be expected from the known values[10] in the chloro-ethylenes.

The bond angles cannot be said to have been determined with accuracy, but it is probable that both ∠Cl—C=C and ∠As—C=C are between 120 and 125°, and that ∠Cl—As—Cl and ∠Cl—As—C are near 100°, the value found for arsenic trichloride.[8]

Summary

An electron diffraction investigation of two

(10) L. O. Brockway, J. Y. Beach and L. Pauling, THIS JOURNAL, 57, 2693(1935).

isomers of β-chlorovinyldichloroarsine (Lewisite) shows that isomer I (b.p. 190° at 760 mm.) has the *trans* structure, and that isomer II (b.p. 150.2° at 760 mm.) has the *cis* structure. The structural assignment depends on the chemical identification of both isomers as β-chlorovinyl-dichloroarsines, since the possibility that isomer II is α-chlorovinyldichloroarsine is not excluded by the electron diffraction data. The interatomic distances found are in accord with those in related substances.

Some Studies in the System AlCl₃–FeCl₃–KCl–NaCl–HCl–H₂O at 25, 30 and 35°

BY GRANT L. MILES

The results described in this report were obtained during an investigation of a hydrochloric acid process for the extraction of alumina from calcined alunite. This process involved the precipitation, through HCl, of $AlCl_3 \cdot 6H_2O$ together with other salts, especially NaCl, from solutions containing approximately 18% $AlCl_3$, 2% $FeCl_3$, 1.5% KCl and 0.5% NaCl, in addition to small amounts of other impurities, especially sulfate. The data presented refer to the compositions of solutions saturated with four solids: $AlCl_3 \cdot 6H_2O$, NaCl, KCl and $2KCl \cdot FeCl_3 \cdot H_2O$. Work on related simpler systems, such as AlCl₃–FeCl₃–KCl–HCl–H₂O and AlCl₃–KCl–HCl–H₂O has been reported by Malquori.[1]

Experimental

Solutions of approximately the correct composition were shaken with excess of the expected solid phases in sealed tubes made from 7 × 1 inch test-tubes. These were rotated in a thermostat maintained at the indicated temperatures (±0.05°) for periods of not less than three days. Duplicate tests showed that this period was ample to ensure complete equilibrium.

Solutions were separated from the solid phases by supporting the tubes vertically in the bath overnight, after which the tubes were quickly unsealed and about 20 ml. of clear supernatant liquor was transferred rapidly to a small weighed conical flask. The transfer was made with a warm predried pipet, the tip of which had been slightly shortened. Losses of hydrogen chloride by fuming were practically eliminated by the addition of about 30 ml. of water to the conical flask, prior to weighing.

Solids were separated by decantation and were dried with blotting paper. Examination of the solid residues was carried out using a petrological microscope. The crystals were ground and mounted in chlorobenzene. The various crystal species were identified by the following properties

$AlCl_3 \cdot 6H_2O$	Colorless and anisotropic
$2KCl \cdot FeCl_3 \cdot H_2O$	Bright orange color and anisotropic
KCl	Isotropic, and refractive index (1.49) below that of chlorobenzene (1.523)
NaCl	Isotropic, and refractive index (1.54) above that of chlorobenzene

(1) G. Malquori, *Gazz. chim. ital.*, 59, 556 (1929).

Reagents.—Analytical Reagent grade potassium chloride, sodium chloride and ferric chloride were used. Aluminum chloride hexahydrate was obtained in a very pure form by passing hydrogen chloride into a solution of aluminum chloride prepared from aluminum metal. The double salt $2KCl \cdot FeCl_3 \cdot H_2O$ was prepared as follows: 320 g. of anhydrous ferric chloride and 148 g. of potassium chloride were dissolved in just sufficient quantities of 6 M hydrochloric acid and water, respectively, at 90°. The two solutions were mixed and allowed to cool slowly. The crystals of the double salt which separated were washed with concentrated hydrochloric acid. A further yield of the double salt could be obtained by adding the appropriate amount of potassium chloride to the heated mother liquor.

Analytical Methods.—Aluminum was estimated by precipitation with oxine, following the separation of the iron by double precipitation with caustic soda. Iron was estimated volumetrically, using potassium dichromate and diphenylamine indicator. Reduction was by stannous chloride. Potassium was estimated by the modified chloroplatinate method in which the potassium chloroplatinate is reduced and weighed as platinum. Sodium was estimated directly by the magnesium uranyl acetate method. Total chloride was estimated by the Volhard method, which was found to give very consistent results.

The free acid content was estimated directly by titration with caustic soda, using methyl orange indicator. The end-point of this titration was made more apparent by carrying out the titration in a blue light. However, the free acid values finally adopted were those calculated from the total chloride content of the solution, and consequently subject to cumulative error. Duplicate estimations for the other analyses agreed within the following limits: Cl, 0.1% (0.04%); K, 1% (0.01%); Na, 2% (0.005%); Fe, 0.5% (0.01%); Al, 1% (0.02%). The parenthesized figures give the calculated deviation in the free acid content, as a percentage of the total sample. The cumulative error involved for the five analyses should therefore be less than 0.1% of the total sample, in terms of free acid content. The calculated values were considered more reliable than those obtained by the direct method, because in iron-containing solutions the value of the free acid as found directly was up to 2% higher than the calculated value, and this discrepancy was found to increase steadily with the iron content. For iron-free solutions the estimated and calculated free acid contents agreed to within 0.1% of the total sample. In those cases where no analyses are recorded in Table I the required chloride equivalents were found by interpolation in the appropriate solubility curve. In all but two instances only the sodium content was involved, and as this sub-

stance was present in small amount, no significant error was introduced. In the other two cases the absence of iron permitted the use of the direct method.

Results

Experimental results are shown in Table I, and are illustrated in Figs. 1 and 2. In Fig. 1 the

TABLE I

SOLUBILITIES IN THE SYSTEM AlCL₃–FeCL₃–KCL–NaCL–HCL–H₂O

Solid phases are denoted in the last column as follows: A, AlCl₃·6H₂O; B, NaCl; C, KCl; D, 2KCl·FeCl₃·H₂O.

Temp., °C.	HCl	FeCl₃	KCl	AlCl₃	NaCl	Solid phases
25	26.1	3.90	1.39	3.38	n. d.ᵃ	ABCD
	26.8	4.55	1.31	2.62	n. d.	ABCD
	27.1	2.26	1.77	2.60	0.30	ABCD
	27.9	2.38	1.58	2.51	n. d.	ABCD
	28.0	2.30	1.64	2.38	n. d.	ABCD
	28.4	Nil	1.47	2.49	n. d.	ABC
	31.7	Nil	1.38	n. d.	n. d.	ABC
	32.4	Nil	1.42	n. d.	n. d.	ABC
	36.5	1.33	1.44	0.16	0.11	ABCD
30	21.3	2.80	2.14	7.45	.49	ABCD
	21.3	2.82	2.21	7.49	.49	ABCD
	25.9	2.66	1.87	3.92	n. d.ᵃ	ABCD
	26.0	2.58	1.93	3.65	n. d.	ABCD
	29.0	2.34	1.63	1.70	0.29	ABCD
30	29.98	Nil	1.65	1.83	.34	ABC
	29.92	Nil	1.68	1.88	.35	ABC
	29.9	0.20	1.66	1.91	.36	ABC
	29.8	0.98	1.65	1.52	n. d.	ABC
	29.1	1.18	1.69	2.02	0.34	ABC
	29.8	1.74	1.68	1.05	n. d.	ABC
	28.6	3.60	1.42	1.58	0.28	ABD
	28.6	3.84	1.38	1.60	n. d.	ABD
	28.5	3.99	1.41	1.49	0.28	ABD
	30.6	2.08	1.51	0.85	.20	ABCD
	34.3	1.73	1.50	.32	.18	ABCD
	35.9	1.62	1.52	.25	.14	ABCD
	36.7	1.51	1.55	.20	.13	ABCD
	38.0	1.38	1.62	.18	.13	ABCD
35	25.7	2.88	2.01 ·	3.61	.42	ABCD
	30.8	2.44	1.74	0.93	.27	ABCD
	32.7	2.23	1.71	.47	.25	ABCD
	36.0	1.93	1.77	.18	.18	ABCD

ᵃ n. d. = not determined.

percentages by weight of aluminum, iron, potassium and sodium chlorides have been plotted against the calculated free acid content of solutions saturated with respect to aluminum chloride hexahydrate, potassium chloride, sodium chloride and potassium iron chloride (2KCl·FeCl₃·H₂O). Results for temperatures of 25, 30 and 35° are shown. It will be noticed that only a single solubility curve for aluminum chloride in the range 25–35° has been drawn. This was because a certain amount of overlap was obtained between results at the three temperatures. The temperature coefficient of the solubility of aluminum chloride is probably very small. This would
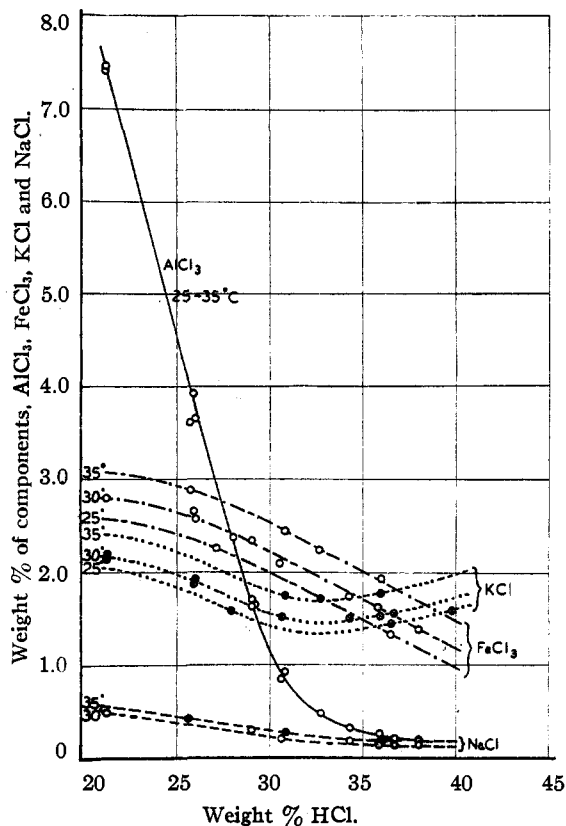

Fig. 1.—The system AlCl₃–FeCl₃–KCl–NaCl–HCl–H₂O: composition of solutions saturated with respect to AlCl₃· 6H₂O, NaCl, KCl and 2KCl·FeCl₃·H₂O.

agree with Malquori's result[2] for the system AlCl₃–KCl–HCl–H₂O, where for example it was found that in solutions saturated with potassium chloride and aluminum chloride hexahydrate, for any particular free acid content in the range 0–35%, the aluminum chloride content remained fairly constant as the temperature was varied between 0 and 50°, decreasing slightly with increasing temperature. It may also be noted that the solubility of aluminum chloride in water increases only by about 5% in the range 0–40°.

Figure 2 gives a general picture of the phase diagram for the system AlCl₃–FeCl₃–KCl–NaCl–HCl–H₂O for solutions saturated with aluminum chloride and sodium chloride. The heavy lines in this figure, which indicate the variation of the "quadruple point" with free acid content, have been drawn from Fig. 1. The points marked on these heavy lines have been obtained by interpolation at intervals of 2% in the free acid content. That the general shape of the potassium chloride solubility curve is approximately a straight line is suggested by the results quoted in Table I for 30°, and the probable shape of the 2KCl·FeCl₃·H₂O solubility curve is also indicated. Because of the considerable variations
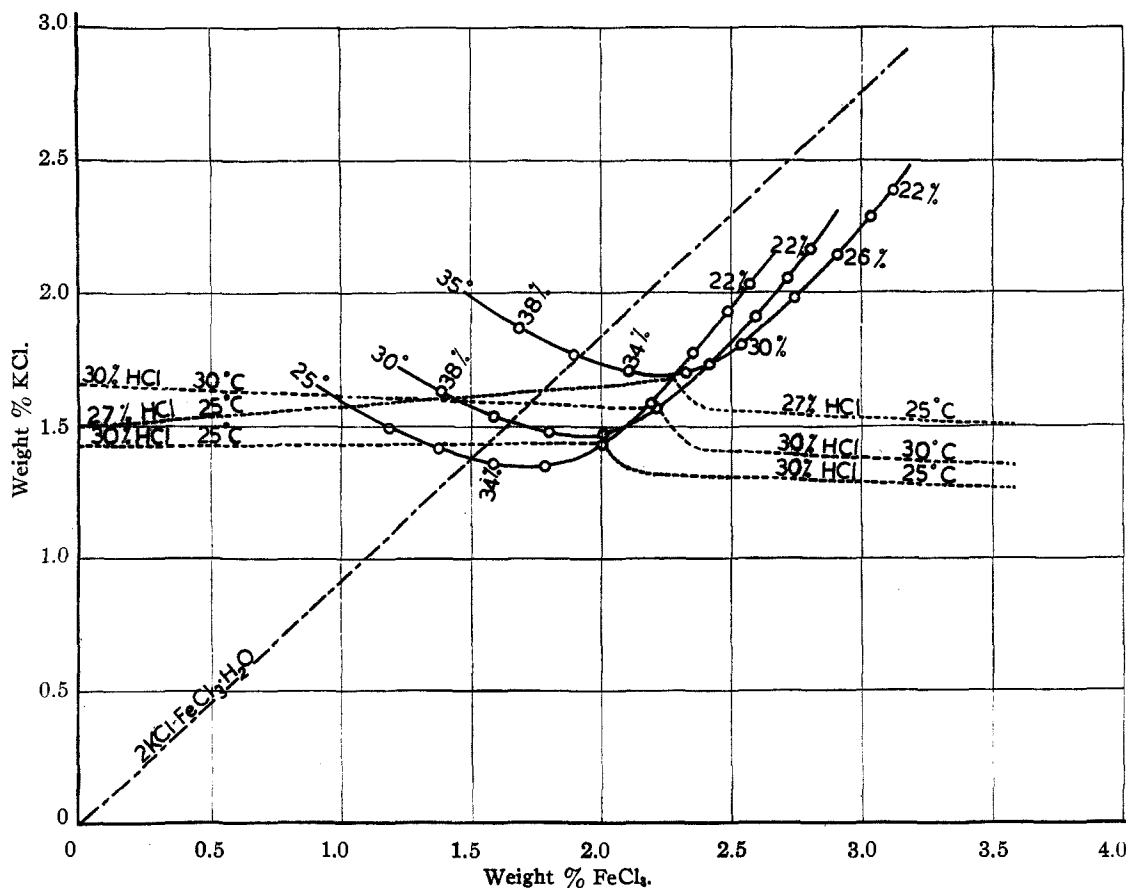
(2) G. Malquori, Gazz. chim. ital., 58, 562 (1928).

Fig. 2.—The system AlCl₃-FeCl₃-KCl-NaCl-HCl-H₂O: concentrations of FeCl₃ and KCl in solutions saturated with respect to NaCl and AlCl₃·6H₂O.

in the free acid content these results are not plotted in Fig. 2, but the probable form of the curves is indicated by dotted lines. However, from the point of view of the separation of iron-free aluminum chloride hexahydrate, it is the position of the "quadruple point" (where the chlorides of aluminum, sodium and potassium, and the potassium iron chloride are all in equilibrium with the solution) that is critical.

Ferric Chloride and Potassium Chloride.— There is some evidence of the formation of solid solutions of ferric chloride in potassium chloride. This possibility was suggested by washing tests and microscopic examination of crystals of potassium chloride separated from ferric chloride solutions which contained 20% of hydrochloric acid. The variation of the ferric chloride content of solid potassium chloride shaken with ferric chloride solutions of different concentrations is given in Fig. 3. The yellow color of aluminum chloride hexahydrate crystallized from liquors containing ferric chloride was also traced to the associated potassium chloride crystals. As will be seen by a comparison of Figs. 2 and 3, the amount of iron which will be associated with aluminum chloride in this way will usually be very slight. Solid solution of ferric chloride in po-

tassium chloride has already been reported by Hinrichsen and Sachsel[3] for solutions at 21°, but Malquori[4] reported no evidence of it at 25, 35 or 60°. However Malquori's results were based on analyses of solutions and not on an examination of the solid residues.

Other Solubility Data.—Malquori[1] has investigated the system AlCl₃-FeCl₃-KCl-HCl-H₂O, by

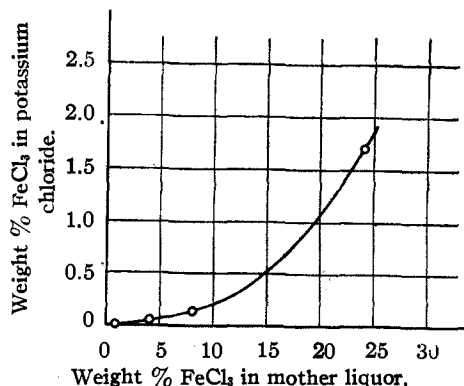Fig. 3.—Composition of solid solutions of ferric chloride in potassium chloride.

(3) Hinrichsen and Sachsel, Z. physik. Chem., **50**, 81 (1905).
(4) G. Malquori, Gass. Chim. Ital., **58**, 891 (1928).

means of a study of the simpler component systems. However, even allowing for slight differences due to the effect of the sodium present in this investigation, only poor agreement was found between the results of this research and Malquori's published data. A review of Malquori's results was commenced, but this is still incomplete. However, it may be pointed out that a preliminary investigation of the system $AlCl_3$–HCl–H_2O at 25° gave results which differed widely from those of Malquori. For example, fair agreement was found with the value for the solubility of aluminum chloride hexahydrate in water, given by Ehret and Frere,[5] of 31.10%. Seidell[6] quotes 31.6% as an average value. On the other hand, Malquori's curves for the solubility of aluminum chloride in this system are based on the value 34.08%, which is almost certainly about 10% higher than the correct value.

Acknowledgments.—The writer acknowledges the collaboration of Mr. W. E. Ewers, of the C. S. I. R. in the preliminary phase rule investigation; and of Professor N. S. Bayliss, under whose supervision this work was carried out. He also wishes to thank Western Australian Industries Department for permission to publish these results.

Summary

A limited study has been made of the system $AlCl_3$–$FeCl_3$–KCl–$NaCl$–HCl–H_2O at 25, 30 and 35°, in solutions saturated with aluminum chloride and sodium chloride, with special reference to the composition of solutions in equilibrium with both solid potassium chloride and the double salt $2KCl\cdot FeCl_3\cdot H_2O$.

(5) W. Ehret and G. Frere, THIS JOURNAL, **67**, 68 (1945).

(6) A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," 3rd ed., Vol. 1, p. 83.

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The Structure of Uranium Hydride and Deuteride[1]

BY R. E. RUNDLE

Uranium metal reacts with hydrogen to form only one hydride. This hydride, established as a compound by X-ray diffraction,[2] has been found chemically to have the composition UH_3.[3]

The hydride of uranium, if existing data on other metallic hydrides be reliable, is unique in that it does not fall in the class of volatile hydrides, salt-like hydrides or interstitial solution hydrides. It is a metal-like hydride of perfectly definite composition, and with a structure completely unrelated to any of the three forms of uranium metal. It has a structure in which the bonding between uranium and hydrogen must play a predominant role, since metal–metal bonds of any strength are almost completely lacking.

Unit Cell and X-Ray Density.—Debye-Scherrer powder diagrams of uranium hydride have been made using $CuK\alpha$ radiation, a camera of 5-cm. radius, and samples sealed in thin-walled glass capillaries. These diagrams may be interpreted in terms of a primitive cubic lattice, $a = 6.63$ Å. The density of the hydride has been measured by helium displacement and found to

be 10.95 g./cc.[4] There are then eight uranium atoms in the cubic unit.

A precise determination of the unit cell has been made using a symmetrical, self-focusing powder camera of 5-cm. radius and unfiltered $CuK\alpha$ radiation. Samples were prepared from purest Ames uranium and carefully purified hydrogen (purified by decomposition of uranium hydride).[5] The samples of Table I were prepared at about 1-atm. hydrogen pressure and at relatively low (200–300°) temperatures. Due to small particle size these samples produced satisfactory but not particularly sharp reflections in the back reflection region.

Other samples, prepared by W. Tucker and P. Figard, were made at pressures up to 1800 p.s.i. and temperatures up to 500–600°. These samples showed considerable growth in particle size and produced very sharp maxima in the back reflection region. The lattice spacing, as determined from these samples (Table II), is more precise but within the limit of experimental error of the spacing of the low pressure hydride.

Uranium metal has been heated with uranium hydride, and two phases are maintained. Changes in spacing of neither uranium metal nor of hydride were great enough to be detected. For example, a sample 50% uranium metal and 50%

(2) R. Rundle, Metallurgical Project Report, CT-609, p. 30, April (1943).

(3) Battelle Memorial Institute, Metallurgical Project Report, CT-818, July, 1943. Other physical and chemical reports on the hydride will be made in THIS JOURNAL by F. Spedding, A. Newton, J. Warf, et al.

(4) A. Newton, J. Warf, O. Johnson and R. Nottorf, Metallurgical Project Report CC-1201, Jan. (1944).

(5) This method of purification, first described by A. Newton, has been shown to be very effective.[4]