[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WESTERN AUSTRALIA AND THE STATE (W. A.) ALUNITE INDUSTRY, CHANDLER]

# The System Potassium–Magnesium–Sodium–Sulfate–Chloride–Water at 90°[1]

BY F. FEAKES

That part of the system, potassium–magnesium–sodium–sulfate–chloride–water, in which sodium chloride is a solid phase has been determined at 90°. It is shown that vanthoffite and langbeinite may coexist at this temperature and that erroneous results may be obtained by interpolating from previous workers' results for invariant points at other temperatures. Some evidence is presented which suggests that under certain conditions magnesium sulfate forms solid solutions with sodium sulfate.

## Introduction

In this quinary system, the results obtained by van't Hoff, Serowy, Koelichen, Przibylla, Leimbach, Blumer, Tollert, Kupper and their coworkers have been summarized by D'Ans.[2] Because of the relation of the system to the oceanic salt deposits of Germany and France, these studies were largely confined to determinations of the solid phases and the compositions of the associated solutions when sodium chloride was present as one of the solid phases.

The present study was initiated to aid the investigation of a process—involving this system at 90°—for the recovery of sodium sulfate, potassium chloride and magnesium salts from alunite. No results are available for the quinary system at 90° and there are but few in the associated quaternary systems involving sulfate and chloride. Serowy[3] has completed polytherms for several points in the quinary system, but the major part of his work at the higher temperatures was with solutions in equilibrium with solid potassium and sodium chlorides. The system $K_2Cl_2$–$Na_2Cl_2$–$MgCl_2$–$H_2O$ has been partially studied by Feit and Przibylla[4] at 90°; their results are plotted in Fig. 1. Since the appearance of D'Ans' publication in 1933, Kurnakov, *et al.*,[5] and Osokoreva, *et al.*,[6] have continued the study of the pure chloride system, while Campbell, *et al.*,[7] restricted their examination to the quaternary system, $K_2Cl_2$–$K_2SO_4$–$MgSO_4$–$H_2O$, at 100°.

Consequently, it was desirable to check the high temperature data as interpolated by D'Ans for the points (invariant at constant temperature and pressure) that represent equilibrium between a solution and four solid phases. Determinations were also made along the univariant lines representing equilibrium between solution and three solid phases. To round off the investigation these studies were carried into the related quaternary systems.

The investigation was confined to systems saturated with respect to sodium chloride.

## Experimental

Analytical reagent grades of the following salts were used: sodium chloride, sodium sulfate, potassium sulfate, potassium chloride, magnesium sulfate, 7-hydrate and magnesium chloride 6-hydrate. From these salts bulk samples were prepared of the other solid phases which appear in this system, namely, glaserite ($3K_2SO_4 \cdot Na_2SO_4$), vanthoffite ($3Na_2SO_4 \cdot MgSO_4$), loewite ($Na_2SO_4 \cdot MgSO_4 \cdot {}^5/_2H_2O$), langbeinite ($K_2SO_4 \cdot 2MgSO_4$), kieserite ($MgSO_4 \cdot H_2O$) and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). In general, the most convenient method of preparation was by isothermal evaporation at a temperature within the range 90–100°.

The following procedure was adopted for each of the experimental points: Water and the appropriate salts, 40 to 50 g. in all, were weighed into a narrow necked Pyrex sample tube of approximately 60 cc. capacity. The quantities were chosen to correspond approximately to the expected composition of the equilibrium solution. Repeated preliminary experiments were, therefore, sometimes necessary. The sample tube was then heated to 90° in the thermostat and the neck sealed. The tube, with others, was then rotated in the thermostat until solution of the salts was complete. Without removing the tube from the thermostat, weighed amounts (about 3 g. each) of the expected solid phases were then introduced, the tube resealed, and rotated in the thermostat for 7 days. (Determinations throughout the course of the examination indicated that 7 days was ample time for the attainment of equillibrium.) The sample tube was then held vertically in the thermostat until the solids had completely settled, whereupon a sample of the clear supernatant liquor was forced up a preheated tube into a tared flask for subsequent analysis. The residual liquor and solids were then shaken up, filtered rapidly under suction, quickly washed with acetone or ethanol and dried between filter paper at room temperature. The solids were reserved for solid phase identification. All solid phases encountered are stable when dry at room temperature.

The thermostat was maintained at 90.0 ± 0.4° for the 8 days prior to sampling. Over the last 4 days of each series the temperature was 90.0 ± 0.2°. The thermometer was calibrated from a standard carrying a National Physical Laboratory certificate.

### Analytical

The solutions were analyzed according to the following procedures: potassium, Hicks' modification[8] of the chloroplatinate method; magnesium, 8-hydroxyquinoline[9]; sulfate, careful precipitation of barium sulfate[10]; chloride, Mohr's method[11]; sodium, by difference. When magnesium and chloride were not present together in solution, a determination of total salts was used either as a check analysis or instead of the sulfate determination.

The individual crystal species in the dried solids were identified by measurement of refractive index ("Becke Line Method)[12] and optical properties.

## Results

The results are plotted in Fig. 1, which is drawn

---

(1) Adapted from a thesis presented for the degree Master of Science in the University of Western Australia.

(2) J. D'Ans, "Die Losungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Kali-Forschungs-Anstalt, Berlin, 1933, p. 168.

(3) F. Serowy, Contribution to *Kali Forschungs Anstalt*, **3**, 21 (1923).

(4) W. Feit and K. Przibylla, *Kali*, **3**, 393 (1909).

(5) N. S. Kurnakov, D. P. Manoev and N. A. Osokoreva, *ibid.*, **2,** 25 (1932); *C. A.*, **26**, 3720 (1932).

(6) N. A. Osokoreva, M. A. Opuikhtina, P. N. Shoikhet, E. F. Plaksina and A. I. Zaslavskii, *Trans. Inst. State Applied Chem.* (*U. S. S. R.*), **16**, 24 (1932); *C. A.*, **29**, 30 (1935).

(7) A. N. Campbell, K. W. Downes and C. S. Samis, THIS JOURNAL, **56**, 2507 (1934).

(8) W. W. Scott, "Standard Methods of Chemical Analysis," Vol. I, 5th ed., D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 870.

(9) Reference 8, p. 535.

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 318.

(11) Reference 10, pp. 449 and 541.

(12) T. R. P. Gibb, "Optical Methods of Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1942, pp. 245–248.

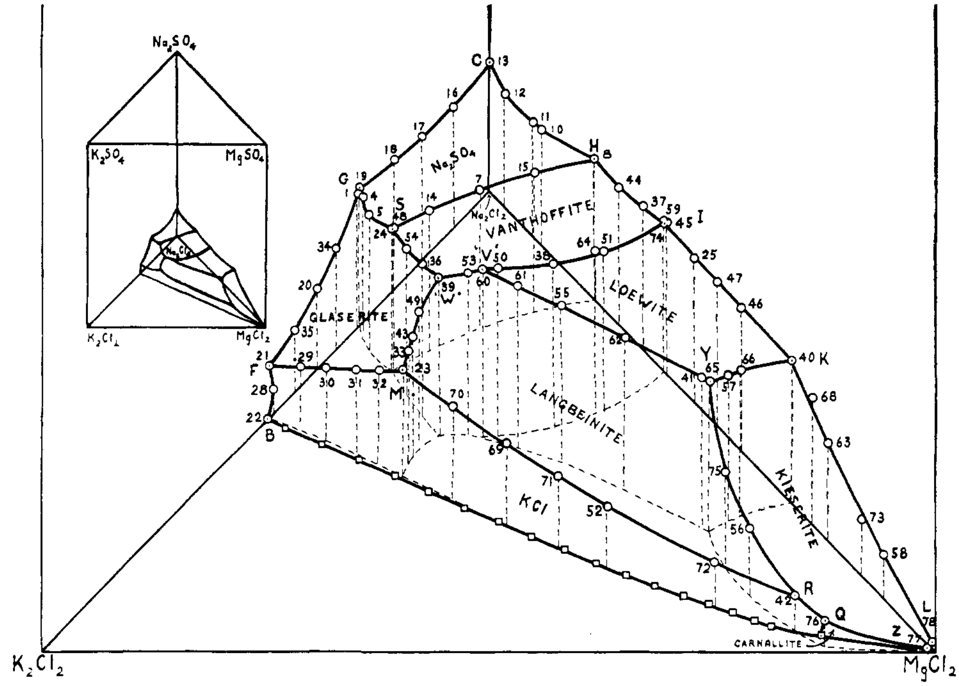

Fig. 1.—The system $K^+$-$Na^+$-$Mg^{++}$-$SO_4^=$-$Cl^-$-$H_2O$ at 90°: □, W. Feit and K. Przibylla; ○, this investigation.

according to Jaenecke's[13] method of representing a right triangular prism. The inset illustrates the section of the prism over which the examination was made (saturation with sodium chloride). The main invariant points have been lettered in conformity with the notation used by D'Ans. The results of Feit and Przibylla cited by D'Ans are also plotted. Projections onto the $K_2Cl_2$–$Na_2Cl_2$–$MgCl_2$ plane are shown by the lighter broken lines.

The numbers adjacent to each determination in Fig. 1 represent the determination or sample no. used during the investigation. They will serve to simplify cross reference to the results which have been fully tabulated and are available through the American Documentation Institute.[14]

## Discussion

For the quaternary system $K_2SO_4$–$K_2Cl_2$–$Na_2Cl_2$–$H_2O$, there is good agreement between these determinations and the values given by D'Ans.[15] In the system: $MgSO_4$–$Na_2SO_4$–$Na_2Cl_2$–$H_2O$, the value given by D'Ans[16] for the point I (NaCl, vanthoffite, loewite) differs considerably from that obtained in this work. The curvature of the phase boundaries HI, IK and I"V," together with the determinations 45, 59 and 74, suggest that D'Ans' figure is incorrect.

When considering the quinary system, good agreement was obtained in the region of high magnesium chloride concentrations, *i.e.*, points R, Q, L and Z. (For the points Q and Z, where the concentration of $MgCl_2$ is very high, the values obtained for the sodium chloride concentration—determined by difference—are open to error.) However, in the region of lower magnesium concentrations, this work showed several major differences. For instance, D'Ans' polytherms[2] indicate that it is possible for glaserite and loewite to coexist at 90° while vanthoffite and langbeinite are not able to do so below 98°. However, the present work proves that, under equilibrium conditions, vanthoffite and langbeinite may coexist at 90°, while glaserite and loewite may not. The range of solution compositions over which vanthoffite and langbeinite are able to coexist would suggest that they are also stable at temperatures somewhat below 90°.

Another feature of the investigation was that in sample no. 5, 6, 8, 10, 11, 12, 14, 15, 24 and 48—that is in all samples (except No. 4) in which sodium sulfate was brought into equilibrium with a magnesium bearing solution—sodium sulfate (thenardite) with properties as described in the literature was not found as a solid phase. Instead, the crystals appeared to be isotropic tetrahedra, the apices of which on occasions were replaced by more numerous plane faces. (Thenardite belongs to the orthorhombic system; refractive indices 1.464, 1.474, 1.485.) The crystals were relatively small (0.002 mm. face length) with a refractive index of 1.487 approx., and they gave positive tests for magnesium. Wienert[17] considers that magnesium sulfate is capable of forming solid solutions with sodium sulfate; it is probable that this crystal species is similar to that described by Wienert. Consequently, throughout this work, this solid phase has been referred to as $Na_2SO_4$ s.s.–$Na_2SO_4$ solid solution.

**Acknowledgments.**—I would like to thank the management of the State (W. A.) Alunite Industry for making available the facilities to carry out this work and Professor N. S. Bayliss for his continued interest and assistance.

PERTH, WESTERN AUSTRALIA RECEIVED MARCH 21, 1951

---

[13] E. Jaenecke, *Z. anorg. Chem.*, **53**, 323 (1907).

[14] For supplementary tables, order Document 3500 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for 35-mm. microfilm, or $1.00 for 6 × 8 photocopies.

[15] Reference 2, p. 113.

[16] Reference 2, p. 141.

[17] F. O. Wienert, *Aust. Chem. Inst. J. Proc.*, **17**, 197 (1950).