The $CaSO_4$–Na_2SO_4–NaCl–H_2O System at 25° to 100° C.

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The $CaSO_4$–Na_2SO_4–H_2O system was studied at temperatures of 25°, 40°, 55°, 70°, 85°, and 100° C. and at salinities of 0.0, 0.5, 1.0, 2.0, and 4.0 molal NaCl. The penta salt ($5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$) appeared at 70° C. at all salinities studied and at 85° C. at 0.0 and 0.5 molal NaCl. This salt was only obtained by starting with calcium sulfate in the gypsum form, and could not be formed from the anhydrite. Glauberite ($CaSO_4 \cdot Na_2SO_4$) was found at all temperatures and all salinities except at 0.0 to 2.0 molal NaCl at 25° C. It formed only at salinities and temperatures at which thenardite was the stable sodium sulfate phase. Under these conditions (of thenardite stability), glauberite can be formed from calcium sulfate in either the gypsum or the anhydrite phase. The "labile salt" ($CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$) was found at 40° C. at all salinities studied and at 25° C. at 3.5 and 4.0 molal NaCl. This salt is generally considered metastable, but there was no evidence of its disappearance after as much as 3 months of reaction time. Two forms of calcium sulfate were observed, gypsum ($CaSO_4 \cdot 2H_2O$) and the insoluble anhydrite ($CaSO_4$). Only at 85° C. at salinities of 1.0 molal NaCl and above, and 100° C. was any conversion of gypsum to anhydrite observed. Sodium sulfate occurred as two phases, mirabalite ($Na_2SO_4 \cdot 10H_2O$) and thenardite (Na_2SO_4). Mirabalite, found only at 25° C. from 0.0 to 2.0 molal NaCl, changed to thenardite at 3.5 and 4.0 molal NaCl.

THE purpose of this investigation was to obtain solubility and phase data on the calcium sulfate–sodium sulfate–sodium chloride system. The effect of sodium chloride concentration and temperature was of prime interest. The study has some practical importance since the information can be applied to sodium sulfate recovery from brines, as well as scale formation in sea water distillation plants.

Sodium sulfate and calcium sulfate form three known double salts: $CaSO_4 \cdot Na_2SO_4$ (glauberite), $5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$ (penta salt), and $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$. The latter salt is generally referred to as the "labile salt" because of its supposed metastability with respect to other double salts.

Hill and Wills (*4*) determined the solubility of the various $CaSO_4$–Na_2SO_4 salts in water and constructed isotherms at 25°, 35°, 50°, and 75° C. These investigators were the first to report the existence of the penta salt, and they confirmed the metastability of the "labile salt." They did state, however, that the "labile salt" can be held unchanged for long periods of time at 25° C.

Lepeshkov and Fradkina (*8*) constructed solubility curves for the $CaSO_4$–Na_2SO_4–NaCl–H_2O system at 35° and 55° C. Using the data of Cameron, Bell, and Robinson (*1*), they also constructed a solubility curve for this system at 25° C. They found the double salt, $CaSO_4 \cdot Na_2SO_4$, to be stable at 35° and 55° C. and $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$ to be metastable.

Kolosov (*5*) studied the system $CaSO_4$–Na_2SO_4–NaCl–H_2O at 25° C. He reported the formation of a metastable $3Na_2SO_4 \cdot 2CaSO_4$. This phase was also reported by Cameron, Bell, and Robinson (*1*) and Druzhinin and Lopina-Shendrik (*2*); however, both Hill and Wills (*4*) and Lepeshkov and Fradkina (*8*) questioned the existence of this salt.

Kydynov and Druzhinin (*7*) studied the ternary system $CaSO_4$–Na_2SO_4–H_2O in 10% NaCl at 0°, 20°, and 40° C. They found that NaCl delays the hydration of the double salts and also delays the formation of $CaSO_4 \cdot Na_2SO_4$. At 20° and 40° C., $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$ and $5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$ were metastable, whereas $CaSO_4 \cdot Na_2SO_4$ was stable.

In the above studies, the solubilities of previously prepared salts were determined. In the present study, calcium sulfate and sodium sulfate were reacted, and the resultant salts, formed in situ, were identified and their solubilities determined.

EXPERIMENTAL

Samples were prepared by adding various quantities of sodium sulfate, calcium sulfate, sodium chloride, and water to 50-ml. screw-cap Erlenmeyer flasks. Calcium sulfate was added as gypsum, and also as the anhydrite for some of the higher temperature studies. Sodium sulfate was added as the decahydrate for the low salinity 25° C. studies and as the anhydrous material for the studies at higher temperatures and salinities. Because of the low calcium sulfate solubility, no more than 1 gram of gypsum was used for each sample. The sodium sulfate solubility is much greater, and as much as 40 grams of the decahydrate and 30 grams of anhydrous material were used in some cases. To prepare the aqueous samples, 35 ml. of water were added to the calcium sulfate–sodium sulfate mixtures. The sodium chloride-containing samples were prepared by adding a saturated sodium chloride solution and water so that the final sodium chloride concentration was either 0.5, 1.0, 2.0, or 4.0 molal in a total volume of about 35 ml.

The samples were placed in constant temperature (±0.1° C.) shaker baths (Warner-Chilcott Model 2156). After at least 3 weeks, portions of the liquids of representative samples were removed and analyzed for calcium. This procedure was repeated at intervals of 1 day or more until the calcium values remained constant within experimental error (±1% relative). The authors assumed that the samples were at equilibrium. (The authors are referring here to equilibrium in terms of solubility, and not necessarily to phase transformations such as $CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 + 2H_2O$, which may have infinitely slow kinetics.) The average time required for equilibrium to be reached was about 4 weeks.

The liquid portions were removed by suction using a rubber bulb and a tared medicine dropper. A fine glass filter was placed on the medicine dropper tip to prevent

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solids from entering the dropper. The dropper and the filter were kept in the constant temperature bath before sampling. Calcium was determined by an EDTA titration with murexide as the indicator; the end point was obtained spectrophotometrically at 620 mμ.

Once equilibrium was established, liquid portions of the remaining samples were removed by the same procedure. The sodium chloride content was determined by the Mohr method. Calcium was then determined on the titrated sample by adding NaCl to remove the excess silver ion, filtering, and titrating the filtrate by the spectrophotometric EDTA procedure. The yellow color of the chromate ion does not interfere. Total water was determined on a second aliquot by evaporation to constant weight at 225° C. Sodium sulfate was then determined by difference.

After the liquids were analyzed, portions of the wet residues were removed with either a polypropylene scoop or a specially designed filtering device, depending on the fineness of the solids. Both the scoop and the filtering device were kept in a constant temperature bath before sampling. The filtering device consisted of a short medicine dropper with a glass wool plug near the tip. Liquids and solids were drawn into the glass wool plug by attaching a pipet and a rubber bulb to the medicine dropper. The liquid was drawn through the glass wool into the pipet, leaving the wet residue in the medicine dropper, which was then expelled by gentle pressure. The wet residue was analyzed by the same methods used on the liquids, with the exception that total water was determined first, followed by the other analyses on the dried sample.

The solid phase composition was determined by Schreinemakers' method of tie-line convergence (*12*). The wet residue values and the liquid values were plotted on triangular coordinates. Since the sum of the three values (% $CaSO_4$, % Na_2SO_4, and % H_2O) representing each point must equal 100%, an "NaCl-free" percentage was obtained using this formula:

$$\text{"NaCl-free" \%} = \frac{\text{Actual \%}}{1.00 - \dfrac{\%\text{NaCl}}{100}}$$

DTA scans were also obtained on some of the solids to confirm the tie-line results. Gypsum, the penta salt, and the disodium salt all produce endotherms upon the loss of water of hydration; each endotherm occurs at a different temperature, thus making identification fairly simple (Figure 1).

RESULTS AND DISCUSSION

The data obtained at 25° C. and 0.0, 0.5, 1.0, 2.0, and 4.0 molal NaCl concentrations are presented in Table I. Some data were obtained at 3.5 molal NaCl and are also included in Table I. Figure 2 is a plot of the invariant points at 25° C. and shows the regions of stability of the various salts.

Between 0.0 and 2.0 molal NaCl, only two solid phases exists: gypsum, $CaSO_4 \cdot 2H_2O$; and mirabilite, $Na_2SO_4 \cdot 10H_2O$. At 3.5 and 4.0 molal NaCl concentrations, three new phases appear: thenardite, Na_2SO_4; and two double salts, the disodium salts, $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$; and glauberite, $CaSO_4 \cdot Na_2SO_4$. Obviously, the transition point from mirabilite to thenardite is lowered from 32.38° C. in H_2O to less than 25° C. in 3.5 and 4.0 molal NaCl. Also, apparently the double salts of $CaSO_4$ and Na_2SO_4 cannot be obtained unless the stable sodium sulfate phase is thenardite.

At 0.0, 0.5, and 1.0 molal NaCl, the solubility of gypsum first decreases and then increases with increasing sodium sulfate concentration. The decrease is normal and can be attributed to the common ion effect; the increase is probably due to complex formation. At 2.0 molal NaCl and above, the salting out effect becomes greater than the opposing effect, and the increase in gypsum solubility is not observed. The sodium sulfate concentration, however, is not appreciably affected by calcium sulfate because of the much lower solubility of calcium sulfate. As expected from the common ion effect, the solubilities of the two double salts decrease with increasing sodium sulfate concentration.

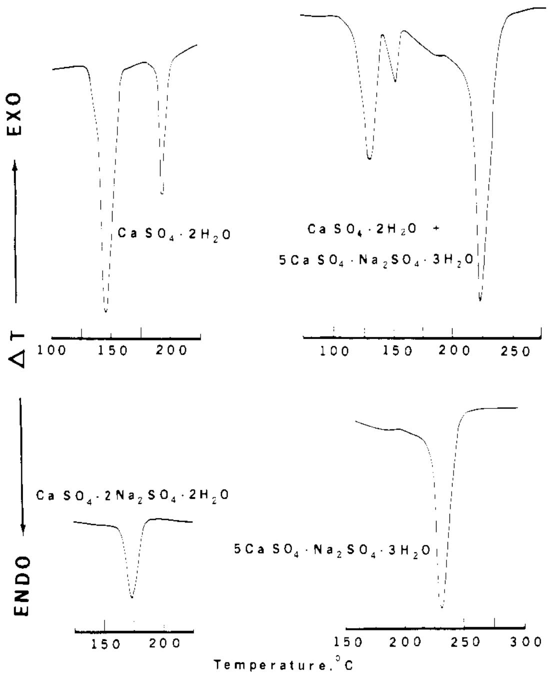

Figure 1. Typical DTA scans
Heating rate 15° C. per minute, reference Al_2O_3

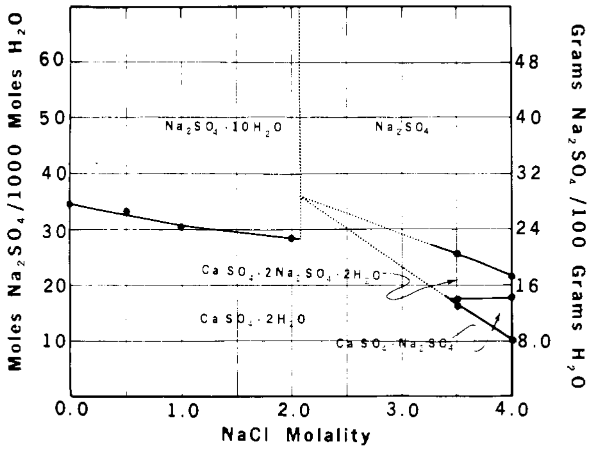

Figure 2. $CaSO_4$–Na_2SO_4 phase diagram at 25° C. and 0.0–4.0 molal NaCl

Of the two double salts formed at 25° C., the disodium salt has a greater region of stability at the lower salinities, and glauberite predominates at the higher salinities (Figure 2). No instability in the disodium salt (the "labile salt") was observed after as much as 3 months of reaction time.

As expected from the salting out effect, the solubilities of the two double salts and both forms of sodium sulfate decrease with increasing salinity. The gypsum solubility, however, increases with increasing salinity until about 3 molal NaCl (possibly due to complexing) and then decreases (salting out).

Much of the data obtained at 25° C. can be compared

Table I. System $CaSO_4$–Na_2SO_4–NaCl–H_2O at 25° C.

Na_2SO_4 Molality	$CaSO_4$ Molality	NaCl Molality	Solid Phase
0.0 Molal NaCl			
0.000	0.0161	0.00	$CaSO_4 \cdot 2H_2O$
0.032	0.0119	0.00	$CaSO_4 \cdot 2H_2O$
0.104	0.0110	0.00	$CaSO_4 \cdot 2H_2O$
0.109	0.0104	0.00	$CaSO_4 \cdot 2H_2O$
0.262	0.0112	0.00	$CaSO_4 \cdot 2H_2O$
0.462	0.0127	0.00	$CaSO_4 \cdot 2H_2O$
0.821	0.0154	0.00	$CaSO_4 \cdot 2H_2O$
1.307	0.0177	0.00	$CaSO_4 \cdot 2H_2O$
1.753	0.0182	0.00	$CaSO_4 \cdot 2H_2O$
1.784	0.0185	0.00	$CaSO_4 \cdot 2H_2O$
1.912	0.0185	0.00	$CaSO_4 \cdot 2H_2O + Na_2SO_4 \cdot 10H_2O$
1.885	0.0082	0.00	$Na_2SO_4 \cdot 10H_2O$
1.919	0.0055	0.00	$Na_2SO_4 \cdot 10H_2O$
1.852	0.0000	0.00	$Na_2SO_4 \cdot 10H_2O$
0.5 Molal NaCl			
0.000	0.0343	0.53	$CaSO_4 \cdot 2H_2O$
0.102	0.0169	0.50	$CaSO_4 \cdot 2H_2O$
0.162	0.0138	0.55	$CaSO_4 \cdot 2H_2O$
0.497	0.0135	0.49	$CaSO_4 \cdot 2H_2O$
0.656	0.0144	0.49	$CaSO_4 \cdot 2H_2O$
1.042	0.0151	0.48	$CaSO_4 \cdot 2H_2O$
1.291	0.0157	0.50	$CaSO_4 \cdot 2H_2O$
1.527	0.0170	0.50	$CaSO_4 \cdot 2H_2O$
1.702	0.0163	0.49	$CaSO_4 \cdot 2H_2O$
1.834	0.0169	0.53	$CaSO_4 \cdot 2H_2O + Na_2SO_4 \cdot 10H_2O$
1.836	0.0140	0.51	$Na_2SO_4 \cdot 10H_2O$
1.807	0.0054	0.56	$Na_2SO_4 \cdot 10H_2O$
1.814	0.0000	0.55	$Na_2SO_4 \cdot 10H_2O$
1.0 Molal NaCl			
0.000	0.0448	0.98	$CaSO_4 \cdot 2H_2O$
0.195	0.0162	0.98	$CaSO_4 \cdot 2H_2O$
0.778	0.0137	0.98	$CaSO_4 \cdot 2H_2O$
1.360	0.0138	0.98	$CaSO_4 \cdot 2H_2O$
1.684	0.0137	1.06	$CaSO_4 \cdot 2H_2O + Na_2SO_4 \cdot 10H_2O$
1.691	0.0107	1.08	$Na_2SO_4 \cdot 10H_2O$
1.698	0.0058	1.09	$Na_2SO_4 \cdot 10H_2O$
1.638	0.0000	1.20	$Na_2SO_4 \cdot 10H_2O$
2.0 Molal NaCl			
0.000	0.0534	1.88	$CaSO_4 \cdot 2H_2O$
0.093	0.0297	1.88	$CaSO_4 \cdot 2H_2O$
0.186	0.0196	1.88	$CaSO_4 \cdot 2H_2O$
0.556	0.0134	1.88	$CaSO_4 \cdot 2H_2O$
1.118	0.0123	1.89	$CaSO_4 \cdot 2H_2O$
1.581	0.0111	2.02	$CaSO_4 \cdot 2H_2O + Na_2SO_4 \cdot 10H_2O$
1.506	0.0059	2.21	$Na_2SO_4 \cdot 10H_2O$
1.528	0.0000	2.06	$Na_2SO_4 \cdot 10H_2O$
3.5 Molal NaCl			
0.000	0.0584	3.59	$CaSO_4 \cdot 2H_2O$
0.239	0.0160	3.52	$CaSO_4 \cdot 2H_2O$
0.483	0.0110	3.50	$CaSO_4 \cdot 2H_2O$
0.933	0.0083	3.49	$CaSO_4 \cdot 2H_2O + CaSO_4 \cdot Na_2SO_4$
0.970	0.0070	3.50	$CaSO_4 \cdot Na_2SO_4 + CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
1.172	0.0044	3.51	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
1.428	0.0030	3.52	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O + Na_2SO_4$
1.432	0.0000	3.52	Na_2SO_4
4.0 Molal NaCl			
0.000	0.0537	4.02	$CaSO_4 \cdot 2H_2O$
0.248	0.0152	4.06	$CaSO_4 \cdot 2H_2O$
0.478	0.0096	4.11	$CaSO_4 \cdot 2H_2O$
0.732	0.0046	4.16	$CaSO_4 \cdot Na_2SO_4$
0.977	0.0039	4.05	$CaSO_4 \cdot Na_2SO_4 + CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
1.187	0.0025	4.08	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O + Na_2SO_4$
1.192	0.0000	4.07	Na_2SO_4

with the data obtained by other workers (Table II). In general, the agreement is good.

The data at 40° C. are presented in Table III. Figure 3 is a plot of the invariant points at 40° C.

At this temperature, there are four phases present at all the salinities studied: gypsum, $CaSO_4 \cdot 2H_2O$; glauberite, $CaSO_4 \cdot Na_2SO_4$; the disodium salt, $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$; and thenardite, Na_2SO_4. Inspection of the data reveals the same decrease and then increase in gypsum solubility that occurred at 25° C. at the low salinities and the simple decrease in solubility at the higher salinities. The two double salts show a normal decrease in solubility with increasing Na_2SO_4 concentration, while the Na_2SO_4 solubility is again little affected by the calcium sulfate concentration.

As the salinity is increased, the stable region for the disodium salt becomes proportionately smaller when compared with glauberite, so that at 4.0 molal NaCl, the disodium salt exits only over a very narrow concentration range (Figure 3). Again, no disappearance of this salt was observed after as much as 3 months of reaction time. Also, with increasing salinity, the gypsum solubility increases to a maximum between 2 and 4 molal NaCl and then decreases, whereas the solubility of all the other phases decrease with increasing salinity. The concentration of sodium sulfate 4. At this temperature, the disodium slat, $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$ disappears, and only three phases appear: $CaSO_4 \cdot$

The pentacalcium sodium salt, $5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$ was not detected at 40° C. in agreement with Hill and Wills (*4*) and Lepeshkov and Fradkina (*8*), as both groups of investigators found that this salt was unstable at 35° C.

The double salt, $3Na_2SO_4 \cdot 2CaSO_4$, reported by some investigators (*1, 2, 5*) was not detected. In agreement with Hill and Wills (*4*), this salt was probably a mixture of glauberite and the disodium salt.

Marshall and Slusher (*9*) found the solubility of gypsum to be 0.0156 molal in water at 40° C. and 0.0462 molal in 1.0 molal NaCl at this temperature. The agreement with these data, 0.0158 molal in water and 0.0452 molal in 1.0 molal NaCl, is good.

The results at 55° C. are given in Table IV and Figure 4. At this temperature, the disodium salt, $CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$ disappears, and only three phases appear: $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot Na_2SO_4$, and Na_2SO_4. Again, gypsum shows the same decrease and increase in solubility with increasing Na_2SO_4 concentration at the low salinities. As expected, the solubility of sodium sulfate and glauberite decrease with increasing salinity, whereas the gypsum solubility increases to a maximum between 2 and 4 molal NaCl and then decreases.

All samples at 55° C. (as well as at 25° and 40° C.) were prepared with gypsum. No change to anhydrite was observed after as much as 3 months of reaction time, even though the thermodynamically stable form of calcium sulfate at temperatures greater than 40° C. is the anhydrite (*3, 10*). The results agree with the results of many others (*3, 4, 10*), who have found the transition from gypsum to anhydrite (and vice versa) extremely slow. The authors decided to use gypsum in the experiments rather than anhydrite, because calcium sulfate occurs as gypsum in nature and would therefore be more likely to be used in a sodium sulfate recovery scheme. Also Salutsky *et al.* (*11*), and the Kurita Industrial Co., Ltd. (*6*), state that it is necessary to start with gypsum for the formation of the double salts. [Some of the experiments at higher temperatures (70°, 85°, 100° C.) did start with anhydrite.]

The disappearance of the disodium salt at 55° C. was also reported by Lepeshkov and Fradkina (*8*), who attributed this effect to the dehydrating action of NaCl. However, this cannot be the case because even in the absence of NaCl the "labile salt" was not observed at 55° C.

The penta salt, $5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$, was observed in

Table II. Comparison of Data on the $CaSO_4$–Na_2SO_4–$NaCl$–H_2O System at 25° C.

NaCl Molality	This Work	*(9)*	*(4)*	*(1)*	*(10)*
$CaSO_4 \cdot 2H_2O$ solubility, molal					
0.0	0.0161	0.0151	0.0154	...	0.0154
1.0	0.0448	0.0457	...	...	0.0451
2.0	0.0534	0.0540	...	...	...
4.0	0.0537	0.0560	...	...	...
$Na_2SO_4 \cdot 10H_2O$ solubility, molal					
0.0	1.898	...	1.953	...	...
Invariant Point $CaSO_4/Na_2SO_4$, molal					
0.0	0.0185/1.912	...	0.0185/1.963	...	...
0.5	0.0169/1.834	...	...	0.0169/1.786	...
1.0	0.0137/1.684	...	...	0.0149/1.647	...

Table III. System $CaSO_4$–Na_2SO_4–$NaCl$–H_2O at 40° C.

Na_2SO_4 Molality	$CaSO_4$ Molality	NaCl Molality	Solid Phase
			0.0 Molal NaCl
0.000	0.0158	0.00	$CaSO_4 \cdot 2H_2O$
0.037	0.0126	0.00	$CaSO_4 \cdot 2H_2O$
0.118	0.0108	0.00	$CaSO_4 \cdot 2H_2O$
0.123	0.0104	0.00	$CaSO_4 \cdot 2H_2O$
0.276	0.0123	0.00	$CaSO_4 \cdot 2H_2O$
0.560	0.0154	0.00	$CaSO_4 \cdot 2H_2O$
1.090	0.0165	0.00	$CaSO_4 \cdot 2H_2O$
1.434	0.0189	0.00	$CaSO_4 \cdot 2H_2O$
2.006	0.0202	0.00	$CaSO_4 \cdot 2H_2O$
2.038	0.0202	0.00	$CaSO_4 \cdot 2H_2O$
2.115	0.0199	0.00	$CaSO_4 \cdot 2H_2O + CaSO_4 \cdot Na_2SO_4$
2.288	0.0144	0.00	$CaSO_4 \cdot Na_2SO_4$
2.474	0.0118	0.00	$CaSO_4 \cdot Na_2SO_4$
2.907	0.0082	0.00	$CaSO_4 \cdot Na_2SO_4$
2.993	0.0100	0.00	$CaSO_4 \cdot Na_2SO_4 + CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
3.023	0.0086	0.00	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
3.290	0.0070	0.00	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
3.386	0.0065	0.00	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O + Na_2SO_4$
3.380	0.0000	0.00	Na_2SO_4
			0.5 Molal NaCl
0.000	0.0356	0.53	$CaSO_4 \cdot 2H_2O$
0.102	0.0170	0.50	$CaSO_4 \cdot 2H_2O$
0.192	0.0138	0.48	$CaSO_4 \cdot 2H_2O$
0.397	0.0137	0.51	$CaSO_4 \cdot 2H_2O$
0.602	0.0145	0.50	$CaSO_4 \cdot 2H_2O$
0.694	0.0151	0.53	$CaSO_4 \cdot 2H_2O$
0.792	0.0150	0.50	$CaSO_4 \cdot 2H_2O$
1.289	0.0163	0.51	$CaSO_4 \cdot 2H_2O$
1.619	0.0159	0.50	$CaSO_4 \cdot Na_2SO_4$
2.076	0.0103	0.49	$CaSO_4 \cdot Na_2SO_4$
2.476	0.0071	0.50	$CaSO_4 \cdot Na_2SO_4$
2.794	0.0056	0.51	$CaSO_4 \cdot Na_2SO_4 + CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
3.026	0.0053	0.50	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O + Na_2SO_4$
3.038	0.0037	0.50	Na_2SO_4
3.027	0.0000	0.51	Na_2SO_4
			1.0 Molal NaCl
0.000	0.0452	0.98	$CaSO_4 \cdot 2H_2O$
0.099	0.0219	0.98	$CaSO_4 \cdot 2H_2O$
0.194	0.0172	0.99	$CaSO_4 \cdot 2H_2O$
0.402	0.0145	1.00	$CaSO_4 \cdot 2H_2O$
0.586	0.0140	0.99	$CaSO_4 \cdot 2H_2O$
0.780	0.0144	0.98	$CaSO_4 \cdot 2H_2O$
1.072	0.0146	0.99	$CaSO_4 \cdot 2H_2O$
1.360	0.0153	0.98	$CaSO_4 \cdot 2H_2O + CaSO_4 \cdot Na_2SO_4$
1.424	0.0143	1.00	$CaSO_4 \cdot Na_2SO_4$
1.528	0.0115	1.01	$CaSO_4 \cdot Na_2SO_4$
1.793	0.0088	0.94	$CaSO_4 \cdot Na_2SO_4$
1.990	0.0076	0.97	$CaSO_4 \cdot Na_2SO_4$
2.183	0.0067	0.98	$CaSO_4 \cdot Na_2SO_4$
2.367	0.0058	0.97	$CaSO_4 \cdot Na_2SO_4$
2.570	0.0055	0.98	$CaSO_4 \cdot Na_2SO_4 + CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
2.714	0.0049	0.96	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O + Na_2SO_4$
2.704	0.0000	0.98	Na_2SO_4
			2.0 Molal NaCl
0.000	0.0527	1.88	$CaSO_4 \cdot 2H_2O$
0.112	0.0272	1.85	$CaSO_4 \cdot 2H_2O$
0.188	0.0197	1.89	$CaSO_4 \cdot 2H_2O$
0.340	0.0153	2.01	$CaSO_4 \cdot 2H_2O$
0.479	0.0134	2.02	$CaSO_4 \cdot 2H_2O$
0.565	0.0135	1.89	$CaSO_4 \cdot 2H_2O$
0.793	0.0126	1.99	$CaSO_4 \cdot 2H_2O$
0.981	0.0122	2.00	$CaSO_4 \cdot 2H_2O + CaSO_4 \cdot Na_2SO_4$
1.010	0.0112	1.88	$CaSO_4 \cdot Na_2SO_4$
1.204	0.0084	1.92	$CaSO_4 \cdot Na_2SO_4$
1.378	0.0067	1.88	$CaSO_4 \cdot Na_2SO_4$
1.563	0.0057	1.88	$CaSO_4 \cdot Na_2SO_4$
1.760	0.0044	1.88	$CaSO_4 \cdot Na_2SO_4$
1.938	0.0052	1.89	$CaSO_4 \cdot Na_2SO_4$
2.010	0.0050	1.89	$CaSO_4 \cdot Na_2SO_4 + CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$
2.141	0.0034	1.88	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O + Na_2SO_4$
2.128	0.0000	1.88	Na_2SO_4
			4.0 Molal NaCl
0.000	0.0557	4.02	$CaSO_4 \cdot 2H_2O$
0.197	0.0218	4.15	$CaSO_4 \cdot 2H_2O$
0.246	0.0174	4.05	$CaSO_4 \cdot 2H_2O$
0.467	0.0103	4.18	$CaSO_4 \cdot 2H_2O + CaSO_4 \cdot Na_2SO_4$
0.552	0.0048	4.14	$CaSO_4 \cdot Na_2SO_4$
0.637	0.0041	4.02	$CaSO_4 \cdot Na_2SO_4$
0.643	0.0040	4.03	$CaSO_4 \cdot Na_2SO_4$
0.834	0.0025	4.01	$CaSO_4 \cdot Na_2SO_4$
1.079	0.0023	4.06	$CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O + Na_2SO_4$
1.096	0.0000	4.03	Na_2SO_4

Table IV. System $CaSO_4$–Na_2SO_4–$NaCl$–H_2O at 55° C.

Na_2SO_4 Molality	$CaSO_4$ Molality	NaCl Molality	Solid Phase
0.0 Molal NaCl			
0.000	0.0149	0.00	$CaSO_4\cdot 2H_2O$
0.107	0.0106	0.00	$CaSO_4\cdot 2H_2O$
0.209	0.0116	0.00	$CaSO_4\cdot 2H_2O$
0.422	0.0132	0.00	$CaSO_4\cdot 2H_2O$
0.836	0.0165	0.00	$CaSO_4\cdot 2H_2O$
1.267	0.0192	0.00	$CaSO_4\cdot 2H_2O$
1.329	0.0194	0.00	$CaSO_4\cdot 2H_2O$
1.423	0.0200	0.00	$CaSO_4\cdot 2H_2O$
1.512	0.0205	0.00	$CaSO_4\cdot 2H_2O$
1.590	0.0189	0.00	$CaSO_4\cdot Na_2SO_4$
2.041	0.0123	0.00	$CaSO_4\cdot Na_2SO_4$
2.166	0.0110	0.00	$CaSO_4\cdot Na_2SO_4$
2.311	0.0096	0.00	$CaSO_4\cdot Na_2SO_4$
2.564	0.0077	0.00	$CaSO_4\cdot Na_2SO_4$
2.802	0.0062	0.00	$CaSO_4\cdot Na_2SO_4$
3.087	0.0052	0.00	$CaSO_4\cdot Na_2SO_4$
3.225	0.0045	0.00	$CaSO_4\cdot Na_2SO_4 + Na_2SO_4$
3.231	0.0000	0.00	Na_2SO_4
0.5 Molal NaCl			
0.000	0.0355	0.53	$CaSO_4\cdot 2H_2O$
0.104	0.0167	0.50	$CaSO_4\cdot 2H_2O$
0.213	0.0145	0.53	$CaSO_4\cdot 2H_2O$
0.412	0.0142	0.52	$CaSO_4\cdot 2H_2O$
0.818	0.0158	0.52	$CaSO_4\cdot 2H_2O$
0.953	0.0172	0.52	$CaSO_4\cdot 2H_2O$
1.016	0.0168	0.51	$CaSO_4\cdot 2H_2O$
1.211	0.0172	0.51	$CaSO_4\cdot 2H_2O$.
1.249	0.0178	0.50	$CaSO_4\cdot 2H_2O$
1.294	0.0180	0.52	$CaSO_4\cdot 2H_2O$
1.298	0.0171	0.51	$CaSO_4\cdot 2H_2O$
1.359	0.0184	0.51	$CaSO_4\cdot 2H_2O + CaSO_4\cdot Na_2SO_4$
1.368	0.0154	0.51	$CaSO_4\cdot Na_2SO_4$
1.487	0.0114	0.53	$CaSO_4\cdot Na_2SO_4$
1.898	0.0076	0.54	$CaSO_4\cdot Na_2SO_4$
2.188	0.0068	0.53	$CaSO_4\cdot Na_2SO_4$
2.374	0.0059	0.52	$CaSO_4\cdot Na_2SO_4$
2.565	0.0050	0.52	$CaSO_4\cdot Na_2SO_4$
2.875	0.0039	0.51	$CaSO_4\cdot Na_2SO_4 + Na_2SO_4$
2.876	0.0000	0.51	Na_2SO_4
1.0 Molal NaCl			
0.000	0.0438	1.01	$CaSO_4\cdot 2H_2O$
0.199	0.0170	1.01	$CaSO_4\cdot 2H_2O$
0.402	0.0150	1.02	$CaSO_4\cdot 2H_2O$
0.601	0.0146	1.01	$CaSO_4\cdot 2H_2O$
0.800	0.0156	1.02	$CaSO_4\cdot 2H_2O$
1.001	0.0158	1.03	$CaSO_4\cdot 2H_2O$
1.074	0.0158	1.02	$CaSO_4\cdot 2H_2O + CaSO_4\cdot Na_2SO_4$
1.254	0.0112	1.02	$CaSO_4\cdot Na_2SO_4$
1.458	0.0088	1.02	$CaSO_4\cdot Na_2SO_4$
1.589	0.0070	1.04	$CaSO_4\cdot Na_2SO_4$
1.748	0.0060	1.01	$CaSO_4\cdot Na_2SO_4$
2.052	0.0052	1.00	$CaSO_4\cdot Na_2SO_4$
2.228	0.0042	1.02	$CaSO_4\cdot Na_2SO_4$
2.323	0.0036	1.00	$CaSO_4\cdot Na_2SO_4$
2.526	0.0032	1.02	$CaSO_4\cdot Na_2SO_4 + Na_2SO_4$
2.516	0.0000	1.02	Na_2SO_4
2.0 Molal NaCl			
0.000	0.0547	2.01	$CaSO_4\cdot 2H_2O$
0.208	0.0194	2.03	$CaSO_4\cdot 2H_2O$
0.410	0.0152	2.04	$CaSO_4\cdot 2H_2O$
0.614	0.0142	2.02	$CaSO_4\cdot 2H_2O + CaSO_4\cdot Na_2SO_4$
0.659	0.0127	2.03	$CaSO_4\cdot Na_2SO_4$
0.874	0.0089	2.05	$CaSO_4\cdot Na_2SO_4$
1.067	0.0065	2.01	$CaSO_4\cdot Na_2SO_4$
1.458	0.0042	2.01	$CaSO_4\cdot Na_2SO_4$
1.656	0.0035	2.01	$CaSO_4\cdot Na_2SO_4$
1.855	0.0030	2.03	$CaSO_4\cdot Na_2SO_4$
1.930	0.0032	2.02	$CaSO_4\cdot Na_2SO_4 + Na_2SO_4$
1.919	0.0000	2.02	Na_2SO_4
4.0 Molal NaCl			
0.000	0.0552	4.07	$CaSO_4\cdot 2H_2O$
0.104	0.0238	4.06	$CaSO_4\cdot 2H_2O$
0.182	0.0183	4.06	$CaSO_4\cdot 2H_2O + CaSO_4\cdot Na_2SO_4$
0.190	0.0138	4.00	$CaSO_4\cdot Na_2SO_4$
0.276	0.0109	4.07	$CaSO_4\cdot Na_2SO_4$
0.338	0.0076	4.06	$CaSO_4\cdot Na_2SO_4$
0.386	0.0062	4.06	$CaSO_4\cdot Na_2SO_4$
0.428	0.0056	4.07	$CaSO_4\cdot Na_2SO_4$
0.540	0.0040	4.05	$CaSO_4\cdot Na_2SO_4$
0.637	0.0031	4.10	$CaSO_4\cdot Na_2SO_4$
0.811	0.0022	4.00	$CaSO_4\cdot Na_2SO_4$
0.958	0.0017	4.17	$CaSO_4\cdot Na_2SO_4 + Na_2SO_4$
0.976	0.0000	4.13	Na_2SO_4

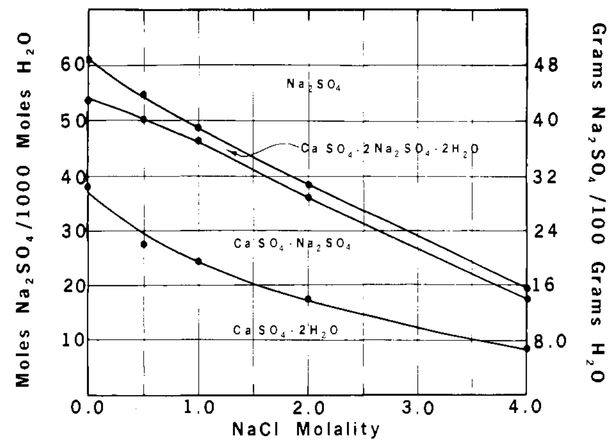

Figure 3. $CaSO_4$–Na_2SO_4 phase diagram at 40° C. and 0.0–4.0 molal NaCl

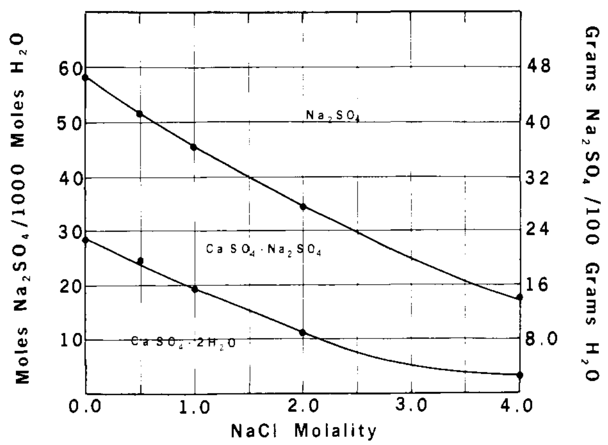

Figure 4. $CaSO_4$–Na_2SO_4 phase diagram at 55° C. and 0.0–4.0 molal NaCl

two samples at 55° C. (both near the $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot Na_2SO_4$ invariant point), one at 0.5 molal NaCl and the other at 4.0 molal NaCl. This salt was not found again in duplicate samples and the authors can only conclude that it is not stable at this temperature. [Hill and Wills (*4*) found that the penta salt was unstable at 50° C. and recommended temperatures of 60° to 75° C. for its preparation.]

The results at 70° C. are presented in Table V and in Figure 5. The penta salt, $5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$, now appears at this temperature at all the salinities studied. Its region of stability increases with increasing salinity to a maximum at about 1.0 molal NaCl and then decreases (Figure 5). The solubility of all the salts present, except gypsum, decrease with increasing salinity. The gypsum solubility increases to a maximum between 2 and 4 molal NaCl and then decreases.

The present value for the solubility of gypsum, 0.0539 molal, in 2.0 molal NaCl at 70° C. is in good agreement with 0.0546 molal reported by Marshall and Slusher (*9*). In the experiments that started with gypsum as the calcium

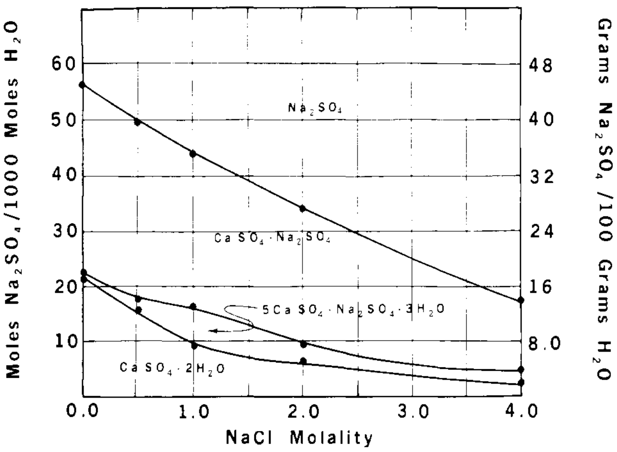

Figure 5. $CaSO_4$–Na_2SO_4 phase diagram at 70° C. and 0.0–4.0 molal NaCl

Table V. System $CaSO_4$–Na_2SO_4–NaCl–H_2O at 70° C.

Na_2SO_4 Molality	$CaSO_4$ Molality	NaCl Molality	Solid Phase
			0.0 Molal NaCl
0.000	0.0149	0.00	$CaSO_4 \cdot 2H_2O$
0.080	0.0103	0.00	$CaSO_4 \cdot 2H_2O$
0.203	0.0117	0.00	$CaSO_4 \cdot 2H_2O$
0.610	0.0156	0.00	$CaSO_4 \cdot 2H_2O$
0.880	0.0176	0.00	$CaSO_4 \cdot 2H_2O$
1.111	0.0180	0.00	$CaSO_4 \cdot 2H_2O$
1.235	0.0187	0.00	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.254	0.0192	0.00	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O + CaSO_4 \cdot Na_2SO_4$
1.308	0.0181	0.00	$CaSO_4 \cdot Na_2SO_4$
1.312	0.0189	0.00	$CaSO_4 \cdot Na_2SO_4$
1.622	0.0135	0.00	$CaSO_4 \cdot Na_2SO_4$
2.071	0.0091	0.00	$CaSO_4 \cdot Na_2SO_4$
2.110	0.0088	0.00	$CaSO_4 \cdot Na_2SO_4$
2.355	0.0074	0.00	$CaSO_4 \cdot Na_2SO_4$
2.646	0.0058	0.00	$CaSO_4 \cdot Na_2SO_4$
2.918	0.0048	0.00	$CaSO_4 \cdot Na_2SO_4$
2.999	0.0044	0.00	$CaSO_4 \cdot Na_2SO_4$
3.113	0.0042	0.00	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
3.108	0.0000	0.00	Na_2SO_4
			0.5 Molal NaCl
0.000	0.0353	0.50	$CaSO_4 \cdot 2H_2O$
0.102	0.0170	0.50	$CaSO_4 \cdot 2H_2O$
0.395	0.0149	0.50	$CaSO_4 \cdot 2H_2O$
0.800	0.0167	0.50	$CaSO_4 \cdot 2H_2O$
0.871	0.0173	0.51	$CaSO_4 \cdot 2H_2O + 5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.970	0.0175	0.51	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.996	0.0168	0.51	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O + CaSO_4 \cdot Na_2SO_4$
1.020	0.0165	0.51	$CaSO_4 \cdot Na_2SO_4$
1.112	0.0156	0.52	$CaSO_4 \cdot Na_2SO_4$
1.275	0.0128	0.49	$CaSO_4 \cdot Na_2SO_4$
1.401	0.0104	0.49	$CaSO_4 \cdot Na_2SO_4$
1.661	0.0067	0.50	$CaSO_4 \cdot Na_2SO_4$
1.812	0.0069	0.50	$CaSO_4 \cdot Na_2SO_4$
2.064	0.0066	0.50	$CaSO_4 \cdot Na_2SO_4$
2.348	0.0048	0.50	$CaSO_4 \cdot Na_2SO_4$
2.595	0.0041	0.51	$CaSO_4 \cdot Na_2SO_4$
2.766	0.0037	0.50	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
2.767	0.0000	0.50	Na_2SO_4
			1.0 Molal NaCl
0.000	0.0439	0.95	$CaSO_4 \cdot 2H_2O$
0.208	0.0174	1.03	$CaSO_4 \cdot 2H_2O$
0.514	0.0152	1.05	$CaSO_4 \cdot 2H_2O + 5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.798	0.0147	1.04	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.897	0.0133	0.98	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O + CaSO_4 \cdot Na_2SO_4$
1.246	0.0085	0.98	$CaSO_4 \cdot Na_2SO_4$
1.513	0.0065	1.04	$CaSO_4 \cdot Na_2SO_4$
1.630	0.0060	0.96	$CaSO_4 \cdot Na_2SO_4$
1.957	0.0045	0.98	$CaSO_4 \cdot Na_2SO_4$
2.155	0.0037	0.98	$CaSO_4 \cdot Na_2SO_4$
2.442	0.0032	1.00	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
2.403	0.0000	1.04	Na_2SO_4
			2.0 Molal NaCl
0.000	0.0539	1.93	$CaSO_4 \cdot 2H_2O$
0.200	0.0201	1.99	$CaSO_4 \cdot 2H_2O$
0.365	0.0159	1.88	$CaSO_4 \cdot 2H_2O + 5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.534	0.0129	1.92	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O + CaSO_4 \cdot Na_2SO_4$
0.704	0.0082	2.05	$CaSO_4 \cdot Na_2SO_4$
0.879	0.0070	1.88	$CaSO_4 \cdot Na_2SO_4$
1.228	0.0043	2.00	$CaSO_4 \cdot Na_2SO_4$
1.468	0.0032	1.99	$CaSO_4 \cdot Na_2SO_4$
1.675	0.0028	1.94	$CaSO_4 \cdot Na_2SO_4$
1.898	0.0025	1.90	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
1.878	0.0000	1.90	Na_2SO_4
			4.0 Molal NaCl
0.000	0.0588	3.99	$CaSO_4 \cdot 2H_2O$
0.130	0.0233	4.02	$CaSO_4 \cdot 2H_2O + 5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.223	0.0138	4.01	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.296	0.0071	4.33	$CaSO_4 \cdot Na_2SO_4$
0.365	0.0053	4.04	$CaSO_4 \cdot Na_2SO_4$
0.487	0.0036	4.03	$CaSO_4 \cdot Na_2SO_4$
0.602	0.0028	4.13	$CaSO_4 \cdot Na_2SO_4$
0.731	0.0019	4.22	$CaSO_4 \cdot Na_2SO_4$
0.836	0.0016	4.24	$CaSO_4 \cdot Na_2SO_4$
0.953	0.0018	4.04	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
0.988	0.0000	3.98	Na_2SO_4

sulfate phase, the gypsum did not change to anhydrite even after a 3-month reaction time. All samples that formed the penta salt at 70° C. started with gypsum as the calcium sulfate phase.

Some samples were prepared with anhydrite as the calcium sulfate phase. The penta salt did not form in any of these samples as is shown in Figure 6. Anhydrite is less soluble than gypsum, so much less that the solubility curve intersects the glauberite solubility line and completely misses the penta salt solubility line. This confirms the findings of the Japanese workers (*6*), who could form the penta salt only from gypsum. Glauberite, however, can be formed from both anhydrite and gypsum.

The results at 85° C. are given in Table VI and in Figure

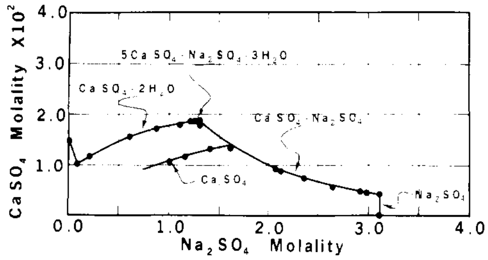

Figure 6. $CaSO_4$–Na_2SO_4 solubility at 70° C. and 0.0 molal NaCl

Table VI. System $CaSO_4$–Na_2SO_4–NaCl–H_2O at 85° C.

Na_2SO_4 Molality	$CaSO_4$ Molality	NaCl Molality	Solid Phase
0.0 Molal NaCl			
0.000	0.0138	0.00	$CaSO_4 \cdot 2H_2O$
0.117	0.0104	0.00	$CaSO_4 \cdot 2H_2O$
0.128	0.0107	0.00	$CaSO_4 \cdot 2H_2O$
0.244	0.0078	0.00	$CaSO_4$
0.319	0.0071	0.00	$CaSO_4$
0.370	0.0105	0.00	$CaSO_4$
0.483	0.0074	0.00	$CaSO_4$
0.623	0.0086	0.00	$CaSO_4$
0.722	0.0092	0.00	$CaSO_4$
0.751	0.0111	0.00	$CaSO_4$
0.870	0.0103	0.00	$CaSO_4$
0.876	0.0139	0.00	$CaSO_4$
1.000	0.0147	0.00	$CaSO_4 + 5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.011	0.0150	0.00	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.080	0.0149	0.00	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.089	0.0154	0.00	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.145	0.0150	0.00	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.337	0.0135	0.00	$CaSO_4 \cdot Na_2SO_4$
1.557	0.0109	0.00	$CaSO_4 \cdot Na_2SO_4$
1.930	0.0081	0.00	$CaSO_4 \cdot Na_2SO_4$
2.031	0.0074	0.00	$CaSO_4 \cdot Na_2SO_4$
2.084	0.0072	0.00	$CaSO_4 \cdot Na_2SO_4$
2.429	0.0056	0.00	$CaSO_4 \cdot Na_2SO_4$
2.655	0.0048	0.00	$CaSO_4 \cdot Na_2SO_4$
2.884	0.0039	0.00	$CaSO_4 \cdot Na_2SO_4$
2.996	0.0040	0.00	$CaSO_4 \cdot Na_2SO_4$
3.045	0.0038	0.00	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
3.034	0.0000	0.00	Na_2SO_4
0.5 Molal NaCl			
0.000	0.0347	0.50	$CaSO_4 \cdot 2H_2O$
0.096	0.0089	0.49	$CaSO_4$
0.210	0.0083	0.50	$CaSO_4$
0.405	0.0074	0.50	$CaSO_4$
0.512	0.0097	0.51	$CaSO_4$
0.652	0.0127	0.54	$CaSO_4$
0.698	0.0131	0.51	$CaSO_4 + 5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.868	0.0148	0.55	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
0.898	0.0143	0.50	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.012	0.0132	0.53	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O$
1.063	0.0128	0.50	$5CaSO_4 \cdot Na_2SO_4 \cdot 3H_2O + CaSO_4 \cdot Na_2SO_4$
1.234	0.0103	0.52	$CaSO_4 \cdot Na_2SO_4$
1.398	0.0093	0.52	$CaSO_4 \cdot Na_2SO_4$
1.698	0.0064	0.54	$CaSO_4 \cdot Na_2SO_4$
2.019	0.0051	0.55	$CaSO_4 \cdot Na_2SO_4$
2.038	0.0046	0.52	$CaSO_4 \cdot Na_2SO_4$
2.326	0.0049	0.53	$CaSO_4 \cdot Na_2SO_4$
2.479	0.0032	0.56	$CaSO_4 \cdot Na_2SO_4$
2.557	0.0035	0.49	$CaSO_4 \cdot Na_2SO_4$
2.716	0.0034	0.52	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
2.695	0.0000	0.51	Na_2SO_4
1.0 Molal NaCl			
0.000	0.0299	1.02	$CaSO_4$
0.198	0.0097	1.01	$CaSO_4$
0.207	0.0082	1.03	$CaSO_4$
0.402	0.0076	1.02	$CaSO_4$
0.598	0.0090	1.01	$CaSO_4$
0.638	0.0084	1.06	$CaSO_4$
0.790	0.0116	1.00	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
0.841	0.0083	1.06	$CaSO_4 \cdot Na_2SO_4$
0.954	0.0088	1.01	$CaSO_4 \cdot Na_2SO_4$
0.998	0.0085	1.07	$CaSO_4 \cdot Na_2SO_4$
1.040	0.0078	1.07	$CaSO_4 \cdot Na_2SO_4$
1.413	0.0052	1.05	$CaSO_4 \cdot Na_2SO_4$
1.612	0.0039	1.09	$CaSO_4 \cdot Na_2SO_4$
1.704	0.0039	1.01	$CaSO_4 \cdot Na_2SO_4$
2.077	0.0034	1.07	$CaSO_4 \cdot Na_2SO_4$
2.227	0.0031	1.03	$CaSO_4 \cdot Na_2SO_4$
2.337	0.0032	1.03	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
2.331	0.0000	1.04	Na_2SO_4
2.0 Molal NaCl			
0.000	0.0378	2.01	$CaSO_4$
0.211	0.0116	1.99	$CaSO_4$
0.247	0.0088	2.09	$CaSO_4$
0.400	0.0092	2.01	$CaSO_4$
0.490	0.0103	2.03	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
0.557	0.0091	2.01	$CaSO_4 \cdot Na_2SO_4$
0.652	0.0067	2.08	$CaSO_4 \cdot Na_2SO_4$
0.664	0.0067	2.01	$CaSO_4 \cdot Na_2SO_4$
0.999	0.0038	2.03	$CaSO_4 \cdot Na_2SO_4$
1.194	0.0030	2.02	$CaSO_4 \cdot Na_2SO_4$
1.478	0.0027	2.12	$CaSO_4 \cdot Na_2SO_4$
1.732	0.0022	2.09	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
1.764	0.0000	2.02	Na_2SO_4
4.0 Molal NaCl			
0.000	0.0353	3.91	$CaSO_4$
0.151	0.0141	4.12	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
0.172	0.0120	4.05	$CaSO_4 \cdot Na_2SO_4$
0.181	0.0118	4.04	$CaSO_4 \cdot Na_2SO_4$
0.209	0.0097	4.03	$CaSO_4 \cdot Na_2SO_4$
0.215	0.0094	4.04	$CaSO_4 \cdot Na_2SO_4$
0.233	0.0081	4.04	$CaSO_4 \cdot Na_2SO_4$
0.241	0.0076	4.01	$CaSO_4 \cdot Na_2SO_4$
0.263	0.0076	4.05	$CaSO_4 \cdot Na_2SO_4$
0.331	0.0036	4.05	$CaSO_4 \cdot Na_2SO_4$
0.487	0.0030	4.13	$CaSO_4 \cdot Na_2SO_4$
0.607	0.0023	4.01	$CaSO_4 \cdot Na_2SO_4$
0.761	0.0016	4.01	$CaSO_4 \cdot Na_2SO_4$
0.883	0.0015	4.03	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
0.913	0.0000	4.03	Na_2SO_4

7. The penta salt and gypsum exist at 0.0 and 0.5 molal NaCl, and disappear at 1.0, 2.0, and 4.0 molal NaCl. Apparently, at 85° C. at the higher salinities, the rate of conversion of gypsum to anhydrite is now appreciable. Once gypsum is dehydrated, the penta salt can no longer be formed owing to the lower solubility of anhydrite compared with gypsum. The solubility of anhydrite shows the same decrease and then increase with increasing Na_2SO_4 concentration at 1.0 molal NaCl as did gypsum at the lower temperatures. The solubility of anhydrite also increases with salinity to a maximum between 2 and 4 molal NaCl, and decreases, similar to gypsum at the lower temperatures. The solubility of the other salts decreases with increasing salinity.

An unidentified double salt was formed by Marshall and Slusher (*9*) at 80° and 95° C., at high salinities. This salt is probably glauberite, the only double salt that was found at these conditions.

Comparison of the solubility data with the data of Power, Fabuss, and Satterfield (*10*) at 85° C. shows good agreement. The present value for the solubility of gypsum in water is 0.0138 molal compared with their 0.0134 molal, and the value for anhydrite in 1.0 molal NaCl is 0.0256 compared with 0.0261 molal obtained by these other investigators.

The 100° C. results are presented in Table VII and Figure

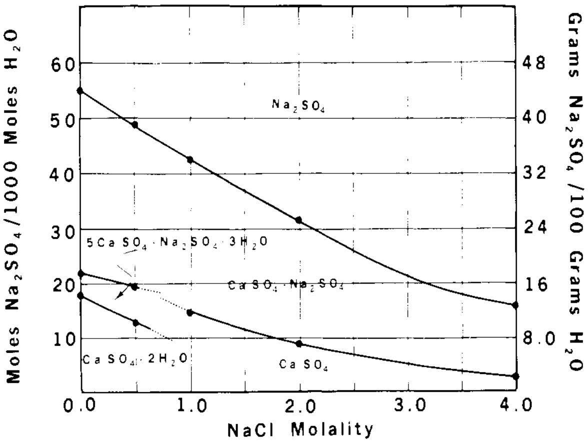

Figure 7. $CaSO_4$–Na_2SO_4 phase diagram at 85° C. and 0.0–4.0 molal NaCl

Table VII. System $CaSO_4$–Na_2SO_4–NaCl–H_2O at 100° C.

Na_2SO_4 Molality	$CaSO_4$ Molality	NaCl Molality	Solid Phase
0.0 Molal NaCl			
0.000	0.0131	0.00	$CaSO_4$
0.052	0.0041	0.00	$CaSO_4$
0.211	0.0039	0.00	$CaSO_4$
0.371	0.0049	0.00	$CaSO_4$
0.643	0.0059	0.00	$CaSO_4$
0.842	0.0070	0.00	$CaSO_4$
1.038	0.0077	0.00	$CaSO_4$
1.283	0.0086	0.00	$CaSO_4$
1.385	0.0101	0.00	$CaSO_4$
1.422	0.0086	0.00	$CaSO_4$
1.496	0.0094	0.00	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
1.624	0.0080	0.00	$CaSO_4 \cdot Na_2SO_4$
2.145	0.0053	0.00	$CaSO_4 \cdot Na_2SO_4$
2.271	0.0052	0.00	$CaSO_4 \cdot Na_2SO_4$
2.387	0.0049	0.00	$CaSO_4 \cdot Na_2SO_4$
2.670	0.0042	0.00	$CaSO_4 \cdot Na_2SO_4$
3.016	0.0036	0.00	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
3.001	0.0000	0.00	Na_2SO_4
0.5 Molal NaCl			
0.000	0.0215	0.50	$CaSO_4$
0.101	0.0061	0.52	$CaSO_4$
0.209	0.0062	0.50	$CaSO_4$
0.420	0.0061	0.53	$CaSO_4$
0.568	0.0062	0.51	$CaSO_4$
0.696	0.0066	0.51	$CaSO_4$
0.726	0.0067	0.50	$CaSO_4$
0.826	0.0071	0.51	$CaSO_4$
0.843	0.0072	0.52	$CaSO_4$
0.916	0.0074	0.50	$CaSO_4$
1.013	0.0076	0.50	$CaSO_4$
1.132	0.0077	0.50	$CaSO_4$
1.224	0.0083	0.50	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
1.346	0.0070	0.53	$CaSO_4 \cdot Na_2SO_4$
1.519	0.0060	0.51	$CaSO_4 \cdot Na_2SO_4$
1.884	0.0050	0.51	$CaSO_4 \cdot Na_2SO_4$
2.259	0.0039	0.51	$CaSO_4 \cdot Na_2SO_4$
2.501	0.0032	0.50	$CaSO_4 \cdot Na_2SO_4$
2.678	0.0030	0.50	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
2.662	0.0000	0.52	Na_2SO_4
1.0 Molal NaCl			
0.000	0.0256	1.03	$CaSO_4$
0.108	0.0088	1.03	$CaSO_4$
0.214	0.0059	1.03	$CaSO_4$
0.475	0.0062	1.08	$CaSO_4$
0.637	0.0063	1.05	$CaSO_4$
0.892	0.0067	1.14	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
0.930	0.0074	1.05	$CaSO_4 \cdot Na_2SO_4$
1.133	0.0061	1.04	$CaSO_4 \cdot Na_2SO_4$
1.314	0.0050	1.02	$CaSO_4 \cdot Na_2SO_4$
1.510	0.0042	1.03	$CaSO_4 \cdot Na_2SO_4$
1.773	0.0037	1.05	$CaSO_4 \cdot Na_2SO_4$
1.933	0.0032	1.02	$CaSO_4 \cdot Na_2SO_4$
2.164	0.0028	1.05	$CaSO_4 \cdot Na_2SO_4$
2.318	0.0025	1.02	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
2.298	0.0000	1.02	Na_2SO_4
2.0 Molal NaCl			
0.000	0.0284	2.03	$CaSO_4$
0.110	0.0101	2.07	$CaSO_4$
0.240	0.0070	2.13	$CaSO_4$
0.416	0.0059	2.06	$CaSO_4$
0.525	0.0063	2.07	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
0.701	0.0050	2.06	$CaSO_4 \cdot Na_2SO_4$
0.906	0.0038	2.16	$CaSO_4 \cdot Na_2SO_4$
1.114	0.0031	2.04	$CaSO_4 \cdot Na_2SO_4$
1.136	0.0029	1.89	$CaSO_4 \cdot Na_2SO_4$
1.509	0.0022	2.05	$CaSO_4 \cdot Na_2SO_4$
1.706	0.0018	2.06	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
1.734	0.0000	2.06	Na_2SO_4
4.0 Molal NaCl			
0.000	0.0296	4.08	$CaSO_4$
0.164	0.0082	4.11	$CaSO_4$
0.177	0.0076	4.20	$CaSO_4$
0.284	0.0054	4.12	$CaSO_4 + CaSO_4 \cdot Na_2SO_4$
0.372	0.0036	4.12	$CaSO_4 \cdot Na_2SO_4$
0.452	0.0030	3.80	$CaSO_4 \cdot Na_2SO_4$
0.501	0.0025	4.11	$CaSO_4 \cdot Na_2SO_4$
0.629	0.0021	4.10	$CaSO_4 \cdot Na_2SO_4$
0.778	0.0017	4.10	$CaSO_4 \cdot Na_2SO_4$
0.913	0.0015	4.08	$CaSO_4 \cdot Na_2SO_4 + Na_2SO_4$
0.893	0.0000	4.09	Na_2SO_4

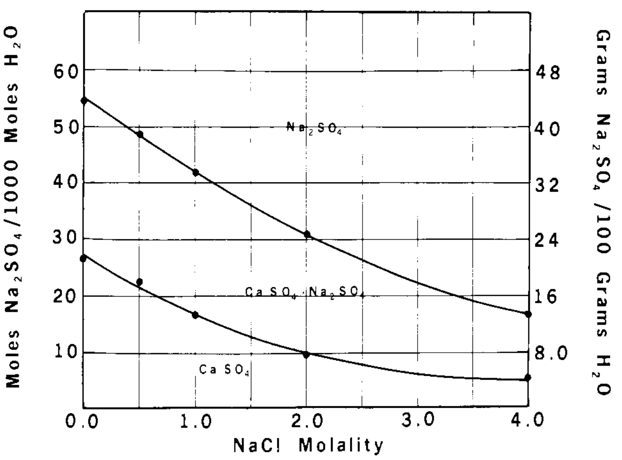

Figure 8. $CaSO_4$–Na_2SO_4 phase diagram at 100° C. and 0.0–4.0 molal NaCl

8. At this temperature, all the salts are dehydrated, leaving only $CaSO_4$, $CaSO_4 \cdot Na_2SO_4$, and Na_2SO_4. The solubility of anhydrite increases with salinity to a maximum above 2.0 molal NaCl and then remains relatively constant thereafter. The solubility of the other two salts decrease with increasing salinity.

No hemihydrate was found at any of the studied conditions except possibly at 85° and 100° C. at the lower salinities. This phase appears to be a transient one between gypsum and anhydrite.

ACKNOWLEDGMENT

The laboratory phase of the research was ably assisted by Lawrence J. Yeager, Mary T. Weymouth, James F. Dunn, and Kenneth R. Kight.

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RECEIVED for review December 7, 1967. Accepted February 19, 1968. Work supported by the Division of the Office of Saline Water, United States Department of the Interior, under Contract No. 14-01-0001-1114.

Pressure-Volume-Temperature Behavior of a Mixture of Difluoromethane and Pentafluoromonochloroethane

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This work presents pressure-volume-temperature properties of a mixture of 73.5 mole % difluoromethane with 26.5 mole % pentafluoromonochloroethane, commonly known as Refrigerant 504. The work includes vapor pressures from −57.72° C., the boiling point, to +66.1° C., the critical point, isochor and isotherm data from 25° to 199° C. at specific volumes between 0.7 and 9.4 cc. per gram, and liquid density data between −30° and +60° C. Correlation equations fit the data to standard deviation of ±0.35% or better, except for the liquid compressibility data which do not obey the Martin-Hou equation used for the vapor density data, and the dew point data where the standard deviation from the vapor pressure equation worsens to ±0.7%.

THE MIXTURE of 0.735 mole of difluoromethane (Refrigerant 32) and 0.265 mole of pentafluoromonochloroethane (Refrigerant 115) is commercially known as Refrigerant 504, which forms a minimum boiling azeotrope at 0° C. (*1*). This work presents its thermodynamic properties, including vapor pressures and liquid and vapor densities, with their correlating equations which include a Martin-Hou equation of state.

No experimental data have been found dealing with the vapor pressure or *PVT* properties of this mixture. Information is available for the components difluoromethane (*3*) and pentafluoromonochloroethane (*4*).

EXPERIMENTAL

Sample Preparation. Both the CH_2F_2 (Genetron 32) and the CF_3CF_2Cl (Genetron 115) were purified and degassed as previously described (*3, 4, 6*). Chromatographic analysis showed them to be better than 99.95 mole % pure.

To prepare the azeotropic mixture, exact weights of each