tubes. The filament consisted of a tungsten coil about 3.5 cm. long, with a coil diameter of 0.8 cm. The coil was coated with a layer of zirconium hydride mixed with an organic binder.

The hydride and binder were decomposed on the coil by heating slowly to 750°, and pumping to obtain a good vacuum. Hydrogen was added until a pressure of 3.2 mm. was obtained holding the temperature constant at 700° until equilibrium was established. Then the temperature was lowered 50° and again held until no more pressure drop occurred. This procedure was repeated to room temperature where a residual pressure of 0.097 mm. resulted, showing that zirconium had taken up practically all of the initial 3.2 mm. of hydrogen on cooling. The volume of the system was in this case approximately 1500 cc.

A dissociation curve was run on this zirconium hydride as shown in Fig. 5, run no. 1, with a residual pressure of 0.773 mm. on cooling. Upon pumping out this residual gas, similar curves could be obtained with rising and falling temperature, as shown by run no. 2.

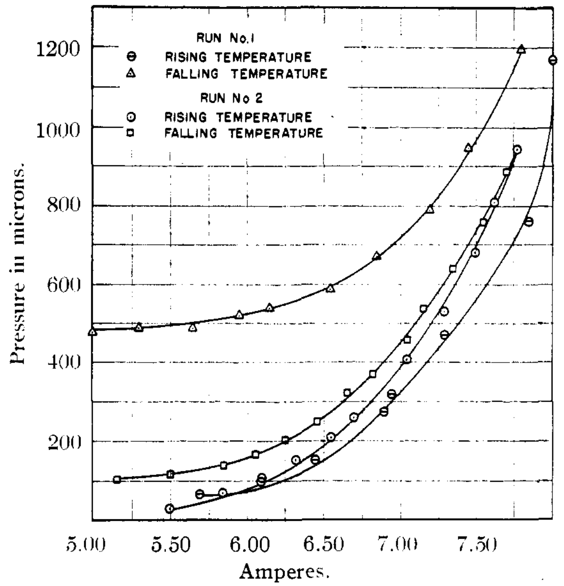

Fig. 5.—Pressure–heater current characteristics of zirconium hydride reservoir for hydrogen thyratron.

Summary

1. In order to provide information concerning the equilibrium conditions of metallic hydrides in hydrogen thyratrons, the equilibrium gas pressures in the barium–hydrogen and zirconium–hydrogen systems have been measured up to 600 and 650°, respectively. Combination of hydrogen with metallic barium occurs readily when the metal is finely divided or in thin layers. The dissociation pressure of barium hydride at 600° appears not to exceed 0.24 mm., which is low in terms of hydrogen thyratron requirements. At this temperature barium metal begins to evaporate rapidly, rendering its use as a hydrogen reservoir impractical.

2. The equilibrium gas pressure in the zirconium–hydrogen system rises from 0.16 mm. at about 150° to 2.1 mm. at 500°. The variation of the pressure with temperature was found to be relatively independent of the pressure at which the hydride was formed initially. The pressures were reproducible with rising and with falling temperature if an excess of hydrogen present was avoided when the hydride was cold.

CAMBRIDGE, MASSACHUSETTS
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WESTERN AUSTRALIA]

The System Potassium Sulfate–Sodium Sulfate–Magnesium Sulfate–Water at 35°

BY N. S. BAYLISS, A. R. H. COLE,[1] W. E. EWERS[2] AND N. K. JONES[1]

Introduction

Previous work on this quaternary system and its three associated ternary systems has been summarized by D'Ans[3] with the exception of Bozza's later investigation[4] of the system K_2SO_4–$MgSO_4$–H_2O at 35°. D'Ans points out that the data on the quaternary system were all obtained before 1915, and furthermore they are confined almost exclusively to the points (invariant at constant temperature and pressure) that represent equilibrium between the solution and three solid phases. The present work was undertaken because the results of another investigation in this Laboratory showed that the previous data needed revision, particularly with respect to the glaserite field.

As well as redetermining the "invariant" points, we have added measurements of a number of points along the "univariant" lines (equilibrium between the solution and two solid phases) and on the "bivariant" surface representing equilibrium between glaserite and saturated solutions. In order to round off the investigation, we found it convenient to re-examine the three related ternary systems K_2SO_4–Na_2SO_4–H_2O, K_2SO_4–$MgSO_4$–H_2O, and Na_2SO_4–$MgSO_4$–H_2O, including measurements of a number of points on the "univariant" lines not hitherto determined.

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(1) Hackett Research Scholar.

(2) Assistant Research Officer, Council for Scientific and Industrial Research.

(3) J. D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Kali-Forschungs-Anstalt, Berlin, 1933, pp. 108, 130, 151, 165.

(4) G. Bozza, *Giorn. chim. Ind. Applicata*, **16**, 109 (1934).

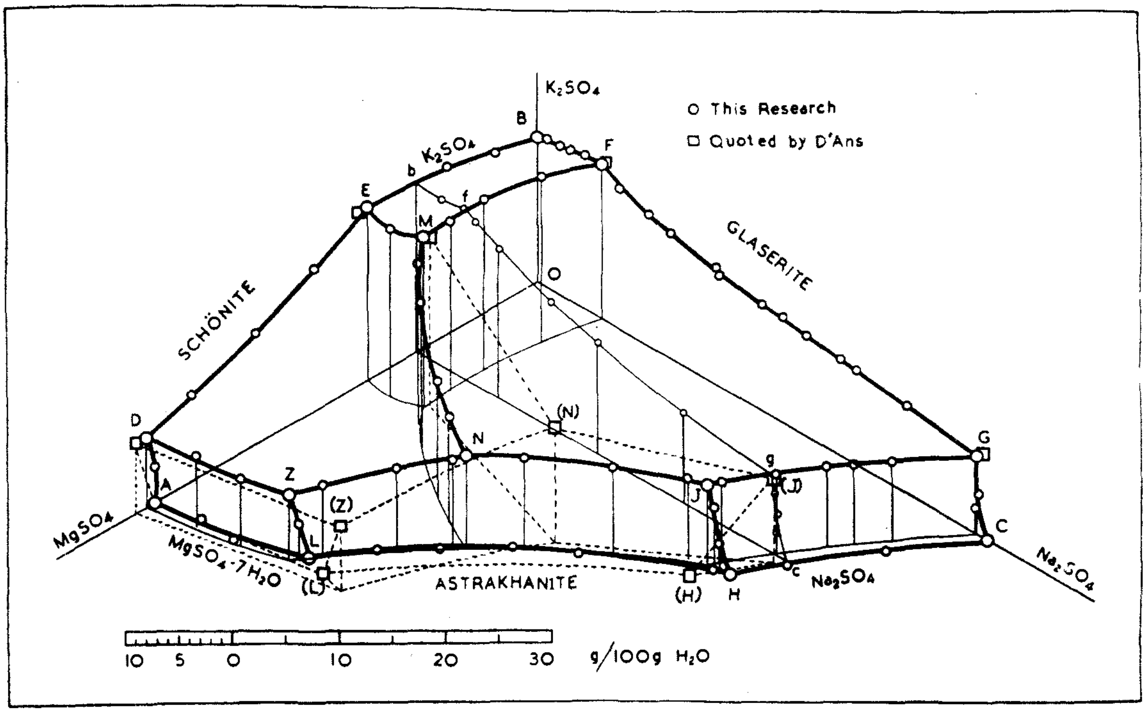

Fig. 1.—Orthogonal projection of the equilibrium diagram of the system K_2SO_4–Na_2SO_4–$MgSO_4$–H_2O. The origin O represents pure water. The scale of concentrations along the K_2SO_4, Na_2SO_4 and $MgSO_4$ axes is shown. Circles are our experimental points; squares are values quoted by D'Ans, and denoted by appropriate letter in parenthesis, thus, (H); broken lines are phase boundaries according to D'Ans.

Experimental

Potassium sulfate, sodium sulfate and magnesium sulfate 7-hydrate of analytical reagent grade were used. From these we prepared bulk samples of the other three solid phases that are concerned in the system, namely, glaserite ($3K_2SO_4 \cdot Na_2SO_4$), schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) and astrakhanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$). The following procedure was adopted for each of the experimental points: Water and the appropriate salts, 60 to 70 g. in all, were weighed into a bottle of 100-cc. capacity, the quantities being chosen to correspond approximately to the expected composition of the equilibrium solution. Repeated preliminary experiments were sometimes necessary to determine this approximate composition. The bottle was well stoppered and rotated with others in the thermostat until the solids had dissolved. Without removing the bottle from the thermostat, weighed amounts (about 3 g. each) of the expected solid phases were then introduced, the bottle was re-stoppered, and rotated in the thermostat for six days. (The preliminary experiments indicated that six days was ample time for equilibrium provided that the required solid phases were added at the beginning of the period.) The bottle was then held vertically in the thermostat until the solids had completely settled, and a sample of the supernatant solution was withdrawn quickly and transferred to a tared flask for subsequent analysis. The solids were then shaken up, filtered rapidly, pressed dry between filter paper, and reserved for identification by the methods described below.

The thermostat was maintained at 35.00 ± 0.05°, and the thermometer was checked against a standard carrying a National Physical Laboratory certificate.

Analytical

The solutions were analyzed for total solids, potassium and magnesium in the case of the quaternary system, for total solids and magnesium in the case of the system Na_2SO_4–$MgSO_4$–H_2O, and for total solids and potassium in the case of the other two ternary systems. Sodium was determined by difference since check analyses showed that the magnesium uranyl acetate method gives high results in the presence of potassium sulfate. Potassium was determined by Hicks' modification[5] of the chloroplatinate method, and magnesium by 8-hydroxyquinoline.[6]

The individual crystal species in the dried solids were identified by measurements of density ("sink and float" method in a centrifuge), refractive index ("Becke line" and "half shadow" methods[7]), and of optical properties.

Results

The results are summarized in the tables, which also show in parentheses the values quoted by D'Ans[3] and by Bozza.[4] Where D'Ans has not quoted a value at 35°, we have cited the value interpolated from his polytherms. Our results are plotted in Fig. 1, which is drawn according to the method of orthogonal projection.[8] The points and lines are lettered in conformity with the notation of D'Ans.[3] In addition to the lines and points in the cöordinate space, we have shown in lighter lines their projections on the Na_2SO_4–$MgSO_4$ plane.

Discussion

Our results for the ternary systems K_2SO_4–Na_2SO_4–H_2O and K_2SO_4–$MgSO_4$–H_2O are in good

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

(6) Ref. 5, p. 535.

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

(8) Ref. 3, p. 33.

TABLE I

THE SYSTEM K_2SO_4–$MgSO_4$–H_2O

Point	Solid phases	Composition of liquid phase g./100 g. H_2O K_2SO_4	$MgSO_4$
B	K_2SO_4	13.80	. . .
B	K_2SO_4	(13.86)[a]	. . .
	K_2SO_4	14.50	4.55
	K_2SO_4	15.90	9.85
E	K_2SO_4, Schoenite	16.30	18.40
E	K_2SO_4, Schoenite	(16.15)[a,c]	(19.30)[a,c]
E	K_2SO_4, Schoenite	(15.95)[b]	(19.30)[b]
	Schoenite	13.30	24.25
	Schoenite	10.45	30.70
	Schoenite	8.05	37.45
D	Schoenite, $MgSO_4 \cdot 7H_2O$	6.55	42.35
D	Schoenite, $MgSO_4 \cdot 7H_2O$	(6.60)[a,c]	(43.55)[a,c]
D	Schoenite, $MgSO_4 \cdot 7H_2O$	(6.45)[b]	(42.50)[b]
	$MgSO_4 \cdot 7H_2O$	3.35	41.45
A	$MgSO_4 \cdot 7H_2O$	. . .	41.65
A	$MgSO_4 \cdot 7H_2O$	. . .	(41.62)[a]
A	$MgSO_4 \cdot 7H_2O$	. . .	(41.25)[b]

[a] D'Ans, ref. 3. [b] Bozza, ref. 4. [c] Interpolated from polytherms.

TABLE II

THE SYSTEM Na_2SO_4–$MgSO_4$–H_2O

Point	Solid phases	Composition of liquid phase g./100 g. H_2O Na_2SO_4	$MgSO_4$
C	Na_2SO_4	49.15	. . .
C	Na_2SO_4	(49.17)[a]	. . .
	Na_2SO_4	44.60	6.60
	Na_2SO_4	40.50	13.30
H	Na_2SO_4, Astrakhanite	38.15	17.25
H	Na_2SO_4, Astrakhanite	(36.1)[a]	(19.7)[a]
	Astrakhanite	36.65	17.60
	Astrakhanite	36.50	17.80
	Astrakhanite	(29.3)[a]	(24.85)[a]
	Astrakhanite	28.00	23.60
	Astrakhanite	23.85	26.50
	Astrakhanite	19.95	30.55
	Astrakhanite	16.55	.34.00
L	Astrakhanite, $MgSO_4 \cdot 7H_2O$	13.60	38.50
L	Astrakhanite, $MgSO_4 \cdot 7H_2O$	(15.8)[a]	(39.25)[a]
	$MgSO_4 \cdot 7H_2O$	7.85	40.90
	$MgSO_4 \cdot 7H_2O$	4.05	40.45
A	$MgSO_4 \cdot 7H_2O$	. . .	41.65

[a] D'Ans, ref. 3.

TABLE III

THE SYSTEM K_2SO_4–Na_2SO_4–H_2O

Point	Solid phases	Composition of liquid phase g./100 g. H_2O K_2SO_4	Na_2SO_4
B	K_2SO_4	13.80	. . .
	K_2SO_4	14.05	1.10
	K_2SO_4	14.00	2.55
	K_2SO_4	14.30	2.50
	K_2SO_4	14.40	3.60
	K_2SO_4	14.80	4.75
	K_2SO_4	14.75	5.15
	K_2SO_4	14.45	6.10
F	K_2SO_4, Glaserite	14.70	7.00
F	K_2SO_4, Glaserite	(14.81)[a]	(7.2)[a]
	Glaserite	13.45	9.00
	Glaserite	12.60	12.25
	Glaserite,	11.90	14.50
	Glaserite	11.10	19.45
	Glaserite	10.65	19.95
	Glaserite	10.15	24.65
	Glaserite	10.05	26.80
	Glaserite	9.55	29.30
	Glaserite	9.15	33.15
	Glaserite	9.00	34.85
	Glaserite	8.30	40.30
G	Glaserite, Na_2SO_4	7.45	48.00
G	Glaserite, Na_2SO_4	(7.9)[a]	(48.7)[a]
	Na_2SO_4	3.95	48.15
	Na_2SO_4	2.30	47.85
C	Na_2SO_4	. . .	49.15

[a] D'Ans, ref. 3.

TABLE IV

THE SYSTEM K_2SO_4–Na_2SO_4–$MgSO_4$–H_2O

Point	Solid phases	Composition of liquid phase g./100 g. H_2O Na_2SO_4	K_2SO_4	$MgSO_4$
	Na_2SO_4, Glaserite	44.05	7.65	5.30
	Na_2SO_4, Glaserite	42.10	7.45	7.55
	Na_2SO_4, Glaserite	40.90	7.65	9.30
	Na_2SO_4, Glaserite	38.85	7.65	12.90
	Na_2SO_4, Glaserite	36.50	7.55	16.50
J	Na_2SO_4, Glas., Astr.	36.10	7.55	17.55
J	Na_2SO_4, Glas., Astr.	(39.25)[a,b]	(8.0)[a]	(13.9)[a]
	Na_2SO_4, Astr.	36.60	5.50	17.30
	Na_2SO_4, Astr.	36.80	2.15	17.15
	Glas., Astr.	34.30	7.65	18.10
	Glas., Astr.	29.90	8.10	21.85
	Glas., Astr.	24.50	8.50	26.00
N	Glas., Astr., Schoen.	21.35	8.80	29.20
N	Glas., Astr., Schoen.	(25.7)[a]	(10.9)[a]	(23.8)[a]
	Schoen., Glas.	17.95	9.95	27.60
	Schoen., Glas.	15.00	11.00	25.85
	Schoen., Glas.	9.30	13.55	21.85
	Schoen., Glas.	7.00	15.20	20.05
M	Schoen., Glas., K_2SO_4	5.75	16.15	18.15
M	Schoen., Glas., K_2SO_4	(6.0)[a]	(16.0)[a]	(17.7)[a]
	Schoen., K_2SO_4	2.90	15.85	18.90
	K_2SO_4, Glas.	5.75	16.05	15.15
	K_2SO_4, Glas.	5.30	16.15	11.20
	K_2SO_4, Glas.	6.15	15.85	5.75
	Schoen., Astr.	20.95	8.70	30.15
	Schoen., Astr.	(22.0)[a]	(8.9)[a]	(30.6)[a]
	Schoen., Astr.	17.80	7.95	33.20
	Schoen., Astr.	13.95	6.60	37.40
Z	Schoen., Astr., $MgSO_4 \cdot 7H_2O$	12.75	6.50	39.80
Z	Schoen., Astr., $MgSO_4 \cdot 7H_2O$	(18.35)[a,c]	(6.0)[a,c]	(39.95)[a,c]
	$MgSO_4 \cdot 7H_2O$, Astr.	13.10	3.30	39.20
	$MgSO_4 \cdot 7H_2O$, Schoen.	9.05	6.60	41.30
	$MgSO_4 \cdot 7H_2O$, Schoen.	4.50	6.60	41.40

[a] D'Ans, ref. 3. [b] D'Ans (p. 167) gives 29.25—probably a misprint for 39.25. [c] Determined at 36°.

agreement with those of previous investigators, although we have determined many additional points along the "univariant" lines. Our data on the ternary system Na_2SO_4–$MgSO_4$–H_2O suggest that previous values require correction where astrakhanite is the stable phase (L, H and intermediate points in Fig. 1). In the quaternary system, we have indicated an extensive revision

TABLE V

THE SYSTEM K_2SO_4–Na_2SO_4–$MgSO_4$–H_2O WITH CONSTANT $MgSO_4$ CONCENTRATION IN THE LIQUID PHASE

This system was determined to indicate the curvature of the glaserite field.

Solid phase	Composition of liquid phase, g./100 g. H_2O K_2SO_4	 Na_2SO_4	 $MgSO_4$
K_2SO_4	15.75	2.75	13.10
K_2SO_4	15.95	5.10	13.10
Glaserite	15.45	6.30	13.10
Glaserite	14.10	8.90	13.10
Glaserite	11.90	14.60	13.10
Glaserite	10.55	19.65	13.10
Glaserite	8.70	29.00	13.10
Na_2SO_4	5.90	38.95	13.10
Na_2SO_4	4.05	39.25	13.10
Na_2SO_4	2.20	39.00	13.10

of the boundaries between the glaserite, schoenite and astrakhanite fields. The correctness of our results is supported by (a) the fact that the experimental points on the lines MN, ZN and JN converge accurately to the experimental point N; and (b) that preliminary experiments on systems made up to correspond with equilibrium according to D'Ans showed that these systems were not in equilibrium, since on rotation in the thermostat some or all of the solid phases disappeared. The preliminary experiments confirmed the experience[9] of previous investigators that equilibrium with respect to glaserite and astrakhanite is established very slowly. This was one reason for our experimental expedient of beginning with a solution of approximately the correct composition and adding ample excess of each of the expected solid phases.

The points representing equilibrium with solutions of constant magnesium content (the line bfgc in Fig. 1) serve to indicate the form of the glaserite surface, and should make it possible to estimate, with reasonable accuracy, the composition of all the solutions that can exist in equilibrium with glaserite.

Acknowledgment.—We are indebted to the Hackett Fund of the University of Western Australia, and to the Commonwealth Research Fund, for the financial support of this project.

Summary

The system K_2SO_4–Na_2SO_4–$MgSO_4$–H_2O has been completely re-determined at 35°. The boundaries between the glaserite, schoenite and astrakhanite fields have been revised, and the shape of the glaserite surface is described in some detail.

[9] Ref. 3, pp. 131, 109.

NEDLANDS, WESTERN AUSTRALIA
RECEIVED DECEMBER 26, 1946

[CONTRIBUTION FROM THE MAGNOLIA PETROLEUM COMPANY]

The Physical and Chemical Properties of Hydrocarbon Solutions of Aluminum Bromide. I. The Solubility of Aluminum Bromide in *n*-Hexane[1]

BY EDWARD R. BOEDEKER[2] AND ALEX G. OBLAD[2]

During the course of a detailed study of a number of hydrocarbon reactions catalyzed by aluminum bromide it was found necessary to determine the solubility of aluminum bromide in *n*-hexane. The results of these solubility determinations are here reported. The solubility of aluminum bromide in *n*-butane has been determined by Heldman and Thurmond.[3] Using their data and those obtained in the present study the solubility of aluminum bromide in normal paraffin hydrocarbons is discussed from a standpoint of an ideal solution and Hildebrand's theory of regular solutions.

Experimental

Because of the ease with which an aluminum bromide–hydrocarbon complex is formed in the presence of water or oxygen,[4] it was necessary to exercise extreme caution so that no water or oxygen was admitted to the ampules while charging them with the aluminum bromide and hydrocarbon.

The hydrocarbon employed was Phillips commercial *n*-hexane which was freed of aromatics by treatment with fuming sulfuric acid. The resulting product was then distilled through a fractionating column of approximately 55 theoretical plates. The middle fraction of the *n*-hexane flat was used and had the following physical properties: b. p. 68.2° (750 mm.), n^{25}_{D} 1.3722 (lit.[5] b. p. 68.3° (750 mm.), n^{25}_{D} 1.3722).

The aluminum bromide was prepared by direct combination of the elements and was distilled twice in the presence of metallic aluminum before being introduced into the reservoir of the vacuum system.

The glass ampules which were used in the solubility studies were charged with aluminum bromide and *n*-hexane in the following manner: The weighed glass ampule was attached to a vacuum system by means of a ground glass joint. The

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[1] Presented as part of a paper given at the Southwest Regional Meeting of the American Chemical Society, Dallas, Texas, December 12 and 13, 1946.

[2] Present address: Texas State Research Foundation, Renner, Texas.

[3] Heldman and Thurmond, THIS JOURNAL, **66**, 427 (1944).

[4] Pines and Wackher, *ibid.*, **68**, 595 (1946); Oblad and Gorin, *Ind. Eng. Chem.*, **38**, 822 (1946); Montgomery, McAter and Franke, THIS JOURNAL, **59**, 1768 (1937).

[5] A. P. I. Project No. 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons, June 30, 1945.