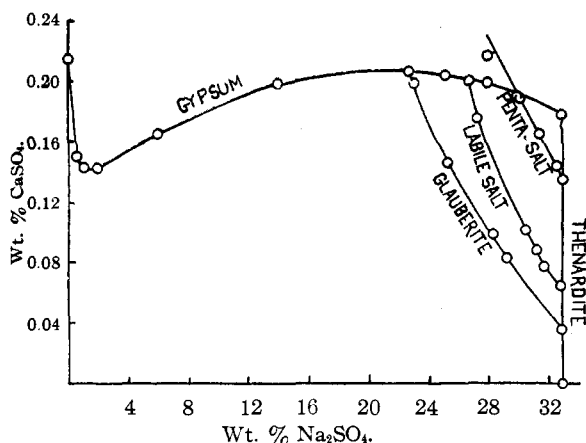


Fig. 2.—$CaSO_4$–$Na_2SO_4$–$H_2O$ at 35°.

The gypsum curve again shows a maximum and a minimum, as it did at 25°. The salt comes to an equilibrium with its solution within a few minutes, but no need for rapid work resulted, as there was no spontaneous occurrence of double salts in eighteen hours' time up to a concentration of 30% sodium sulfate. In the presence, however, of solid thenardite at the invariant point (32.85%) the formation of labile salt begins immediately and the system becomes constant at the invariant concentration for labile salt and thenardite, the change toward glauberite being suspended. The change of labile salt to glauberite at this temperature is very slow under all conditions of concentration, for which reason some of the points on the glauberite curve were obtained with samples of that salt made at 75°. The labile salt formed from gypsum at 35°, upon seeding, within two to four days, but the extrapolations of the tie-lines fail to agree with the accepted formula by two to three per cent., which may be due either to the presence of unchanged gypsum or to that of glauberite, each of which is higher in

calcium sulfate, that being the direction in which the experiments with the labile salt regularly err. Anhydrite was not included in the isotherm. The new pentasalt[15] is found to be metastable with respect to both labile salt and glauberite; the points on its curve were obtained by rotating the salt with sodium sulfate solution until the maximum content of calcium was found by analysis, which point was usually reached between five and twenty-four hours. During this period there was sometimes the appearance of a few glauberite crystals and more frequently formation of the labile salt set in.

**The 50° Isotherm.**—The isotherm at 50°, which includes a solubility curve for anhydrite in addition to the salts included at lower temperatures, is shown in Table III and Fig. 3. In this table and others which follow, the results in parentheses were obtained by interpolation.
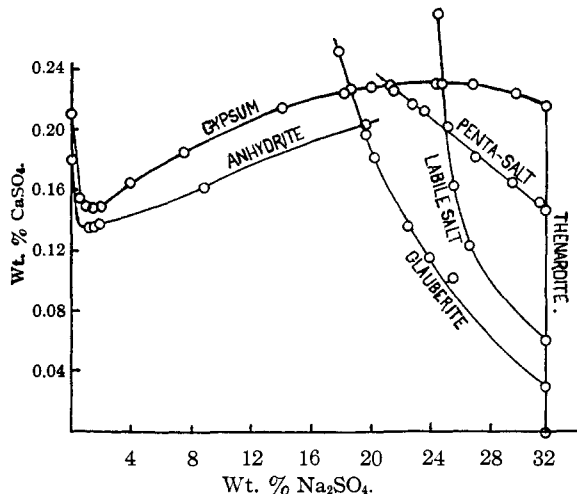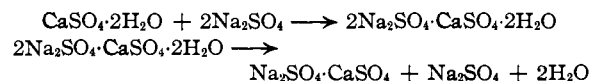


Fig. 3.—$CaSO_4$–$Na_2SO_4$–$H_2O$ at 50°.

The gypsum curve again shows a minimum and maximum. No spontaneous formation of glauberite from gypsum occurred at any concentration of sodium sulfate; our observation is that it occurs only as a second step after labile salt (or pentasalt) has formed, according to the two equations

$$CaSO_4 \cdot 2H_2O + 2Na_2SO_4 \longrightarrow 2Na_2SO_4 \cdot CaSO_4 \cdot 2H_2O$$
$$2Na_2SO_4 \cdot CaSO_4 \cdot 2H_2O \longrightarrow$$
$$Na_2SO_4 \cdot CaSO_4 + Na_2SO_4 + 2H_2O$$

In obtaining the points on the gypsum curve any length of time was found possible up to about 25% sodium sulfate; beyond that concentration not more than ten minutes could be allowed

(15) We are indebted to Dr. John E. Ricci and Dr. Thomas W. Davis for the experimental work with this salt at 35 and at 50°.

TABLE III

CaSO₄–Na₂SO₄–H₂O AT 50°

| Original complex Wt. % | | Saturated solution Wt. % | | |
|---|---|---|---|---|
| Na₂SO₄ | CaSO₄ | Na₂SO₄ | CaSO₁ | Solid phases |
| ---- | ---- | ---- | 0.210 | Gypsum |
| 0.449 | 8.437 | 0.521 | .154 | Gypsum |
| .894 | 7.576 | .989 | .149 | Gypsum |
| 1.431 | 3.758 | 1.521 | .148 | Gypsum |
| 1.889 | 3.743 | 1.981 | .149 | Gypsum |
| 3.712 | 3.672 | 3.908 | .164 | Gypsum |
| 7.160 | 3.540 | 7.496 | .185 | Gypsum |
| 13.36 | 3.774 | 14.05 | .214 | Gypsum |
| 18.20 | 0.657 | 18.28 | .224 | Gypsum |
| 19.94 | .403 | 20.07 | .228 | Gypsum |
| 23.11 | 3.810 | 24.40 | .230 | Gypsum |
| 26.43 | 1.755 | 26.93 | .230 | Gypsum |
| 29.76 | 0.539 | 29.75 | .224 | Gypsum |
| 33.59 | .525 | 31.77 | .216 | Gypsum + thenardite |
| --- | ---- | 31.73 | --- | Thenardite |
| --- | --- | 1.236 | .135 | Anhydrite |
| 1.941 | .594 | 1.529 | .135 | Anhydrite |
| 1.945 | .856 | 1.942 | .138 | Anhydrite |
| 8.978 | 1.006 | 8.923 | .162 | Anhydrite |
| 35.38 | 0.641 | 31.70 | .040 | Thenardite + glauberite |
| 29.49 | .967 | 29.08 | .058 | Glauberite |
| 25.84 | .522 | 25.49 | .102 | Glauberite |
| 26.71 | 5.286 | 23.93 | .115 | Glauberite |
| 22.77 | 0.749 | 22.53 | .136 | Glauberite |
| 20.14 | .195 | 20.24 | .182 | Glauberite |
| 20.33 | 1.172 | 19.68 | .197 | Glauberite |
| 19.79 | 1.299 | 19.66 | .203 | Glauberite + anhydrite |
| 18.65 | 1.096 | 18.71 | .227 | Glauberite + gypsum |
| 18.23 | 1.068 | 18.44 | .233 | Glauberite |
| 18.10 | 0.722 | 17.88 | .252 | Glauberite |
| 33.71 | .807 | 31.67 | .060 | Labile salt + thenardite |
| --- | --- | 26.61 | .124 | Labile salt |
| --- | --- | 25.51 | .163 | Labile salt |
| --- | --- | 24.8 | .230 | Labile salt + gypsum |
| --- | --- | 24.51 | .277 | Labile salt |
| --- | ---- | 31.7 | .147 | Pentasalt + thenardite |
| --- | --- | 31.3 | .153 | Pentasalt |
| --- | --- | 29.4 | .165 | Pentasalt |
| --- | --- | 27.0 | .182 | Pentasalt |
| --- | --- | 25.2 | .202 | Pentasalt + labile salt |
| --- | --- | 23.6 | .213 | Pentasalt |
| --- | --- | 22.8 | .217 | Pentasalt |
| --- | --- | 21.6 | .226 | Pentasalt |
| --- | --- | (21.4) | ( .229) | Pentasalt + gypsum |

before the solubility began to drop, and at 31.77% (the invariant concentration) a still shorter time was necessary. The points on the curve for the labile salt were all obtained from undersaturation with material made at 35° and about 30% sodium sulfate; when the attempt was made to obtain results by formation of the labile salt from gypsum, the formation of glauberite began before the formation of the labile salt was complete. Glauberite, it will be observed, is the stable salt over a considerable range of concentrations; at about 25% sodium sulfate it could be formed completely in about two days from gypsum, via the labile salt, and from anhydrite in about two weeks. The invariant point with gypsum could be approached only from lower concentrations of sodium sulfate, that is, by decomposition of glauberite to gypsum, but not from the higher concentrations (change of gypsum to glauberite) because of the non-existence at this concentration of the apparently necessary intermediate compound, the labile salt. The curve for anhydrite was included, this being the lowest temperature at which it was thought feasible to work with that salt. It recently has been shown[11] that anhydrite is stable with respect to gypsum at temperatures down to 42°, as had previously been indicated in the systems containing potassium sulfate and ammonium sulfate.[9] The solid used was an artificial anhydrite made by dehydration of gypsum by sulfuric acid as previously described;[9] the solubility figures represent approach from undersaturation for one week's time, and were found constant for two months; approach from supersaturation did not prove feasible. Experiments were not successful in the region where the anhydrite is metastable with respect to glauberite or the labile salt. The points on the pentasalt curve are all obtained from undersaturation, using a sample of the salt made at 75° and periods of from two to eighteen hours, the time being limited usually by the spontaneous appearance of the labile salt.

**The 75° Isotherms.**—Table IV and Fig. 4 show the results at 75°, which include curves for the two forms of calcium sulfate and the three double salts.

The gypsum curve has apparently lost the maximum. In obtaining the curve, gypsum could be left in contact with solutions containing up to 12–13% of sodium sulfate for a half day without appearance of double salts; from that point on, there was almost immediate formation of double salts (probably pentasulfate, or labile salt at the higher concentrations) as shown by the extra-

polation of the tie-lines; the last four points on the gypsum curve show the presence of double salt, although the filtrations were made within a minute or two. For this reason it is possible that the true solubility curve is slightly higher than we have found; Barre's[5] two figures are very

### TABLE IV

#### CaSO₄–Na₂SO₄–H₂O AT 75°

| Original complex Wt. % | | Saturated solution Wt. % | | |
|---|---|---|---|---|
| Na₂SO₄ | CaSO₄ | Na₂SO₄ | CaSO₄ | Solid phases |
| —— | —— | —— | 0.192 | Gypsum |
| 0.488 | 2.257 | 0.506 | .142 | Gypsum |
| .978 | 2.212 | 1.009 | .143 | Gypsum |
| 1.461 | 2.309 | 1.505 | .145 | Gypsum |
| 1.944 | 2.306 | 1.996 | .148 | Gypsum |
| 3.890 | 2.316 | 4.036 | .168 | Gypsum |
| 7.766 | 2.300 | 8.046 | .199 | Gypsum |
| 10.05 | 2.747 | 10.38 | .224 | Gypsum |
| 12.17 | 2.870 | 12.06 | .238 | Gypsum |
| 17.96 | 1.892 | 17.20 | .270 | Gypsum |
| 22.56 | 2.494 | 23.15 | .300 | Gypsum |
| 29.61 | 0.511 | 29.62 | .308 | Gypsum |
| —— | —— | 30.32 | .308 | Gypsum + thenardite |
| —— | —— | 30.38 | —— | Thenardite |
| 0.991 | 0.980 | 1.002 | .070 | Anhydrite |
| 4.955 | 1.243 | 5.017 | .086 | Anhydrite |
| 7.94 | 4.671 | 8.93 | .113 | Anhydrite |
| 9.099 | 2.536 | 9.205 | .103 | Anhydrite |
| 9.62 | 3.309 | 9.95 | .113 | Anhydrite |
| 15.82 | 0.824 | 14.47 | .117 | Anhydrite |
| 18.94 | .577 | 18.92 | .128 | Anhydrite + glauberite |
| 19.78 | .895 | 19.95 | .129 | Anhydrite |
| —— | —— | 30.32 | .042 | Glauberite + thenardite |
| 28.88 | 4.619 | 27.14 | .052 | Glauberite |
| 28.57 | 3.815 | 26.76 | .054 | Glauberite |
| 28.96 | 5.253 | 26.35 | .056 | Glauberite |
| 25.94 | 0.410 | 25.78 | .060 | Glauberite |
| 23.39 | 1.756 | 22.45 | .086 | Glauberite |
| 19.23 | 0.808 | 19.20 | .123 | Glauberite |
| —— | —— | 18.16 | .138 | Glauberite |
| 16.42 | .354 | 16.30 | .175 | Glauberite |
| 15.43 | .523 | 15.12 | .198 | Glauberite |
| 14.36 | .521 | 14.16 | .225 | Glauberite |
| 13.76 | 2.006 | 13.85 | .247 | Glauberite + gypsum |
| —— | —— | 30.38 | .081 | Labile salt + thenardite |
| —— | —— | 29.06 | .103 | Labile salt |
| —— | —— | 28.46 | .110 | Labile salt |
| —— | —— | 26.17 | .154 | Labile salt |
| —— | —— | 25.94 | .169 | Labile salt |
| —— | —— | 25.20 | .210 | Labile salt |
| —— | —— | 24.20 | .292 | Labile salt |
| —— | —— | (24.0) | (.302) | Labile salt + gypsum |
| —— | —— | 10.2 | .221 | Pentasulfate + gypsum |

| | | | | |
|---|---|---|---|---|
| 10.85 | 1.386 | 10.81 | .217 | Pentasulfate |
| 11.11 | 1.478 | 11.05 | .201 | Pentasulfate |
| 12.39 | 5.355 | 12.10 | .208 | Pentasulfate |
| 12.99 | 0.430 | 13.06 | .207 | Pentasulfate |
| 13.74 | 6.490 | 13.60 | .200 | Pentasulfate |
| 14.36 | 2.605 | 14.25 | .197 | Pentasulfate |
| 15.00 | 3.433 | 15.07 | .201 | Pentasulfate |
| 14.99 | 1.117 | 15.10 | .198 | Pentasulfate + glauberite |
| 16.97 | 0.354 | 17.03 | .189 | Pentasulfate |
| 19.01 | .472 | 19.08 | .185 | Pentasulfate |
| —— | —— | (26.2) | (.160) | Pentasulfate + labile salt |
| 33.76 | .510 | 30.28 | .146 | Pentasulfate + thenardite |

much lower than ours, probably on this same account. The anhydrite figures were obtained from undersaturation, the time being a few days to a week; two points standing slightly above the curve represent approach from supersaturation by a month's decomposition of the pentasulfate. In
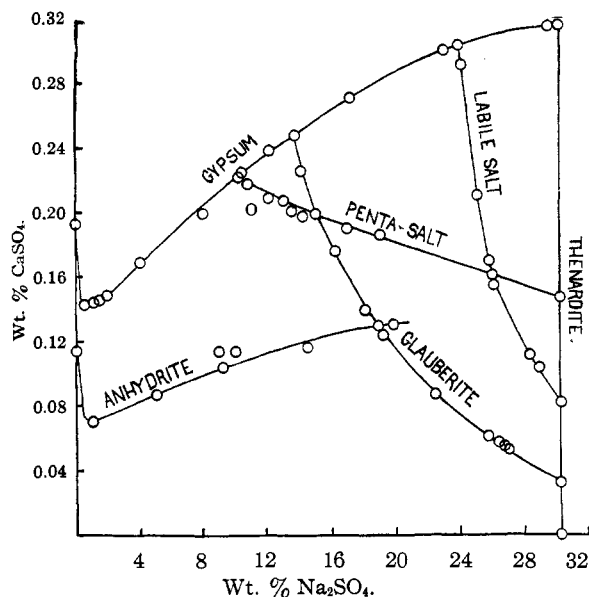


Fig. 4.—CaSO₄–Na₂SO₄–H₂O at 75°.

the region in which anhydrite is metastable with respect to glauberite, it changes to that salt in surprisingly short time, so that the curve could not be continued to higher concentrations. The point on the glauberite curve at 25.78% sodium sulfate was obtained from anhydrite in two days. The points on the curve for the labile salt were obtained wholly from undersaturation, using material obtained at lower temperatures and were contaminated with excess sodium sulfate, for which reason the exact composition of the original complexes is not known; the time was restricted to one-half hour or less to avoid too extensive

<div align="center">

TABLE V

ISOTHERMALLY INVARIANT POINTS IN SYSTEM

$CaSO_4-Na_2SO_4-H_2O$

</div>

| | I<br>Gypsum<br>+<br>mirabilite | II<br>Thenardite<br>with<br>any Ca-salt | III<br>Labile salt<br>+<br>pentasalt | IV<br>Labile salt<br>+<br>gypsum | V<br>Glauberite<br>+<br>anhydrite | VI<br>Glauberite<br>+<br>pentasalt | VII<br>Glauberite<br>+<br>gypsum | VIII<br>Pentasalt<br>+<br>gypsum |
|---|---|---|---|---|---|---|---|---|
| 25° | 21.7 | 33.9 | .. | 29.8 | .. | .. | 25.9 | ... |
| 35° | .. | 32.8 | .. | 26.7 | .. | .. | 22.65 | 30.0 |
| 50° | .. | 31.7 | 25.2 | 24.8 | 19.7 | .. | 18.7 | (21.4) |
| 75° | .. | 30.3 | (26.2) | (24.0) | 18.9 | 15.1 | 13.85 | 10.2 |

formation of glauberite. The glauberite curve represents formation of the salt from gypsum, by way of labile salt, for periods of approximately one day. The figures for the pentasalt were obtained mostly by formation of the compound from gypsum and glauberite, in a few cases from undersaturation with pure pentasulfate. In general,



Fig. 5.—Polytherm of system $CaSO_4-Na_2SO_4-H_2O$. Curve I, gypsum and mirabilite; II, thenardite and any calcium salt; III, labile salt and pentasalt; IV, labile salt and gypsum; V, glauberite and anhydrite; VI, glauberite and pentasalt; VII, glauberite and gypsum; VIII, pentasalt and gypsum.

the time allowed for formation was from two to five days at concentrations of sodium sulfate between 10 and 14%; in no case is any extensive decomposition of the pentasalt indicated by the extrapolation of the tie-lines, which show a solid with a sodium sulfate content of 10.84 to 17.7%

(16.2 by theory). At higher concentrations, however, where it is metastable with respect to glauberite, its decomposition is very rapid, and the points on the curve were obtained in times of an hour or less.

**The Polythermal Diagram.**—The results at the four temperatures are collected in Table V and in the polythermal diagram, Fig. 5, showing the concentration of sodium sulfate at each point and omitting the small concentrations of calcium sulfate. A corresponding diagram showing the concentrations of calcium sulfate can be constructed from the foregoing tables, but with less clarity.
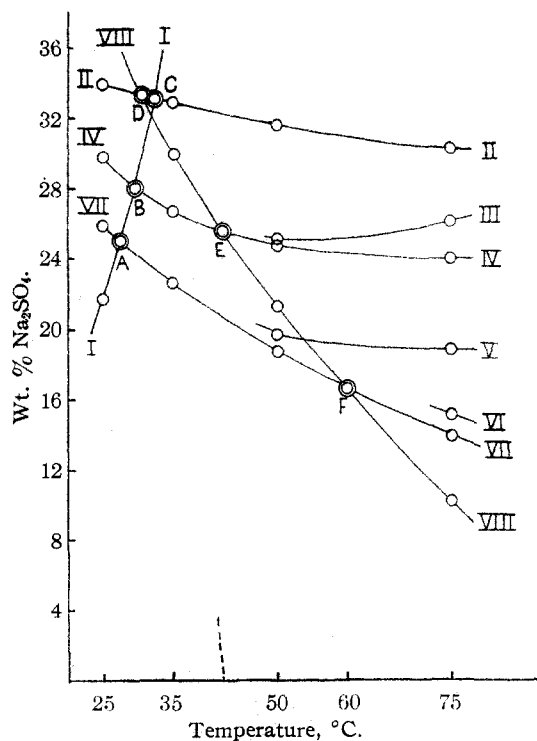
In Fig. 5, the lines represent saturation with respect to the two salts indicated in each case by the Roman numeral in Table V, but it is to be noted that the areas between lines do not represent fields of saturation with respect to a single salt, as in the usual diagram, since the many degrees of metastability occurring in this system make impossible that simple method of representation. Curve I is the curve for mirabilite and gypsum. Curve II represents saturation with thenardite and any one of the calcium-containing salts; since their solubility is in all cases so slight, it is found that the solutions saturated with two salts show the solubility of thenardite within the errors of analysis. The curves for the labile salt with other salts make a pair (III and IV) running increasingly close together at lower temperatures; Barre's figures[6] for one of these pairs (gypsum and labile salt) are slightly above ours at the lower temperature and below ours at 75°, which we attribute to partial change of his salt to glauberite or pentasalt. The curves for glauberite with another salt make a trio (V–VI–VII) lower down in the diagram; Barre's figures for the gypsum–glauberite curve are above 2% higher than ours, as is also D'Ans' figure at 60°. The curve for gypsum and pentasalt (VIII) shows a markedly different direction, in accord with

the fact that the solubility curve of the pentasalt (Figs. 2–4) does not parallel the curves for the other salts.

The system shows a relatively small number of invariant points of saturation with respect to three salts within the temperature range studied. That the number is small may be seen from the four isotherms, in which it appears that four of the seven salts considered change their relative solubility but slightly with change of temperature. The exceptions are anhydrite, mirabilite and pentasalt. With respect to anhydrite, it has been shown lately[11] that its transition temperature with gypsum is 42° instead of the higher temperature (63.5°) assigned at an earlier date by van't Hoff;[16] there must therefore be a series of invariant points below that temperature for anhydrite and gypsum with each of the other salts of the system. Because of the difficulty in obtaining saturation with anhydrite at these lower temperatures, this series of points has not been determined. Mirabilite increases its solubility greatly between 25° and its transition temperature to thenardite, 32.4°, so that its solubility curve (Fig. 1 and Fig. 5, curve I) passes through the solubility curves for gypsum–glauberite (VII), gypsum–labile salt (IV) and gypsum–thenardite (II), giving rise to invariant points A, B and C. A similar change in the solubility of the pentasalt gives rise to the invariant points D, E and F. The interpolated values of the temperature and the concentration of sodium sulfate are collected in Table VI.

The invariant points A and B of this table were

(16) Van't Hoff, *Z. physik. Chem.*, **45**, 257 (1903).

### TABLE VI

INVARIANT POINTS IN SYSTEM $CaSO_4$–$NaSO_4$–$H_2O$

| Letter in Fig. 5 | Saturating salts | Temp., °C. | Wt. % $Na_2SO_4$ |
|---|---|---|---|
| A | Gypsum, Mirabilite, Glauberite | 27.5 | 25.0 |
| B | Gypsum, Mirabilite, Labile salt | 29.5 | 28.0 |
| C | Mirabilite, Thenardite, Gypsum | 32.4 | 33.0 |
| D | Pentasalt, Gypsum, Thenardite | 31 | 33.2 |
| E | Pentasalt, Gypsum, Labile salt | 44 | 25.5 |
| F | Pentasalt, Gypsum, Glauberite | 60 | 16.6 |

determined previously by van't Hoff[7] and set at 29 and 30.2°, respectively; it is possible that the interpolated figures of Table VI from equilibrium experiments may be closer to the true values. The interpolated values which we have obtained for points D, E and F probably are less close to the true values, since they depend upon equilibria which were less clearly established.

### Summary

The system $CaSO_4$–$Na_2SO_4$–$H_2O$ has been studied and isotherms constructed at four temperatures, 25, 35, 50 and 75°, including solubility determinations for gypsum, anhydrite, glauberite, the labile salt and a new hydrated sodium pentacalcium sulfate, $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$. The metastability and the composition of the labile salt, $2Na_2SO_4 \cdot CaSO_4 \cdot 2H_2O$, have been confirmed, and a polythermal diagram of the system sketched.

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