sodium caprylate (Fig. 3) and caprate (Fig. 4), the critical points are at 0.0002 and 0.00008 N, respectively. The values for the equivalent conductance of the mixtures below the critical concentration in each case approximate the sum of the values for the original quaternary ammonium chloride and the sodium salt. In the system containing sodium oleate (Fig. 5), the critical point is evidently below the lowest concentration investigated (0.000005 N).

A recent report[6] on the compatibility of N-alkyl-N-methylmorpholinium methosulfates with soaps prompted investigation of this type of compound as well as the corresponding chloride. Conductance curves for mixtures of the N-dodecyl-N-methylmorpholinium salts with sodium oleate are shown in Figs. 6 and 7 together with curves for the sums. Extrapolation of the curves for the mixtures indicates a critical concentration not greater than 0.000025 N. On the basis of this value the morpholinium salts cannot be considered as compatible with sodium oleate.

Summary

A conductometric method for estimating the solubility of slightly soluble quaternary ammonium salts has been presented.

Solubilities, as indicated by the critical concentrations, of trimethylhexadecylammonium salts of fatty acids in the presence of equimolecular quantities of sodium chloride are as follows: acetate 0.0012 N, caproate 0.0007 N, caprylate 0.0002 N, caprate 0.00008 N, and oleate < 0.000005 N.

Evidence is presented that N-dodecyl-N-methylmorpholinium salts are not compatible with sodium oleate.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 13, 1950

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[6] Hart, McGreal and Niederl, Abstracts of the Atlantic City Meeting of the American Chemical Society, September 19–23, 1949.

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

The System Ammonium Fluoride–Potassium Fluoride–Water at 25°[1]

BY HELMUT M. HAENDLER AND ALBERT W. JACHE

Few complete studies have been made of systems involving two inorganic fluorides and water. Kurtenacker, Finger and Hey[2] have reported several systems with ammonium or potassium

TABLE I

ANALYSES OF SOLUTIONS AND WET RESIDUES

Solutions, weight %			Wet residues, weight %		
NH_4F	KF	H_2O	NH_4F	KF	H_2O
0.00	48.96	51.04	...	...	...
1.70	48.76	49.54	0.27	63.08	36.65
3.49	48.63	47.88	0.69	60.31	39.00
6.53	48.15	45.32	1.41	59.32	39.27
8.04	48.42	43.44	1.32	61.80	36.88
8.75	48.44	42.40	1.60	62.93	35.47
8.97	47.63	43.40	5.79	53.01	41.20
10.08	47.88	42.04	2.99	58.65	38.30
10.77	47.93	41.30	52.39	25.96	21.95
10.94	47.04	42.02	43.46	29.58	26.96
11.09	47.39	41.52	43.69	30.03	26.28
11.98	44.88	43.04	67.94	16.57	15.49
12.14	45.09	42.77	52.41	25.83	21.76
12.92	42.93	44.15	61.14	19.50	19.30
13.12	43.28	43.60	58.57	19.13	22.30
13.62	41.45	44.93	55.08	20.79	24.13
13.77	41.26	44.97	59.74	18.37	21.65
13.93	40.82	45.15	70.00	14.96	15.04
14.41	39.29	46.30	56.24	20.03	23.73
14.85	38.63	46.52	60.34	18.01	21.65
16.88	35.43	47.69	64.50	15.02	20.48
17.07	35.01	47.92	60.53	16.43	23.04
18.60	31.41	49.94	77.90	10.15	11.95
20.37	29.92	49.71	70.48	10.99	18.63
22.52	27.57	49.91	78.64	10.23	11.23
26.44	23.76	49.80	41.23	18.83	39.94
28.49	19.65	51.84	67.61	11.25	21.14
31.59	16.85	51.66	76.99	5.43	17.68
36.03	10.69	53.28	79.04	4.00	10.36
41.27	4.57	54.16	80.74	1.64	17.66
42.92	1.48	55.60	78.50	0.61	20.59
44.85	0.00	55.15	...	...	...

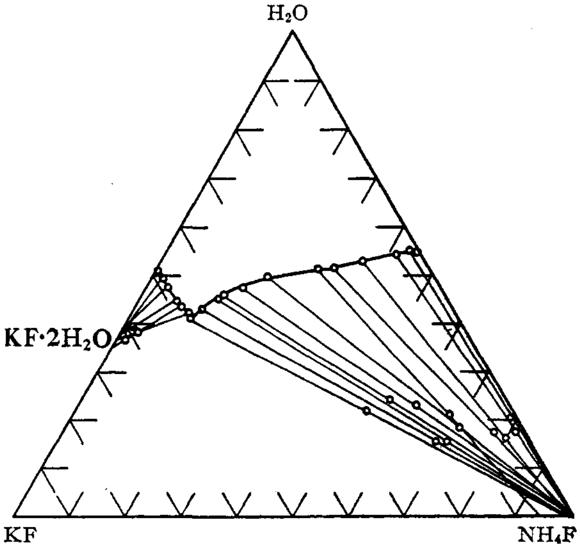

Fig. 1.—The system ammonium fluoride–potassium fluoride–water at 25°.

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[1] This work was part of a program of fluoride research supported by a Research Corporation grant-in-aid and is taken in part from the M.S. thesis of A. W. Jache.

[2] Kurtenacker, Finger and Hey, *Z. anorg. allgem. Chem.*, **211**, 281 (1933).

fluoride as one salt component and zinc, cobalt, copper, cadmium and nickel fluoride as the other. Novoselova[3] has studied systems containing ammonium, aluminum and beryllium fluorides. As part of a general program of research on inorganic fluorides, we have studied the system ammonium fluoride–potassium fluoride–water at 25°. The system is a simple one; no double salts are formed, the solid phases being ammonium fluoride, potassium fluoride and potassium fluoride dihydrate.

Experimental

The Schreinemakers wet residue method, as discussed by Purdon and Slater,[4] was used. The C. P. materials were weighed into polyethylene cups fitted with rubber stoppers bearing entrance tubes for a pipet and for a motor-driven lucite stirrer. Samples were withdrawn through a paper filter held onto the end of a glass pipet by a lucite cap. Teflon pipets were used at first, but it was found that glass contributed no observable error if the samples were handled quickly.

The solutions and wet residues were analyzed for ammonium ion and potassium ion. Ammonia was determined by distillation from strongly alkaline solution into boric acid and titration with standard hydrochloric acid. Potassium was determined by ignition with sulfuric acid, followed by treatment of the sulfate with ammonium carbonate at 600°.

Results

The results of the analyses of the solution and wet residues are given in Table I and representative points have been plotted in Fig. 1.

Summary

The system ammonium fluoride–potassium fluoride–water has been studied at 25°.

No new compound is formed by the two fluorides.

DURHAM, N. H. RECEIVED MARCH 29, 1950

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[3] Novoselova, *J. Gen. Chem. U. S. S. R.*, **9**, 1063 (1939); **10**, 1547 (1940); *C. A.*, **33**, 7687 (1939); **35**, 3186 (1941).

[4] Purdon and Slater, "Aqueous Solutions and the Phase Rule," Edward Arnold and Co., London, 1946, p. 63.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ILLINOIS INSTITUTE OF TECHNOLOGY]

The Oxidation of Zirconium at High Temperatures[1]

BY DANIEL CUBICCIOTTI

Zirconium metal can react with oxygen in two ways: (a) to form a solid solution of oxygen in the metal phase and (b) to form a new phase of zirconium dioxide. When oxygen is admitted at pressures of a micron or less to a sample of zirconium at 1000 to 1500°, the oxygen dissolves in the metal and no new phase is formed. DeBoer and Fast[2,3] have established the solubility of oxygen in the metal to be about 38 atom per cent. This reaction has been studied to determine the "gettering" power of the metal. Thus Ehrke and Slack[4] and Hukagawa and Nambo[5] measured the residual pressures of gas over a heated zirconium filament. Guldner and Wooten[6] found that no new phase was formed until after the metal was saturated with oxygen.

Hickman and Gulbransen[7] found a new phase of monoclinic zirconium dioxide formed on the surface of the metal at 600° under an oxygen pressure of 1 mm. At the lower temperature and higher pressure of this experiment the rate of reaction of the metal with oxygen is apparently greater than the rate of solution of the oxide into the metal phase, and a new phase is formed on the metal surface. Gulbransen and Andrew[8] give an excellent review of the literature on the reactions of zirconium with gases.

The present investigation of the oxidation was made to study the reaction in the intermediate temperature range of 600 to 900°. The two types of reactions, one occurring at low temperatures, the other at high temperatures, indicate that at some intermediate temperature there must be a point at which both reactions occur simultaneously.

Experimental

Method.—To measure the rate of reaction between zirconium and oxygen, the rate of consumption of oxygen by a specimen of metal at high temperature was measured. The apparatus consisted of two silica glass bulbs, connected by de Khotinsky-cemented rubber connectors to a glass manometer system, which was connected through stopcocks to a vacuum system and a gas buret. The silica bulbs were kept at constant high temperature by an electric muffle furnace regulated with a Wheelco Capacitrol. The manometer fluid was a commercial non-volatile oil, Amoil, with a density of 0.93 g. per cc. The pressure in the bulb containing the sample was prevented from dropping to a low value by periodic additions of oxygen, in known amounts, to the bulb.

In a typical run, a piece of 0.0054″ thick sheet zirconium about 3 × 15 mm. was cleaned with acetone, rubbed shiny with a clean cloth, weighed and its surface area measured. The sample was placed in one of the silica glass bulbs which was then connected to the glass system with a rubber connector and cemented. The system was evacuated to about 10^{-5} mm. and the furnace brought to temperature, oxygen at known low pressure was admitted to the two bulbs. The decrease of pressure due to the consumption of the oxygen by the sample was measured with the Amoil manometer. When the pressure in the bulb dropped by 0.05 cm. of mercury below the original value, additional oxygen was admitted to the bulb and

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[1] This research was conducted under the sponsorship of the Office of Naval Research.

[2] DeBoer and Fast, *Rec. trav. chim.*, **55**, 459 (1946).

[3] DeBoer and Fast, *ibid.*, **59**, 161 (1940).

[4] Ehrke and Slack, *J. Applied Phys.*, **11**, 129 (1940).

[5] Hukagawa and Nambo, *Electrotech. J. (Japan)*, **5**, 27 (1941).

[6] Guldner and Wooten, *Trans. Electrochem. Soc.*, **93**, 223 (1948).

[7] Hickman and Gulbransen, *Anal. Chem.*, **20**, 158 (1948).

[8] Gulbransen and Andrew, *AIME, J. of Metals*, **185**, 515 (1949); *J. Electrochem. Soc.*, **96**, 364 (1949).