numerous concentrations up to about 0.1 normal.

3. The measurements confirm Onsager's limiting conductance equation and his prediction of the presence of C (concentration) and a $C \log C$ term at increasing concentrations.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Ternary Systems. XIX. Calcium Sulfate, Potassium Sulfate and Water

BY ARTHUR E. HILL

The finding of deposits of polyhalite, $(CaSO_4)_2 \cdot K_2SO_4 \cdot MgSO_4 \cdot 2H_2O$, in the southwest of this country, has in it possibility of value as a commercial source of potash. It was suggested to me by Dr. Everett P. Partridge, of the U. S. Bureau of Mines, New Brunswick, N. J., that information on the ternary system consisting of calcium sulfate, potassium sulfate and water would be helpful in attacking the problem. I am indebted not only to Dr. Partridge for the suggestion, but to him, Mr. John E. Conley and Mr. Loyal Clarke of the same station for much valuable help during the course of the work, and particularly to Dr. Alton Gabriel for the petrographic examination of solid phases in nearly all the experiments reported, without which the work would have dragged and might easily have gone astray.

The system in question has been studied in part by a number of investigators, who have laid out its general outline from 0 to 83°, but with considerable omission and occasional error. It was first studied as part of the work on the Stassfurt salts, by van't Hoff and his co-workers,[1] later by Cameron and Breazeale,[2] by Barre[3] and by Anderson and Nestell.[4] This large amount of work however includes no isotherms at any temperature except the 25° isotherm of Cameron and Breazeale, all other points given being for saturation with two or with three solid phases; there is no guide as to which equilibria are stable and which are metastable; there are some erroneous points given, doubtless because of lack of information as to the phases present; and, finally, there has been no attention paid to the occurrence of anhydrite, $CaSO_4$, which is the dominating stable phase at all the higher temperatures. The present work gives complete isotherms at 40, 60 and 100°, and makes it possible to determine the stability or metastability of the various phase-complexes.

Between 0 and 100°, the solid phases which were found by the earlier workers, and to which no new compounds have been added, are the following

Gypsum, $CaSO_4 \cdot 2H_2O$
Hemihydrate, $CaSO_4 \cdot 0.5H_2O$
Anhydrite, $CaSO_4$
Syngenite, $CaSO_4 \cdot K_2SO_4 \cdot H_2O$
Pentacalcium potassium sulfate, $(CaSO_4)_5 \cdot K_2SO_4 \cdot H_2O$

The last-named salt, first found by van't Hoff and Geiger,[1] has been commonly called the "pentasalt." In dealing with aqueous systems containing any of the complex salts, one finds the solubility always very low with respect to calcium ion, as is well known for calcium sulfate in all its forms; there is also met with the problem of slow attainment of equilibrium. Successful work has been possible only with knowledge of and consistent use of the principle laid down by van't Hoff,[5] as the "Verzögerungs-regal," which, though entirely empirical as far as I have been able to find, is a rule of the greatest usefulness in solubility determinations, and very rarely has been quoted. It is to the effect that the retardation of salts in attaining equilibrium, presumably not only external equilibrium with solution but also internal equilibrium as to the stable phases, is expressed by the mean valence, which is calculated by dividing the total valence representing all ions in the formula by the total number of such ions. In this calculation, water of hydration is regarded as hydrogen oxide and given arbitrarily a mean valence of 4/3. By this treatment uni-univalent salts, which usually attain equilibrium

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(1) Van't Hoff and Wilson, *Sitzungsberichte der Preuss. Akad.*, 1142 (1900); van't Hoff and Geiger, *ibid.*, 935 (1904); van't Hoff, Voerman and Blasdale, *ibid.*, 305 (1905); D'Ans, *Z. anorg. Chem.*, **62**, 129 (1909). For a complete tabulation, see D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Verlagsgesellschaft für Ackerbau, Berlin, 1933.

(2) Cameron and Breazeale, *J. Phys. Chem.*, **8**, 335 (1904).

(3) Barre, *Compt. rend.*, **148**, 1604 (1909); *Ann. chim. phys.*, (V111) **24**, 145, 1911.

(4) Anderson and Nestell, *J. Ind. Eng. Chem.*, **12**, 243 (1920); Anderson, *ibid.*, 11, 327 (1919).

(5) Van't Hoff, "Zur Bildung der ozeanischen Salzablagerungen," Braunschweig, 1905, Vol. 1, p. 32; Vol. II, p. 17.

quickly, have a mean valence of 1, and di-divalent salts, which usually are exceedingly slow in attaining equilibrium, have a mean valence of two. Of the salts treated in this research gypsum has a mean valence of 1.5, syngenite also one of 1.5, pentasalt one of 1.75 and anhydrite one of 2.0. It should be pointed out that this retardation index, as far as it can be given quantitative expression, would have to be regarded as an exponential function. In entire accord with van't Hoff's experience, it has been found that gypsum and syngenite can be brought to equilibrium in moderate time at all temperatures, pentasalt requires considerable time even at favorable temperatures and anhydrite is exceedingly slow under all conditions. Knowledge of these relations has made it possible to attain certain metastable equilibria with ease; others have been found quite impossible of attainment.

Materials and Apparatus

The potassium sulfate used was a Kahlbaum zur Analyse preparation as was also the gypsum; the latter was found to vary only slightly in water content from that required by the formula. Syngenite was easily prepared at any temperature, by the addition of gypsum to potassium sulfate solutions of suitable concentration, as shown by the isotherms; the formation of the double salt starts immediately, and is complete within a few hours, even at room temperature. Lower temperatures are preferable to avoid formation of pentasalt. The pentasalt was prepared at 100°, by addition of gypsum (about 50 g. per liter of solution) to a boiling solution of potassium sulfate, of such concentration that the final solution did not fall below 5.5%. There was immediate formation of syngenite, which after about one hour began visibly to change into the more granular pentasalt. After six hours of boiling, the salt was filtered, washed with 1:1 alcohol–water solution, then with 95% alcohol, dried in air and finally in the drying oven at 100°. Analyses of the double salts were found to accord with the formulas within very narrow limits; microscopic inspection showed absence of any second salt.

The extremely low vapor tension of these two hydrates does not appear to have been noted or mentioned before. A 3-g. sample of syngenite placed over concd. sulfuric acid underwent no measurable loss of weight in forty-eight days. Placed in a drying oven at 100°, there was a loss of 1.3 mg. the first day, and no subsequent loss during fifteen days, indicating that the small loss was due to extraneous moisture. Put in an open electric oven at 220° under atmospheric conditions of moisture, the loss was 0.76% in four days and proceeded slowly and without completion; after eleven months the loss was 4.93%, distinctly lower than the 5.49% required by the formula. This would indicate that its vapor tension at 220° is but slightly above the prevailing aqueous tension of the atmosphere. However, when placed in an oven at 220° in a stream of air dried by sulfuric acid, the loss was 5.38% in two days. It was easily possible to dehydrate it completely at a red heat over the Bunsen burner in fifteen minutes. The vapor tension of the pentasalt is still lower; not only was no detectable loss found over sulfuric acid or in the 100° oven, but heating at 170° in a partial vacuum in a slow stream of dried air gave absolutely no loss in seven days. With the Bunsen burner, however, losses close to (but a little higher than) the theoretical 2.06% were obtained in thirty minutes. It is evident that these salts possess vapor tensions notably lower than is commonly found in salt hydrates.

In the solubility experiments, the original complex was made up by careful weighing of the components, gypsum being used sometimes and dehydrated calcium sulfate at other times, and at still others syngenite or pentasalt. The potassium sulfate was always brought into solution and the temperature brought up to the temperature of the experiment before any calcium salt was added, to prevent the initiation of undesired phases by temporary conditions of wrong temperature or concentration. The experiments at 40° were conducted in a large water-thermostat in which 250-cc. Pyrex bottles were slowly tumbled end-over-end. The 60° work was done in stoppered bottles in a small glycerin-filled thermostat, stirring being attained by whirling the bottles about their vertical axis by means of a wind-mill. For the 100° work, some of the experiments were conducted in the whirled bottles, others in Pyrex or quartz flasks of larger dimensions which were kept boiling over a small flame; good reflux condensers kept the loss of water by evaporation down to a small amount, and the boiling point elevation brought about by even high concentrations of potassium sulfate was never greater than 1°, which is not of consequence at this temperature. For analysis, samples were pipetted or siphoned out through small filters made by tying a filter paper over the end of the glass tube and covering it with a thin layer of pure cotton; the filtration was therefore always at the temperature of the experiment, and crystallization in the pipets or siphons did not occur. A sample of from 10 to 15 cc. was run into a small glass-stoppered weighing flask, and after weighing was evaporated to dryness at 100° and subsequently for a few hours at 220°; this gave complete expulsion of water except for what might be retained by any syngenite or pentasalt formed, as shown above, but as the total of the calcium sulfate is never above 0.2%, it follows that the resultant error in water content would never be greater than 0.01%. A second larger sample of 50–100 cc. was analyzed for calcium by precipitation as oxalate and ignition to calcium oxide, then calculated to sulfate. The potassium sulfate was found by difference. At the lower temperatures, the weight of the pipetted sample was used to calculate an approximate density.

Preparation and Study of Anhydrite.—The preparation of anhydrite suitable for solubility measurements required extended study. Hara[6] found that anhydrite obtained by dehydrating gypsum by any method disintegrated into very fine crystals when in contact with water and gave high and discordant solubility values. Results obtained by using selected pure crystals of natural anhydrite he found mutually concordant. My own experience with the best natural anhydrite available to me was less happy; it gave all the physical characteristics of colloidal solutions,

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(6) Tanaka, Nakamura and Hara, *J. Soc. Chem. Ind. Japan*, **34**, Supplement binding, 284–287 (1931).

and the solubility figures were wholly unreliable. Dehydration of gypsum at 100°, even for very long periods, gives material which is quickly hydrated to hemihydrate in contact with water. Gypsum dehydrated over the Bunsen burner at temperatures estimated roughly as between 600 and 800° gave material identified by the microscope as anhydrite, but which in solubility measurements gave erratic results, although less so than the natural anhydrite; the explanation may lie in the existence of polymorphic forms of the mineral, in the presence of calcium oxide which was definitely established by experiment, or even in the matter of surface tensions due to incomplete annealing, which factor might easily be sufficient to affect measurably the behavior of so insoluble a substance. It was clearly indicated that suitable material ought to be prepared under conditions as nearly as possible like those under which it was to be used, which would suggest a dehydration by boiling with salt solutions of low enough vapor tension to bring about the conversion. Many of these were tried without success; sodium chloride solutions and several others gave either hemihydrate or material which quickly reverted to hemihydrate in contact with water. Success was attained with two only: potassium sulfate solutions of about 5% concentration brought about the conversion in about two weeks' time, but much more convenient was a boiling sulfuric acid solution of 15 to 20% concentration, which effected complete conversion in three days or less. The crystals were of 20 to 30 microns in length, quite uniform in character, and possessed essentially the indices of natural anhydrite ($\alpha = 1.571$, $\beta = 1.576$, $\gamma = 1.614$).

A preliminary report only can be made upon the solubility of anhydrite in water at varying temperatures. It is to be noted that the solubility has previously been measured only at temperatures higher than 100°;[7] the recent and more accurate measurements of Partridge and White[8] also are at temperatures of 100° and above. The known exceptions to this statement are two measurements of Hara,[6] at 75 and 50°, concerning which language difficulties leave uncertainty as to whether they are experimental figures or extrapolations of Partridge's curve, and a measurement by Roller[9] at 20° and one by Haddon and Brown[10] at 33°. The transition temperature of gypsum to anhydrite was set by van't Hoff[11] at 63.5°, on the basis of vapor tension and tensimeter measurements. Partridge[12] has called attention to the fact that the transition temperature given by van't Hoff has but meager experimental support, and that the solubility data indicate a transition temperature very much lower, namely, at about 38°. It is clear that exact determinations from 100° downward are much needed. These can be supplied at present only in small part, because of the exceedingly slow approach to equilibrium of anhydrite–water systems, which might be expected from the high mean valence of the salt. In such a case, approach to equilibrium from both undersaturation and supersaturation is absolutely essential; constancy of composition, over even long periods, is no criterion whatever. Up to this date, I have been able to attain equilibrium in water at 100° within reasonable time, as will be shown; the presence of other salts, particularly of other sulfates, accelerates the process very greatly, so that work at 60° has been successful in the three-component systems; but in pure water, only an upper and lower limit have been established at the lower temperatures. These point beyond question to a transition not far from 40°, in accord with Partridge's opinion. The baffling behavior met with, however, is that after a measurable approach toward equilibrium for a few days the solutions reach a concentration which does not appear to vary with the time; at 50°, the solutions from supersaturation and undersaturation, being still some 5% apart, did not approach toward each other measurably over a three-month period. A similar phenomenon in the case of calcite and aragonite was observed by Bäckström;[13] about the equilibrium value there is a region amounting to several per cent. of the total concentration in which the reaction velocity is zero; the times considered, however, were much shorter than in these experiments with anhydrite. The experiments with anhydrite are being continued, in an effort to determine whether a true solubility curve can be attained, and will be reported on at a later time.

The 40° Isotherm.—The results of the experimentation at 40° are shown in Table I and in Fig. 1.

Equilibrium with respect to gypsum or syngenite was established within a day or two in all cases. The consistency of the results was tested by extrapolation of the tie-lines through the two points representing the saturated solution and the original complex taken; using the method of algebraic extrapolation,[14] the lines met the composition of gypsum and of syngenite very closely indeed, except for the points on lines 7, 12 and 16, where apparently chance error intervened;

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[7] "Int. Crit. Tables," N. Y. 1928, Vol. IV, p. 229.

[8] Partridge and White, THIS JOURNAL, **51**, 360 (1929).

[9] Roller, *J. Phys. Chem.*, **35**, 1142 (1931).

[10] Haddon and Brown, *J. Soc. Chem. Ind.*, **43**, 11 (1924).

[11] Van't Hoff *et al.*, *Z. physik. Chem.*, **45**, 257 (1903).

[12] Ramsdell and Partridge, *Amer. Mineralogist*, **14**, 59 (1929).

[13] Bäckström, *Z. physik. Chem.*, **97**, 179 (1921).

[14] Hill and Ricci, THIS JOURNAL, **53**, 4305 (1931).

TABLE I

$CaSO_4$–K_2SO_4–H_2O:40° ISOTHERM

		Original Complex Wt. %		Satd. Solution Wt. %			
Point	Line	K_2SO_4	$CaSO_4$	K_2SO_4	$CaSO_4$	Density	Solid phase
A	1	....	...	0.00	0.212	0.9960	Gypsum
	2	1.000	3.000	1.027	.149	....	Gypsum
	3	1.993	2.994	2.066	.147	1.0108	Gypsum
	4	2.513	3.013	2.596	.154	1.0152	Gypsum
B	5	....	...	2.917	.155	1.0187	Gypsum + Pentasalt
	6	2.998	3.003	3.123	.159	1.0192	Gypsum (m)
	7	3.528	1.959	3.526	.163	1.0210	Gypsum (m)
C	8	....	...	3.71	.165	....	Gypsum + Syngenite (m)
D	9	....	...	3.956	.143	1.0252	Syngenite + Pentasalt
	10	5.045	0.775	4.061	.134	1.0258	Syngenite
	11	8.000	3.000	4.666	.101	1.031	Syngenite
	12	7.01	2.10	4.797	.094	1.032	Syngenite
	13	8.00	2.00	5.754	.070	1.039	Syngenite
	14	11.00	3.00	7.763	.040	1.056	Syngenite
	15	11.71	2.20	9.376	.029	1.069	Syngenite
	16	14.00	2.00	11.284	.020	1.086	Syngenite
E	17	13.997	0.467	12.895	.014	1.099	Syngenite + K_2SO_4
	18	15.002	.011	12.897	.010	1.099	K_2SO_4
F	19	....	...	12.86	.00	1.099	K_2SO_4

m = metastable equilibrium.

the average variation for the other lines is ±0.24%. The points B and D, representing the ends of the solubility curve for pentasalt, required especial attention. Efforts to reach the points from two directions each, that is, by the opposite phase reactions which raise the potassium sulfate concentration and lower it, respectively, proved futile; it was found impossible to form pentasalt from gypsum and solutions on the curve BC, which would lower the potassium sulfate concentration, or from syngenite and solutions on the curve CD, which would raise it; not only was there no spontaneous formation of pentasalt, but complexes containing large quantities of the salt left the solutions entirely unchanged during a three-months period of rotation. It is apparent that the velocity of formation of pentasalt by these two reactions is practically zero at 40°, although the temperature is distinctly above the transition point, which van't Hoff[1] and D'Ans[1] placed at 31.8°. No evidence of formation of the salt was found in any experiments at this temperature, except that when solutions of the composition C were taken with gypsum, syngenite and pentasalt present, microscopic examination seemed to indicate a slow growth of pentasalt. Why the formation of the salt requires the presence of the other two phases is not clear; an answer might explain the fact that pentasalt has not been found, according to van't Hoff, in any of the natural deposits containing gypsum or syngenite. Because of the non-formation of pentasalt, it was possible to locate the points B and D only by decomposition of the salt in solutions along the curves AB and DE, respectively. Point B represents the result of a four-months' experiment, which was probably unnecessarily prolonged; point D was obtained by two concordant experiments, one lasting for three months, the other only six days. Van't Hoff[1] located the point B at a much higher concentration, namely, 3.55% (3.8 moles of K_2SO_4 per 1000 moles of water). It has previously been remarked by Anderson[4] that van't Hoff's value is out of line with the values for this two-salt equilibrium at other temperatures. The new value of 2.92% seems to be more probable.

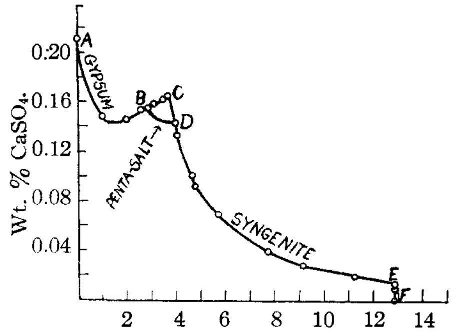

Fig. 1.—Isotherm at 40°.

No effort was made to consider equilibria involving anhydrite at this temperature. If Partridge's view and my own are correct as to the transition temperature for anhydrite, its solubility curve at 40° would be very close to the curve ABC.

The 60° Isotherm.—The results obtained at 60° are shown in Table II and Fig. 2.

The metastable invariant point C for gypsum and syngenite is lower than that found by Barre[3] by about 0.008% calcium sulfate and about 0.15% potassium sulfate; Barre's figures for the calcium sulfate at this invariant point plot somewhat irregularly. Equilibrium on the curves AC and CE for gypsum and for syngenite were obtained in about three days; the algebraic extrapolations of the tie lines gives the composition of the pure salts with considerable accuracy, the average deviation being ±0.57%, the maximum being 1.5%. The deviations in all cases except one indicate deficiencies in potassium sulfate content of the solid phase, which points toward small losses of water from the solution during filling and sam-

TABLE II

$CaSO_4$–K_2SO_4–H_2O:60° ISOTHERM

Point	Line	Original Complex Wt. % K_2SO_4	Original Complex Wt. % $CaSO_4$	Satd. Solution Wt. % K_2SO_4	Satd. Solution Wt. % $CaSO_4$	Solid phases
A	1	0.000	...	0.000	0.2015	Gypsum (m)
	2	0.501	1.994	0.518	.155	Gypsum (m)
	3	1.204	1.800	1.239	.148	Gypsum (m)
B	4	....	...	1.660	.150	Gypsum + Pentasalt (m)
	5	1.801	2.003	1.854	.151	Gypsum (m)
	6	2.400	2.002	2.449	.156	Gypsum (m)
	7	3.500	2.001	3.599	.169	Gypsum (m)
C	8	....	...	4.440	.176	Gypsum (m) + Syngenite (m)
	9	6.325	1.171	5.178	.134	Syngenite (m)
	10	7.501	2.000	5.429	.118	Syngenite (m)
D	11	....	...	5.660	.106	Syngenite + Pentasalt
	12	8.451	2.000	6.172	.099	Syngenite
	13	11.787	1.794	10.044	.041	Syngenite
E	14	....	...	15.40	.019	Syngenite + K_2SO_4
F	15	....	...	15.40	.000	K_2SO_4
G	16	0.000	...	(0.00	.160)	Anhydrite
	17	....	...	1.007	.101	Anhydrite
	18	....	...	2.013	.107	Anhydrite
	19	....	...	3.000	.111	Anhydrite
	20	....	...	3.562	.114	Anhydrite
H	21	....	...	(4.10	.116)	Anhydrite + Pentasalt
	22	....	...	4.745	.119	Anhydrite (m)
I	23	....	...	(5.32)	.121	Anhydrite + Syngenite (m)
	24	43.30	1.626	4.035	.117	Pentasalt
	25	....	...	2.840	.123	Pentasalt (m)

m = metastable equilibrium, ( ) = by graphic interpolation.

pling. Microscopic examination showed pure gypsum or pure syngenite in every case. The invariant point B was obtained only by decomposition of pentasalt, in two experiments covering nine days and nineteen days, respectively; formation of pentasalt at these low concentrations could not be obtained. For the point D, the values were obtained both by decomposition and formation of pentasalt, in experiments lasting five and eighteen days, respectively. The pentasalt equilibria on the line CD were obtained by agitating the pure salt with potassium sulfate solutions for periods of two to six days; the extrapolated tie lines showed the composition of the salt unchanged, within narrow limits, and microscopic examination showed no impurity.

For the solubility curve GH for anhydrite, the point G, representing solubility in pure water, is an approximation only, as discussed earlier. The other points represent results obtained from undersaturation over periods of five to ten days; as will be shown in the discussion of the 100° isotherm, the approach to equilibrium from undersaturation, in the presence of excess sulfate ion, is moderately rapid and reliable. The invariant points H and I are obtained by graphic interpolation; the equilibrium at H was experimentally unattainable because of retardation in formation of both salts concerned, while that at I could not be obtained because the decomposition of syngenite (mean valence 1.5) into pentasalt is so much more rapid than the attainment of equilibrium by anhydrite (mean valence 2.0).

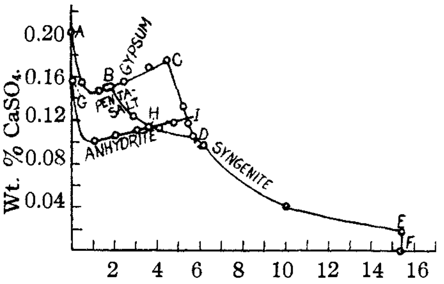

Fig. 2.—Isotherm at 60°.

The position of the anhydrite curve, so markedly below the gypsum curve, appears to be clear proof that the transition point for gypsum–anhydrite is not only distinctly lower than the 63.5° found by van't Hoff, but also much lower than the 60° of this isotherm.

The 100° Isotherm.—Table III and Fig. 3 show the results obtained at 100°.

TABLE III

$CaSO_4$–K_2SO_4–H_2O:100° ISOTHERM

Point	Line	Original Complex Wt. % K_2SO_4	Original Complex Wt. % $CaSO_4$	Satd. Solution Wt. % K_2SO_4	Satd. Solution Wt. % $CaSO_4$	Solid phase
A	1	0.00	...	0.00	0.167	Gypsum
	2	.243	3.053	.260	.135	Gypsum
	3	.730	2.558	.787	.133	Gypsum
B	4	....	...	1.090	.136	Gypsum + Pentasalt
	5	1.454	2.446	1.521	.140	Gypsum (m)
	6	....	...	2.016	.148	Gypsum (m)
	7	2.934	1.941	2.962	.162	Gypsum (m)
	8	4.368	2.939	4.522	.184	Gypsum (m)
	9	5.145	2.189	5.312	.198	Gypsum (m)
C	10	....	...	(5.37)	(.199)	Gypsum (m) + Syngenite (m)
	11	5.344	2.323	5.523	.200	Gypsum (m)
	12	6.569	1.371	5.322	.203	Syngenite (m)
	13	6.363	1.095	5.511	.191	Syngenite (m)
	14	6.442	0.974	5.547	.186	Syngenite (m)
	15	6.581	.984	5.719	.177	Syngenite (m)
	16	6.946	1.011	6.019	.163	Syngenite (m)
	17	7.487	0.571	7.030	.127	Syngenite (m)
	18	9.505	1.692	8.019	.102	Syngenite (m)
	19	8.643	0.586	8.110	.100	Syngenite (m)
I	20	....	...	(9.1)	(.084)	Syngenite (m) + Anhydrite (m)
	21	10.658	0.952	9.851	.076	Syngenite (m)
D	22	....	...	10.62	.066	Syngenite + Pentasalt
	23	....	...	11.62	.055	Syngenite
	24	15.640	2.400	13.608	.042	Syngenite
	25	....	...	14.150	.039	Syngenite
	26	....	...	14.375	.038	Syngenite
	27	16.994	1.038	16.221	.033	Syngenite

TABLE III (*Concluded*)

Point	Line	Original Complex Wt. %		Satd. Solution Wt. %		Solid phase
		K_2SO_4	$CaSO_4$	K_2SO_4	$CaSO_4$	
E	28	....	...	19.317	0.026	Syngenite + K_2SO_4
F	29	....	...	19.368	..	K_2SO_4
G	30	....	...	0.00	.067	Anhydrite
	31	....	...	.448	.051	Anhydrite
	32	....	...	.728	.047	Anhydrite
	33	....	...	1.932	.051	Anhydrite
	34	....	...	2.953	.055	Anhydrite
	35	....	...	4.500	.060	Anhydrite
H	36	....	...	5.46	(.067)	Anhydrite + Pentasalt
	37	....	...	6.52	.071	Anhydrite (m)
	38	....	...	7.323	.084	Anhydrite (m)
	39	....	...	8.10	.086	Anhydrite (m)
	40	....	...	8.50	.085	Anhydrite (m)
	41	....	...	8.43	.079	Anhydrite (m)
	42	....	...	2.558	.090	Pentasalt (m)
	43	....	...	4.021	.082	Pentasalt (m)
	44	....	...	5.221	.069	Pentasalt (m)
	45	....	...	6.817	.064	Pentasalt
	46	....	...	8.336	.064	Pentasalt
	47	....	...	9.598	.063	Pentasalt

m = metastable, ( ) = graphic interpolation.

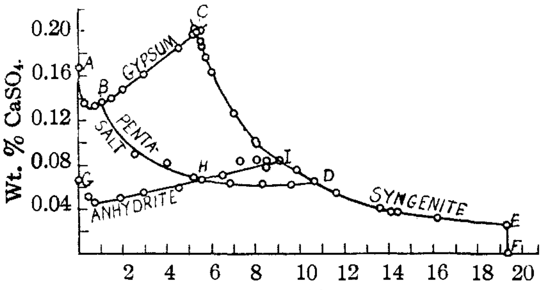

Fig. 3.—Isotherm at 100°.

The curves BC and CD represent sections of the gypsum curve and the syngenite curve which are metastable with respect to pentasalt; experimentally it was necessary to treat the systems not as merely metastable but as actually unstable, for at all points where the calcium sulfate concentration is high the formation of pentasalt starts immediately when either gypsum or syngenite is added to the potassium sulfate solution. However, the reaction is not so rapid but that the solubility of the gypsum or syngenite is reached before a large enough proportion of the solid phase has changed to pentasalt to alter the concentration of the solution. That such unstable mixed systems can give the true solubility of the more soluble salt is clearly indicated by the smooth curves found, as well as by the reproducibility of the results. The stirring in the thermostat was conducted for thirty to sixty minutes in these cases, before samples were taken for analysis. The tie-lines of course do not extrapolate to the composition of the pure salts, but show admixture of from 1 to 10% of pentasalt in most cases, as was confirmed by the microscopic examination. The invariant point C was obtained graphically from the two solubility curves, each of which was carried somewhat beyond the invariant point; when trials were made to obtain it experimentally with mixtures of the two salts, the resulting points were always low in calcium sulfate and irregular in potassium sulfate, apparently because of the very rapid formation of pentasalt, which is always most rapid when the two solid phases composing it are present. Barre's[3] figure at 99° is very close to the value here given.

The curve GHI represents the solubility of anhydrite derived by using the preparation obtained by boiling with sulfuric acid solution, as described previously. At this temperature of 100° only, and at no lower temperature, has it thus far been found possible to reach approximate equilibrium from supersaturation and from undersaturation. The figure for solubility in pure water, 0.067%, is a mean between 0.066 and 0.068%, reached in eleven days. As the concentration of potassium sulfate was increased the rate of approach to equilibrium was accelerated and good concordance (for this compound) attained; up to the point H, the results from undersaturation and supersaturation differed by not more than 0.002%. The approach from undersaturation was much more rapid than from supersaturation. As soon, however, as equilibria involving both anhydrite and pentasalt were investigated, or equilibria in the metastable region H to I, the systems proved out of accurate control. For the point H, the potassium sulfate concentration was definitely found; the value 5.46% was obtained from lower and from higher concentrations, but the calcium sulfate concentrations were erratic and not reproducible, all of them being higher than the point H as given. This is, in my belief, due to continuous decomposition of the pentasalt into some form of solid calcium sulfate other than anhydrite, which is constantly replenished before the change to anhydrite is complete; some evidence for this view will be given below. The solubility figures between H and I were also erratic and do not fall exactly upon any probable smooth curve. For that reason, the points H and I are taken by somewhat arbitrary graphic methods, while that for H is probably nearly right, that for I (metastable syngenite and metastable anhydrite) may be in error by some 0.005% calcium sulfate, and as a result by as much as 0.5% potassium sulfate. Attempts to obtain I experimentally were a failure; the results were quite erratic, the change to stable pentasalt occurring before equilibrium as to metastable anhydrite was reached, as might be anticipated from the much lower mean-valence of pentasalt.

The behavior of pentasalt, for which the line BHD stands, was similar to that of anhydrite. The isothermally invariant point D, for stable syngenite and pentasalt, was obtained without difficulty from higher and from lower concentrations of potassium sulfate. On the curve DH for stable equilibrium for the salt, results were obtained from supersaturation and from undersaturation with respect to calcium sulfate, in fair concordance. In the metastable region from H to B, however, the results were highly erratic. Samples taken for analysis over a period of days showed irregular increases and decreases in calcium sulfate content, although microscopic examination of the solids did not disclose anhydrite in any case. The invariant point B was obtained by boiling pentasalt and gypsum for periods of five to twenty-one hours with potassium sulfate solutions more concentrated than 1.09%; formation of pentasalt occurred, the potassium sulfate solution dropped to 1.09% and the solid phases showed no impurities. The attempt to decompose pentasalt, however, beginning either with pure water or with low concentrations of potassium sulfate, gave a surprisingly slow rise in potassium sulfate, requiring more than six days to reach 1.09%; the calcium sulfate concentration showed an initial rise to 0.144% in four hours and to 0.162% in two days, then diminishing to 0.106% in six days. From this it seems quite clear that the decomposition of pentasalt at 100° is not immediately into gypsum, which would show a solubility not higher than 0.136%, nor to hemihydrate, which must have a solubility very close to gypsum since the transition point is so close to 100°, but to some metastable form which may perhaps be regarded as amorphous; this slowly changes to the stable form, anhydrite. This hypothesis contradicts no known facts, and has further experimental confirmation in the work of Anderson and Nestell[4] for this equilibrium; their results are very erratic, but show calcium sulfate concentrations varying from 0.155 to 0.202%, values which cannot possibly be attributed to gypsum or hemihydrate and of course not to anhydrite. The decomposition therefore may be written, with considerable surety, as $(CaSO_4)\cdot K_2SO_4\cdot H_2O \longrightarrow 5CaSO_4$ (amorphous) + K_2SO_4 solution $\longrightarrow 5CaSO_4$ (anhydrite) + K_2SO_4 solution. In further confirmation is the fact that the residues from these experiments were found to contain, in addition to pentasalt, small splinters of dehydrated hemihydrate, that being the term adopted to describe the product which is obtained by dehydrating gypsum at low temperatures, and which shows the variable refractive index and other properties because of which Grengg,[15] and also Linck and Jung,[16] regard it as a solid solution; whether it be a solid solution or an amorphous form, it would obviously be metastable and show a higher solubility than the other forms. Considering the work done at all temperatures between 40 and 100° with pentasalt, it should be stated that in no case has it been possible to obtain a completely reversible equilibrium between that salt and either gypsum or anhydrite, whereas the equilibrium with syngenite (point D) has been shown reversible at 60 and at 100°.

It was considered necessary to repeat a few two-salt equilibrium points obtained by others which did not plot well with the results here obtained; these are given in Table IV.

TABLE IV

Point	Temp., °C.	Satd. Solution Wt. % $CaSO_4$	Satd. Solution Wt. % K_2SO_4	Solid phases
C	25	0.148	3.067	Gypsum + syngenite
C	31.8	.155	3.363	Gypsum + syngenite
D	83	.076	8.505	Syngenite + pentasalt

The 25° equilibrium found is slightly lower in calcium sulfate than in the figures of Cameron and of D'Ans; the potassium sulfate concentration is distinctly lower at 83° than previously reported, and also at 31.8°.

The Temperature–Concentration Diagram.—From the data in the four tables, Fig. 4 has been drawn to show the fields of stability of the various salts from 0 to 100°. Stable equilibria have been indicated by full lines, metastable by dotted lines. The points for equilibria involving anhydrite are of course conjectural except at 60 and 100°; but from their curvature and general relationship to the other curves, it becomes apparent that the point Q for gypsum, anhydrite

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(15) Grengg, *Z. anorg. Chem.*, **90**, 327 (1914).

(16) Linck and Jung, *ibid.*, **137**, 407 (1924).

and pentasalt must be below 40° and not far above 31.8° (point O).

With regard to the general problem of separating potassium sulfate from calcium sulfate by solubility differences, the complete diagram gives a somewhat disappointing picture; it indicates that as far as stable equilibria are concerned, the rise of temperature from 25 to 100° improves the possibilities only slightly; at 25° potassium sulfate could be concentrated in solution up to 3.067%, which could be increased at 100° only up to 5.46% (points on line H) without leaving some of the potash in one of the insoluble double salts. However, the very low rate at which anhydrite combines to form pentasalt or syngenite makes it seem probable that if any of the complex salts could be so decomposed at higher temperatures as to convert the calcium sulfate into anhydrite, solutions might be concentrated up toward the neighborhood of 10.6% at 100° (point D) or at least to 9.1% (point I).

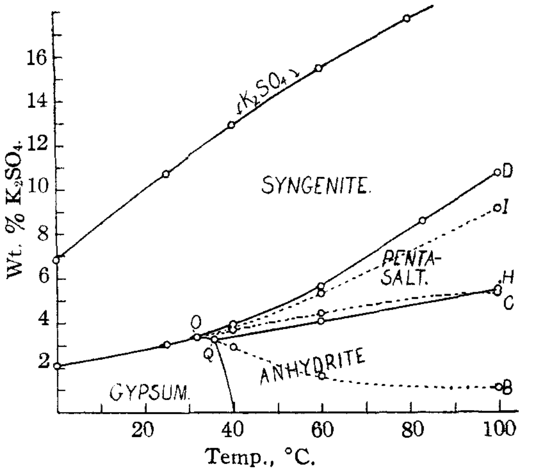

Fig. 4.—Polytherm for $CaSO_4$–K_2SO_4–H_2O.

Summary

1. Complete isotherms for the system $CaSO_4$–K_2SO_4–H_2O have been studied at 40, 60 and 100°, and the fields for the various equilibria, stable and metastable, between 0 and 100° have been indicated.

2. A preliminary report is made on the determination of the solubility of anhydrite in water; the solubility appears to vary with the mode of preparation of the salt, and the approach to equilibrium is extremely slow.

3. The results in the ternary system indicate that so far as the stable equilibria are concerned the separation of potassium sulfate from calcium sulfate in natural polyhalite, by solubility differences, is not materially favored by increase in temperature, but that a substantial concentration of potassium sulfate may prove possible through the metastable precipitation of anhydrite, in view of the great retardation in the formation of pentasalt and syngenite even at 100°.

New York, N. Y. Received February 2, 1934

[Contribution from the Kettering Laboratory of Applied Physiology, University of Cincinnati]

Microdetermination of Fluorine in Organic Substances

By Donald M. Hubbard and Albert L. Henne

The present method was devised to titrate fluorine in small quantities of gaseous organic fluorides. As it may be applied to the titration of halogens in any substance which can be volatilized or burned, its publication may be justified.

The principle of the method consists in decomposing the organic molecule over silica heated to 900° in a combustion tube. Under these conditions, the decomposition is rapid and complete and the fluorine of the organic molecule is transformed into silicon tetrafluoride. The latter is then collected in water or in a weak alkaline solution where the fluorine ion is then titrated by means of cerous nitrate. To ensure correct results it is essential to sweep the combustion tube with hydrogen in order to remove adsorbed silicon fluoride and to reduce silicon oxyfluoride.

Procedure.—The gases analyzed were organic substances containing both fluorine and chlorine. As the method used to titrate fluorine permits a simultaneous measurement of the chlorine, and as the chlorine and fluorine are present in the organic molecule in a known ratio, it is convenient to check the accuracy of the fluorine titration by the titration of chlorine. (The Volhard method is a very sensitive and well-known procedure.) The following paragraphs describe the analysis