[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Ternary Systems. XX. Calcium Sulfate, Ammonium Sulfate and Water

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The system consisting of calcium sulfate, ammonium sulfate and water has had partial investigation by D'Ans,[2] who determined some of the points of saturation with respect to two salts, and sketched a probable outline of the system between the temperatures of 20 and 83°; no isotherms were studied. Sullivan[3] has furnished a partial isotherm at 25°, up to 33% concentration of ammonium sulfate. Bell and Taber[4] contributed an isotherm at 50°, which we have found to be incomplete through omission of at least two of the phases. Barre[5] also has given a number of points of saturation with respect to two salts, between 3 and 100°.

After completing recently[6] a study of the related system in which potassium sulfate is present in place of ammonium sulfate, and showing that the work of D'Ans[2] and others had led to many errors through the incompleteness of their study, it was decided to make a complete study of the system described in this paper, with sufficient isotherms to ensure that errors of interpretation might not occur. This procedure is of course always the wisest; but in cases like the two mentioned, where there is frequently great retardation in the formation of double salts, it seems to be an actual necessity. The following complete isotherms at 100, 75, 50 and 25° make it probable that no existing equilibria between those temperatures have been overlooked, and the orderly sequence of invariant points makes it improbable that any have been greatly misplaced, as appears to be the case with some of those reported by D'Ans.[2]

The system was found to produce the following solid phases, all of which have been reported by the previous investigators. These differ from each other greatly in their rapidity of formation and in the time required to reach equilibrium. For each a mean valence can be calculated according to the "Retardation Rule" proposed by van't Hoff,[7] which was found indispensable in determining the time to be allowed for equilibrium, which in our work has varied from as little as five minutes to as much as several weeks. The index is calculated by dividing the total valence representing all ions in the formula by the total number of such ions; water of hydration is regarded as hydrogen oxide and given arbitrarily, according to van't Hoff, a mean valence of $^4/_3$.

	Index
Ammonium sulfate, $(NH_4)_2SO_4$	1.33
Gypsum, $CaSO_4 \cdot 2H_2O$	1.50
Syngenite, $CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$	1.50
Di-calcium salt, $2CaSO_4 \cdot (NH_4)_2SO_4$	1.71
Penta-calcium salt, $5CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$	1.75
Anhydrite, $CaSO_4$	2.00

The three first-named salts form from supersaturation quickly and attain external equilibrium with solution quickly; the di-calcium salt forms more slowly, the penta-calcium salt very slowly and anhydrite shows a retardation in formation and in dissolving which makes it frequently impossible to attain equilibrium at the lower temperatures. To this list of existing compounds should be added the calcium sulfate hemi-hydrate, $CaSO_4 \cdot 0.5H_2O$, which in spite of its somewhat high retardation index, 1.6, is so labile that its equilibria could not be studied.

Materials and Apparatus

The materials used were Kahlbaum ammonium sulfate and gypsum, "zur Analyse." Where the equilibria involved these salts, or the formation of others from them, they were weighed with water into 250-cc. glass-stoppered Pyrex bottles, the ammonium sulfate being allowed to dissolve before the gypsum was added. Care was given to the weighing so that this original complex, with the composition of the saturated solution as found by analysis, might be used in algebraic extrapolation of the tie-line to find the composition of the solid phase; it was found in this case, as in some others, that extrapolation through the point for the original complex is more accurate than when the point selected is a wet residue.[8] Equilibrium was attained by rotating the bottles in a water thermostat at 25 and 50°, in a glycerol-filled thermostat at 75 and 100°. The temperature control was ±0.05° at the lower temperatures, ±0.1° at the higher. For analysis, samples were filtered through cotton and filter paper by suction

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(1) The material of this paper is from the thesis of Mr. Yanick, presented to the Graduate School of New York University, January, 1935, in partial fulfilment of the requirements for the degree of Ph.D.

(2) D'Ans, *Z. anorg. Chem.*, **62**, 129 (1909).

(3) Sullivan, THIS JOURNAL, **27**, 529 (1905).

(4) Bell and Taber, *J. Phys. Chem.*, **10**, 119 (1906).

(5) Barre, *Ann. chim. phys.*, [VIII] **24**, 145 (1911).

(6) Hill, THIS JOURNAL, **56**, 1071 (1934).

(7) Van't Hoff, "Zur Bildung der ozeanischen Salzablagerungen," F. Vieweg und Sohn, Braunschweig, 1905, Vol. I, p. 32; Vol. II, p. 17.

(8) Hill and Ricci, THIS JOURNAL, **53**, 4305 (1931).

into pipets at 25 and 50°, by air-pressure through electrically heated tubes at 75 and 100°; no tendency to crystallize during transfer was noted. The samples for analysis were delivered directly into Erlenmeyer flasks, which were stoppered at once and weighed after cooling. The calcium sulfate was determined in a large sample by precipitation as calcium oxalate and weighed as calcium oxide; a small sample was evaporated to constant weight in a partially evacuated oven at 90°, which required about twenty-four hours. With these very accurate determinations of calcium sulfate and water, the ammonium sulfate was known by difference, with errors that can rarely have exceeded 0.02%. For equilibria involving di-salt, pentasalt or anhydrite, these compounds were especially prepared by methods noted later and substituted for gypsum in the original weighings. The equilibrium solids were removed in small amounts and inspected for homogeneity by a petrographic microscope.

The 100° Isotherm.—In Table I are given the data for the 100° isotherm. In column one are given the points of saturation with respect to two solid phases, lettered as shown in Fig. 1. The second and third columns give the composition of the original complexes used, in weight per cent.; the fourth and fifth columns give the composition of the equilibrium solution and the last column gives the saturating solid phase or phases, as determined by algebraic extrapolation of the tie-lines and confirmed by examination under the microscope.

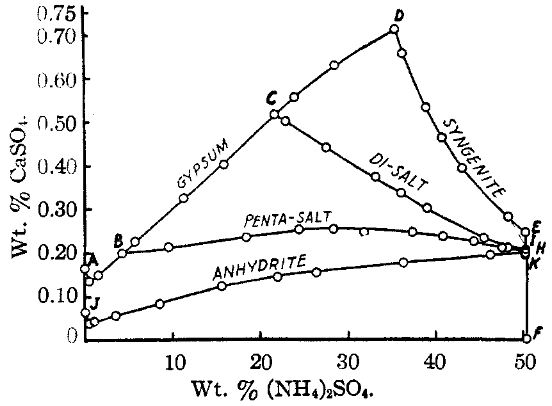

Fig. 1.—100° Isotherm.

The gypsum curve, A-B-C-D, was obtained by stirring the salt for periods of fifteen to thirty minutes. The change of the salt to stable anhydrite in the region AB cannot be detected in long periods of time; the change to pentasalt in the region BC and to di-salt in the region CD is detectable after thirty minutes, the formation of di-salt being the more rapid as indicated by its retardation index. The curve DE for syngenite was obtained in all cases by use of gypsum as reacting phase; the formation of syngenite starts instantaneously and is completed in less than thirty minutes, after which time crystals of the di-salt were detectable under the microscope. By using time intervals of less than thirty minutes points falling on the smooth curve DE were obtained. Extrapolations of the tie-lines at this temperature do not give convincing evidence of the composition of the salt, as they fall to pass through the composition of the salt by an average deviation of −3.1% (max. deviation, −6.6%), the errors being attributed to partial decomposition of the salt and to possible evaporation in withdrawal of samples. The isothermally invariant point D was obtained with solid phases present recognized as gypsum and syngenite.

TABLE I

$CaSO_4$–$(NH_4)_2SO_4$–H_2O: 100° ISOTHERM

	Original complex		Saturated solution		
Point in Fig. 1	Wt. % $CaSO_4$	Wt. % $(NH_4)_2$-SO_4	Wt. % $CaSO_4$	Wt. % $(NH_4)_2$-SO_4	Solid phase
A	...	....	0.167	...	Gypsum
	2.227	0.507	.136	0.56	Gypsum
	2.977	1.505	.152	1.63	Gypsum
B	2.006	4.286	.200	9.24	Gypsum + pentasalt
	6.971	5.089	.226	5.69	Gypsum
	10.152	9.986	.327	11.40	Gypsum
	8.686	14.827	.404	16.07	Gypsum
C	2.243	21.870	.518	21.81	Gypsum
	9.818	21.419	.555	24.21	Gypsum
	5.111	27.119	.630	28.79	Gypsum
D	3.000	34.933	.715	35.77	Gypsum + syng.
	4.992	37.025	.657	36.46	Syng.
	3.922	39.127	.532	39.12	Syng.
	2.663	41.112	.461	41.09	Syng.
	3.111	43.091	.392	43.26	Syng.
	2.019	48.528	.280	48.51	Syng.
E	2.014	53.396	.245	50.41	Syng. and $(NH_4)_2SO_4$
	2.011	23.082	.505	22.98	Di-salt
	2.047	27.868	.441	27.90	Di-salt
	2.274	33.261	.372	33.37	Di-salt
	2.996	39.004	.300	39.36	Di-salt
	3.006	45.039	.229	45.68	Di-salt
	2.868	47.786	.212	48.44	Di-salt
I	2.024	52.878	.204	50.40	Di-salt and $(NH_4)_2SO_4$
	2.507	10.000	.214	9.76	Pentasalt
	3.999	18.000	.236	18.53	Pentasalt
	2.001	24.499	.254	24.68	Pentasalt
	2.781	28.291	.252	28.55	Pentasalt
	8.194	30.011	.248	32.15	Pentasalt
	2.010	37.028	.244	37.48	Pentasalt
	2.012	40.506	.237	41.03	Pentasalt
	2.002	44.013	.223	44.64	Pentasalt
	2.005	47.041	.212	47.74	Pentasalt
H	2.008	53.063	.201	50.37	Penta and $(NH_4)_2SO_4$
J	...	....	.066	...	Anhydrite
	3.020	0.504	.042	0.53	Anhydrite
	2.544	1.019	.047	1.09	Anhydrite
	5.064	3.376	.058	3.61	Anhydrite
	5.007	8.013	.085	8.52	Anhydrite
	3.486	15.007	.125	15.61	Anhydrite
	4.045	21.088	.145	22.02	Anhydrite
	4.999	24.964	.155	26.56	Anhydrite
	4.005	35.092	.177	36.52	Anhydrite
	4.004	44.860	.193	46.59	Anhydrite
K	2.904	64.174	.198	50.41	Anhydrite + $(NH_4)_2SO_4$
F	...	....	...	50.45	$(NH_4)_2SO_4$

The curve for the solubility of the di-salt, C-I, was obtained by use of prepared samples of the salt, made from gypsum in boiling solutions of 40% ammonium sulfate or higher; the change to syngenite is complete in a few minutes, and that to the di-salt in a few hours, whereas at this concentration any further change to pentasalt was found to be extremely slow, requiring several days for its completion. The crystals were quickly filtered by suction, washed with 95% alcohol and then with ether, and dried in an oven at 95°. Microscopic examination showed no foreign salts present and analysis confirmed the purity; $CaSO_4$ found, 67.20 and 67.25%, calcd. for $2CaSO_4 \cdot (NH_4)_2SO_4$ 67.33%; total SO_4 found, 71.13 and 71.12%, calcd. 71.26%. Material of this composition was stirred with solution for one hour for points near C, for several hours for points near I, where the change to pentasalt is slower. The invariant points C and I were obtained with mixtures of the appropriate salts. It was found that the di-salt forms directly from gypsum (without the intervention of syngenite) at ammonium sulfate concentrations between C and D, but the reaction could not be used either to prepare the salt or for solubility determinations, since a change to pentasalt begins before the formation from gypsum is complete. Because of the intermediate positions of the di-salt as regards stability, the extrapolated tie-lines at this temperature do not indicate the composition of the salt at all well, but the smoothness of the curve indicates, as has been found throughout this study, that external equilibrium with solution is rapidly attained even when internal equilibrium as to solid phases is slow of attainment.

For the solubility curve for the pentasalt, B-H, a few points in the range 25–35% ammonium sulfate were obtained by formation from gypsum over one to two days of stirring; for the other points, it was found more suitable to prepare the salt in larger quantities by boiling a 30% ammonium sulfate solution with gypsum for twenty-four hours. The salt thus obtained, after washing with alcohol and drying, was found free from other salts on microscopic examination and gave good analytical results; $CaSO_4$ found, 81.65 and 81.91%, calcd. for $5CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$ 81.93%; total SO_4 found, 69.39 and 69.38%, calcd. 69.37%. This salt was stirred with ammonium sulfate solutions for twenty-four hours for attainment of solubility equilibrium; the extrapolated tie-lines pass close to the composition of the salt, with average deviation of only ± 0.5%. This behavior, in contrast with that of the di-salt and of syngenite, is in agreement with our general observation that the change of this salt to the stable anhydrite is very slow.

The only stable calcium salt at this temperature is anhydrite, for which we obtained the curve J-K. Here it was necessary to use that salt directly as the solid phase, since its formation from gypsum is a matter of many days. The anhydrite was prepared by a technique already described,[6] by boiling gypsum with 20% sulfuric acid for three to seven days. The solubility in water (J) found in three experiments averaged 0.066%, in good agreement with the 0.067% reported before. For the points on the line J-K, three to six days of rotation were used, it already having been established by experiments at 75° that that time was sufficient even at the lower temperatures.

It is to be noted that at this temperature, 100°, there is no crossing of the solubility curves for syngenite, di-salt, penta-salt or anhydrite. It is true that the points I, H and K fall so close together that a clear differentiation could not be claimed, but the position of the curves at lower concentrations of ammonium sulfate makes it probable that no equilibrium between any two of these salts exists.

The 75° Isotherm.—The experimental results at 75° are shown in Table II and in Fig. 2.

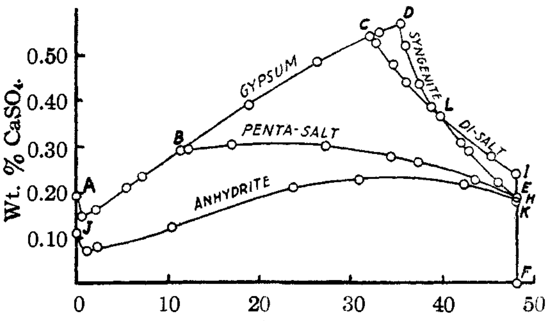

Fig. 2.—75° Isotherm.

At this temperature, as at 100°, the solubility curves for anhydrite, pentasalt and di-salt were determined with prepared specimens of the solid phase; the syngenite was formed in the solubility experiment from gypsum. For gypsum, periods of one hour to twenty-four hours were used; at this temperature its change into the other salts

TABLE II

$CaSO_4$–$(NH_4)_2SO_4$–H_2O: 75° ISOTHERM

Point	Original complex Wt. % $CaSO_4$	Original complex Wt. % $(NH_4)_2$-SO_4	Saturated solution Wt. % $CaSO_4$	Saturated solution Wt. % $(NH_4)_2$-SO	Solid phase
A	...	...	0.191	..	Gypsum
	4.025	0.503	.147	0.53	Gypsum
	4.002	2.002	.162	2.12	Gypsum
	4.024	5.028	.208	5.29	Gypsum
	2.003	7.007	.235	7.16	Gypsum
B	2.005	11.241	.294	11.33	Gypsum + Pentasalt
	4.004	18.019	.391	18.93	Gypsum
	4.013	25.068	.486	26.26	Gypsum
C	3.012	32.061	.539	32.22	Gypsum + Di-salt
	4.014	32.091	.545	33.58	Gypsum
D	1.997	34.666	.568	32.28	Syngenite + Gypsum
	2.003	36.062	.522	35.72	Syngenite
	2.008	38.156	.438	37.90	Syngenite
L	3.003	39.670	.371	39.88	Syngenite + Di-salt
	2.004	42.016	.308	42.01	Syngenite
	2.997	42.934	.289	42.82	Syngenite
	3.005	45.998	.224	45.94	Syngenite
E	2.049	50.079	.185	48.00	Syngenite + $(NH_4)_2SO_4$
	2.000	12.002	.295	11.94	Pentasalt
	2.001	16.983	.303	17.04	Pentasalt
	2.001	27.012	.300	27.24	Pentasalt
	2.141	33.903	.276	34.38	Pentasalt
	2.132	36.731	.267	37.21	Pentasalt
	1.797	43.053	.229	43.55	Pentasalt
H	1.991	50.114	.181	47.96	Penta + $(NH_4)_2SO_4$
	2.010	32.613	.530	32.71	Di-salt
	1.992	34.581	.482	34.62	Di-salt
	2.012	35.834	.442	35.91	Di-salt
	2.006	38.995	.380	39.17	Di-salt
	2.002	44.994	.279	45.35	Di-salt
I	1.999	49.986	.243	47.93	Di-salt + $(NH_4)_2SO_4$
J	...	....	.114	...	Anhydrite
	2.995	0.500	.074	0.52	Anhydrite
	2.995	2.005	.082	2.07	Anhydrite
	3.011	10.042	.133	10.35	Anhydrite
	2.601	23.099	.212	23.62	Anhydrite
	2.997	29.987	.231	30.86	Anhydrite
	2.997	41.023	.221	42.20	Anhydrite
	2.026	50.182	.180	47.95	Anhydrite + $(NH_4)_2SO_4$
F	...	....	..	48.00	$(NH_4)_2SO_4$

cannot be detected within that period. Pentasalt was rotated for two days; experiment showed no change in solubility with an additional two days. An experiment carried out with solution supersaturated with respect to calcium sulfate gave the same result as from undersaturation within this period. For the di-salt, rotation for seven to twelve hours gave equilibrium in the region CL, where the salt is stable with respect to syngenite, but in the metastable region L-I detectable amounts of syngenite were found after thirty minutes; for the invariant point I, stirring could be continued for only five minutes, after which syngenite began to form and the solubility began to fall toward the point E. For syngenite, periods of four to twenty-two hours were used, the shorter period in the region DL where syngenite is metastable with respect to di-salt. Anhydrite in pure water gave evidence of incomplete attainment of equilibrium after three weeks; the figure 0.116% is the mean of four determinations, not in very close agreement. This behavior of anhydrite has been pointed out in our earlier investigation.[6] On addition of ammonium sulfate however, the necessary time becomes much shortened; results after two weeks show no variation from those after one week.

At this temperature the improvement in control over that at 100° is indicated by the more satisfactory extrapolation of tie-lines; for gypsum the deviation from the composition of the solid phases is less than ±0.5%, for pentasalt ±0.8%, for di-salt ±1.1%, and for syngenite −0.57% (except in one case). The most marked change in relations brought about by the change of temperature from 100 to 75° is the opposite movement of the syngenite and di-salt curves, bringing about a crossing of the two and a new two-solid equilibrium (L) which is non-existent at the higher temperature.

The 50° Isotherm.—The results obtained at 50° are shown in Table III and Fig. 3.

TABLE III

$CaSO_4$–$(NH_4)_2SO_4$–H_2O: 50° ISOTHERM

Point	Original complex Wt. % $CaSO_4$	Original complex Wt. % $(NH_4)_2$-SO_4	Saturated solution Wt. % $CaSO_4$	Saturated solution Wt. % $(NH_4)_2$-SO_4	Solid phase
A	...	...	0.210	...	Gypsum
	3.000	0.500	.155	0.53	Gypsum
	7.620	1.037	.154	1.15	Gypsum
	7.972	1.990	.162	2.21	Gypsum
	5.012	6.019	.210	6.43	Gypsum
	3.000	7.995	.233	8.32	Gypsum
	5.016	10.035	.260	10.69	Gypsum
	2.996	15.962	.321	16.57	Gypsum
	4.994	17.984	.346	19.16	Gypsum
B	2.007	23.688	.390	24.15	Gypsum + Pentasalt
	5.000	24.013	.400	25.47	Gypsum
	2.390	30.209	.432	30.96	Gypsum
D	3.000	35.040	.449	34.90	Gypsum + Syngenite
N	2.115	49.649	.468	45.39	Gypsum + $(NH_4)_2SO_4$ (m)
	2.998	37.002	.381	36.44	Syngenite
	2.996	38.965	.313	38.55	Syngenite
M	2.007	39.384	.294	39.12	Syngenite + Pentasalt
	2.965	40.554	.267	40.22	Syngenite
	2.504	44.010	.201	42.91	Syngenite
	2.506	43.084	.180	43.88	Syngenite
E	2.504	46.066	.157	45.31	Syngenite + $(NH_4)_2SO_4$
	2.306	22.956	.394	23.14	Penta (m)
	2.220	29.469	.361	29.80	Pentasalt
	2.143	33.890	.331	34.40	Pentasalt
	2.007	36.087	.315	36.50	Pentasalt
	2.025	38.079	.298	38.54	Pentasalt
	1.713	43.169	.246	43.65	Pentasalt
H	1.698	50.268	.222	45.61	Penta + $(NH_4)_2SO_4$
	1.975	36.444	.485	36.54	Di-salt (m)
C	1.994	36.995	.452	37.54	Gypsum + Di-salt
	2.025	39.365	.399	39.54	Di-salt
	1.999	42.938	.310	43.22	Di-salt
I	2.007	49.511	.244	45.51	Di-salt + $(NH_4)_2SO_4$
F	...	....	...	45.65	$(NH_4)_2SO_4$

m = metastable

In the work at this temperature, the change of a metastable salt to a more stable one is much slower than at the higher temperatures. This fact permitted the establishment of one point each on the curves for pentasalt and di-salt in the region above A-B-C, where the salts are metastable with respect to gypsum; the pentasalt remained wholly unchanged for four days, with no sign of formation of gypsum, but for the di-salt only a few minutes of rotation were possible before gypsum began to appear. There was also obtained the metastable invariant point N for gypsum and ammonium sulfate, after five minutes of stirring.

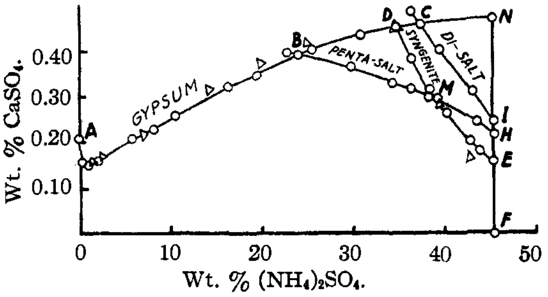

Fig. 3.—50° Isotherm: ∇, Bell and Taber.

The position of this point indicates that, despite the rapid initiation of double-salt formation, the solubility equilibrium for the two simple salts is very quickly attained. Necessity for rapid treatment occurred elsewhere in the system in the region MH, where pentasalt is metastable with respect to syngenite, and for the di-salt throughout, which begins to change rapidly into syngenite or pentasalt.

TABLE IV

$CaSO_4$–$(NH_4)_2SO_4$–H_2O: 25° ISOTHERM

	Original complex		Saturated solution		
Point	Wt. % $CaSO_4$	Wt. % $(NH_4)_2SO_4$	Wt. % $CaSO_4$	Wt. % $(NH_4)_2SO_4$	Solid phase
A	...	...	...	0.21	Gypsum
	2.989	0.150	0.172	0.16	Gypsum
	7.654	1.000	.146	1.12	Gypsum
	8.000	3.000	.162	3.33	Gypsum
	7.986	4.992	.183	5.51	Gypsum
	8.000	10.004	.242	11.09	Gypsum
	8.330	20.000	.335	22.22	Gypsum
	2.026	28.062	.373	28.66	Gypsum
D	6.909	33.476	.386	34.85	Gypsum + Syngenite
B	2.014	35.611	.386	36.13	Gypsum + Pentasalt
N	1.845	45.789	.378	43.29	Gypsum + $(NH_4)_2SO_4$
	7.920	36.630	.379	35.06	Syngenite
	5.255	36.783	.347	35.74	Syngenite
	2.380	37.080	.310	36.67	Syngenite
	2.361	39.723	.224	39.41	Syngenite
	3.158	41.050	.200	40.70	Syngenite
	3.273	41.430	.191	41.20	Syngenite
E	2.998	44.943	.142	43.24	Syngenite + $(NH_4)_2SO_4$
	2.133	34.385	.429	34.77	Pentasalt
	2.275	37.989	.337	38.52	Pentasalt
	2.210	40.430	.303	41.01	Pentasalt
	2.268	40.863	.299	41.47	Pentasalt
H	1.830	46.174	.259	43.24	Pentasalt + $(NH_4)_2SO_4$
F	...	....	..	43.46	$(NH_4)_2SO_4$

In Fig. 3, the results of Bell and Taber[4] for the gypsum and syngenite curves are shown by triangles. We have here omitted study of anhydrite because of the great difficulty in obtaining equilibrium, although it has been shown probable[6] that it is the stable salt at this temperature. The diagram shows the presence of a two-salt equilibrium point (M) for syngenite and pentasalt, and the disappearance of the syngenite–di-salt equilibrium found at 75°.

Algebraical extrapolation of tie-lines, as a test of consistency in results,[8] gave for gypsum deviations of less than 1% except for a few points; for penta-salt 1.0%, for di-salt ± 0.7%, and for syngenite never more than ± 0.37%.

The 25° Isotherm.—The results of the determinations at 25° are shown in Table IV and Fig. 4; in the latter, the figures of Sullivan[3] for the solubility of gypsum are indicated by triangles.

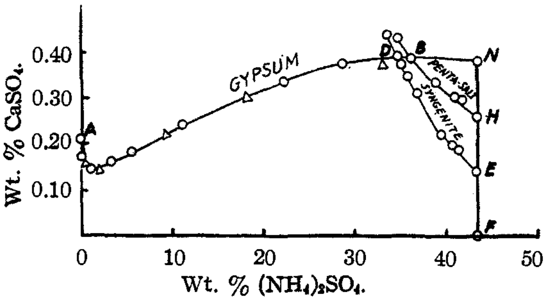

Fig. 4.—25° Isotherm: ∇, Sullivan.

At this temperature the various points could be attained in a few hours, and remained unchanged in value after several days, with the following exceptions. Point N (metastable gypsum and ammonium sulfate) could be maintained only from five to twenty minutes. Point H likewise can be maintained for only twenty minutes, the pentasalt beginning quickly to change to syngenite. In general, even at low temperatures, the presence of solid ammonium sulfate seems to initiate very rapid formation of the stable salt. It should be noted however that the curves for syngenite and for pentasalt were extended into the region of metastability with respect to gypsum; examination after six hours and after four days showed no gypsum present. The attempt to locate the metastable invariant point for the two salts, *i. e.*, the intersection of the two solubility curves, resulted in failure; the mixture of the two salts changed wholly to syngenite or to gypsum.

A curve for the di-salt could not be established at this temperature; attempts to use that salt showed rapid change of the salt to other bodies and gave solubility figures which were clearly not representative of any equilibrium. The salt is evidently metastable with respect to both gypsum and ammonium sulfate, its temperature of formation from those components being evidently somewhat higher than 25°. A curve for anhydrite is also missing from the diagram, but for another reason; experience has shown the extreme difficulty of obtaining reliable solubility figures for that compound at low temperatures. The salt is doubtless metastable with respect to gypsum at this temperature and has a higher solubility in water; as the transition point to gypsum is lowered by the presence of ammonium sulfate, it is probable that its solubility curve crosses that of gypsum at some point between A and D.

The extrapolations of the tie-lines to the composition of the solid phases was found quite accurate throughout the whole isotherm.

Composition of the Ammonium Syngenite.—There has been conflicting evidence as to the degree of hydration of this salt. Bell and Taber,[4] on the basis of extrapolation of tie-lines, ascribed to it the formula $CaSO_4 \cdot (NH_4)_2SO_4 \cdot 2H_2O$. D'Ans[2] analyzed the dry salt, after washing with alcohol, and found it a true syngenite, $CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$. Bell and Taber[9] raised the objection that this procedure resulted in a partial decomposition of the salt, and gave additional experiments in which the extrapolated tie-lines indicated the dihydrate composition. Quite recently Merz, Hardesty and Hendricks[10] gave a single value by extrapolation of the tie-line which also agreed excellently with the formula for a dihydrate.

Our own attempts to prepare the pure salt by washing with alcohol–water solutions following the procedure of D'Ans were as unsuccessful as Bell and Taber had found; there was always evidence of decomposition of the salt, rather more with respect to the ratio of the two sulfates than with respect to water. This does not of course preclude that D'Ans was successful through chance or through more skilful procedure. At the same time, it became clear to us in the regular progress of the work that the compound could not possibly be a dihydrate; omitting our results at 100°, where evaporation and rapid change of solid salt diminished the accuracy, it was found that at 75° four of the five experiments extrapolate to the formula of the monohydrate with an average deviation of −0.57% in ammonium sulfate content, which would be an error of −3.39% if the compound were a dihydrate. At 50°, the comparable deviations are, for six points; for monohydrate, average +0.14% (max. +0.37%), for dihydrate average, −3.1%; at 25°, for 6 points, for monohydrate, average −0.17% (max. −1.32%) and for dihydrate, −3.2%. The evidence of these sixteen experiments could not be passed by.

The experiments of Bell and Taber and of Merz and collaborators are of course in principle exactly the same as ours, with the experimental difference that one of their points for the extrapolation is from the analysis of a wet residue, our corresponding point being the composition of the original complex as weighed on the balance. We have previously expressed the opinion[8] that the analysis of a wet residue, unless conducted with a special technique, is likely to bring in errors due to loss or gain of water in transfer of the pasty mass, which errors may more than counterbalance the mathematical advantage of the greater difference in the two points taken for extrapolating the straight line. In our routine determinations, it is true that our two points are very close together, so that the errors of the analysis are multiplied on the average some twenty-fold; this choice of complexes was made in order to prevent clogging of our bottles with the very voluminous precipitate. We have therefore conducted three additional experiments with especial care, using as large amounts of solid phase as seemed possible. The results are given in Table V.

TABLE V

COMPOSITION OF THE AMMONIUM SYNGENITE (50°)

Original complex, wt. %	$CaSO_4$	5.008	5.003	4.899	
	$(NH_4)_2SO_4$	40.990	41.139	41.223	
Satd. soln. wt. %	$CaSO_4$	0.254	0.253	0.222	
	$(NH_4)_2SO_4$	40.484	40.582	40.706	
Devn. in compn. of monohydrate, %		−0.575	−0.137	−0.167	Av. −0.293

The multiplication of errors here is reduced to about ten-fold. The experiments give an average deviation from the formula of the monohydrate of only −0.3%, while that from the dihydrate would be about −3.3%. There seems to be no question but that the salt is a true syngenite,

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(9) Bell and Taber, *J. Phys. Chem.*, **11**, 492 (1907).

(10) Merz, Hardesty and Hendricks, THIS JOURNAL, **55**, 3571 (1933).

$CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$, as is also strongly indicated by the crystallographic examination of Dr. Gabriel in this issue.[11]

The Temperature–Concentration Diagram.—The isothermally invariant points (solution saturated with two salts) have been collected in Table V. The concentration of the solution with respect to ammonium sulfate alone has been included; that of the calcium sulfate is of course small in all cases and can be found in Tables I–IV. An additional experiment at 83° for the syngenite–di-salt equilibrium is included.

TABLE VI

$CaSO_4$–$(NH_4)_2SO_4$–H_2O: TEMPERATURE–CONCENTRATION DIAGRAM

Line	F-F′	D-D′	B-B′	C-C′	M-M′	L-L′
Solid phases	$(NH_4)_2SO_4$	Gyps. Syng.	Gyps. Penta	Gyps. Di-salt	Syng. Penta	Syng. Di-salt
Temp., °C.						
100	50.45	35.77	4.24	21.81	...	...
83	...	...	...	...	...	43.62
75	48.00	35.28	11.33	32.22	48.00	39.88
50	45.65	34.87	24.15	37.54	39.13	...
25	43.46	34.85	36.13	...	...	...
0[a]	41.50	34.33	...	...	...	...

[a] By extrapolation.

The results are also indicated in Fig. 5. In interpreting this diagram, it should be remembered that the various areas indicated are *not* areas of stable existence of salts; throughout the greater part of the temperature range only anhydrite and ammonium sulfate are stable, and the other salts are at the same time stable with respect to one or more salts and metastable with respect to others; the fields for stability and metastability are therefore superimposed in part upon each other. The continuous lines, marked with the same lettering as in Tables I–IV, show the various two-salt equilibria. That for anhydrite–gypsum (J-J′) is wholly hypothetical, on the assumption that the transition point is at about 40°. At two points only is there intersection of these lines—at X, representing invariant equilibrium between gypsum, syngenite and disalt, which is placed by graphical means at about 62°, and at Y, representing equilibrium between gypsum, syngenite and pentasalt, which is placed at about 29°. The other apparent intersections are unreal, since the lines are in different planes.

The diagram differs not only quantitatively but also qualitatively from that given by D'Ans[2] in that he placed the line M-M′ for the syngenite–pentasalt equilibrium as practically coincident with D-D′, for gypsum–syngenite. Such a condition is shown by the various isotherms to be impossible. D'Ans also includes an equilibrium between disalt and pentasalt, which is also shown by the isotherms to be non-existent.

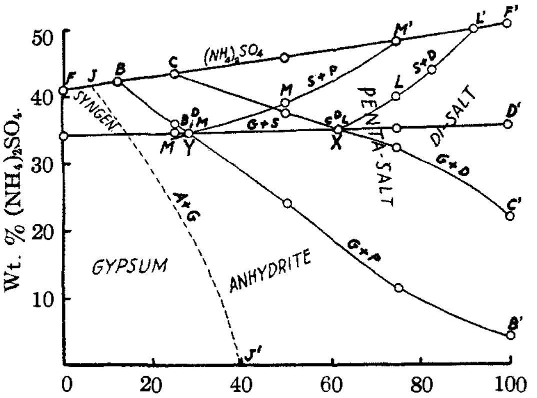

Fig. 5.

The crystallographic properties of the three double salts found in this investigation have been studied and are reported upon in this issue by Dr. Anton Gabriel, of the U. S. Bureau of Mines, New Brunswick, N. J.

Summary

The solubility relationships of the various simple salts and double salts occurring in the system $CaSO_4$–$(NH_4)_2SO_4$–H_2O have been determined between 25 and 100°. It has been found possible, by making use of van't Hoff's retardation rule, to adjust time relationships so that a consistent solubility isotherm could be determined where there were as many as four degrees of metastability present at a given temperature and concentration, and where the time necessary for equilibrium varied from five minutes to several weeks.

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[11] Gabriel, THIS JOURNAL, 57, 686 (1935).